MAGNETRON SPUTTERING OF MULTICOMPONENT REFRACTORY THIN FILMS

A Dissertation in
Materials Science and Engineering
by
Trent M. Borman

© 2020 Trent M. Borman

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

August 2020
The dissertation of Trent M. Borman was reviewed and approved by the following:

Jon-Paul Maria  
Professor of Materials Science and Engineering  
Dissertation Advisor  
Chair of Committee

Susan Sinnott  
Professor of Materials Science and Engineering and Professor of Chemistry

Joshua Robinson  
Professor of Materials Science and Engineering

Brian Foley  
Assistant Professor of Mechanical and Nuclear Engineering

John Mauro  
Professor of Materials Science and Engineering  
Chair, Intercollege Graduate Degree Program in Materials Science and Engineering
Abstract

A resurgence of interest in hypersonic flight has led to an increased demand for new refractory materials that possess a complex blend of physical, thermal, chemical, and mechanical properties. The selection of materials for use at extreme temperatures (>3000 °C) is dominated by the Group IVB and VB carbides, diborides, and nitrides. While these ultra high temperature ceramics (UHTCs) provide an excellent basis from which to start, new compositions are necessary for the envisioned applications.

As complexity increases from binary carbides, diborides, and nitrides to ternary, quaternary, and high entropy compositions, the breadth of the compositional space grows exponentially. These new and vast, multi-dimensional phase diagrams pose a few important questions: what are the metal stoichiometries of interest? and how do the property-chemistry trends observed in binary systems translate to these complex compositions?

Studying these new materials systems and answering these questions is not a trivial undertaking. Throughout the history of UHTC synthesis, the intrinsic properties of these ultra refractory materials have been convoluted with extrinsic factors, such as microstructure, phase purity, and defects. A valid study of the roles of metal and anion stoichiometry in these materials requires synthesis of UHTCs over broad compositional ranges while limiting the impacts of extrinsic characteristics.

Physical vapor deposition has been widely used to study high entropy systems including alloys, oxides, carbides, and nitrides. This work expands on previous studies and focuses on understanding and improving the sputter deposition process for multicomponent carbides. The advantages and limitations of conventional sputtering techniques were investigated; avenues to improve the process, ranging from gas flows to pulsed power techniques, were explored; and finally, the benefits of high power impulse magnetron sputtering inspired the development of new co-sputtering techniques.

(HfNbTaTiZr)C$_x$ has received significant research interest in the UHTC community, as it combines 5 of the most refractory carbide systems; however, researchers had not studied the influence of carbon stoichiometry in this, or other, high entropy compositions. In this work, (HfNbTaTiZr)C$_x$ films were synthesized over a broad range of carbon stoichiometries with reactive RF sputtering. These films exhibited broad crystallographic and microstructural transitions from metallic to carbide and finally nanocomposite films, simply by changing carbon content. Carbon vacancies were observed to cluster into stacking faults in substoichiometric films, despite the chemical disorder of the metal sublattice. A near-stoichiometric film with a hardness of 24 ± 3 GPa was synthesized, closely matching the rule of mixtures for the binary constituents. Additionally, ab-initio calculations validated the experimental mechanical property findings. Overall, the synthesis and property trends of (HfNbTaTiZr)C$_x$ closely mirrored those of binary counterparts. Unfortunately, as with other carbides, excess carbon rapidly precipitated at methane flow rates slightly (2.5%) higher than the stoichiometric flow rate.

The sudden onset of excess carbon precipitation stymied the rapid and facile synthesis of near-stoichiometric multicomponent carbides. Consequently, the deposition process needed to be improved...
before studying other compositions. A study of gas flows and pressures determined that operating with a modest fixed argon pressure (5–10 mT) increased deposition rate and could reduce target poisoning and carbon precipitation. Additionally, the results indicated that most of the methane was being consumed by the growing carbide film; however, partial pressure control was not feasible with the chamber's configuration. As a result, the best carbon control strategy was determined to be a combination of carefully regulated methane (flow rate) and metal (sputter rate) fluxes.

Conventional temperature and pressure based microstructural development strategies were not feasible for use with reactively sputtered high entropy carbides. Fortunately, tunable high energy ion bombardment was demonstrated to be a viable alternative, influencing the microstructure, stress, and crystallography of the growing carbide films. The increased plasma densities, fixed energetics, and consistent energetics of high power impulse magnetron sputtering (HiPIMS) produced carbide films which were more microstructurally and crystallographically consistent than conventionally sputtered films. Simultaneous power and voltage regulation of the HiPIMS process resulted in more consistent deposition rates than the power regulation of conventional sputtering processes. Furthermore, films deposited with HiPIMS exhibited a much more gradual onset of excess carbon precipitation than RF sputtered counterparts.

Asynchronously patterned pulsed sputtering (APPS) was developed based on the flux and energetic decoupling of HiPIMS. Conventional co-sputtering is rife with tedious calibrations and changing energetics. With conventional sputtering techniques, flux is changed by power which changes the sputtering voltage and the energetics of the deposition, resulting in inconsistent film quality. During HiPIMS, the flux is controlled by the frequency, while the energetics are dominated by the pulsing parameters (width and voltage). Asynchronously patterned pulsed sputtering consists of two HiPIMS supplies operating at the same frequency but phase shifted so the plasmas don't interact. One supply skips a fraction of the pulses, changing the time average flux and thus controlling the stoichiometry independently of energetics. APPS was demonstrated to produce linear compositional trends, consistent deposition energetics, and uniform film qualities across the entire stoichiometry range. The development of APPS and reactive APPS enabled the rapid synthesis of ternary systems, facilitating the search for properties of interest such as ductility in (NbW)C.
# Table of Contents

List of Figures viii  
List of Tables xiv  
Acknowledgments xvii  

## Chapter 1  
Introduction 1  
1.1 Motivation .......................................................... 1  
1.2 Dissertation Outline .................................................. 2  

## Chapter 2  
Literature Review 4  
2.1 Ultra-High Temperature Ceramics (UHTCs) .............................. 4  
2.1.1 Introduction to Refractory Materials .................................. 4  
2.1.2 History of UHTCs ...................................................... 5  
2.1.3 Present Challenges and Research in UHTCs .................................. 11  
2.1.4 Carbon Content in Carbide UHTCs ........................................ 16  
2.2 High Entropy Materials .................................................. 18  
2.2.1 High Entropy Alloys .................................................... 18  
2.2.2 High Entropy Ceramics ................................................ 22  
2.3 Sputtering .............................................................. 24  
2.3.1 Diode and Magnetron Sputtering ........................................ 24  
2.3.2 Reactive Sputtering .................................................... 26  
2.3.3 High Power Impulse Magnetron Sputtering (HiPIMS) ....................... 28  
2.3.4 Sputter Deposition of Transition Metal Carbides ........................... 32  

## Chapter 3  
Experimental Methods 36  
3.1 Thin Film Deposition ...................................................... 36  
3.2 X-ray Diffraction (XRD) and Reflectivity (XRR) ............................ 39  
3.3 Scanning Electron Microscopy ............................................. 40  
3.4 Energy Dispersive Spectroscopy (EDS) .................................... 41  
3.5 Raman Spectroscopy ...................................................... 41  
3.6 X-ray Photoelectron Spectroscopy (XPS) .................................. 41  
3.7 Nanoindentation Testing ................................................ 42
## Chapter 4
### Physical and Mechanical Properties of RF Sputtered (HfNbTaTiZr)C

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 Preface</td>
<td>44</td>
</tr>
<tr>
<td>4.2 Introduction</td>
<td>44</td>
</tr>
<tr>
<td>4.3 Experimental Methods</td>
<td>46</td>
</tr>
<tr>
<td>4.3.1 X-ray Photoelectron Spectroscopy (XPS)</td>
<td>46</td>
</tr>
<tr>
<td>4.3.2 Nanoindentation</td>
<td>47</td>
</tr>
<tr>
<td>4.3.3 Computational Methods</td>
<td>47</td>
</tr>
<tr>
<td>4.4 Results and Discussion</td>
<td>49</td>
</tr>
<tr>
<td>4.5 Conclusions</td>
<td>62</td>
</tr>
<tr>
<td>4.6 Acknowledgements</td>
<td>63</td>
</tr>
</tbody>
</table>

## Chapter 5
### Refining the High Entropy Carbide Reactive Sputtering Process

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.1 Introduction</td>
<td>64</td>
</tr>
<tr>
<td>5.2 Regulating the Methane to Carbide Reaction</td>
<td>65</td>
</tr>
<tr>
<td>5.2.1 Decoupling Methane and Argon Partial Pressure</td>
<td>66</td>
</tr>
<tr>
<td>5.2.2 Exploring the Role of Sputtering Gas Partial Pressure</td>
<td>69</td>
</tr>
<tr>
<td>5.2.3 Determining the Flow Rate and Gas Consumption Regime</td>
<td>71</td>
</tr>
<tr>
<td>5.2.4 Understanding the Contribution of Methane Flow</td>
<td>73</td>
</tr>
<tr>
<td>5.2.5 Refining the Gas Control Approach</td>
<td>76</td>
</tr>
<tr>
<td>5.3 Influence of Tunable Deposition Energetics on Carbide Film Growth</td>
<td>78</td>
</tr>
<tr>
<td>5.3.1 Microstructural Trends in Physical Vapor Deposited Films</td>
<td>78</td>
</tr>
<tr>
<td>5.3.2 Impact of High Energy Ion Bombardment During Sputtering of Carbide Films</td>
<td>79</td>
</tr>
<tr>
<td>5.4 Prospect of Expanding the Stoichiometric Process Window with High Power Impulse Magnetron Sputtering (HiPIMS)</td>
<td>84</td>
</tr>
<tr>
<td>5.4.1 Precedent for the HiPIMS Deposition of Transition Metal Carbides</td>
<td>84</td>
</tr>
<tr>
<td>5.4.2 Sputtered Flux Stability During HiPIMS</td>
<td>85</td>
</tr>
<tr>
<td>5.4.3 Reactive Bipolar HiPIMS of High Entropy Transition Metal Carbides</td>
<td>87</td>
</tr>
<tr>
<td>5.4.4 Influence of Bipolar HiPIMS on Sputtered Transition Metal Carbides</td>
<td>92</td>
</tr>
<tr>
<td>5.5 Conclusions</td>
<td>94</td>
</tr>
</tbody>
</table>

## Chapter 6
### Asynchronously Patterned Pulsed Sputtering (APPS): A Novel Co-Sputtering Technique

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.1 Preface</td>
<td>95</td>
</tr>
<tr>
<td>6.2 Introduction</td>
<td>95</td>
</tr>
<tr>
<td>6.3 Design</td>
<td>97</td>
</tr>
<tr>
<td>6.4 Operation and Application to NbW</td>
<td>97</td>
</tr>
<tr>
<td>6.5 Results</td>
<td>103</td>
</tr>
<tr>
<td>6.6 Conclusions</td>
<td>106</td>
</tr>
</tbody>
</table>

## Chapter 7
### Exploring the (NbW)C System with Reactive Asynchronously Patterned Pulsed Sputtering

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.1 Preface</td>
<td>107</td>
</tr>
<tr>
<td>7.2 Introduction</td>
<td>107</td>
</tr>
<tr>
<td>7.3 Experimental Details</td>
<td>109</td>
</tr>
</tbody>
</table>
7.4 Results and Discussion ................................................. 114
7.5 Conclusions ............................................................. 120

Chapter 8
Conclusions and Future Work ........................................... 121
8.1 Conclusions ............................................................. 121
  8.1.1 Microstructure-Stoichiometry-Property Relations in High Entropy Carbide Films 121
  8.1.2 Refining the High Entropy Carbide Deposition Process ................................. 122
  8.1.3 Development of Novel Pulsed Co-Sputtering Techniques ............................. 123
8.2 Future Work ............................................................ 125
  8.2.1 Advancing Asynchronously Patterned Pulsed Sputtering ......................... 125
  8.2.2 Investigating Tough Carbonitrides ....................................................... 127
  8.2.3 Exploring High Power Pulsed Radio Frequency (RF) Magnetron Sputtering .... 128

Appendix A
Supplementary Data for the Properties of RF Sputtered (HfNbTaTiZr)C .............. 131
  A.1 Quantifying Stoichiometry of the Carbide Films ........................................ 131
  A.2 Verifying the Precipitation of Excess Carbon ........................................... 132
  A.3 Changes in Cross-Sectional Microstructure ............................................. 132

Appendix B
Python Script for Generation of APPS Waveforms ........................................ 134

References ................................................................. 137
List of Figures

2.1 Henri Moissan and an electric arc furnace used to synthesize many of the transition metal carbides during his pursuit of synthetic diamond. Photograph is in the public domain.37 .......................................................... 6

2.2 Prototypical crystal structures for UHTC materials. Large red atoms represent a transition metal, and smaller gray atoms are boron, carbon, or nitrogen. The rocksalt structure, left, is formed by most of the nitrides and carbides. The aluminum diboride structure, right, is a layered structure formed by the refractory diboride systems. Metal-metal bonds are hidden for clarity. ........................................................................................................ 7

2.3 Schematic representations of the oxide scale (light gray) on a metal (dark blue) as a function of Pilling-Bedworth ratio. Below 1, the scale is patchy with regions of exposed metal between oxide grains. Between 1 and 2, the oxide forms over the entire surface, protecting the underlying metal. Above 2, the oxide grains impinge with high stresses, causing cracking and delamination. ............................................................................................... 9

2.4 Schematic representation of the phases present during high temperature oxidation of a diboride/SiC composite. Oxides form near the interface with atmosphere, with evaporation occurring at the very surface. The inward diffusion of oxygen is hindered by the borosilicate glass phase. Gasses build beneath the oxide layers and diffuse to the surface through the glass. The skeletal MO$_2$ phase helps retain the molten borosilicate glass layer. Figure adapted from Parthasarathy et al.65 ......................................................... 10

2.5 Photograph of a three-component UHTC strake used during the SHARP-B2 test. The three compositionally distinct segments are labeled. Image is in the public domain.15 ........................................... 12

2.6 Isothermal mass gain at 1300°C plotted as a function of time for ZrB$_2$/SiC composites with various diboride additives (10 mol.%). Additions of oxidation prone diborides reduces the total oxidative mass gain of the composite. Data replotted from Talmy et al.59,79,80 .................................................................................................................. 13

2.7 Hardness as a function of carbon content for and metal species for Group IVB and VB metal carbides. Monotonic increases are seen for Group IVB metals and VC while parabolic trends are observed for NbC and TaC. The origins of this trend remain under investigation to this day.103,104 Data replotted from Vinitskii.80,103,105 ................................................ 17
2.8 Annual publications on the topics "high entropy alloy" and "high entropy alloys" by year, since 2004. Publications in the field have grown exponentially over the last 15 years. Data is from Web of Science analysis tools. .......................................................... 21

2.9 Schematic representation of the mechanism of sputtering. The plasma body contains positive ions (in this case Ar\(^+\)) which are accelerated across the cathode sheath by an electrostatic potential from the power supply. The impact of the ion with the target surface causes a cascade of collisions in the target. This cascade leads to the ejection or sputtering of atoms from the target into a vapor. Figure adapted from Mahan.\(^{156}\) ........ 24

2.10 Schematic diagram of a sputtering system with DC and RF sputtering capability. DC sputtering uses a DC power supply while RF sputtering uses an RF power supply in conjunction with a capacitive matching network that maximizes power transfer while developing a DC self-bias. This DC self-bias arises from the asymmetry in the I-V response of the diode sputtering process. In this system the substrate and vacuum chamber are grounded together and serve as the anode of the system. Figure adapted from Mahan.\(^{156}\) .......................................................... 25

2.11 Schematic representations of the hysteretic behavior observed in reactive sputtering processes. (a) reactive gas pressure, (b) reactive gas consumption rate, and (c) sputtering rate are plotted as a function of reactive gas flow rate. Flow \(f_1\) is the point at which the process switches from metallic to compound mode with increasing reactive gas flow. Flowrate \(f_2\) is the point at which the process returns to a metallic sputtering mode with decreasing reactive gas flow. The no discharge trace represents the partial pressure of the reactive gas if none of it was consumed by the sputtering process. Figure adapted from Safi.\(^{161}\) .......................................................... 27

2.12 Plot of pulsed sputtering techniques in duty cycle–peak power density space. Direct current magnetron sputtering (DCMS), pulsed DCMS, modulated pulsed power (MPP), high power impulse magnetron sputtering (HiPIMS) are plotted in filled shapes. The high power pulsed magnetron sputtering (HPPIPS) and direct current magnetron sputtering (DCMS) ranges are shown at the bottom. The DCMS limit represents the maximum peak power density at 100% duty cycle before target and cathode damage occur. The average power density indicates the maximum peak power density that can be applied as a function of reduced duty cycle. Figure adapted from Gudmundsson et al.\(^{168}\) ....... 29

2.13 Comparison of ion energy fluxes measured during DCMS and HPPIPS of a Cr-Al-C target. Both techniques used the same time-averaged power density but a 162-fold difference in peak power density (labeled). An increased energy flux and transition from gas species to target species is observed with this increase in peak power density. Data replotted from Rueß et al.\(^{175}\) .......................................................... 30

2.14 Ion energy distribution functions (IEDFs) for \(^{48}\text{Ti}^+\) measured during bipolar HiPIMS plotted as a function of positive pulse voltage. Replotted from Keraudy et al.\(^{80,182,184}\) ....... 31
2.15 Illustrated representation of the microstructural development in sputtered carbide films as a function of increasing carbon content. Small, dark circles represent carbon while large, light circles represent a transition metal. At low carbon contents, films are phase pure carbide. At moderate carbon contents, excess carbon begins to form a thin layer along grain boundaries. At high carbon contents, the excess carbon region broadens, and the film becomes a carbide-carbon nanocomposite. In all cases some carbon vacancies are present, albeit decreasing in concentration with increasing carbon content. Illustration inspired by Jansson & Lewin.19

2.16 Carbon stoichiometry as a function of acetylene flow for TiC films synthesized by DCMS (black) and HiPIMS (red). Left shows the total carbon to titanium ratio, right shows the excess carbon (C-C bonds) to total carbon ratio. DCMS results in a rapid increase in total carbon and excess carbon with increasing acetylene flow. HiPIMS films exhibit a process window where total carbon content changes gradually and excess carbon content is low (<20%). Data replotted from Samuelsson et al.80,201

3.1 External view of reactive magnetron sputtering chamber with key components labeled.

3.2 XPS spectra as a function of carbon content for the Ta4f and C1s orbitals. The Ta 4f is split into the 4f_{5/2} and 4f_{7/2} orbitals. The C 1s peak is split in a lower binding energy C-M bonding peak and a higher binding energy C-C bonding peak. The black dots are experimental data, the blue and green lines are individual peak fits, and the red line is the sum of both peak fits. For the C1s peaks with only a red line, a single peak was fit.

4.1 X-ray diffraction patterns from (HfNbTaTiZr)C_x films deposited at a range of methane flows using HiPIMS. Patterns are arranged as a function of increasing methane flow from 0.5 sccm (bottom, light red) to 5.5 sccm (top, blue). RS denotes peaks which correspond to the rocksalt carbide crystal structure. X-ray artifacts and secondary wavelengths (CuKβ, W Lα) are denoted by ‡.

4.2 High resolution XPS spectra as a function of carbon content for the C1s and Ta4f orbitals. The C1s peak is split in a lower binding energy C-M bonding peak and a higher binding energy C-C bonding peak. The Ta4f is split into the 4f_{5/2} and 4f_{7/2} orbitals. The black dots are experimental data, the blue and green lines are individual peak fits, and the red line is the sum of both peak fits. For the C1s peaks with only a red line, a single peak was fit.

4.3 Carbon stoichiometry analysis from the high resolution XPS data as a function of methane flow. The black trace is the as-measured metal-bonded carbon content, the red trace is the estimated metal-bonded carbon content after accounting for presputtering effects, and the blue trace is the as-measured total carbon content.

4.4 SEM micrographs of (HfNbTaTiZr)C_x films deposited with a range of methane flows.

4.5 Low angle annular dark field (LAADF) and annular dark field (ADF) transmission electron micrographs of (HfNbTaTiZr)C_x samples deposited with 2.5 (left) and 3.0 (right) sccm of methane. Some of the stacking faults and twin boundaries present in the 2.5 sccm sample are circled or labeled with arrows.
4.6 HAADF micrograph and corresponding STEM energy dispersive spectroscopy (EDS) elemental maps collected from the (HfNbTaTiZr)C_x film deposited with 2.5 sccm of methane. A titanium-rich grain boundary region is circled in the titanium map.

4.7 Atomic resolution micrographs and STEM electron energy loss spectroscopy (EELS) maps of (HfNbTaTiZr)C_x films deposited with 2.5 and 3 sccm of methane. The EELS maps for carbon, titanium, and oxygen were collected in the boxed regions of each micrograph.

4.8 4D STEM diffraction patterns (left) from a grain (G) and grain boundary (GB) in the (HfNbTaTiZr)C_x film deposited with 3 sccm of methane. The squares in the micrograph (right) denote the locations that these patterns were collected from.

4.9 Hardness values from nanoindentation experiments (Exp.) and density functional theory calculations (DFT) plotted as a function of the methane flow rate.

4.10 The electronic density of states (DOS) of (HfNbTaTiZr)C_x presented as a function of carbon stoichiometry. The total density of states with 50, 70, 90, and 100% carbon occupancy (left). The partial density of states (pDOS) with 100% of carbon sites occupied (middle). The partial density of states (pDOS) with 70% of carbon occupancy (right). E_f marks the Fermi level in the density of states (fixed at 0 eV). P_gap denotes the location of the pseudogap, a minimum in the DOS that occurs between bonding and non-bonding/anti-bonding states. ‡ indicates the position of new energy states generated due to carbon vacancies.

5.1 X-ray diffraction patterns from (HfNbTaTiZr)_x films deposited with a total pressure (bottom, red) or argon partial pressure (top, black) of 5 mT. Both films were deposited with 20 sccm of Ar and 2.75 sccm of CH_4. RS denotes peaks which correspond to the rocksalt carbide crystal structure. X-ray artifacts and secondary wavelengths (Cu_Kβ, W_Lα) are denoted by †.

5.2 Scanning electron micrographs of (HfNbTaTiZr)_x films deposited with a total pressure (left) or argon partial pressure (right) of 5 mT. Both films were deposited with 20 sccm of Ar and 2.75 sccm of CH_4.

5.3 X-ray diffraction patterns from (HfNbTaTiZr)C_x films deposited with 2.5 (bottom, red), 5 (middle, black), and 10 (top, blue) mT of argon while maintaining a fixed methane flow (2.75 sccm) and partial pressure (1.2 mT). RS denotes peaks which correspond to the rocksalt carbide crystal structure. X-ray artifacts and secondary wavelengths (Cu_Kβ, W_Lα) are denoted by †.

5.4 X-ray diffraction patterns from (HfNbTaTiZr)C_x films deposited across an 8 fold change in flow magnitude (doubling with each successive trace from bottom to top) while maintaining a fixed 20:2.75 Ar/CH_4 flow ratio and argon partial pressure (5 mT). RS denotes peaks which correspond to the rocksalt carbide crystal structure. X-ray artifacts and secondary wavelengths (Cu_Kβ, W_Lα) are denoted by †.
5.5 X-ray diffraction patterns from (HfNbTaTiZr)C<sub>x</sub> films deposited with fixed argon (5 mT) and reactive gas (1.2 mT) partial pressures arranged as a function of increasing gas flow (bottom to top). RS denotes peaks which correspond to the rocksalt carbide crystal structure. X-ray artifacts and secondary wavelengths (Cu<sup>Kβ</sup>, W<sup>Lα</sup>) are denoted by ♦. 75

5.6 Scanning electron micrographs of (HfNbTaTiZr)<sub>x</sub> films deposited with fixed argon (5 mT) and reactive gas (1.2 mT) partial pressures arranged as a function of increasing gas flow (left to right). 75

5.7 X-ray diffraction patterns from (HfNbTaTiZr)C<sub>x</sub> films deposited using bipolar HiPIMS. Patterns are arranged as a function of increasing kick voltage from 20 V (bottom, red) to 150 V (top, light blue). RS denotes peaks which correspond to the rocksalt carbide crystal structure. X-ray artifacts and secondary wavelengths (Cu<sup>Kβ</sup>, W<sup>Lα</sup>) are denoted by ♦. 80

5.8 Scanning electron micrographs of (HfNbTaTiZr)C<sub>x</sub> films deposited using bipolar HiPIMS with a range of positive pulse voltages from 20 (upper left) to 150 (lower right) volts. 82

5.9 X-ray diffraction patterns from (HfNbTaTiZr)C<sub>x</sub> films deposited at a range of methane flows using HiPIMS. Patterns are arranged as a function of increasing methane flow from 1.0 sccm (bottom, light red) to 2.8 sccm (top, light blue). RS denotes peaks which correspond to the rocksalt carbide crystal structure. X-ray artifacts and secondary wavelengths (Cu<sup>Kβ</sup>, W<sup>Lα</sup>) are denoted by ♦. 89

5.10 Raman spectra of (HfNbTaTiZr)C<sub>x</sub> films deposited with HiPIMS, plotted as a function of methane flow. D and G correspond to the locations of the D and G Raman modes of excess carbon in the system. Spectra are linearly offset for clarity. 90

5.11 Scanning electron micrographs of (HfNbTaTiZr)C<sub>x</sub> films deposited with HiPIMS, arranged as a function of methane flow. 91

6.1 Schematic representation of applied voltage as a function of time for (a) DC sputtering, (b) HiPIMS operating at different rates leading to variable degrees of overlap, (c) HiPIMS operating at the same rate leading to no overlap but restricting energetic control (narrower pulse width), and (d) APPS leading to no overlap and independent energetic and flux control. 96

6.2 Schematic layout of the experimental setup. Arrows point in the direction of power or information transfer. Solid and dotted lines distinguish between connections to the two supplies. Colors correspond with the connections. 98

6.3 X-ray diffraction patterns of NbW alloys as a function of increasing intended at. % niobium. Peaks associated with the BCC metal phase shift to lower angles as the fraction of Nb increases the lattice parameter. Variations in the presence and intensity of the \{2 2 2\} BCC peak are observed as a function of composition. X-ray artifacts and secondary wavelengths (Cu<sup>Kβ</sup>, W<sup>Lα</sup>) are denoted by ♦. 104

6.4 Experimental niobium concentration (blue, left) and film density (red, right) of APPS deposited NbW films as a function of intended niobium concentration. Linear regression coefficients are listed and plotted for both datasets. 105
7.1 Concentration of niobium (metals basis) as a function of the percentage of total APPS mass flow rate. The three traces represent samples with intended Nb concentrations of 30% (red, bottom), 50% (blue, middle), and 70% (blue, top).

7.2 X-ray diffraction patterns of (Nb,W)_{1-y}C_x films deposited with reactive APPS. Patterns are clustered into 3 groups of 5 by intended niobium content: 30% (red, bottom), 50% (black, middle), and 70% (blue, top). Within each of these groups of 5, the patterns are stacked in order of increasing methane flow: 80% of the total APPS mass flow rate (bottom, lightest) to 120% (top, darkest) in steps of 10%. RS denotes peaks which correspond to the rocksalt carbide crystal structure. X-ray artifacts and secondary wavelengths (CuK\beta, WL\alpha) are denoted by †.

7.3 SEM micrographs of (Nb,W)_{1-y}C_x films deposited with reactive APPS arranged by increasing niobium content (left to right) and percentage of total APPS mass flow rate (m_R,T, top to bottom).

A.1 Raman spectra for (HfNbTaTiZr)C_x films plotted as a function of the methane flow rate. D and G correspond to the locations of the D and G Raman modes of excess carbon in the system. Spectra are linearly offset for clarity.

A.2 SEM cross-sectional micrographs of (HfNbTaTiZr)C_x samples deposited with 3.0 and 5.5 sccm of methane.
# List of Tables

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Elemental and binary materials with melting points in excess of 3000 °C.²,³,²³</td>
<td>4</td>
</tr>
<tr>
<td>3.1</td>
<td>X-ray diffraction and reflectivity slit and mask configurations</td>
<td>39</td>
</tr>
<tr>
<td>3.2</td>
<td>Iridium sputtering conditions used to coat samples for scanning electron microscopy</td>
<td>41</td>
</tr>
<tr>
<td>5.1</td>
<td>Flow rates and partial pressures used to study the impact of sputtering gas flow rate and partial pressure on the carburization of (HfNbTaTiZr)Cx films.</td>
<td>69</td>
</tr>
<tr>
<td>5.2</td>
<td>Flow rates and partial pressures used to study the impact of flow rate magnitude (at fixed flow ratio) on the carburization of (HfNbTaTiZr)Cx films.</td>
<td>72</td>
</tr>
<tr>
<td>5.3</td>
<td>Flow rates and partial pressures used to study the impact of flow rate magnitude (at fixed partial pressures) on the carburization of (HfNbTaTiZr)Cx films.</td>
<td>74</td>
</tr>
<tr>
<td>5.4</td>
<td>Source conditions used to deposit (HfNbTaTiZr)Cx films with a range of ionic bombardment energies</td>
<td>80</td>
</tr>
<tr>
<td>5.5</td>
<td>Chamber conditions and sputtering durations used to deposit (HfNbTaTiZr)Cx films with a range of ionic bombardment energies</td>
<td>80</td>
</tr>
<tr>
<td>5.6</td>
<td>Interplanar spacing, integrated intensity, and full width at half maximum measured from the {1 1 1} peak of the X-ray diffraction patterns plotted in Figure 5.7 Out-of-plane strain (positive is tensile) and relative intensity are calculated with respect to the sample deposited with a 20 V positive pulse.</td>
<td>82</td>
</tr>
<tr>
<td>5.7</td>
<td>Source conditions used to deposit (HfNbTaTiZr)Cx films with HiPIMS over a range of methane flow rates.</td>
<td>88</td>
</tr>
<tr>
<td>5.8</td>
<td>Chamber conditions and sputtering durations used to deposit (HfNbTaTiZr)Cx films with HiPIMS over a range of methane flow rates.</td>
<td>88</td>
</tr>
<tr>
<td>6.1</td>
<td>Source parameters for Nb and W flux calibration film depositions</td>
<td>99</td>
</tr>
<tr>
<td>6.2</td>
<td>Chamber conditions and sputtering durations for Nb and W flux calibration film depositions</td>
<td>99</td>
</tr>
</tbody>
</table>
6.3 Calculation of metal pulse flux for Nb and W films. Volume per formula unit of Nb and W determined from International Center for Diffraction Data (ICDD) PDF cards. The volume per formula unit of WO$_3$ was derived from the density and molar mass.

6.4 Sample order, intended composition, theoretical volume (Vegard’s law) per formula unit, total dose for 100 nm, and pulse quantities for NbW alloys.

6.5 Control frequency and pulse rates (rounded to 1 Hz) of each target based on intended composition. The deposition time is determined from the pulses (Table 6.4) divided by pulse rate.

6.6 The patterned species, pulse ratio, pulse train length, and quantity of pulses and skips used to deposit NbW films with APPS. The pulse train length, pulses, and skips have already been divided by the greatest common denominator.

6.7 Pulse and skip patterns used for each composition in this work. The patterns are structured as n[p,s,p,s,…] where n (if present) is the number of times to repeat the portion in brackets, p is the number of pulses in a row, and s is the number of skipped pulses in a row. Asterisks between n and opening brackets, and commas after closing brackets are required for the Python script but omitted for clarity.

7.1 Source parameters and methane flows for NbC and WC flux calibration film depositions.

7.2 Chamber conditions and sputtering durations for NbC and WC flux calibration film depositions.

7.3 Calculation of metal atom pulse fluxes used to deposit (Nb$_{0.5}$W$_{0.3}$)$_x$ films with R-APPS.

7.4 Calculation of metal atom pulse fluxes used to deposit (Nb$_{0.7}$W$_{0.3}$)$_x$ and (Nb$_{0.3}$W$_{0.7}$)$_x$ films with R-APPS.

7.5 APPS pulsing parameters used to deposit (Nb$_y$W$_{1-y}$)$_x$ films, listed in order of deposition. The tungsten source always operates at the control frequency and niobium is always the patterned source.

7.6 Frequency ratios and R-APPS methane mass flow rates for the (Nb$_y$W$_{1-y}$)$_x$ films deposited in this work.

7.7 Linear regression coefficients for the dependence of atomic percent Nb on the percentage of flux normalized methane flow. The right most column is the mean measured W percentage.

8.1 Tungsten deposition rate as a function of pre-sputtering time following deposition conditions in Chapter 6. The volume per formula unit of W is ~30% that of WO$_3$. The equivalent thickness (of metal) is calculated as $d_W + 0.3d_{WO_3}$.

A.1 Metal stoichiometry of the sample deposited with 2.5 sccm of methane, as determined by electron probe microanalysis.
A.2 Metal to bonded carbon stoichiometry of commercially available TaC and TiC powders before and after 3 keV Ar⁺ presputtering. .............................. 132
I would like to thank my parents Karen and Todd and my sister Brittany for their unwavering support of me throughout this entire process.

Throughout my first 8 years of knowing him, Professor Jon-Paul Maria has been highly influential on my career path and a valuable mentor. His lab provided by first introduction to thin films back in 2012 and I have been in the field ever since. In addition to training me as a scientist, he gave me opportunities to flourish as an engineer. Additionally, I always appreciated his "revisionist history," approach to presentations; he is a master of organizing data in a way that tells a compelling story.

The Office of Naval Research, our program manager Dr. Eric Wuchina, and the National Science Foundation have my gratitude for supporting this work. This material is based on work supported by the Office of Naval Research Multidisciplinary University Research Initiative under Grant No. N00014-15-1-2863 and the National Science Foundation Graduate Research Fellowship under Grant No. DGE-1255832. Any opinions, findings, and conclusions or recommendations expressed in this material are those of the author(s) and do not necessarily reflect the views of the Office of Naval Research or the National Science Foundation.

I had the opportunity to collaborate with a team that spanned many states and universities as part of the MURI grant that funded this work. I would like to thank the members of the Curtarolo group at Duke University; the Brenner group at North Carolina State University; the Vecchio and Luo groups at the University of California, San Diego; and the Hopkins and Opila groups at the University of Virginia for their valuable collaboration and feedback throughout this project.

Thank you to all of the staff at Penn State's Materials Characterization Laboratory and Huck Life Sciences Core Facilities. I would especially like to acknowledge Julie Anderson, Wes Auker, and Trevor Clark for helping me make the most of my time on the electron microscopes.

I would like to thank all of friends and colleagues over my 3 stints in the Maria group: Angela Cleri, Nicole Estrich, Kevin Ferri, Richard Floyd, Petra Hanusova, David Harris, John Hayden, David Hook, Delower Hossain, Xiayou Kang, Kyle Kelley, George Kotsonis, Sarah Lowum, William Luke, Edward Mily, Joshua Nordlander, Elizabeth Paisley, Christina Rost, Evyn Lee Routh, Evan Runnerstrom, Edward Sachet, Christopher Shelton, and Alexander Smith. A special thanks goes to Delower Hossain, who worked closely with me on this project for the majority of my studies.

Finally, I would like to thank my innumerable friends I made throughout my graduate school career including, but not limited to, the members of the Susan Trolier-McKinstry Group, my cohort from 2014, and my office and lab mates in Steidle Building and the Millennium Science Complex.
Dedication

To my grandparents Dave, JoAnn, Kenny, and Lee who saw me begin this chapter of my life but were unable to see me complete it.
1.1 Motivation

The demand for new refractory materials is increasing in tandem with the growing spaceflight industry and resurgence of interest in hypersonic flight. Ultra-high temperature ceramics (UHTCs) exhibiting a complex balance of mechanical, thermal, chemical and physical properties are necessary for both the leading edges (heated by friction from the air) and the propulsion systems of hypersonic vehicles.\textsuperscript{1,2}

There are a large range of materials available for use at temperatures up to 2000 °C, including numerous metals, oxides, nitrides, carbides, silicides, and other binary compounds. However, when temperatures exceed 3000 °C, the quantity of materials that merely won't melt (ignoring all other property requirements) drops to under 20.\textsuperscript{2,3} At these temperatures, a few elements, one oxide, boron nitride, and a range of binary Group IVB and VB transition metal carbides, nitrides, and diborides remain solidified.\textsuperscript{2,3} Unfortunately, many of these materials are no longer suitable once other property requirements are considered, leaving very few options. Thus, extensive efforts to develop new UHTC compositions with the proper balance of properties are underway.\textsuperscript{1}

New compositions with several (typically 5) constituents in relatively even quantities are receiving significant research interest. These high entropy alloys and ceramics often have enhanced properties relative to their constituents, including improved hardness,\textsuperscript{4–7} oxidation and corrosion resistance,\textsuperscript{4,8} strength at high temperatures,\textsuperscript{9} and reduced thermal conductivity.\textsuperscript{10–12} Furthermore, some researchers have computationally and experimentally demonstrated that some ternary alloys, such as HfCN and HfTaC, may exhibit melting point enhancement due to entropic effects.\textsuperscript{13,14}

While these high entropy materials systems show great promise for refractory applications, a study on the fundamentals of these materials is necessitated. Studies of bulk UHTCs are often hindered by challenging synthesis processes. The extreme synthesis conditions and reactive nature of the metal constituents often result in materials where the properties are dominated by extrinsic factors, such as uncontrolled microstructure and phase impurities.\textsuperscript{1,15,16} This leads to uncertainty whether the material itself is intrinsically unsuitable, or if processing is limiting the final properties.
These processing challenges are exacerbated when making materials with a large degree of disorder, such as high entropy or sub-stoichiometric carbides. In bulk form, a mixture of metal carbide, metal, and/or carbon powders are reactively sintered and annealed into a ceramic sample. The extreme refractory nature inhibits diffusion and poses significant challenges for the homogenization of these materials into a single phase. Additionally, high entropy phases are often only stable at elevated temperatures, requiring quenching in order to retain the phase at room temperature. The study of these disordered materials necessitates a processing strategy that consistent synthesis of a broad range of compositions, thereby limiting the impacts of extrinsic factors.

Physical vapor deposition (PVD) is a valuable technique for the synthesis of complex, disordered, ultra-refractory materials, such as refractory carbides. Vapor phase synthesis allows for deposition of materials at significantly lower temperatures than conventional processing (often 0.2T_{\text{melt}}) while maintaining intimate chemical mixing.\textsuperscript{17} Additionally, the condensation of high energy gas particles (often several eV) on a comparatively cold substrate tends to favor high temperature phases over low temperature counterparts.\textsuperscript{17–19} This rapid quenching is particularly advantageous for the formation of high entropy phases, which are often metastable at room temperature.\textsuperscript{17,18,20}

Of the physical vapor deposition techniques, sputtering is the most promising strategy for carbide synthesis. Reactive sputtering of a metallic target in a hydrocarbon gas enables control of the carbon content of the resulting film, facilitating fundamental studies on the properties of multicomponent carbides as a function of carbon stoichiometry. However, sputter deposition of complex carbides does pose some challenges with respect to accurate stoichiometry control. Unlike other reactive sputtering processes, such as those for oxides or nitrides, carbon can precipitate as a secondary phase in the films, hindering functional properties.\textsuperscript{19,21} Furthermore, the strong covalent metal-carbon bonds change the sputter yield of the target surface, making co-sputtering of targeted compositions a challenge.\textsuperscript{19,22} Thus, it is necessary to establish a thorough understanding of the processing science required to synthesize multicomponent carbides and other refractory materials before their properties can be fully studied.

1.2 Dissertation Outline

This dissertation focuses on the development of techniques that can be used to deposit multicomponent refractory films. From this central goal, the dissertation can be split into two sections: 1. Reactive deposition of high entropy carbides from alloy targets across broad ranges of carbon stoichiometry and 2. Development of a new pulsed co-sputtering technique to accurately deposit alloys and carbides from elemental targets with considerably simpler calibration than conventional methods.

Chapter 2 is a literature review to provide greater context for the motivation and procedures used in this work. The first section focuses on the common definitions, history, and continuing challenges in the field of ultra-high temperature ceramics. Despite significant research efforts over many decades, there are key limitations which must be overcome or circumvented to further increase operation temperatures.
Some of the most viable strategies at this moment involve the engineering of new compositions. Section 2.2 discusses high entropy alloys, the numerous advantages that have been observed, and possible explanations for these properties. The latter half of this section focuses on high entropy ceramic materials field, including the promising early work on high entropy UHTC materials. The final section introduces sputter deposition with a review of the mechanics of sputtering, an introduction to reactive and high power impulse magnetron sputtering (HiPIMS), and an overview of important considerations when sputtering transition metal carbides.

Chapter 3 discusses the experimental procedures used in this work. This includes the design and configuration of the sputtering chamber, sputtering procedures, sample preparation, and process parameters used for characterization measurements. Experiment specifics such as pressures, flow rates, and sputter parameters will be tabulated when the relevant data are discussed in later chapters.

Chapter 4 describes the synthesis and characterization of radio frequency (RF) magnetron sputtered (HfNbTaTiZr)C_x thin films with chemistries ranging from extremely sub-stoichiometric carbides to carbide-carbon nanocomposite structures. The properties of these films were studied with a wide range of characterization techniques and computational modeling. Unfortunately, stoichiometric films were only achievable over a very narrow methane flow range. This result motivated a thorough study of the processing science of high entropy carbides.

Chapter 5 presents some of the experiments that were undertaken to understand and improve the high entropy carbide sputtering process. The impacts of partial pressure and mass flow of both the sputtering gas and reactive gas were studied to determine which factors in the chamber atmosphere affect carburization. High energy adatom bombardment was examined as an alternative to conventional thermal or pressure based structural modification techniques. Finally, the effects of HiPIMS on the carbon stoichiometry and structural uniformity of films deposited with a broad range of carbon contents were explored. The advantages observed with HiPIMS motivated the development of the new co-sputtering schemes in the following chapters.

Chapter 6 describes development of a new co-sputtering technique, asynchronously patterned pulsed sputtering (APPS). Conventional co-sputtering is fraught with tedious calibrations, nonlinear power-composition trends, and variable deposition energetics. APPS was developed to enable simple calibrations, linear compositional trends, and fixed plasma energetics across the entire composition range. In this chapter, the theory and operation of APPS are introduced and applied to NbW alloys.

Chapter 7 focuses on the application of asynchronously patterned pulsed sputtering to the reactively sputtered (NbW)C_x system. Reactive APPS (R-APPS) enables facile synthesis of broad regions of ternary phase diagrams. This chapter details the synthesis of films with 30, 50, and 70 at. % Nb (metals basis) as a function of carbon stoichiometry.

Chapter 8 summarizes the primary conclusions of this work and provides guidance for further research investigating the sputter deposition of complex and refractory materials systems.
Chapter 2

Literature Review

2.1 Ultra-High Temperature Ceramics (UHTCs)

2.1.1 Introduction to Refractory Materials

There are 100's of refractory materials ($T_{\text{melt}} > 2000\, ^\circ C$) including ceramics and metals, such as $\text{Al}_2\text{O}_3$, Mo, and SiC. Once the threshold of $T_{\text{melt}} > 3000\, ^\circ C$ is crossed, around 20 elemental and binary materials remain (Table 2.1). However, this list rapidly dwindles when a few basic requirements are considered. For instance, Re and Os are too rare and expensive, $\text{ThO}_2$ is radioactive, W and Ta are too dense, and graphite burns at low temperatures. These simple criteria leave only ultra-high temperature ceramics as the final candidates.\textsuperscript{1–3}

Ultra-high temperature ceramics (UHTCs) are most commonly defined as ceramics with melting points in excess of 3000\,^\circ C. However, the use of this definition is not without its uncertainty. There are a broad range of reported melting points for any given UHTC as a consequence of the difficulty in measuring such extreme temperatures, reactions or decompositions that may go undetected, and extreme sensitivity to stoichiometry. For instance, the reported melting points of $\text{TaC}$ and $\text{HfC}$ have varied by 200\,^\circ C while $\text{ZrB}_2$'s has spanned nearly 500\,^\circ C over a century of measurement efforts.\textsuperscript{13,23,24}

Thus, many researchers have considered other definitions for UHTCs. One alternative criterion uses the maximum service temperature in air (frequently above 2000\,^\circ C) to distinguish UHTCs from more

<table>
<thead>
<tr>
<th>Elements</th>
<th>C, Os, Re, Ta, W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borides</td>
<td>$\text{HfB}_2$, $\text{TaB}_2$, $\text{TiB}_2$, $\text{ZrB}_2$</td>
</tr>
<tr>
<td>Carbides</td>
<td>$\text{HfC}$, $\text{NbC}$, $\text{TaC}$, $\text{TiC}$, $\text{ZrC}$</td>
</tr>
<tr>
<td>Nitrides</td>
<td>$\text{HfN}$, $\text{TaN}$, $\text{TiN}$</td>
</tr>
<tr>
<td>Oxides</td>
<td>$\text{ThO}_2$</td>
</tr>
</tbody>
</table>

Table 2.1: Elemental and binary materials with melting points in excess of 3000\,^\circ C.\textsuperscript{2,3,23}
traditional refractory ceramics, such as Al₂O₃, MgO, SiC, and Si₃N₄. A second approach is chemistry based, considering all early transition metal carbides, nitrides, and diborides.²⁴

While the extreme refractory nature of UHTCs is arguably their most renowned property, they exhibit many other desirable characteristics. The strong covalent bonds between metals and nonmetals lead to high hardness, moduli, and strength at extreme temperatures.¹ ² The small size of the nonmetals enables metallic bonding between next-nearest neighbor metal atoms, which leads to higher thermal conductivity and electrical conductivities than refractory oxide counterparts.¹ Additionally some ionic character is present between the metals and nonmetals, ranging from to 7% for TaB₂ to 53% for HfN.²⁵ This mixed covalent-metallic-ionic character leads to a combination of properties typically found in either ceramics or metals rather than a single material, making UHTCs one of the strongest candidates for extreme (thermal, mechanical, chemical, radiation, etc.) environments.

Ultra-high temperature ceramics have received cyclical bursts of research interest. The most notable research efforts, since their discovery at the turn of the 20th century, stem from the United States and USSR during the Cold War/Space Race and contemporary efforts coinciding with the resurgence of interest in hypersonic flight. Prior to the adoption of the term "ultra-high temperature ceramics," this class of materials was known by a broad range of terms including: transition metal borides and carbides, refractory borides and carbides, cermets, and hard metals, among others.²⁴,²⁶–²⁸ In this work, this class of materials will be primarily referred to as UHTCs and the subclasses (refractory) carbides or (di)borides. The following sections will discuss the field of UHTCs and the waves of research interest that have led to the current state of the art. While this dissertation focuses on carbides, discussion of the competing diboride systems is included to provide context with respect to the greater UHTC field.

### 2.1.2 History of UHTCs

#### Discovery of UHTCs

Many of the early developments and discoveries in the field of carbides directly resulted from the chemical study of hardened steel. While blacksmiths have hardened steel since the eras of the Greek and Roman empires, it wasn't until the late 18th century that the roles of carbon in steel were discovered. In 1774, chemist Sven Rinman dissolved iron and steel in acids, leaving behind a substance he called plumbago.²⁹ He attributed the presence of this substance to the charcoal used to fuel the furnaces.²⁹,³⁰ As more scientists studied this substance over the course of the 19th century, they began to conclude that a specific structure, not just presence, of carbon was responsible for the hardening effect.²⁹,³¹ Finally, in the late 19th century, cementite (Fe₃C) was successfully isolated by chemists.²⁶,³²–³⁶

Following this discovery of iron-carbide, other binary carbides, including TiC,²⁷,³⁸ VC,²⁶ and WC,²⁶,³⁹ were quickly isolated by chemists. These "hard metals" piqued the interest of scientists around the

---

¹ In addition to the high phonon thermal conductivity from the strong covalent bonds.
² Plumbago obtained its modern name, carbon, a few decades later.²⁹
world at the turn of the 20th century. Henri Moissan, known for his eponymous phase of SiC, expanded his studies of carbides to include nearly every region of the periodic table (Figure 2.1). His work on the transition metal carbides covered MoC, TiC, VC, WC, and ZrC, among others. Although not the first to discover some of these carbides (NbC, TiC, and ZrC, for instance), Moissan is widely regarded for his prolific contributions to early progress in the field. Shortly thereafter, Tucker & Moody reported the synthesis of ZrB$_2$ in 1901.

Research during the first two decades of the 20th century focused on understanding the chemistry and fundamentals of the hard metals, spearheaded by the works of Moissan and Hönigschmid. In the 1930s, Hägg classified structural trends by systemically studying the X-ray diffraction data of carbides, nitrides, and borides. He found that when the radius ratio of the nonmetal to metal was around 0.59 or less, the resultant structure could be described as a conventional metal lattice (generally FCC or HCP, occasionally BCC or simple hexagonal) with the nonmetals in the interstices. Conversely, when the radius ratio was over 0.59, more complex phases were observed. This critical radius ratio of 0.59 was later termed "Hägg's rule." The UHTCs in Table 2.1 typically form the interstitial FCC / rocksalt (carbides and nitrides) or layered hexagonal AlB$_2$ (diborides) structures shown in Figure 2.2.

---

[III] In his book, *The Electric Furnace*, Moissan summarizes his work on transition metal carbides as well as investigations in alkali, alkaline earth, lanthanide, and uranium carbides. Some of these carbides stemmed from his extensive, albeit unsuccessful, attempts to make synthetic diamond with his electric arc furnace.

[IV] Moissan authored over 600 publications on carbides at the turn of the century.
Ultra-high temperature ceramics were considered to have no practical use when they were first discovered. However, a few decades later, as the incandescent lightbulb rose into prominence, the carbides, nitrides, and diborides were viewed as candidates for filaments, due to their refractory and electrically conductive characteristics. Through these efforts by the lighting industry, the melting points and electrical properties of many UHTCs were established. Additional research during this era investigated the bonding and electronic structures of these compounds.

During this time, synthesis also transitioned from high-temperature fusion of metals and nonmetals to the carbothermal, nitrocarbothermal, and borocarbothermal reduction processes still used today. These solid-state synthesis methods enabled higher yields and purer material than the previous fusion techniques. However, despite these advances in processing and characterization, the use of refractory hard metals as filaments never came to fruition. Nonetheless, carbides eventually found use in the lighting industry as hard materials (WC-Co) for use in tungsten filament drawing dies. The adoption of carbide cermets as industrial tooling was followed by a lull in UHTC research until the 1950s and 60s.

Cold War / Space Race Development of UHTCs

As the Space Race and moon mission rose to prominence in the 50s and 60s, NASA (then NACA) and their Soviet Union counterparts began to look for materials that could be used for both propulsion and atmospheric re-entry. Both agencies quickly realized that the materials technologies available at the time were inadequate for their envisioned applications. For instance, predictions indicated that rocket motors would need materials with melting points in excess of 3300 °C, limiting material choices.
to just a small handful. At the same time, there was a need for thermal protective systems that could span a broad range of temperature and property requirements dependent on geometry and landing configuration. It was clear to NASA and the U.S. Air Force that a study of candidate materials and their properties was necessary to make these visions a reality.

Throughout the 1960s, the U.S. Air Force (USAF) funded a number of studies to develop the refractory carbides and diborides for use as aerospace materials. During this time, a great deal of thermodynamic data, mechanical properties, oxidation behavior, and phase equilibria were measured for carbides, nitrides, and diborides. Rudy investigated over 75 binary and ternary systems, characterizing phases, liquidus projections, and lattice parameters across broad regions of compositional space. The fundamental thermodynamic and thermochemical data produced by Rudy and others during these studies continue to be referenced to this day. During this period it was recognized that many of the carbides, which previously received extensive research interest as hard materials, were significantly less oxidation resistant than diboride counterparts. As such, most research efforts began to focus on understanding the synthesis and processing of diboride based materials.

Around a similar time, the performance of UHTCs in lab environments (i.e. furnace testing with a uniform temperature) began to be correlated with tests that more closely simulated the application environment (i.e. arc-jet tests that impose a heat flux and temperature gradient). During this time characteristics such as oxidation rates, material erosion rates, and oxide stability in extreme, dynamic environments were established. The carbides did receive some renewed interest due to this testing; HfC and ZrC were found to form a protective oxide scale above 1900 °C. However, the diborides were not subject to this narrow temperature range; diborides continued to resist oxidation at the lower temperatures that would also be encountered in a flight plan.

Based on these studies, efforts to understand and improve oxidation resistance were centered around ZrB₂ and HfB₂, the most oxidation resistant diborides. At low temperatures oxygen diffusion is limited by the B₂O₃ liquid, while at high temperatures it is limited by ZrO₂ and HfO₂. Many researchers focused on reducing the oxidation of Zr or Hf by adding materials with low high-temperature oxidation rate, such as Si, Al, Be, and Cr. These elements are typically predicted to produce dense, protective oxide scales by the Pilling-Bedworth ratio:

\[
R_{PB} = \frac{V_{oxide}}{V_{metal}} = \frac{M_{oxide}}{nM_{metal}}\rho_{oxide} \rho_{metal}
\]

The Pilling-Bedworth ratio \( R_{PB} \) is related to the ratio of molar volumes \( V \), or the molar masses \( M \), densities \( \rho \) and number of metal atoms per formula unit of oxide \( n \). The oxide layer does not

---

\(^{(V)}\)Arc-jet testing provides gas and heat fluxes similar to those experienced on a hypersonic craft. Arc-jets consist of a high power (0.1–100 MW) plasma torch fed with a range of gas mixtures from inert to the composition of air. The velocity of the plasma can be in excess of Mach 5 with temperatures of 1000s of degrees. Typically, the UHTC sample is mounted to a cooled mounting stub (simulating the inside of the craft) that leads to a large temperature gradient across the surface. Temperatures at the surface can exceed 3000 °C with temperature gradients in excess of 100 °C/mm.
fully cover the surface when the ratio is less than 1, allowing further oxidation to occur. When the ratio is greater than 2 the molar volume change of the oxide coating is too large, leading to high stresses and flaking of the oxide layer. At intermediate values of 1-2 the oxide coating fully covers and remains on the surface, protecting the metal. This behavior is schematically represented in Figure 2.3.62

At low temperatures these additives did successfully produce an oxide scale that protected the UHTC from oxidation; unfortunately, the same could not be said at higher temperatures. Curiously, researchers found that many of these oxides failed catastrophically at temperatures far lower than anticipated.59 Recently, Opeka et al. sought to explain this behavior by analyzing the vapor phase equilibria of the metal-metal oxide systems. They found that these sacrificial metal additions formed a high suboxide vapor pressure at the metal–metal oxide interface. Underneath the protective oxide scale, the oxygen activity was too low to fully oxidize the suboxide while the scale was too dense for the suboxide vapor to diffuse to regions of higher oxygen activity, providing no means to alleviate pressure. Further increases in the suboxide partial pressure eventually caused delamination of the oxide scale.59

The requisite vapor pressure for this failure event would logically be assumed to be near atmospheric pressure — the force of the scale being pushed onto the metal would equal the force of the vapor pushing it off of the metal. This criterion would predict maximum temperatures ranging from 1865 °C for Si/SiO$_2$ to 2690 °C for Cr/Cr$_2$O$_3$. However, experiments yielded vastly different results: Si/SiO$_2$ failed where expected, but Cr/Cr$_2$O$_3$ failed at 980 °C.59,63

Rather than following the classical mechanics treatment (balance of forces), researchers have found that pressures as low as $10^{-4}$ Pa are adequate to disturb protective oxide scales.59,64 At this pressure all the aforementioned materials would fail under 1000 °C, with the Si/SiO$_2$ interface failing at 750 °C. Yet, the Si/SiO$_2$ based interface is resilient up to near atmospheric pressure (1865 °C).59

To explain this discrepancy, the atomic structure of the scale must be considered. Silica forms a glassy scale instead of a dense crystalline scale, like the other metal oxides. The open, amorphous structure of SiO$_2$ enables the diffusion of molecular SiO vapors through the scale, alleviating pressure at the interface. This diffusion process enables the SiO$_2$ scale to remain resilient and protective until the vapor pressure reaches atmospheric levels.59

However, this analysis (rooted in thermodynamic and vapor pressure equilibria) does not fully explain the behavior of diboride/SiC composites. These composites don’t experience catastrophic
Figure 2.4: Schematic representation of the phases present during high temperature oxidation of a diboride/SiC composite. Oxides form near the interface with atmosphere, with evaporation occurring at the very surface. The inward diffusion of oxygen is hindered by the borosilicate glass phase. Gasses build beneath the oxide layers and diffuse to the surface through the glass. The skeletal MO₂ phase helps retain the molten borosilicate glass layer. Figure adapted from Parthasarathy et al.⁶⁵

oxidation at temperatures in excess of 2000 °C, despite pure SiO₂ scales failing much sooner.⁵⁹,⁶¹,⁶⁵ In order to understand the resilience of these diboride/SiC composites, the roles of all constituent elements must be considered.

Regions of the starting materials (MB₂/SiC) persist at the bottom of the scale, with the first layers of oxide primarily consisting of porous MO₂. The MB₂/MO₂ interface has a relatively low vapor pressure of MO₂(g) (~10 Pa at 2227 °C), preventing delamination of the MO₂ scale from the underlying composite.⁵⁹ The boron from MB₂ oxidizes into B₂O₃ and forms a liquid at the surface of the scale. The temperature gradient across the scale prevents the B₂O₃ vapor pressure from rising to catastrophic levels at the interface, although evaporation does occur at the surface. Some of the boria wets the porous zirconia scale, resisting shear forces due to the favorable surface energy.⁶⁶ SiC oxidizes into CO or CO₂ gas and SiO₂, which forms a glassy layer at the surface. This SiO₂ glass mixes with the molten boria, forming a borosilicate glass, which is silica rich at the surface due to evaporation of the B₂O₃. The porous MO₂ structure prevents the molten glass from sliding off the surface by providing resistance to flow.⁵⁹ Meanwhile, the glass hinders oxygen diffusion through the porous MO₂, reducing the oxidation rate of the underlying material. Further increases in temperature will cause the glass to evaporate from the surface, exposing the porous MO₂ scale (Figure 2.4).

The symbiosis between the crystalline MO₂ and glassy SiO₂/B₂O₃ results in hindered oxidation. At extreme temperatures, the protective scale gradually melts or evaporates away, rather than catastrophically failing from high vapor pressures.⁶¹,⁶⁵,⁶⁷ Since its discovery, many researchers have sought to improve this synergy and further increase the oxidation resistance of diboride/SiC composites (Section 2.1.3).⁵⁹

Research during the Cold War and Space Race produced the compendium of phase diagrams that are used to guide compositional and alloy development in UHTC systems to this day. HfB₂ or ZrB₂/SiC composites were developed, and continue to be investigated, for hypersonic applications due to their favorable oxidation characteristics over broad temperature ranges. These composites also
demonstrated that unpredictable synergistic interactions between materials can lead to significantly enhanced oxidation resistance. Throughout the course of these discoveries, researchers made many advancements in UHTC synthesis and microstructure-processing relationships. Despite significant developments during the Cold War, these discoveries were followed by another hiatus in research activity until the recent resurgence of interest in hypersonic flight. A detailed history of the field of UHTCs from the 1900s through the 1960s can be found in the work of Fahrenholtz.

2.1.3 Present Challenges and Research in UHTCs

Researchers have made significant progress on improving the synthesis, mechanical properties, and oxidation behaviors of UHTC materials over the past few decades. Despite these advancements, there are still a number of limitations in the scientific community's understanding that have both hindered the application of UHTCs and steered the trajectory of on-going research efforts.

During the 1980s, the interest in UHTCs was centered primarily around hypersonic applications, such as scramjets, rocket motors, and atmospheric re-entry vehicles. This interest culminated in programs such as NASA's/USAF's X-15 and X-51 hypersonic vehicles, tested at speeds in excess of Mach 5 (5300 km/h). These designs contained sharp leading edges that could see temperatures in excess of 2000 °C, high heat fluxes (>100 W/cm²), and reactive dissociated gasses. Diboride/SiC composites were seemingly the perfect candidates for the exterior surfaces of these aircraft due to their high thermal conductivities, relatively oxidation resistant scales, and reasonable high temperature strengths. Despite this, more conventional, well-established, materials (e.g. super alloys, carbon-based composites, and silica-based protection) were used for these mission critical components.

While not applied as key structural components, UHTCs have been tested in some real-world hypersonic re-entry scenarios. The SHARP-B2 test conducted by NASA and the USAF used a modified Mk-12A reentry vehicle that could extend and retract UHTC specimens arranged in sharp strakes. Each strake consisted of a ZrB₂/C/SiC tip, ZrB₂/SiC middle, and HfB₂/SiC trailing section (Figure 2.5). A Minuteman III ICBM deployed the reentry vehicle at 740 km above the earth so it could begin its 23 minute, > Mach 22 (>27 000 km/h) flight back to sea level. In order to avoid complete loss of the specimens, one pair of strakes was retracted before ablation began and the other shortly after ablation began (around 2800 °C). Ex-situ analysis, after the recovery, found that half of the specimens failed thermomechanically due to inadequate processing.

The SHARP-B2 test demonstrated the unfortunate reality that UHTCs still aren't suitable for mission critical applications. Oxidation and thermomechanically induced failures are all too frequent and would have devastating consequences on the operation of hypersonic craft. As a result, many researchers are focused on engineering oxidation resistance and improving the synthesis and processing of UHTCs to achieve more consistent mechanical properties.
Oxidation

While diboride-SiC composites have been found to exhibit improved oxidation resistance relative to pure diborides, there is a limited amount that can be achieved without further compositional modifications. Additives that lower oxygen diffusion could hinder the consumption of UHTC or loss of the scale. This can be accomplished by modifying the MO$_2$ at the interface or the glassy SiO$_2$ scale at the surface.

Skeletal MO$_2$ serves as the final barrier to further oxidation of the diboride. At these extreme temperatures MO$_2$ forms a fluorite structured oxide with a large concentration of oxygen vacancies, which facilitate fast oxygen diffusion.\textsuperscript{70–72} Doping can hinder oxygen diffusion by reducing the oxygen vacancy concentration or inducing a structural transition to a low diffusivity phase. Oxygen vacancies are a positive defect (V$_{O}^{\bullet}$) that can be eliminated by adding other positive defects, such as metal dopants of higher valence (M$_2$O$_5$, M = V, Nb, Ta).\textsuperscript{73,74}

Additions of rare earth or alkaline earth elements can make the pyrochlore structure more favorable than the fluorite structure.\textsuperscript{59} The pyrochlore structure is a A$_2$B$_2$O$_7$ or A$_2$B$_2$O$_6$ derivative of the fluorite structure, where the cations occupants and anion vacancies (1/8 or 1/4 of all oxygen sites) are crystallographically ordered. Since the vacancy locations are structural, rather than randomly dispersed, oxygen diffusion is significantly limited relative to a disordered fluorite structure where percolation pathways for oxygen ion conductivity may exist. This strategy was successfully demonstrated in ZrO$_2$ based thermal barrier coatings and shows promise in diboride ceramics.\textsuperscript{59,75–78}
The other approach involves modifying the SiO$_2$/B$_2$O$_3$ glass to inhibit the diffusion of oxidation to the lower layers of the scale. Additives that modify the viscosity, O$_2$ diffusion, or vapor pressure of suboxides would make it more protective. Potential candidates include rare earth or early transition metal oxides.\cite{Talmy1989,Talmy1994,Talmy1996} Talmy et al. demonstrated that modifying ZrB$_2$/SiC ceramics with additions of MB$_2$ (M = Cr, Nb, Ta, Ti, or V) or Ta$_x$Si$_y$ led to enhanced oxidation resistance of the complex ceramic.\cite{Talmy1989,Talmy1994,Talmy1996} Each of these additives are much more oxidation prone than pure ZrB$_2$ when tested individually, but when combined the sum is greater than its parts.\cite{Talmy1989} For instance, ZrB$_2$/SiC modified with 10 mol\% TaB$_2$ gained half the mass that pure ZrB$_2$/SiC did during high temperature oxidation experiments (Figure 2.6).\cite{Talmy1989,Talmy1994}

This behavior occurs because these additives form oxides that are immiscible with the borosilicate glass, leading to the precipitation of microdroplets and creating an "opal glass."\cite{Talmy1989,Talmy1994} The opal glass has increased viscosity and reduced oxygen diffusion relative to the pure borosilicate glass, providing additional protection to the underlying UHTC.\cite{Talmy1989} Talmy et al. found that the characteristics of the surface scale were strongly dependent on the modifier, with some forming core shell structures (Cr) and others multiple crystalline oxides (Nb). In the TaB$_2$ modified composite, 100 µm droplets of borosilicate glass were encapsulated by a matrix of crystalline Ta and Zr oxides.\cite{Talmy1989,Talmy1994} This glass modifying strategy has been successfully applied to a range of other diborides including those of Cr, Ti, and Ta.\cite{Talmy1989}

Carbides were largely written off during the Cold War due to their inferior oxidation resistance relative to diboride counterparts. The pursuit of hypersonic flight has led to renewed interest, with carbides
envisaged for niche applications including rocket nozzles and thrusters. These roles typically require higher thermal and mechanical loads in a significantly less oxidizing environment than aerodynamic control surfaces.\textsuperscript{1,84} Many of the carbides have melting points 500–700 °C higher than the most refractory diborides, making them particularly suitable for the extreme heat fluxes in these roles.\textsuperscript{1,3} Despite interest in less oxidizing applications, researchers are still seeking to improve the oxidation resistance of the carbides. A key limiting factor is the formation of CO and CO\textsubscript{2} gas at the carbide-oxide interface. These gasses lead to large vapor pressures (1 atm at 1730 °C) and formation of a porous metal oxide scale.\textsuperscript{59,85}

One avenue to alleviating this problem is engineering the thin oxycarbide layer at the interface between the carbide and oxide. Oxycarbides have been observed to have a consistent oxygen stoichiometry (i.e. line compound), suggesting they could act as a barrier to oxygen diffusion.\textsuperscript{59,86–88} Rare-earth elements can form both stable carbide and oxycarbide phases; thus, alloying the refractory carbide with rare-earth carbides could provide a path to engineer the oxycarbide layer to inhibit oxygen diffusion and protect the refractory carbide.\textsuperscript{59,89–92} Furthermore, the lanthanide contraction enables the choice of additives that closely match the size of host lattice.\textsuperscript{93}

The exploration of compositional modifications and their ability to hinder oxidation continues to receive significant research interest. High entropy ceramics provide another compositional strategy to tune UHTCs for increased oxidation resistance. These complex compositions provide nearly limitless degrees of freedom to tailor oxidation behavior without sacrificing the critical mechanical or thermal characteristics necessary for an application. High entropy UHTCs are described in greater depth in Section 2.2.2.

**Starting Materials**

The properties of UHTC ceramics are often hindered by factors extrinsic to the UHTC compound itself, including microstructure or secondary phases. The processing behavior of UHTC ceramics, such as sintering characteristics, are often directly related to the quality of the starting materials. Most UHTC ceramics are synthesized from commercially available, carbothermal reduction (Equation (2.2)) derived powders.\textsuperscript{1,27} These powders are typically relatively coarse and have high concentrations of oxygen, nitrogen, and metal impurities (>0.1 wt.%). While it is possible to process these powders into a ceramic, these impurities often hinder sintering, lead to unwanted inclusions, and impair mechanical properties.\textsuperscript{1,15} Many of the thermomechanical failures during the SHARP-B2 test were attributed to these processing limitations.\textsuperscript{15,16} Subsequently, researchers are developing alternative synthesis pathways in order to exact greater control over purity, grain size, surface chemistry, and other characteristics.

\[
\text{MO}_2(s) + \text{B}_2\text{O}_3(l) + 5 \text{C}(s) \rightarrow \text{MB}_2(s) + 5 \text{CO}(g)
\]  \hspace{1cm} (2.2)

Other reduction reaction routes, such as borothermal (Equation (2.3)) and borocarbothermal (Equation (2.4)), have been investigated as alternatives to the carbothermal route. Researchers have reported
that very fine diboride powders (150 nm) can be synthesized from ZrO$_2$ nanopowders and boron at temperatures as low as 1000–1200 °C. However, these powders had residual boron that required temperatures in excess of 1500 °C to remove. This high temperature purification step was associated with growth to 660 nm and a change from faceted to spherical morphology. While high purity (<0.5 wt.% oxygen) powders were obtained, the particle size was larger than desired for sintering.\textsuperscript{94,95} Although the high temperature reduction routes have limitations for powder synthesis, they have been utilized to reduce oxygen content in the final ceramics. For instance, B$_4$C can act as a sintering aid, reducing oxide impurities during the sintering process.\textsuperscript{95}

$$3\text{MO}_2(s) + 10\text{B}(s) \rightarrow 3\text{MB}_2(s) + 2\text{B}_2\text{O}_3(l) \quad (2.3)$$

$$2\text{MO}_2(s) + \text{B}_4\text{C}(s) + 3\text{C}(s) \rightarrow 2\text{MB}_2(s) + 4\text{CO}(g) \quad (2.4)$$

Alternatively, the energetically favorable reaction between metals and boron has been used to synthesize diboride powders near room temperature, with oxygen contents near those of the starting reagents. In some cases, high energy milling provides sufficient energy to instigate the reaction, diffusing boron through the MB$_2$ surface layer into the underlying metal. This diffusion process results in diboride powders that exhibit similar sizes and shapes to the starting metal powders.\textsuperscript{95–97} One limitation of this technique arises from the ductility of the metal species; ball milling can flatten metal particles, leading to elongated diboride powders. However, brittle metal hydrides or chlorides, which decompose to release H$_2$(g) or Cl$_2$(g), can be used to produce a more equiaxed diboride powder.

A third strategy for the creation of UHTC powders is chemical (solution) synthesis. These processes are used when the utmost purity is desired, producing powders ranging from 10–200 nm. Chemical synthesis requires no milling, which avoids incorporation of oxygen or impurities from the milling media. Chemical solution routes typically involve a metal chloride reacting with a boron containing precursor.\textsuperscript{95} Hydrothermal processing of the chemical reaction in Equation (2.5) produced both ZrB$_2$ and HfB$_2$ at temperatures between 500–700 °C.\textsuperscript{98} Meanwhile, sol-gel carbothermal processing has produced 100–200 nm powders at 1500 °C. The intimate mixing of the precursors in solution based techniques favors small particle sizes and low temperature processing relative to solid state approaches.\textsuperscript{99} These processes and polymeric precursor routes also provide an avenue to infiltrate woven SiC fabric with UHTC material, enabling production of fiber strengthened composites with increased fracture toughness.\textsuperscript{1,95}

$$\text{MCl}_4(g) + \text{NaBH}_4(g) \rightarrow \text{MB}_2(s) + 2\text{NaCl}(s) + 3\text{H}_2(g) \quad (2.5)$$

A final area of research, which combines many of the above techniques, is the direct synthesis of composites. Typically, when manufacturing a ZrB$_2$/SiC composite, ZrB$_2$ and SiC powders are synthesized separately, mixed together, and sintered into a ceramic.\textsuperscript{95} A growing area of research is focused on direct synthesis of a composite powder. Displacement reactions, such as Equation (2.6), can produce a ZrB$_2$/SiC
This processing route has enabled direct synthesis of diboride composites with ZrC, MoSi$_2$, BN, and ZrN additives. Additionally, researchers have used sol gel routes to directly produce ZrB$_2$/SiC ceramic powders with other additives.

$$2 \text{Zr} + \text{Si} + 4\text{C} \rightarrow 2\text{ZrB}_2 + \text{SiC}$$

While all of the aforementioned processes have many reports in the literature, they have yet to be applied on an industrial scale. This is primarily a consequence of cost, as carbothermal reduction of transition metals and boron oxide remains the most economical route. As the demands for high temperature properties, purity, sinterability, and microstructural control continue to increase, it is likely that researchers will continue to improve these methods and develop new ones. Some routes, such as solution processing, may find themselves particularly advantageous in the field of ternary to high entropy UHTCs, as they provide a means to achieve intimate mixing of many components while avoiding contamination. Nevertheless, the quality of precursor materials continues to pose a problem to the ultra-high temperature ceramics field.

### 2.1.4 Carbon Content in Carbide UHTCs

Early transition metal carbides are unique in their ability to remain phase stable under extreme carbon deficiency. Fluorite structured cubic ZrO$_2$ is renowned for its ability to accept large concentrations of oxygen vacancies (20% of oxygen sites vacant in its pure form). The transition metal carbides can exceed this vacancy concentration by a factor of 3 with as many as 60% of the carbon sites vacant, albeit sometimes in ordered arrangements.

The bonding of transition metal carbides primarily consists of covalent bonds between the metal-d and carbon-p orbitals. These extremely strong bonds give rise to many of the observed functional properties, including high hardness, melting point, and moduli. Each carbon vacancy removes six covalent bonds from the system, causing the octahedra of metal atoms to distort closer together and compensate with increased metallic bonding character.

In order to maximize the benefits of covalent bonding, carbides are typically synthesized with a stoichiometric ratio of metal and carbon. However, the resulting material typically has a carbon vacancy concentration of a few percent. This is a consequence of the low vacancy formation energy and large entropy gain that make it energetically preferable to form sub-stoichiometric material. Furthermore, the extreme temperatures during processing and use can increase carbon vacancy concentrations. An unexpected increase in the carbon vacancy concentration can have significant impacts on the properties. For instance, the reduction in covalent bonding associated with a carbon vacancy concentration of 30% in HfC can reduce thermal conductivity by 50%, decrease elastic modulus by 20%, and lower the ductile to brittle transition temperature by 1000 °C. Thus, it is critical to understand both how to limit the concentration of carbon vacancies as well as the impacts of those that form.
It is worth noting that the impact of carbon vacancies is not always intuitive in the refractory carbides. For instance, an increased concentration of carbon vacancies results in a monotonic decrease in the hardness of Group IVB carbides, correlating with the removal of covalent bonds (Figure 2.7). However, there are numerous reports that NbC and TaC increase in hardness at some level of substoichiometry, before undergoing the decrease observed in other materials.\textsuperscript{103,105} This trend has been observed by multiple authors, although different amounts of hardening and vacancy concentrations have been reported.\textsuperscript{103,105,106} Some of the early theories for this behavior included filling of d-bands without filling antibonding states,\textsuperscript{103,105} and changing slip systems due to d-d interactions between metal atoms across vacancies.\textsuperscript{103,107}

Since this trend was observed in the 1970s, many researchers have sought to explain this anomalous behavior.\textsuperscript{101,103,104,108,109} More recently, Yu \textit{et al.}, used density functional theory to probe the formation energies and elastic constants of a broad range of substoichiometric carbides. They found a monotonic decrease in both moduli and hardness, as well as a relatively consistent softening rate, in rocksalt carbides with disordered carbon vacancies. Furthermore, they found no anomalous increase in hardness for any of the known ordered substoichiometric phases, including $M_2C$, $M_3C_2$, $M_4C_3$, $M_6C_5$, and $M_8C_7$.\textsuperscript{103}
Many researchers have noticed that the peak in hardness occurs around the stoichiometry of M₆C₅. Prior researchers postulated that both the interaction of ordered M₆C₅ domains with other microstructural features and the higher cohesive energy of the M₆C₅ phase contributed to the enhanced hardness.¹¹⁰,¹¹¹ Yu et al. modified this conclusion, finding that the anomalous hardening is dictated by the domain hardening effects of the ordered M₆C₅ phase precipitating in a disordered rocksalt matrix.¹⁰³

The rise of computational materials science has led to numerous papers expanding on the experimental carbon stoichiometry studies from decades past.⁸⁴,¹⁰³–¹⁰⁵,¹⁰⁸,¹⁰⁹ These efforts have significantly improved the community's understanding of the complex behaviors observed when carbon vacancies are introduced into a binary carbide. With the rapid rise of more complex carbides, it will become important to understand what, if any, changes occur as a consequence of the multicomponent metal sublattice. For instance, carbon vacancies could preferentially cluster around particular metal atoms, or ordered domains could form with a subset of the metal species. Presently, very little research attention has been devoted to carbon stoichiometry in carbides with 2 or more metal species.¹⁴,¹¹²,¹¹³ The importance of studying carbon content in high entropy carbides will be discussed further in Section 2.2.2.

2.2 High Entropy Materials

2.2.1 High Entropy Alloys

With the advent of Bragg's Law in 1913, scientists began to determine the structures of crystalline materials and atomic sizes using diffraction.¹¹⁴ Armed with this new knowledge of atomic sizes and structures, many researchers began to observe trends in the formation of phases and solid solutions, formulating sets of rules that governed these processes. For instance, Goldschmidt analyzed ionic crystals and published the following rules for solid solution formation:¹¹⁵

1. Ions of one element can extensively substitute for another ion in a crystal if the ionic radii are within 15%.
2. Ions within one unit of charge will substitute as long as electroneutrality is preserved. Ions differing by more than one unit of charge will exhibit very limited solubility.
3. When one site of a crystal could be occupied by two different ions, the ion with a higher ionic potential will form a stronger bond and is the preferred occupant.

Pauling expanded on the work of Goldschmidt, developing a set of rules to predict the structure of ionic compounds:¹¹⁶,¹¹⁷

1. Coordination geometry of cations is determined by the cation/anion radius ratio. There is a critical radius ratio for each coordination geometry that will keep the anions from touching.
2. The electrostatic bond strength (charge divided by coordination) of each bond to an ion must add up to the ion's charge. This preserves local electroneutrality in the structure.
3. Corner sharing is preferred over edge and face sharing of polyhedra. Corner sharing keeps cations far apart, lowering electrostatic repulsion.

4. In crystals with multiple cation, cations with high charge and low coordination number tend not to share corners with each other. This increases the distance and decreases the repulsion between highly charged species.

5. Structures are kept simple, with a small quantity of unique repeat units. Each ionic species in the crystal will be most stable in a specific coordination geometry.

Similarly, Hume-Rothery focused on metallic solid solutions, postulating the following criteria for solid solution formation:118

1. The atomic radii of the solute and solvent must be within 15%.
2. The crystal structures of the solute and solvent must be similar.
3. Complete solubility will be achieved when solute and solvent have the same valence. A lower valence solute is more likely to dissolve in a higher valence solvent.
4. The solute and solvent should be similarly electronegative. Large differences can lead to intermetallic formation.

For decades, these rules served as the foundation for the development of new material compositions. They were also capable of predicting the phase stability of many materials far before their industrial relevance was known.20 To this day, these rules continue to be applied when using solid solutions to tune properties of interest such as bandgap in the III-V semiconductor alloy AlN-GaN. Similarly, they can be applied to intentionally form intermetallic structures that will precipitation harden Ni superalloys. The basis of these rules is strongly rooted in the enthalpic term of the Gibbs free energy. The energy of the system can be reduced by limiting strain and electrostatic repulsion, among other factors.

Throughout the advancement of metallurgy, highly engineered alloys with a large diversity of alloying additions have become commonplace. However, most of these elements make up only a small fraction of the total chemical composition. As a result, most alloys are based around a primary element (i.e. Fe, Al, or Ni) or pair of elements (Cu-Zn, Pb-Sn). The primary element(s) provide(s) the core characteristics, while numerous alloying additions fine tune the properties for a particular application.

In the mid-2000s researchers began to break this paradigm, synthesizing alloys with as many as 20 elements in equimolar concentrations. These "high entropy alloys" presented a new multidimensional compositional space that was unexplored by researchers.119,120 Traditionally, mixing a variety of dissimilar elements in equimolar concentrations would be avoided unless a brittle, intermetallic dominated microstructure was desired.

However, Boltzmann's hypothesis indicates that entropy can contribute significantly to the phase stability of a multicomponent, equimolar system.20,119,121,122 The calculation of the configurational entropy for an $n$ component equimolar system is shown in Equation (2.7), where $k_B$ is the Boltzmann
constant, \(x_i\) is the atomic fraction, and \(n\) is the number of species. This leads to a configurational entropy of \(1.61k_B\) for a five-element equimolar system. This entropy of \(1.61k_B\) can provide a meaningful reduction in the Gibbs free energy at realizable temperatures: approximately 13.4 kJ/mol per 1000 K of temperature.

\[
S = -k_B \ln(w) = -k_B \sum_{i=1}^{n} x_i \ln(x_i) \\
= -k_B \left[ \frac{1}{n} \ln \left( \frac{1}{n} \right) + \frac{1}{n} \ln \left( \frac{1}{n} \right) + \frac{1}{n} \ln \left( \frac{1}{n} \right) + \cdots + \frac{1}{n} \ln \left( \frac{1}{n} \right) \right] \\
= -k_B \ln \left( \frac{1}{n} \right) = k_B \ln(n) 
\]  

(2.7)

Yeh et al. defined "high-entropy alloys" (HEAs) as alloys with five or more elements in significant molar fractions (>5 at. %). Equimolar quantities would maximize the entropy of mixing, while fractions of 5-35 at. % would extend the scope of alloy design.\(^{119}\) They reported that high entropy alloys tended to exhibit simple solid solution structures rather than intermetallic phases, contrary to conventional alloys. For instance, CuCoNiCrAlFe alloys formed FCC \((x \leq 0.5)\), FCC and BCC \((0.5 \leq x \leq 0.8)\) and multiple BCC phases \((x \geq 0.8)\) dependent on the Al content. Despite these changes in phase, no complex intermetallic structures were observed at any point.\(^{119}\) At a similar time, Cantor et al. found that equimolar FeCrMnNiCo formed an FCC solid solution during solidification. They also observed that this alloy could dissolve numerous other metals that would not normally dissolve in an FCC lattice, including Nb, Ti, and V.\(^{120}\)

High entropy alloys provided a new, vastly uncharted, compositional space for materials exploration. Researchers rapidly explored this multidimensional space in the years that followed, producing countless alloys that had never been reported before. Since the introduction of the term in 2004, there has been an exponential growth of research as visualized in Figure 2.8. This has led to new studies on fundamental science of high entropy systems as well as countless reports on a wide spectrum of properties of interest. Researchers have developed alloys with enhanced cryogenic fracture toughness, hindered grain growth in nanocrystalline alloys, reduced oxidation, and increased wear resistance among other properties of interest. Furthermore, researchers began to study alloys with boron additions and high entropy alloy-based nitride coatings.\(^{130,131}\)

\(^{[V]}\) The definition "high-entropy" alloys is a topic of contentious debate. The common composition-based definition states that an HEA contains five or more elements in concentrations of 5-35 at. % each.\(^{119,123}\) There is also the entropy definition: the entropy of the ideal solid solution must be \(\geq 1.61R\) (5 elements equimolar), although some relax this to \(1.5R\). Some contend that high-entropy alloys should always be focused on maximizing entropy and thus be equimolar. Others narrow this down further, maintaining that only alloys that form a single solid solution are truly high entropy, while the precipitation of secondary phases indicates a lower entropy state. Many researchers suggest that while some complex compositions may not form a single phase, the newly unlocked regions of phase and microstructural space are still advantageous. This debate has led to alternative names such as multi-principal element alloys (MPEAs) and complex concentrated alloys (CCAs). These terms seek to avoid the controversy of "high-entropy" and instead focus on exploration of this highly multidimensional compositional space, regardless of the phase and microstructural outcomes.\(^{123}\) The term high entropy alloys will refer to equimolar solid solutions in this work.
These novel properties were followed by attempts to determine what features of these new alloys were responsible for the often unpredictable, albeit desirable, outcomes. The scientific community has hypothesized that these unique behaviors are a manifestation of four effects: high entropy, lattice distortion, sluggish diffusion, and the 'cocktail' effect.\textsuperscript{123}

The high entropy effect is the lead concept and argues that the high ideal configurational entropy of a solid solution makes it significantly more energetically favorable than any of the intermetallic phases, enabling the stabilization of elements in atypical crystal structures. The lattice distortion effect hypothesizes that the large range of atom sizes and the randomization of occupancies lead to heavily distorted lattice sites. This distortion is purported to be more extreme than conventional alloys and may further contribute to the configurational entropy of the system. As a consequence of this extreme distortion, hardness and strength should increase due to hindered dislocation motion, while electrical and thermal conductivities will be reduced by scattering from the distorted lattice.\textsuperscript{123,132} Diffusion is predicted to be sluggish, as atoms struggle to diffuse through a highly distorted lattice.\textsuperscript{123} Limited diffusion rates are supported by observations of reduced grain growth\textsuperscript{9,126} and increased oxidation resistance.\textsuperscript{123,127,128}

Finally, the "cocktail" effect, which was coined by Ranganthan, refers to the tendency of HEAs to yield unexpected results.\textsuperscript{123,133} The "cocktail" effect is based on the comparison of HEA metallurgy to gastronomy. Frequently, culinary and bartending experts use combinations of ingredients which seem counter-intuitive, but provide an unpredictable, yet desirable, final outcome. Preconceived notions,
rooted in hundreds of years of metallurgy, often suggest that a mixture of many elements would never yield a desirable outcome. As a result, most metallurgists would shy away from ever synthesizing such an alloy. However, the field of HEAs has demonstrated that unassuming combinations of numerous elements can frequently produce desirable outcomes.

The field of high-entropy alloys is a promising and rapidly evolving field. This section provided only a brief glimpse of a field which is thoroughly covered in the reviews of Miracle & Senkov, Praveen & Kim, Tsai & Yeh, and numerous others.\textsuperscript{(VII)}

2.2.2 High Entropy Ceramics

After the rise of high entropy alloys, researchers began to investigate ceramic counterparts. Some of the earliest work consisted of sputtering high entropy alloy targets in a nitrogen atmosphere to make nitride films.\textsuperscript{131} This was followed by the sputter deposition of HEAs in an oxygen containing atmosphere, forming HCP metal films with dissolved oxygen.\textsuperscript{135} Eventually carbide films were reported in the literature in the early 2010s.\textsuperscript{4,5,22} At this point, reports on high entropy ceramics were relatively sparse and primarily focused on whether additions of carbon, nitrogen, or oxygen could further enhance the properties of the starting HEA.

In 2015, Rost et al. reported the synthesis of an entropy-stabilized oxide. This was the first report in the literature that unambiguously demonstrated the role of high configurational entropy in stabilizing the solid solution phase of a high entropy ceramic composition. Cations with the same charge (2+) were chosen so that electroneutrality could be preserved in any stoichiometry. Additionally, the oxides of these cations had different crystal structures, coordination geometries, and electronegativities, making a solid solution enthalpically unfavorable. The resulting mixture of oxides, (MgCoNiCuZn)O, contained limited solid solubility pairs, such as MgO-ZnO and CuO-NiO.\textsuperscript{17,20}

The transition to the single-phase structure was found to be reversible below a transition temperature, a requirement of an entropy driven transition. Compositional deviations from the equimolar stoichiometry were found to increase the transition temperature, as anticipated from the reduction in configurational entropy (Equation (2.7)). The transition was also found to be endothermic by calorimetry, an indication that the transition is enthalpically unfavorable. Finally, transmission electron microscopy and extended x-ray absorption fine structure (EXAFS) demonstrated that all of the cations were randomly distributed, with no clustering. Given that the high entropy solid solution phase was fully disordered and the transition was enthalpically unfavorable, the rocksalt (MgCoNiCuZn)O phase was reported to be entropy-stabilized.\textsuperscript{17,20}

Rost’s demonstration that it was possible to make ionic solutions that were not only high entropy, but entropy-stabilized, led to numerous reports on high entropy ionic and ceramic systems.\textsuperscript{(VIII)} The transition from high entropy metal alloys to high entropy ceramics was followed by a shift in applications of

\textsuperscript{(VII)}Reported as over 100 on Web of Science as of the time of publication.

\textsuperscript{(VIII)}∼250 citations on Web of Science
interest. Rather than focusing predominately on mechanical properties, as with metal alloy counterparts, researchers began to report advances in many other functional properties. Derivatives of the original entropy-stabilized oxide, as well as entirely new compositions, have been reported to exhibit colossal dielectric constants,\textsuperscript{136} room temperature lithium superionic conductivity,\textsuperscript{137} enhanced magnetic exchange coupling,\textsuperscript{138} amorphous-like thermal conductivity,\textsuperscript{11,12} thermochemical water splitting,\textsuperscript{139} and more.\textsuperscript{140–142}

Since the advent of bulk high entropy ceramics, reports of many other high entropy ceramic systems have been published including carbides,\textsuperscript{7,10,22,143–146} higher valence and complex oxides,\textsuperscript{147,148} nitrides,\textsuperscript{8,22,149,150} silicides,\textsuperscript{151} carbonitrides,\textsuperscript{152} and diborides.\textsuperscript{6,153,154} Many of these high entropy ceramics have exhibited common trends\textsuperscript{142} including diminished thermal conductivities,\textsuperscript{10,11,147,155} enhanced mechanical properties,\textsuperscript{6,7,144} and reduced oxidation rates.\textsuperscript{6,8,127,146}

With the transition from high entropy alloys to high entropy ceramics comes an additional important consideration, the role of anion stoichiometry. As previously discussed in Section 2.1.4, carbon stoichiometry can play a substantial role in the properties of binary UHTC carbides. Presently carbon stoichiometry is receiving little attention, with most reports focusing on stoichiometric or nominally-stoichiometric (i.e. batched stoichiometrically) specimens.

With the addition of the high entropy effects (cocktail, sluggish diffusion, distortion, etc.) it is unknown how significant the role of carbon stoichiometry will be relative to binary or ternary counterparts. This leads to a number of uncertainties about how the high entropy sublattice modifies the conventional understanding of compositional trends in carbides. For instance, can vacancy ordered carbides still form or does the high entropy metal sublattice disrupt this behavior? Could vacancies preferentially segregate on a local chemistry basis, congregating around certain elements? What are the implications of such chemical ordering on mechanical, thermal, and oxidation properties? Does the disordered metal sub-lattice overwhelm the impacts of the carbon lattice in properties such as thermal conductivity?

All of these questions are prudent to investigate; however, they are challenging to approach experimentally. This study requires a method to synthesize a broad range of compositions (both metal and carbon stoichiometry) while limiting the impacts of extrinsic factors. Unfortunately, the synthesis of bulk UHTC ceramics often results in impurities, oxide inclusions, secondary phases, and low density. High entropy materials exacerbate many of these issues by requiring additional high energy milling, spark plasma sintering, and high temperature anneals to fully homogenize the elements. This all makes the study of carbon content in bulk high entropy UHTCs extremely cost and time prohibitive. Thus, another approach is necessary to study the impacts of carbon stoichiometry in high entropy carbide. Sputter deposition can overcome many of these limitations, as will be discussed in the following section. Furthermore, physical vapor deposition techniques have already been established as a highly effective synthesis method for high entropy materials.\textsuperscript{4,17,18,22,123,142}
2.3 Sputtering

2.3.1 Diode and Magnetron Sputtering

The films deposited in this work were synthesized using a range of sputtering techniques. Sputtering is a physical vapor deposition process where energetic ions bombard a sputtering target, causing a cascade of atomic collisions and ejection of the target material (Figure 2.9). This target vapor condenses on the surface of a substrate, creating a film.\textsuperscript{156}

Sputter deposition of thin films was first reported by Grove in 1852, as a result of his experiments with glow discharges.\textsuperscript{157,158} In those experiments, a steel needle cathode was placed in close proximity to a silver coated plate acting as an anode. Upon the application of a large DC voltage, a thin film of iron oxide was reactively sputtered onto the silver plate. This experiment demonstrated the simplest form of sputtering - direct current (DC) diode sputtering.\textsuperscript{157,158}

Diode sputtering consists of two electrodes (most commonly planar) in a vacuum system. One electrode, the target, acts as a cathode, while the substrate and/or remainder of the system operates as an anode. A glow discharge occurs when the chamber is filled with a sputtering gas,\textsuperscript{(IX)} and a large DC voltage is applied.\textsuperscript{156,158,159} The target material must be conductive in order to maintain a current

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{sputtering_diagram.png}
\caption{Schematic representation of the mechanism of sputtering. The plasma body contains positive ions (in this case Ar\textsuperscript{+}) which are accelerated across the cathode sheath by an electrostatic potential from the power supply. The impact of the ion with the target surface causes a cascade of collisions in the target. This cascade leads to the ejection or sputtering of atoms from the target into a vapor. Figure adapted from Mahan.\textsuperscript{156}}
\end{figure}

\textsuperscript{(IX)} Argon is most commonly used due to its abundance (around 1\% of air), ease of ionization, and modest atomic mass, which facilitates momentum transfer to most elements.\textsuperscript{158}
between the anode and cathode via the glow discharge. If the target is insulating, positive ions will build up on the target surface. Eventually, the electric field from these built up ions will stop the flow of current and extinguish the discharge. Additionally, DC diode sputtering topically requires several kV of DC bias and pressures on the order of 100 mT to establish a glow discharge. This high pressure makes DC diode sputtering more prone to gas phase scattering and reduced deposition rates.\textsuperscript{156,159}

Radio frequency (RF) diode sputtering enables the deposition of insulating materials by dissipating the target's surface charge with each cycle of the alternating RF voltage. As an added benefit, the RF electric field increases the collision rate between secondary electrons and the sputtering gas in the glow discharge. This increased collision rate can sustain the glow discharge at 1% of the pressure required for DC diode sputtering, decreasing scattering effects.\textsuperscript{156,159}

However, RF sputtering can be more challenging to implement than DC sputtering. RF sputtering requires more complicated power supplies and the use of a matching network to ensure maximum power transfer into the glow discharge. These components do not scale to high powers as easily as their DC counterparts. Additionally, a blocking capacitor is necessary to develop a negative DC self-bias on conducting target. This self-bias occurs because of the difference in ion and electron currents.

\textbf{Figure 2.10:} Schematic diagram of a sputtering system with DC and RF sputtering capability. DC sputtering uses a DC power supply while RF sputtering uses an RF power supply in conjunction with a capacitive matching network that maximizes power transfer while developing a DC self-bias. This DC self-bias arises from the asymmetry in the I-V response of the diode sputtering process. In this system the substrate and vacuum chamber are grounded together and serve as the anode of the system. Figure adapted from Mahan.\textsuperscript{156}
lighter electrons move faster than the heavy ions, resulting in a greater electron current and inducing a negative charge and bias on the capacitor and target surface. This negative bias increases the sputtering time per RF cycle above the half cycle that would occur with no bias and a symmetric waveform. A schematic of the setup for DC and RF diode sputtering is shown in Figure 2.10.\textsuperscript{156,158,159}

Magnets are used extensively in modern sputtering cathodes to create magnetron sputtering cathodes. These cathodes consist of strong (often rare earth) magnets oriented such that the magnetic field lines cross over the surface of the target. This magnetic field traps the secondary electrons in a helical path over the target, increasing the rate of collisions and ionization of gas molecules. This increased collision rate enables glow discharges at lower pressures than diode counterparts.\textsuperscript{158,159} Lowering the sputtering pressure has numerous benefits including higher bombardment energies, enhanced deposition rates, and less embedded gas in the resulting film. Magnetron sputtering cathodes are ubiquitously in modern deposition systems due to their many benefits.\textsuperscript{156,158–160}

2.3.2 Reactive Sputtering

Reactive sputtering is a process where a compound film is deposited by sputtering with a reactive gas, such as oxygen, nitrogen, or hydrocarbons. This process enables stoichiometry control, increased deposition rates, higher purities, and less expensive targets than sputtering from compound targets.\textsuperscript{161,162} These combined characteristics have made reactive sputtering an industrially important technique for optical, electronic, and tribological thin films.\textsuperscript{158,161,163–165} At first glance, reactive sputtering seems simple to implement. However, development and control of reactive processes is typically far more involved than non-reactive counterparts. The reactions between the sputtered material or sputtering target and the reactive gas can result in nonlinear behavior and process instabilities.\textsuperscript{162,164}

One of the key causes of reactive process instability is target poisoning. Reactions between the target and the reactive gas can form a compound, poisoning the target surface. This compound typically has a lower electrical conductivity and sputter yield than the target, leading to sputtering characteristics that vary with reactive gas flow. Poisoning often results in a hysteretic response of parameters such as reactive gas partial pressure, sputtering rate, and optical emission when reactive gas flow is changed.\textsuperscript{161}

Target poisoning and the resulting hysteresis are best explained schematically. In Figure 2.11(a) the partial pressure of the reactive gas remains constant as the reactive gas flow is increased up to f\textsubscript{1}. In this metallic regime, all of reactive gas is gettered by the metal. This forms a metal rich thin film while preventing an increase in reactive gas pressure. Once the flow rate exceeds f\textsubscript{1}, the amount of reactive gas surpasses the gettering capacity of the sputtered metal. At this point, the surface of the target begins to form a compound with the reactive gas. The formation of this compound coincides with a significant, often 10-20x, decrease in sputtering rate. The decreased sputtering rate leads to an even greater reduction in the gettering rate of the system. As a result, the reactive gas partial pressure increases suddenly, and the film becomes gas rich.\textsuperscript{161}
Figure 2.11: Schematic representations of the hysteretic behavior observed in reactive sputtering processes. (a) reactive gas pressure, (b) reactive gas consumption rate, and (c) sputtering rate are plotted as a function of reactive gas flow rate. Flow $f_1$ is the point at which the process switches from metallic to compound mode with increasing reactive gas flow. Flowrate $f_2$ is the point at which the process returns to a metallic sputtering mode with decreasing reactive gas flow. The no discharge trace represents the partial pressure of the reactive gas if none of it was consumed by the sputtering process. Figure adapted from Safi.\textsuperscript{161}
The reactive gas partial pressure changes linearly with gas flow in the compound regime. The partial pressure is $\Delta P$ lower than it would be with no glow discharge, as the sputtered compound consumes some reactive gas. Once the target is poisoned, the target no longer returns to the metallic mode when the flow is decreased below $f_1$. Instead, the flow rate must be reduced to an even lower level ($f_2$). At this flow, the compound is finally sputtered from the target surface faster than it is formed by the reactive gas.\textsuperscript{161} This path dependent behavior is known as sputtering hysteresis. The effects of hysteresis can also be observed in reactive gas consumption and sputtering rates (Figure 2.11(b & c), respectively)\textsuperscript{161}

Sputter hysteresis can have significant implications on process stability and reproducibility. A process that uses a flow rate poised between $f_1$ and $f_2$ will result in films with stoichiometries that depend on the prior process. If the target was left poisoned after the last deposition, then the following deposition will sputter slowly and form a gas rich film. Conversely, if the prior deposition occurred in the metallic regime, then the next film will be metal rich and deposit at a high rate.

Researchers have developed a number of approaches to limit the impacts of target poisoning including increasing the pumping speed, altering the target-to-substrate distance, shielding the cathode from reactive gas, bipolar pulsed DC power, or pulsing the reactive gas flow. Some processes continuously modulate the reactive gas flow via a feedback loop which monitors the optical emission or target voltage.\textsuperscript{161,162,164,166} Alternatively, the target can be presputtered in an inert atmosphere, removing residual compound from the surface. While this does not avoid target poisoning, it does ensure a consistent starting point in the hysteresis plots (Figure 2.11).\textsuperscript{166,167}

### 2.3.3 High Power Impulse Magnetron Sputtering (HiPIMS)

Conventional magnetron sputtering (DCMS, pulsed DCMS, and RFMS) operates with low power densities (~50 W/cm\textsuperscript{2}) and high duty cycles (typically 25-100\%).\textsuperscript{168,169} These techniques are plotted in the upper left corner of Figure 2.12, below the DCMS power limit. The DCMS power limit represents the point at which it is no longer possible to operate at 100% duty cycle. Above the DCMS limit, the time-averaged power exceeds the cooling capacity of the cathode and target, resulting in thermal damage.

All techniques above the DCMS limit are referred to as high power pulsed magnetron sputtering (HPPMS). These methods require a reduction in duty cycle to avoid thermal damage to components and targets. The first technique above the DCMS limit is modulated pulsed power (MPP). In this method, the target power is modulated with pulses that start at low powers (near DCMS limits) for 100s of microseconds before increasing to high power densities (0.05–0.5 kW/cm\textsuperscript{2}) for similar time frames. These several hundred microsecond pulses are made up of "sub-pulses" on the order of microseconds. The duty cycle of these sub-pulses controls the power of the main pulses. The modest overall duty cycle of MPP allows for peak powers in the range of 0.5–1 kW/cm\textsuperscript{2}.\textsuperscript{158,168,170} High power impulse magnetron sputtering (HiPIMS) operates with a peak power density 100-1000x higher than DCMS and a duty cycle of 0.5-5% (bottom right of Figure 2.12). This extreme increase in peak power density results in a much
Figure 2.12: Plot of pulsed sputtering techniques in duty cycle–peak power density space. Direct current magnetron sputtering (DCMS), pulsed DCMS, modulated pulsed power (MPP), high power impulse magnetron sputtering (HiPIMS) are plotted in filled shapes. The high power pulsed magnetron sputtering (HPPMS) and direct current magnetron sputtering (DCMS) ranges are shown at the bottom. The DCMS limit represents the maximum peak power density at 100% duty cycle before target and cathode damage occur. The average power density indicates the maximum peak power density that can be applied as a function of reduced duty cycle. Figure adapted from Gudmundsson et al.\textsuperscript{168}

denser plasma with a large fraction of ionized target and gas species. The highly reactive HIPIMS plasma enables controlled ion bombardment of the growing film.\textsuperscript{168,171–173} HiPIMS discharges typically operate with voltages in excess of 500 V, modest frequencies (50–5000 Hz) and short pulse widths (5–200 \(\mu\)s).\textsuperscript{168,174} This operating regime provides HiPIMS with a unique advantage relative to DCMS: although the time-averaged power of a DCMS and HiPIMS process are subject to the same limits, the plasma parameters can vary dramatically. With conventional sputtering techniques, the voltage, current, and power are all coupled together by the plasma characteristics. As a result, the maximum applied voltage and current during a DCMS process are limited by the thermal power limit of the target and cathode. Conversely, with HiPIMS, the voltage and pulse width can be freely adjusted to tailor the plasma characteristics. Meanwhile, the repetition frequency (i.e. duty cycle) independently reigns in the extreme peak powers to a usable time-averaged power. This enables researchers to use pulse parameters and voltages that yield a dense and highly ionized plasma without exceeding power limitations. There are also several other advantages from HiPIMS including the transition from a gas to metal ion plasma, tunable bombardment energies, and a reduction of hysteresis.
Figure 2.13: Comparison of ion energy fluxes measured during DCMS and HPPMS of a Cr-Al-C target. Both techniques used the same time-averaged power density but a 162-fold difference in peak power density (labeled). An increased energy flux and transition from gas species to target species is observed with this increase in peak power density. Data replotted from Rueß et al.\textsuperscript{175}

Rueß et al. measured the time-averaged ion energy fluxes during from DCMS and HPPMS of a Cr-Al-C target. Both techniques used the same time-averaged power of 2.3 W/cm\textsuperscript{2} but a 162 fold difference in peak power (2.3 and 373 W/cm\textsuperscript{2} respectively).\textsuperscript{(X)} The transition from DCMS to HPPMS increased the total energy flux by a factor of 3.4. Furthermore, they found that the composition of ionic species responsible for the energy flux changed dramatically, as plotted in Figure 2.13. With DCMS the energy flux was carried mostly (84.7\%) by gas species with the remaining energy from target species. HPPMS resulted in the opposite behavior, with the almost all of the plasma energy carried by target species (98.6\%). This transition from gas to metal ion species can have significant influences on the chemistry, structure, and growth modes of the deposited film.\textsuperscript{168,175}

Ion assisted growth typically uses bombardment from ionized inert gas to control stress, adhesion or functional properties.\textsuperscript{172} The most common methods include ion sources, such as Kaufman sources,\textsuperscript{172,176} or substrate biasing.\textsuperscript{175,177,178} Bombardment with noble gas species does have some limitations: high energy gas species can implant in the growing film and the efficiency of momentum / energy transfer depends on the mass ratio of the film and gas.\textsuperscript{158,179}

\textsuperscript{(X)}While the peak power density of 373 W/cm\textsuperscript{2} is slightly lower than plotted in Figure 2.12, the duty cycle of 1.25\% falls in the HiPIMS regime.
The large fraction of metal ions present in a HPPMS/HiPIMS plasma enables self-bombardment (i.e. with target atoms) of the growing film. The energies of these metal species can be tuned with either substrate bias or bipolar HiPIMS. Bipolar HiPIMS (B-HiPIMS) is a process where the high power sputter pulse is followed by a positive low voltage pulse (typically <200 V). This positive pulse adds energy to all of the ionic species in the plasma and directs them towards the substrate and other anodes in the system. Bipolar HiPIMS achieves many of the benefits of stage bias without its drawbacks: the necessity of an electrically isolated substrate manipulator and a conductive substrate or RF bias to avoid surface charging.

Keraudy et al. examined the ion energy distribution functions for $^{48}$Ti$^+$ (Figure 2.14), $^{48}$Ti$^{2+}$, and $^{36}$Ar$^+$ as a function of the applied positive voltage during the secondary pulse. With no positive pulse, all species had a narrow peak in the ion energy distribution near 3 eV, with the metal species exhibiting a large shoulder to higher energies. Upon application of positive pulse, the narrow peak at 3 eV decreased in intensity while a similarly narrow peak grew at an energy corresponding to $qV_+$ (the ion’s charge and the voltage of the positive pulse). For the metal species the shoulder also increased in energy by $qV_+$.

Further analysis indicated that half of the metal ions accelerate across the full potential while the other half were not significantly influenced by the positive voltage pulse. Conversely, the gas species were only partially influenced by the magnitude of the field, accelerating to only a fraction of $qV_+$. Nevertheless, this work indicates that B-HiPIMS can be used to tune the peak in the ion energy distribution and control bombardment of the growing film.

![Figure 2.14:](image)

**Figure 2.14:** Ion energy distribution functions (IEDFs) for $^{48}$Ti$^+$ measured during bipolar HiPIMS plotted as a function of positive pulse voltage. Replotted from Keraudy et al.\textsuperscript{80,182,184}
Some researchers have explored the impacts of this controllable energy flux on film properties. Wu et al. found that altering just the positive pulse increased the deposition rate of Cu films while reducing residual stresses from 1000 MPa to 450 MPa. Similarly, Velicu et al. found that the positive pulse significantly increased the Cu flux to the substrate. This increased flux improved density, adhesion and mechanical properties while reducing roughness. A recent structure zone model, published by Anders, presents many interesting energy assisted growth regimes including ion assisted epitaxial growth, textured nanocrystalline films, ion etching to induce renucleation and residual stress control. At this point few reports on B-HiPIMS exist, primarily focusing on elemental carbon and metals. It remains to be seen how effective this technique is for materials systems with several components.

Finally, HiPIMS has been observed to lessen hysteretic behavior in reactive processes (i.e. R-HiPIMS). Wallin & Helmersson reported reduced or eliminated hysteresis during reactive HiPIMS of an Al target in an Ar/O₂ atmosphere. This behavior was observed by a number of other researchers in a wide variety of materials systems, but only under certain conditions. This reduced hysteresis is most commonly attributed to the pulsed nature of HiPIMS; the extreme erosion rates clean the target surface of any contaminants, while the reaction rate is too low to cause significant compound formation between pulses.

Strijckmans et al. modeled reactive DCMS and HiPIMS to explain these experimental observations. From their models, they determined that the poisoning rate is not significantly lower with HiPIMS than DCMS. Additionally, they found the target surface cleaning time to be significantly longer than the pulses. This indicated that the fast erosion rates of HiPIMS were not responsible for lessened hysteresis. Instead, they hypothesized that a large fraction of ionized metal species implant in the target surface, reducing the amount of compound formation. They concluded that while HiPIMS does change the hysteresis in reactive sputtering, additional experiments and models are necessary to conclusively determine the exact mechanisms. Finally, they suggested that hysteresis may not be fully prevented, but rather more difficult to observe, in R-HiPIMS.

High power impulse magnetron sputtering and its derivatives (B-HiPIMS and R-HiPIMS) are rapidly growing fields being approached from many angles by researchers around the world. While many unknowns still remain, the advantages HiPIMS presents for a wide range of materials systems are quickly being discovered.

2.3.4 Sputter Deposition of Transition Metal Carbides

Sputter deposition typically involves kinetically controlled nucleation and growth, with the resulting films far from equilibrium. The condensation of vapor phase species at quench rates near ∼10¹² K/s affords little time for adatoms to rearrange on the surface. It is possible to drive the process closer to equilibrium by increasing the substrate temperature or bombardment, as demonstrated by the structure zone model. Typically, a substrate temperature in excess of 0.3Tₘₑₙₙ is necessary to cause significant
changes in film growth morphology. For UHTCs with melting points of 3300–4000 K, substrate heating has significant limitations. Thus, many researchers use high energy deposition techniques including substrate bias, high plasma densities, or HiPIMS to drive the system towards equilibrium.

This non-equilibrium nature does have some advantages for the synthesis of transition metal carbides. The Group VIB elements Mo and W would be expected to form hexagonal MC and M_2C phases; these are the equilibrium phases at modest temperatures. Instead, rocksalt MoC_{1-x} and WC_{1-x} readily deposit over a broad range of conditions despite being unstable below 2000 °C. This is likely a consequence of both the limited time for structural rearrangement and the broader carbon stoichiometry window in the rocksalt structure. These results suggest that sputter deposition may favor high temperature high entropy structures over phase segregation, making it suitable for the synthesis of high entropy carbides.

However, sputter deposition of transition metal carbides does present a unique challenge that is not applicable to many reactive processes: the reactive gas can precipitate a secondary phase if the process is not carefully controlled. Carbides are reactively sputtered in hydrocarbon gases, often methane or acetylene, with excess gas flow resulting in secondary carbon phases. Excessive carbon leads to the microstructural progression illustrated in Figure 2.15. As carbon content increases, carbon begins to precipitate at the carbide grain boundaries in layers a few angstroms thick. With further increases in carbon content, the excess carbon regions become several nanometers thick while the carbide grains are reduced to 5–20 nm, forming a nanocomposite.

These high carbon content, nanocomposite films are not without their utility. Carbide-carbon nanocomposites are often used to modify the tribological properties of carbides for low friction applications, such as contacts. However, this secondary carbon phase has detrimental effects on the mechanical, thermal, and chemical properties of interest for UHTC applications. Thus, it is important to synthesize carbide films without any secondary carbon phases.

The equilibrium phase diagrams for the Group IVB carbides exhibit the following regions: metal, (metal + MC_{1-x}), MC_{1-x}, (MC + C), and C, as carbon content increases. Based on the phase diagram, fully stoichiometric films should form prior to the precipitation of excess carbon. Thus, stoichiometric films should form within a narrow window of carbon flux. Finding and remaining in this window should present a difficult, but not intractable, process to develop.

Unfortunately, the difficulty in controlling carbon flux and stoichiometry is exacerbated by the non-equilibrium nature of sputter deposition. This often results in carbon precipitation far before the carbide phase reaches full stoichiometry. For instance, Lewin et al. found that carbon precipitated with carbide stoichiometries as low as TiC_{0.47}. However, not all processes have precipitated carbon this early; there are numerous reports of at or near stoichiometric carbide films without excess carbon.

Analysis of this variability indicates that the characteristics of the plasma strongly influence the resulting stoichiometry. Carbon precipitation is often observed in low-energy or low-density plasma processes. Lewin et al. used small sources (50 mm) a large distance (15 cm) from the substrate; this resulted
Figure 2.15: Illustrated representation of the microstructural development in sputtered carbide films as a function of increasing carbon content. Small, dark circles represent carbon while large, light circles represent a transition metal. At low carbon contents, films are phase pure carbide. At moderate carbon contents, excess carbon begins to form a thin layer along grain boundaries. At high carbon contents, the excess carbon region broadens, and the film becomes a carbide-carbon nanocomposite. In all cases some carbon vacancies are present, albeit decreasing in concentration with increasing carbon content. Illustration inspired by Jansson & Lewin.\(^{19}\)

Conversely, the synthesis of films at or near stoichiometry often involves the increased energetics and plasma density afforded by stage bias, small target-substrate distances, or high instantaneous power density processes (HiPIMS or laser assisted sputtering).\(^{19,201–204}\)

Samuelsson et al. demonstrated the benefits of high plasma densities by synthesizing TiC films with DCMS and HiPIMS supplies calibrated for the same metal deposition rate. This methodology was chosen so the fluxes of metal and carbon (acetylene flow) would be constant, with only the energetics and ion concentration of the plasma changing between power sources.\(^{201}\) The carbon stoichiometry of the resulting films are plotted in Figure 2.16 as a function of acetylene flow rate.

At low (sub-stoichiometric) flow rates, the total carbon concentration increased similarly for both power sources. However, the stoichiometry of DCMS films increased rapidly with further increases in acetylene flow, peaking at over 300 carbon atoms per titanium atom at 8 sccm. Conversely, the C/Ti ratio of HiPIMS remained relatively stable over a broad range of flow rates, before rapidly increasing above 15 sccm. Both techniques resulted in excess carbon; however, the onset was significantly slower for HiPIMS, allowing for stoichiometric films with as little as 5% excess carbon. Furthermore, the excess carbon experienced a plateau near 20% in HiPIMS deposited films while DCMS films became almost entirely excess carbon over the same flow regime.\(^{201}\)
Figure 2.16: Carbon stoichiometry as a function of acetylene flow for TiC films synthesized by DCMS (black) and HiPIMS (red). Left shows the total carbon to titanium ratio, right shows the excess carbon (C-C bonds) to total carbon ratio. DCMS results in a rapid increase in total carbon and excess carbon with increasing acetylene flow. HiPIMS films exhibit a process window where total carbon content changes gradually and excess carbon content is low (<20%). Data replotted from Samuelsson et al.\textsuperscript{80,201}

The data suggest that HiPIMS provides a broad transition zone between metallic and compound sputtering modes. This behavior may be a consequence of reduced hysteresis from hindered reactions at the target surface, as described in Section 2.3.3. Alternatively, the window of stability may occur due to processes at the film surface. Samuelsson et al. suggested that the excess carbon may be chemically etched by hydrogen, as in CVD growth of diamond.\textsuperscript{201,207} The HiPIMS plasma produces both the large concentration of hydrogen and the intense ion bombardment necessary for chemical sputtering.\textsuperscript{201,208} Alternatively, preferential physical sputtering of carbon could occur due to the high energy ion flux during HiPIMS.\textsuperscript{201}

The literature indicates that sputter deposition of stoichiometric carbides with minimal excess carbon requires careful planning. Equipment should be configured to maximize the plasma interactions with the substrate in conjunction with the use of techniques that increase the reactivity and energy of the plasma.\textsuperscript{19} With that in mind, there are only a few reports on the synthesis of high entropy carbides by sputtering\textsuperscript{4,5,22}. Thus, it is relatively uncertain how the synthesis of high entropy compositions compares to binary counterparts. Particularly, if the added complexity of the high entropy metal sub-lattice will alter the compositional or microstructural trends observed in binary counterparts.
Chapter 3
Experimental Methods

3.1 Thin Film Deposition

The films in this work were deposited in a custom-built magnetron sputtering chamber (Figure 3.1), built in the shape of an 18” diameter sphere. Six ports, located on the bottom half of the chamber (40° off the vertical axis), are aimed confocally to a point 2.38” above the center of the chamber. 2” circular magnetron sputtering sources (Kurt J. Lesker Torus® Mag KeeperTM) are installed in five of these ports, allowing for 5 source materials to be installed and sputtered simultaneously. The 6th port contains a 1” germanium window with 7–12 µm antireflective coating (ThorLabs WG91050-G mounted in VPCH12-FL) which serves as an access point for a far IR pyrometer (Omega Engineering OS554A-MV-5) to measure substrate temperature.

The top, central port of the chamber contains a heating stage which can be lowered to the confocal point of the lower 6 flanges. The heating stage (NBM Design Inc.) uses a 2” diameter pyrolytic-BN/graphite heating element (Momentive 2109925) with a 1200 °C temperature limit, as measured by a K-type thermocouple in physical contact with the backside of the element. The chamber is turbo pumped at 240 L/s and load locked (pumped to 10–50 mT prior to transferring the sample). The base pressure of the chamber is 10−9–10−7 Torr with the stage at 650 °C after pumping overnight. Immediately after an extended deposition the base pressure is in the range of 10−6–10−5 Torr due to the H2 generated by ionization of CH4 during sputtering.1

All targets used in this work were metallic, rather than compound targets such as TiC. Carbide targets often produce films with stoichiometries which are different than the starting target.19,102,175,210 Furthermore, metallic targets enable the independent control of carbon flux and metal flux, and thus the carbon content of the growing films. Elemental metal targets were typically purchased in the highest purity sold, ranging from Grade 702 for Zr to 99.995% Ti, (Kurt J. Lesker Inc.). High entropy metal alloy targets were arc-melted from an equimolar composition and machined to size. All of the alloy targets have a 99.5% nominal purity (ACI Alloys Inc).

1This is exacerbated by the lower relative compression ratio and pumping speed of H2 relative to Ar and air.209
Targets were mounted with silver epoxy (Chemtronics CircuitWorks® Conductive Epoxy) to copper backing plates with a magnetic keeper (MeiVac Inc.). The best results were obtained by mixing a 1:1 volume ratio of the epoxy components in SpeedMixer™ (Flacktek Inc. DAC 150.1 FV), spreading a thin layer onto the target and wringing the target and backing plate together to remove any air pockets. The epoxy was dried in a vacuum oven at 80 °C under a pressure of 125–250 Torr for 10 min. Silver thermal contact paste (Noelle E903-64) was spread on the copper hearth of the magnetron to provide high thermal conductivity between the backing plate and hearth. Targets were removed from the vacuum oven, cooled, and installed on the magnetrons. After magnetically attaching, the targets were rotated several times to ensure an even coating of the thermal grease. The chamber was then sealed and allowed to pump down overnight with the stage heated to 650 °C, serving as a means to bake the chamber out.

Both sputtering and reactive gasses were introduced through the gas chimney of one of the sputter guns using mass flow controllers (Alicat Scientific MC-20SCCM-D & MC-50SCCM-D). 99.999% purity

---

$I$ All bonded targets, whether using metallic or elastomeric bonds, are limited by heat dissipation and bond failure which can result in the targets falling off mid-deposition. This procedure resulted in the most resilient bonds (allowing 250 W+ of power on a 2" target for many hours). Ideally a magnetic keeper would be directly screwed into the back of the target; however, machining a #4-40 or smaller screw in alloys of W, Mo, Ta, and other metals is challenging and costly.

$II$ Presumably this allowed for out-gassing of any volatile organic compounds still remaining in the bond that would pressurize under heating from the sputtering process and cause the bond to mechanically fail.
Argon (Praxair Ultra High Purity 5.0) was used as the sputter gas, while 99.99% methane (CH$_4$) was used for the carbon source (Praxair Ultra High Purity Plus 4.0). Methane was chosen despite its low C:H ratio as it is readily available in high purities and easily stored. Acetylene is another common choice, but it is dissolved in acetone or dimethylformamide for safety, which means a finite vapor pressure of the solvent could flow into the chamber and introduce oxygen.$^{19,189,204,211}$

Substrates were cleaved with a diamond scribe (Ted Pella Inc. 54482) prior to cleaning. Samples were cleaned with ACS reagent grade isopropanol and methanol (Fisher Scientific) and dried with a spin coater (Specialty Coating Systems G3 Spin Coater) operating at 4000 RPM. After solvent cleaning, substrates were transferred to a UV-ozone cleaner (Jetlight UVO-Cleaner® 42) for 10 min to remove any residual organic compounds.

Substrates were mounted to the Inconel sample stage using silver paint (Ted Pella Inc. "Leitsilber" 200 Silver Paint) and dried for 10 min on a hot plate at 120°C. After the silver paint was dried, the Inconel sample stage was placed in the stage holder and loaded into the main chamber via the load-lock. The stage is continuously rotated at 6 RPM throughout the heating and deposition process. Depositions started after the temperature reading on the optical pyrometer stabilized (15–20 min).

Sputter magnetrons were powered by different power supplies depending on the type of sputtering (RF or HiPIMS). Radio frequency (RF) power at 13.56 MHz (Kurt J. Lesker R301) was supplied through a match network (Kurt J. Lesker EJAT3) to the sputtering cathode. An additional 120 pF capacitor was installed in parallel with the adjustable tune air capacitor to enable matching with metallic targets. The match network was tuned to minimize reflected power on the match network controller (Kurt J. Lesker EJMC2) and RF power supply.

High power impulse magnetron sputtering (HiPIMS) power was controlled by an external pulsing unit (Starfire Industries IMPULSE$^{\text{TM}}$ 2-2) which received input power from a DC power supply (Advanced Energy MDX 5 kW). When multiple HiPIMS units were run simultaneously, supplies were synced either with the built-in master-slave configuration (fixed frequency) or powered by an external arbitrary waveform generator (RIGOL DG1022Z) to enable asynchronously patterned pulsed sputtering (see Chapter 6). The power and current waveforms were monitored via the built in voltage and current monitor outputs by using an oscilloscope (RIGOL DS1054Z).

In all cases sputtering started with a 2–5 min presputter in pure Ar gas (20 sccm) at 5–7.5 mT to clear the target surface of any poisoning or contamination from prior depositions.$^{(IV)}$ This was followed by presputtering with Ar and CH$_4$ (at the chosen flowrate) for 2 min to allow the plasma, target surface, and chamber environment to equilibrate prior to the film deposition. Next, the stage shutter was opened and the film was deposited. After deposition, all sputter sources were powered down and gas flow was stopped. Samples were allowed to cool in the load-lock for 30 min prior to venting in order to limit oxygen contamination.$^{(V)}$

$^{(IV)}$A pneumatically actuated dome shutter blocked the majority of target contamination from other sources.

$^{(V)}$This process evolved with time, at first samples cooled in the load-lock with it isolated from the main chamber (10–100 mT),
Specific deposition process parameters (e.g. powers, pulsing parameters, flow rates, pressures, etc.) will accompany the resulting data in the subsequent chapters.

3.2 X-ray Diffraction (XRD) and Reflectivity (XRR)

X-ray diffraction (Malvern Panalytical Empyrean) patterns were collected in order to determine the phase(s) of the deposited films and glean qualitative information on the carbon content of the carbide structure. X-ray reflectivity was used to quantify thickness, density, and roughness of films under ~150 nm thick. All samples were placed on a (5 1 0) Si zero diffraction plate for measurement.

XRD spectra were measured in Bragg-Brentano geometry using a Bragg-Brentano\textsuperscript{HD} incident beam optic to provide a divergent beam. The diffracted beam passed through programmable anti-scatter slits into a PIXcel\textsuperscript{3D} area detector operating in scanning line (strip) mode. The typical slit and mask configuration used for XRD is tabulated in Table 3.1. Deviations from these settings followed Malvern Panalytical documentation to maximize the spot size on larger samples.

Diffraction patterns were collected over the range of 10–120° (2θ). The full 3.347° range of the PIXcel\textsuperscript{3D} strip detector was used with a step size of 0.0263–0.525° and a count time of 25–75 s, depending on the sample and purpose of the scan. Peak positions were indexed with HighScore Plus (Malvern Panalytical) using the PDF-2 2010 database (International Centre for Diffraction Data). Many of the carbides discussed in this work have never been made or indexed before and thus do not have specific reference cards in this database. For these materials, powder diffraction file (PDF) cards containing a combination of the constituents were used for indexing. Typically, a low entropy composition in the database would have a crystal structure and lattice parameter matching the higher entropy composition sufficiently for indexing.

X-ray reflectivity spectra were collected using the same optical modules as XRD; however, the PIXcel\textsuperscript{3D} detector was operated in receiving slit mode (0.055 mm active length) with a narrow anti-

| Table 3.1: X-ray diffraction and reflectivity slit and mask configurations |
|--------------------------|----------------|----------------|
| Optics setting           | XRD            | XRR            |
| Incident divergence slit (°) | 1/8            | 1/8            |
| Incident beam mask (mm)  | 2              | 2              |
| Incident anti-scatter slit (°) | 1/2        | 1/2            |
| Receiving anti-scatter slit (°) | 1/4          | "Follow" (55 μm) |

Then with the gate valve to the main chamber open (10⁻⁵ Torr), and most recently for 10 minutes in the load lock at 10⁻⁵ Torr, followed by isolating the load lock and backfilling with forming gas (95% Ar 5% H₂) to near atmospheric pressure (500 Torr). This progression aimed to reduce surface oxide formation, allowing for surface level XPS to determine metal to bonded-carbon stoichiometry prior to sputtering off adventitious carbon.
scatter slit (Table 3.1). This optic and detector configuration collects predominately the same signal that would be collected with a parallel plate collimator, providing sufficient resolution and dynamic range for the needs of this work. XRR patterns were measured over a 1–1.4° ($\omega$) range centered around 0.7–0.9° ($\omega$) using a step size of 0.003–0.005° ($\omega$) and a count time of 0.25–0.5 s, with exact parameters depending on the density, anticipated thickness, and roughness of the film. Reflectivity data were fit with the X'Pert Reflectivity (Malvern Panalytical) software package. The electron density is necessary to calculate the refractive index and accurately model the mass density. The electron densities of high entropy carbides were calculated by assuming stoichiometric M$_1$C$_{1}$ structures containing an equimolar metal distribution. While many films were not fully carburized, the effects of carbon content variation on the x-ray refractive index are minimal, owing to the comparatively low electron density of carbon.

Thickness, density, and roughness were manually iterated until the simulation was close to the measured data. Next, the density, thickness and roughness of the film were fit, while only the roughness of the substrate was fit (the density was assumed to be theoretical and thickness could be considered infinite). Additionally, the software was allowed to fit the instrument intensity, background, and divergence. The best results were obtained using the genetic algorithm with increased population and generation limits (10 and 1,000 respectively). Furthermore, the cutoff for termination of the fitting process was substantially lowered (0.0005 rather than 5) as the square log difference scheme resulted in fit values below 0.01 for strong fits and 0.5 for fits which were visually poor. In some cases (most frequently for metals) a native oxide layer <5 nm thick improved the fit quality.

### 3.3 Scanning Electron Microscopy

Field emission scanning electron microscopy (FE-SEM) was used to observe microstructural trends in the growing films as a function of deposition parameters (Zeiss Sigma, ThermoFisher Scientific Apreo S or Verios G4 UC). For the Sigma, an accelerating voltage of 1–5 kV was used with secondary electrons collected using the in-lens detector. In the case of the Apreo and Verios, a landing energy of 1 keV and a stage bias of 0 to -4 kV was used in conjunction with the in-column detectors. This configuration favored surface sensitivity while enhancing signal strength for the in-column secondary and backscattered electron detectors. In all cases, a working distance of 2 ± 1 mm was used. For thickness measurements of samples beyond the limitations of X-ray reflectivity, samples were cleaved and mounted on 90° stubs with the fracture surface facing the electron beam. The thickness was measured in several cross-sectional micrographs spanning >5 mm of the substrate in order to reduce error.

Due to the oxidation prone nature of many of the elemental constituents (Group IVB in particular) and the insulating substrate ($\text{Al}_2\text{O}_3$), samples were sometimes coated with Ir metal after mounting. The thin layer of iridium <5 nm grounded the films and substrate, reducing drift in the SEM. This was used primarily when trying to obtain accurate thickness measurements. Samples were coated with Iridium in a DC magnetron sputtering system following conditions outlined in Table 3.2.
Table 3.2: Iridium sputtering conditions used to coat samples for scanning electron microscopy

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Condition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power</td>
<td>10 W DC</td>
</tr>
<tr>
<td>Pressure</td>
<td>10 mT</td>
</tr>
<tr>
<td>Ar flow</td>
<td>15 sccm</td>
</tr>
<tr>
<td>Distance</td>
<td>50 mm</td>
</tr>
<tr>
<td>Target size</td>
<td>25.4 mm</td>
</tr>
<tr>
<td>Time&lt;sup&gt;(VI)&lt;/sup&gt;</td>
<td>15–30 s</td>
</tr>
<tr>
<td>Thickness&lt;sup&gt;(VII)&lt;/sup&gt;</td>
<td>3–5 nm</td>
</tr>
</tbody>
</table>

3.4 Energy Dispersive Spectroscopy (EDS)

The ratio of metal species in co-sputtered samples (Chapters 6 and 7) was quantified using energy dispersive spectroscopy (EDS). Spectra were collected using an 80 mm<sup>2</sup> Oxford X-Max<sup>N</sup> detector on the Thermo Fisher Scientific Verios G4 UC, or a 100 mm<sup>2</sup> Oxford Ultim Max detector on the Thermo Fisher Scientific Apreo S. Characteristic x-rays were generated with a 3.2 nA, 10 keV electron beam rastered over an area of ~0.1 mm<sup>2</sup>. Spectra were collected for 60–120 s of live time, with a dead time fraction of 25-35%. The peaks of all species (i.e. film and substrate) were fit with the Aztec software package. The atomic fractions of the metals were extracted and normalized to determine the metal ratio in the films.

3.5 Raman Spectroscopy

Raman spectroscopy (Horiba LabRam HR Evolution) was used to quickly and qualitatively establish the presence of excess carbon in carbide films. Spectra were collected using a 4 mW 488 nm argon ion laser, a 600 g/mm grating, and a 30 s collection time. Spectra were analyzed for the intensity of the D-peak (1350 cm<sup>-1</sup>) and G-peak (1580 cm<sup>-1</sup>).<sup>212,213</sup> There would often be relatively broad and low features at these wavenumbers for all films; however, the precipitation of excess carbon would lead to an abrupt and substantial (~10-fold) increase in intensity over a relatively small change in methane flow.

3.6 X-ray Photoelectron Spectroscopy (XPS)

Carbon stoichiometry was quantified with x-ray photoelectron spectroscopy (XPS) spectra measured on a Physical Electronics VersaProbe II. Spectra were collected using monochromatic Al Kα<sub>1</sub> radiation (1486.6 eV) and a hemispherical analyzer (58.7 eV pass energy). All samples were etched using a 3 keV

<sup>(VI)</sup>Dependent on target wear and erosion track depth. The deposition rate was calibrated via XRR on a witness specimen.

<sup>(VII)</sup>Typically, thicker for cross-sectional images in order to suppress charging at the substrate-film interface.
Figure 3.2: XPS spectra as a function of carbon content for the Ta4f and C1s orbitals. The Ta 4f is split into the 4f\textsubscript{5/2} and 4f\textsubscript{7/2} orbitals. The C 1s peak is split in a lower binding energy C-M bonding peak and a higher binding energy C-C bonding peak. The black dots are experimental data, the blue and green lines are individual peak fits, and the red line is the sum of both peak fits. For the C1s peaks with only a red line, a single peak was fit.

Ar\textsuperscript{+} beam for 5 minutes to remove any adventitious C and native oxide prior to the measurement. Ion and electron neutralization sources were used to prevent charging of the insulating Al\textsubscript{2}O\textsubscript{3} substrate during the measurement. Metal peaks were selected based on the elements present in order to avoid the peak overlaps that are common when measuring elements in the same region of the periodic table. The resulting spectra were fit with the CasaXPS software package using a modified Lorentzian line shape and a Shirley background. Sample spectra for Ta 4f and C 1s are presented in Figure 3.2. The metal spectra are fit while constraining the anticipated intensity ratio (1:2, 2:3 and 3:4 for p, d, and f orbitals respectively). The carbon peaks corresponding to C-M and C-C (if present) bonds were fit independently in order to quantify the amount of carbon bonded to metal atoms in the carbide structure and excess carbon, respectively.

3.7 Nanoindentation Testing

Hardness and elastic moduli were measured via nanoindentation (Bruker Hysitron TI-980) with a Berkovich indenter. Polycarbonate was used for the tip-optic calibration step while the tip area was calibrated with a fused-silica sample. The Oliver-Pharr method was used to calculate the moduli data.
with a maximum applied load of 5.5 mN. The loading and unloading cycle durations were 5 s, with a hold of 2 s at the maximum load. Nine indents were performed on each sample in a linear arrangement, with a spacing of 20 μm. The actual elastic modulus was calculated using the relationship in Equation (3.1) where $E_r$, $E_i$, and $E_s$ are the reduced, indenter, and sample elastic moduli, respectively, and $\nu_i$ and $\nu_s$ are the Poisson’s ratio of the indenter and sample, respectively.

$$
\frac{1}{E_r} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_s^2}{E_s}
$$

(3.1)

The elastic moduli and Poisson’s ratio of the diamond indenter were taken as 1141 GPa and 0.07 based on the work of Pharr & Oliver. The Poisson’s ratio for the carbide was assumed to be 0.22, based on data from Jain et al. in the Materials Project, or taken from density functional theory (DFT) calculations.
Chapter 4

Physical and Mechanical Properties of RF Sputtered (HfNbTaTiZr)Cx

4.1 Preface

The contents of this chapter are intended for publication as follows:

Trent Borman,1,* Mohammed Delower Hossain,1* Abinash Kumar,2,3 Xi Chen,2,3 Ali Khosravani,4 James LeBeau,2,3 Donald Brenner,2 & Jon-Paul Maria,1 Physical and Mechanical Properties of RF Sputtered (HfNbTaTiZr)C

1Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802
2Department of Materials Science and Engineering, North Carolina State University, Raleigh, NC 27695
3Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, MA 02139
4The George W. Woodruff School of Mechanical Engineering, Georgia Institute of Technology, Atlanta, GA 30332
* Denotes equal contribution

4.2 Introduction

Ultra-high temperature ceramics (UHTCs) are often defined as ceramic materials with melting points in excess of 3000 °C.2 The selection of UHTCs is dominated by elements from Groups IVB and VB in carbide, nitride and diboride forms.13,14,23,24,217 High performance UHTCs are critical for applications in extreme environments, such as heat shields for hypersonic vehicles and engines and use in nuclear reactors.24 In addition to high melting temperatures, this class of materials exhibits high hardness, thermal conductivity, (I) and chemical resistance.19,218 The extreme demands of the envisioned applica-

(I) For a ceramic.
tions necessitate consideration of the strength, thermal expansion, and thermal conductivity of UHTCs across a wide range of temperatures. Furthermore, the UHTC must also satisfy the manufacturability, cost, and density requirements of the application at hand. Consequently, there has been a renewed focus on the development of UHTC materials with tailored combinations of physical, mechanical, and chemical properties in order to enable these new applications. In the recent past, the development of new materials via compositional exploration has been dominated by the concept of high entropy alloys (HEAs). These new materials typically contain five distinct metals in a solid solution FCC or BCC structure, with configurational entropy favoring the formation of a single phase over the precipitation of intermetallics. The concept of HEAs was extended to ceramics with the first entropy stabilized oxide synthesized by Rost et al.

Since then, the field of high entropy ceramics has grown to include UHTCs, such as high entropy diborides (HEBs), high entropy carbides (HECs), and high entropy nitrides (HENs), with numerous favorable findings. Gild et al. demonstrated that HEBs possess enhanced mechanical and chemical properties relative to any of the binary constituents. Castle et al. reported that bulk quinary carbides exhibited enhanced hardness compared to both binary and ternary counterparts. (HfNbTaTiZr)C was observed to have improved oxidation resistance and thermal stability by Zhou et al. Malinovskis et al. reported that physical vapor deposited (CrNbTaTiW)C films exhibited increased hardness and corrosion resistance. The hardnesses of bulk spark plasma sintered HECs were reported to exceed the rule of mixtures by Sarker et al. Finally, Yan et al. reported atypically low thermal conductivity in (HfNbTaTiZr)C, which they attributed to severe phonon scattering by the distorted anion sublattice.

The diverse functional properties of transition metal carbides result from the combination of covalent, ionic, and metallic bonding characteristics. However, the presence of carbon vacancies in the binary carbides can have profound effects on both the melting temperature and the mechanical properties. A computational study of the Hf-Ta-C system by Hong & van de Walle found that the entropy from a carbon vacancy concentration between 10-20% had a positive effect on the energetic stability of binary and ternary carbides, thereby increasing the melting point. Carbon vacancy induced hardening has also been reported in transition metal nitrides and carbides, increasing the hardness through a variety of mechanisms.

High entropy carbides show promise as a means to develop UHTC materials with a unique combination of properties including enhanced oxidation and chemical resistance, high melting temperature, and improved mechanical properties relative to their binary constituents. The strong impact of carbon vacancies on the properties of binary and ternary carbides necessitates a complimentary study in a chemically disordered high entropy carbide. This work describes how the types and amount of carbon affect the mechanical properties and microstructure of a sputter deposited HEC. Additionally, the experimental mechanical property findings are validated through ab-initio investigations.
4.3 Experimental Methods

Thin Film Synthesis

Thin films were deposited with reactive radio frequency (RF) magnetron sputtering in a high vacuum chamber. A 99.5% HfNbTaTiZr alloy target (2" diameter) containing an equimolar fraction of each transition metal element was sputtered at 200 W to provide the metal flux. Carbon was introduced in the form of 99.99% CH$_4$ gas, with the flow rate used to control the total carbon content of the films. The carbide films were grown on epi-polished c-plane sapphire substrates at a temperature of 500 °C, using a rotating substrate stage to ensure uniformity. Ultra-high purity (99.999%) argon was introduced to the chamber at a constant rate of 20 sccm, while the total pressure during the deposition was fixed at 5 mT. Deposition rates were calibrated to determine the time necessary to achieve an approximate thickness of 2 µm, with actual thicknesses measured ex-situ post deposition. Before each deposition the target was presputtered for 5 minutes in argon to clean the target surface, followed by 2 minutes in the mixed Ar + CH$_4$ flow to allow the pressure to equilibrate.

X-ray Diffraction (XRD)

X-ray diffraction patterns of the films were collected with a Panalytical Empyrean X-ray diffractometer using Cu Kα radiation (operating at 45 kV / 40 mA). The incident beam was shaped by a Bragg-Brentano$^{\text{HD}}$ optic equipped with a 4 mm mask, 0.04 rad sollar slits, and 1/8° and 1/2° divergence and anti-scatter slits, respectively. The diffracted beam passed through a 1/4° anti-scatter slit and 0.04 rad sollar slits before being collected by a PIXcel$^{\text{3D}}$ detector operating in 1D scanning line mode. The data were collected with a count time of 75 seconds per 0.0263° 2θ step.

Scanning Electron Microscopy (SEM)

Field-emission scanning electron microscopy was used to analyze the surface and cross-sectional microstructures of the samples. Micrographs were collected with the in-lens detector of a Zeiss Sigma VP-FESEM, using a beam energy of 5 keV and a working distance of 3 mm. Cross sections were sputter coated with 5 nm of iridium to ground the insulating sapphire substrate, preventing image drift. Film thicknesses were measured from multiple cross-sectional images across the sample.

4.3.1 X-ray Photoelectron Spectroscopy (XPS)

The types of carbon in the film and their relative amounts were determined from X-ray photoelectron spectra collected with a Physical Electronics Versaprobe II. A monochromatic Al K$_{\alpha}$ X-ray source with an energy of 1486.6 eV was used to generate the photoelectrons for measurement. The spectra were measured with a hemispherical analyzer (pass energy of 58.7 eV) and analyzed with the CasaXPS 2.3.19
software package. Data were fit with modified Lorentzian line shape (LF) with and Shirley background. All samples were presputtered for 5 minutes with a 3 keV Ar\textsuperscript{+} beam to remove any adventitious carbon and native oxide from the surface. High resolution XPS spectra were collected for the C 1s, Hf 4f, Ta 4f, Zr 3d, Nb 3d, and Ti 2p shells in order to avoid peak overlaps.

4.3.2 Nanoindentation

Mechanical properties of the films were measured using a Hysitron TI-900 nanoindenter with a load resolution of 1 nN. A 5.5 mN load was applied to a Berkovich indenter to produce the indentations. Loading and unloading cycles occurred in 5 seconds, with a 2 second hold at the maximum load. Nine indentations were performed on each sample, and the Oliver-Pharr method was employed to calculate the hardness and modulus of the films.\textsuperscript{214,215} A polycarbonate sample was used to calibrate the tip to optic distance, and a fused silica specimen was used to determine the tip area function. The elastic moduli of the samples were calculated with the relationship in Equation (4.1), where \( E_r \) is the reduced (measured) elastic modulus, \( \nu_i \) and \( E_i \) are the Poisson's ratio and elastic modulus of the diamond indenter, and \( \nu_s \) and \( E_s \) are the Poisson's ratio and elastic modulus of the sample. The Poisson's ratios of the samples (\( \nu_s \)) were determined with DFT calculations, while the elastic properties of diamond were obtained from Pharr & Oliver.\textsuperscript{215}

\[
\frac{1}{E_r} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_s^2}{E_s}
\]  

(4.1)

4.3.3 Computational Methods

The first principles calculations used the generalized gradient approximation (GGA) method implemented in Quantum Espresso v6.2.\textsuperscript{220,221} An 80 atom rocksalt structured supercell was populated with transition metal atoms (Hf, Nb, Ta, Ti, Zr) based on the experimental compositions. The Alloy Theoretic Automated Toolkit (ATAT) was used to distribute the metal atoms in a special quasirandom structure (SQS).\textsuperscript{222,223} The anion sites were occupied by randomly distributed carbon atoms and vacancies (if applicable). A 3×3×3 k-point grid based on the Monkhorst-Pack scheme was used for energy calculations, and an 8×8×8 k-point grid was used for electronic structure generation. The plane wave energy cutoff was set to 120 Ry, and convergence with respect to the energy cutoff and k-points was confirmed. The energy convergence value was set to \( 10^{-4} \) Ry. Normconserving Perdew-Burke-Ernzerhof (PBE) exchange-correlation functionals with non-relativistic pseudopotentials were used for every element.

The 80-atom supercell was chosen for its modest size, geometric simplicity (tetragonal symmetry with lattice parameters of \( \sqrt{5}a \), \( \sqrt{5}a \), and \( 2a \), where \( a \) is the lattice parameter of the rocksalt unit cell), and ability to evenly distribute 5 metal atoms. Supercells of this size, generated with SQS techniques, are frequently used in the high entropy literature.\textsuperscript{142,224–227} The enthalpies of formation of multiple 80 and 240 atom supercell configurations were found to be within 0.01 eV or ~0.7% of each other, indicating
that 80 atom supercells were sufficiently sized. Furthermore, the enthalpy, electronic structure, and mechanical properties closely matched the work of Sarker et al., who used the Automatic Flow (AFLOW) technique on the same composition. All of this suggests that the 80 atom supercell appropriately captures the characteristics of the disordered material.

Bulk moduli were calculated using the Murnaghan equation of state by curve fitting the energy vs. volume data. Calculations of elastic moduli used unit cells distorted by Equation (4.2) in conjunction with the strain tensors found in Equations (4.3) and (4.4). The variables $R$ and $R'$ are the original and distorted lattice vectors, respectively. In all cases, the total distortion of the structure was kept to less than 1%.

$$R' = (1 + \epsilon)R$$

$$\epsilon_{tet} = \frac{1}{3} \begin{pmatrix} -\delta & 0 & 0 \\ 0 & -\delta & 0 \\ 0 & 0 & 2\delta \end{pmatrix}$$

$$\epsilon_{orth} = \frac{1}{3} \begin{pmatrix} -0 & \delta & 0 \\ \delta & 0 & 0 \\ 0 & 0 & \delta^2 \end{pmatrix}$$

The three independent elastic constants of the cubic system ($C_{11}, C_{12}, C_{44}$) were calculated from the energy-strain relationships of the distorted cells and the bulk modulus using Equations (4.5) to (4.7)

$$U_{tet} = \frac{1}{3}(C_{11} - C_{12})\delta^2$$

$$U_{orth} = 2C_{44}\delta^2$$

$$B = \frac{1}{3}(C_{11} + C_{12})$$

The resulting elastic constants and bulk modulus were used to calculate the theoretical hardness with the model developed by Chen et al. Equation (4.8) defines the theoretical hardness as a function of the Pugh modulus ($k$) and the shear modulus ($G$). The Pugh modulus is in turn a function of the shear and bulk moduli, as shown in Equation (4.9). The shear modulus was calculated from the three independent elastic moduli using Equation (4.10).

$$H_v = 2(k^2 G)^{0.585} - 3$$

$$k = \frac{G}{B}$$

$$G = \frac{3(C_{11} - C_{12}) + C_{44}}{5}$$

48
4.4 Results and Discussion

The crystallographic structures of the high entropy carbide films were examined to ascertain phase purity and any preferential growth orientations. The large configurational entropy and similarity of the binary constituents was expected to favor formation of a \((\text{HfNbTaTiZr})_x\) solid solution over phase segregation or intermetallic formation. The structural transformation of \((\text{HfNbTaTiZr})_x\) as a function of methane flow is shown by the X-ray diffraction patterns plotted in Figure 4.1.

At the lowest methane flow (0.5 sccm), a polycrystalline mixture of BCC and HCP metallic structures was observed. An increase of the methane flow rate from 0.5 to 1.5 sccm transformed the metallic structure into an extremely carbon deficient rocksalt high entropy carbide with polycrystalline texture and broad diffraction peaks. Further increases in the methane flow resulted in sharp, polycrystalline textured rocksalt peaks up through a flow rate of 2.75 sccm. Above this flow rate, the films grew epitaxially with \{1 1 1\} texture and continued to grow epitaxially until a methane flow rate of 3.5 sccm. Finally, the rocksalt carbide reverted to polycrystalline texture at the highest methane flow rates (4.5 & 5.5 sccm), producing broader diffraction peaks with diminished intensity. The methane flow into the chamber had a profound effect on the final structure of the carbide films, with some large structural transformations occurring over small changes in flow rate. All samples formed single phase high entropy rock salt carbides to the detection limits of the instrument, except for the lowest flow rate (0.5 sccm) sample that exhibited mixed metallic structures.

The observed structural transformation in Figure 4.1 arose from the gradual increase of carbon in the high entropy carbide film. Carbon can be incorporated into the film in two distinct forms: it can occupy the anion lattice sites in the rocksalt structure and form C-M bonds, or it can precipitate and form C-C bonds elsewhere in the film (excess carbon). An x-ray photoelectron spectroscopy (XPS) investigation of concentration and relative fractions of bonded and excess carbon was critical to explain the structure property relationships in high entropy carbide films. High resolution XPS spectra of the C1s and Ta4f peaks are plotted with the corresponding peak fits in Figure 4.2.

At low methane flows (0.5–2.75 sccm), there was a single C1s peak present at \(\sim 282.5\) eV, except for the development of a slight high energy shoulder in the 2.75 sccm spectrum. This peak represents the carbon that is bonded to the metal, and the intensity increased with the methane flow rate. The system transitioned from a metallic structure with interstitial carbon to a rocksalt carbide as the amount of bonded carbon increased. A higher energy shoulder began to develop at 2.75 sccm due to the precipitation of excess carbon (C-C bonding) in the film. The shoulder developed into an excess carbon peak (\(\sim 284.8\) eV) and maintained a constant intensity through the 3 sccm spectra. Further increases in the methane flow rate (4.5–5.5 sccm) amplified the contribution of excess carbon.

The structural development of the carbide films (Figure 4.1) is strongly linked to the carbon stoichiometry. At low flow rates, the carbide structure is being populated with carbon atoms. A small amount of excess carbon precipitated when the structure saturated, followed by rapid precipitation at
Figure 4.1: X-ray diffraction patterns from (HfNbTaTiZr)C<sub>x</sub> films deposited at a range of methane flows using HiPIMS. Patterns are arranged as a function of increasing methane flow from 0.5 sccm (bottom, light red) to 5.5 sccm (top, blue). RS denotes peaks which correspond to the rocksalt carbide crystal structure. X-ray artifacts and secondary wavelengths (CuKα, WLa) are denoted by †.
Figure 4.2: High resolution XPS spectra as a function of carbon content for the C1s and Ta4f orbitals. The C1s peak is split in a lower binding energy C-M bonding peak and a higher binding energy C-C bonding peak. The Ta4f is split into the 4f_{5/2} and 4f_{7/2} orbitals. The black dots are experimental data, the blue and green lines are individual peak fits, and the red line is the sum of both peak fits. For the C1s peaks with only a red line, a single peak was fit.

higher flow rates. The amount of carbon also affected the relative peak positions of the metal peaks. At low flow rates, the Ta4f peaks (Figure 4.2) were at a lower binding energy due to the increased metallic bonding in these samples. The peak positions and intensities saturated at 2.75 sccm, coinciding with the development of the excess carbon shoulder. Further increases in methane flow produced no significant change in the spectra, indicating that the maximum quantity of Ta-C bonds had formed.

Sputtering is a non-equilibrium synthesis process; thus, the quantity of carbon in the structure, before excess carbon precipitates, is not necessarily indicative of a thermodynamic limit. Moreover, transition metal carbides and high entropy carbides are stable under extreme substoichiometry: the rocksalt structure can tolerate carbon vacancy concentrations as high as 50%, which substantially alters the properties. With these facts in mind, the bonded and total (bonded + excess) carbon contents (normalized by metal atoms) are plotted in Figure 4.3.

The bonded and total quantities of carbon deviated substantially at methane flow rates above 2.75 sccm. According to the data plotted in Figure 4.3, the fraction of bonded carbon increased until 4.5 sccm; conversely, the Ta4f spectra (Figure 4.2) suggested that the Ta-C bonds were saturated at 2.75 sccm. It is important to note that preferential sputtering of carbon from carbide films has been reported in the literature and these samples were presputtered with 3 keV Ar+ in the XPS. Consequently,
the spectra collected from presputtered samples resulted in a C/M ratio of 0.72 for the sample deposited with 2.75 sccm of methane. However, after accounting for this preferential sputtering (see Appendix A.1), the bonded carbon to metal ratio was ~0.96 in the 2.75 sccm sample. This indicated that the precipitation of excess carbon followed the occupation of nearly all carbon lattice sites in the rocksalt structure. The estimated bonded carbon content after accounting for the effects of presputtering can be found in Figure 4.3 as the red C-M (est.) trace.

Excess carbon precipitation led to the formation of a two-phase microstructure. Although the carbon phase was not discernable with the XRD measurements, the emergence of epitaxial growth (2.92 sccm of methane) coincided with the detection of a substantial amount of excess carbon by the XPS measurements. The precipitation of excess carbon and the transition from polycrystalline to epitaxial growth drove the corresponding microstructural transformation in Figure 4.4. Large metallic grains were observed at the lowest methane flow rate (0.5 sccm). The polycrystalline rocksalt structure at increased methane flows (1.5–2.75 sccm) resulted in a reduced grain size and wide range of grain shapes. Carbide grains began to favor a triangular morphology when excess carbon first precipitated (2.82 sccm), and further progression into the epitaxial methane flow regime (2.92–3.5 sccm) resulted in an entirely triangular-grained microstructure. Triangular grains formed in two domains (pointing roughly upwards or downwards), reflecting the 6-fold symmetry of the underlying c-plane sapphire substrate.
Figure 4.4: SEM micrographs of (HfNbTaTiZr)Cₓ films deposited with a range of methane flows.
As discussed above, XRD data revealed that the films deposited with 2.92 to 3.5 sccm of methane grew as \{1 1 1\} oriented epitaxial rocksalt carbide films. Cross-sectional scanning electron micrographs (Figure A.2) verified columnar growth of the films from the substrate surface. The lattice mismatch of the \{0 0 1\} sapphire and \{1 1 1\} rocksalt (HfNbTaTiZr)C_x planes is approximately 14\%, which allows for several degrees of in-plane (\phi) rotation of the triangular grains.\textsuperscript{7,143} Further increases in the methane flow suppressed columnar growth and produced a very fine-grained microstructure.

The observed grain size reductions (starting with 2.82 sccm) are linked with the precipitation of excess carbon at the grain boundaries. The precipitation of a significant amount of carbon can both restrict the growth of carbide grains and provide large quantities of nucleation sites, resulting in a nanocomposite structure. Similar microstructural features have been observed in sputtered binary carbides, with researchers determining that the amount of excess carbon controls both the grain size and grain separation.\textsuperscript{19,204,239} A diverse range of grain sizes can be produced in the nanocomposite regime simply by controlling the amount of excess carbon in the film. As a result, the amount of bonded and excess carbon governs the bonding, microstructure, and subsequently the functional properties of high entropy carbide films.\textsuperscript{19,189,201–206}

Transmission electron microscopy (TEM) analysis is necessary to detect any elemental or phase segregation on the nanometer length scale in high entropy materials.\textsuperscript{20,123} Furthermore, the degree of carbon vacancy ordering, which occurs in several transition metal carbides, can be explored in a chemically disordered crystal with high resolution imaging.\textsuperscript{112,240,241} The samples deposited with 2.5 and 3 sccm of methane were selected for TEM investigation. The former enabled the exploration of carbon vacancy induced defects (point, line, and area defects) present in a chemically disordered rocksalt carbide. The higher flow sample (3 sccm) allowed for examination of the amount and form of excess carbon which precipitates at higher flow rates.

A significant population of stacking faults and twin boundaries were discovered in the 2.5 sccm sample during low angle annular dark field (LAADF) imaging (Figure 4.5). Subsequent atomic resolution micrographs substantiated the presence of both stacking faults and twin boundaries in this \(~7\%\) carbon deficient carbide film. The atomic resolution scanning transmission electron microscopy (STEM) data provided evidence that carbon vacancies prefer to cluster and form stacking faults rather than randomly distribute, despite the chemically disordered lattice. In contrast, no defects were observed in the carbide structure from atomic to microstructural length scales in the sample deposited with 3 sccm of methane.

The chemical uniformity of the films was first examined with STEM energy dispersive spectroscopy (EDS). A cross-sectional micrograph and EDS maps from a region of the sample deposited with 2.5 sccm of methane can be found in Figure 4.6. The distribution of metal elements was mostly uniform across the film for both samples (3 sccm not pictured); however, there were some slight striations of titanium at the grain boundaries of both films (circled).

The compositions of the grain boundaries of both samples were investigated more closely with STEM electron energy loss spectroscopy (EELS). The STEM-EELS maps in Figure 4.7 indicated the presence of
Figure 4.5: Low angle annular dark field (LAADF) and annular dark field (ADF) transmission electron micrographs of (HfNbTaTiZr)Cₓ samples deposited with 2.5 (left) and 3.0 (right) sccm of methane. Some of the stacking faults and twin boundaries present in the 2.5 sccm sample are circled or labeled with arrows.

carbon, oxygen, and titanium in the grain boundary region of both samples. The grain boundary region of the 2.5 sccm sample was crystalline, as shown in the accompanying atomic resolution micrograph. Conversely, the grain boundaries of the 3 sccm sample appeared amorphous. Diffraction patterns were collected from the grain and grain boundaries of the 3 sccm sample with 4D STEM (Figure 4.8) in order to examine the crystallinity of each region. The carbide grain diffracted strongly, producing a diffraction pattern consistent with the \{111\} oriented epitaxial growth of the carbide grains. Conversely, the diffraction pattern from the grain boundary consisted of diffuse scattering, confirming that the grain boundary carbon phase is amorphous or poorly-crystalline.
Figure 4.6: HAADF micrograph and corresponding STEM energy dispersive spectroscopy (EDS) elemental maps collected from the (HfNbTaTiZr)C<sub>x</sub> film deposited with 2.5 sccm of methane. A titanium-rich grain boundary region is circled in the titanium map.

Titanium is the smallest and lightest of the constituent elements, as well as quite oxidation prone. Both of these factors support the observed preferential segregation of titanium to the grain boundaries at the modest deposition temperature (500 °C). Although titanium, oxygen, and carbon were detected in the grain boundary region via STEM EELS, there were no indications that any crystalline titanium oxides or oxycarbides had formed. This suggests that the deposition temperature or stoichiometry were insufficient to crystallize any Ti-C-O phases.

Raman spectroscopy further confirmed both the onset and the poorly-crystalline nature of excess carbon in the (HfNbTaTiZr)C<sub>x</sub> films (Figure A.1). The Raman spectra for films deposited with 2.75 sccm of methane or less were relatively flat and featureless in the region of interest (800–2000 cm<sup>-1</sup>). Samples deposited with methane flow rates at or above 2.82 sccm developed intense, broad peaks which corresponded to the D (1350 cm<sup>-1</sup>, defect induced breathing mode) and G (1565 cm<sup>-1</sup>, sp<sup>2</sup> bonding) modes of carbon. The onset of the carbon Raman peaks directly aligns with the onset of excess carbon.
Figure 4.7: Atomic resolution micrographs and STEM electron energy loss spectroscopy (EELS) maps of (HfNbTaTiZr)Cₓ films deposited with 2.5 and 3 sccm of methane. The EELS maps for carbon, titanium, and oxygen were collected in the boxed regions of each micrograph.

Figure 4.8: 4D STEM diffraction patterns (left) from a grain (G) and grain boundary (GB) in the (HfNbTaTiZr)Cₓ film deposited with 3 sccm of methane. The squares in the micrograph (right) denote the locations that these patterns were collected from.
precipitation determined by XPS (Figures 4.2 and 4.3) The XPS, TEM, and Raman data conclusively 
established the onset of excess carbon precipitation (2.82 sccm), and the poorly-crystalline and defective 
nature of the carbon at the grain boundaries. This behavior matches that of sputter deposited binary 
carbide counterparts in the literature.$^{5,19,22,234,244}$

Relationships between microstructure, carbon content, and hardness in the ($\text{HfNbTaTiZr})_x\text{C}_x$ films 
were studied using nanoindentation. Figure 4.9 compares the theoretical and density functional theory 
calculated (based on XPS bonded carbon stoichiometry) hardness data of high entropy carbide films 
as a function of increasing methane flow rate. The experimental hardness increased linearly with 
increasing methane flow rates up to 2.75 sccm, reaching a maximum value of 24 ± 3 GPa. Further 
increases in the methane flow resulted in a sharp drop of the hardness to around 10 GPa, which persisted 
throughout the epitaxial regime (2.82-3.5 sccm). The hardness rose back to ~15 GPa with the transition 
to a carbon-carbide nanocomposite microstructure at the highest methane flow rates (4.5–5.5 sccm).

The observed hardness trend in Figure 4.9 is strongly coupled with both the amount of bonded and 
excess carbon and the microstructural features of the carbide films. At low methane flows all of the 
carbon occupied the anion sites of the rocksalt structure, this continued until the structure was nearly 
carbon saturated by the 2.75 sccm methane flow rate (Figure 4.3). As the flow rate increased, the density 
of carbon-metal bonds in the structure also increased (Figure 4.2). The strong covalent bonds between

![Figure 4.9: Hardness values from nanoindentation experiments (Exp.) and density functional theory calculations (DFT) plotted as a function of the methane flow rate.](image)
metal and carbon linearly hardened the material until all of the carbon sites in the lattice were occupied in the 2.75 sccm sample, which was the hardest.

The measured hardness dropped sharply at flow rates in excess of 2.75 sccm, corresponding with the precipitation of excess carbon in the microstructure (Figures 4.2, 4.3, and A.1). The epitaxial films were substantially weakened by the thin layer of poorly crystalline excess carbon decorating the grain boundaries throughout the entire thickness of the film (Figure 4.5).

However, the carbide films rehardened at the highest flow rates (4.5–5.5 sccm of CH$_4$), coinciding with the formation of a nanocomposite microstructure. This behavior can be explained as the combination of three separate effects: grain size reduction, charge transfer from the nanocrystals to the excess carbon, and strengthening from a small fraction of sp$^3$ bonding. As described in the SEM analysis (Figure 4.4), the transition from 3.5 to 4.5 sccm of methane is accompanied by a microstructural transformation from large triangular grains to a carbide-carbon nanocomposite. The substantial quantity of carbon in the grain boundaries restricted grain growth and fostered nucleation of nanocrystalline carbide grains.$^{19,204}$

The metal-carbon bonds have a degree of ionicity, transferring a fraction of the metal's electrons to the neighboring carbon species. The quantity of charge transferred per metal atom depends on both the degree of ionicity and the surrounding coordination environment. All metal sites are octahedrally coordinated; thus, the charge transfer within the bulk of the crystal depends only on the elemental species.$^{(II)}$ At the edges of the crystal, the coordination environment changes. While the metal atom may still have half an octahedra tying it to the rocksalt crystal, the other half is exposed to the poorly crystalline carbon matrix.$^{245}$

The increased quantity of carbon nearest neighbors results in a greater amount of electron charge transfer, reducing the net charge on the metal. The enhanced charge transfer to the carbon increases the interfacial bonding at carbide-carbon boundary, strengthening the interface. Additionally, the net electron transfer from the metal atoms causes states at the Fermi level to empty at in the carbide phase. In Group IVB carbides the Fermi level is located in a region between bonding states and anti-bonding states, so this charge transfer would lower the amount of covalent bonding in the carbide.

However, the Fermi level is higher for the mixed Group IVB-VB carbide of this work, populating some non-bonding and anti-bonding states with electrons. A modest increase in electron transfer would empty these non or anti-bonding states, changing the shear strength of the material.$^{101,108}$ Furthermore, this electron depletion would be spread out across the entire carbide grain since the rocksalt carbides are metallic conductors. As a result, an appropriately high surface area (electron transfer) to volume (total electrons) ratio of the carbide grains could empty all non-bonding or anti-bonding states in the carbide material. The grain size reduction in the high methane flow samples should increase the impacts of this charge transfer mechanism.$^{19,245,246}$

Finally, the D and G peak positions and intensities from the Raman spectra (Figure A.1) suggest a small quantity ($<10\%$) of sp$^3$ bonding in the defective carbon matrix.$^{212,213,247-249}$ As more carbon

$^{(II)}$ Neglecting the effects of second-nearest neighbor metal species in a high entropy crystal.
precipitates, the mechanical properties of the nanocomposite are increasingly dominated by the matrix phase. However, the presence of sp$^3$ bonding would strengthen the carbon matrix, preventing the facile intergranular fracture observed in the epitaxial films. This theory is supported by the hardness values of the nanocomposite films (~15 GPa), which are near the reported and rule of mixtures values for carbide and a-C/DLC nanocomposite thin films.$^{19,164,244,249-251}$

The mechanical property evolution shown in Figure 4.9 is impacted by both the changes in bonding properties as well as the wide variation in microstructure features observed as a function of carbon content. Ab-initio calculations provide an avenue to validate the given explanations for the property trends by decoupling bonding and microstructural effects. The impacts of carbon vacancies on the bonding and hardness of the high entropy carbide were studied with density functional theory (DFT). The calculations predicted that the hardness would increase with an increasing carbon content and density of covalent bonds, as plotted in Figure 4.9. The calculated hardness for the stoichiometric carbide is comparable to the experimentally measured hardness value for the sample deposited with 2.75 sccm of methane as well.

However, there are limitations to the approach used to calculate hardness with DFT, as evidenced by the substantial deviation at low methane flows. The method used to calculate hardness, as developed by Chen et al., is based solely on the elastic constants of the material, more specifically the shear and bulk moduli.$^{232}$ The hardness of covalently bonded materials is dictated by the covalent bond strength, which is directly related to the elastic constants of the material. Conversely, the hardness of a metallically bonded material is dependent on plastic flow, dislocation formation, glide, and interactions with defects (dislocations, vacancies, grain boundaries, etc.). Consequently, the DFT predictions under-predicted the hardness of carbon deficient samples, which trade covalent bonds for metallicity. Predictions were accurate for stoichiometric or nearly stoichiometric compositions, as the high density of strong covalent bonds controlled the plastic deformation process and hardness of the material. Finally, the calculations indicated that the substantial drop in hardness above 2.75 sccm of methane is due to microstructural effects and excess carbon, rather than changes in the carbide stoichiometry.

The effects of anion vacancies on the bonding properties of (HfNbTaTiZr)C$_x$ were probed by evaluating the DFT calculated electronic structure. Figure 4.10 shows the electronic density of states as a function of carbon stoichiometry. Carbon stoichiometries were chosen based on the XPS data, with 1:1, 1:0.9, and 1:0.5 coinciding roughly with the 2.75, 2.5, and 1.5 sccm CH$_4$ samples, respectively. Additionally, an intermediate composition of 1:0.7 was added, which would occur around 2 sccm of methane.

The electronic structure of the stoichiometric composition (Figure 4.10, bottom left) represents a sample deposited with around 2.75 sccm of methane. In this composition, the Fermi level is significantly above the psuedogap (the minima between the pseudo-valence and pseudo-conduction bands), indicating the occupation of some non-bonding and anti-bonding states; conversely, states below the pseudogap are bonding in nature.$^{231,252-254}$
Figure 4.10: The electronic density of states (DOS) of (HfNbTaTiZr)C\textsubscript{x} presented as a function of carbon stoichiometry. The total density of states with 50, 70, 90, and 100% carbon occupancy (left). The partial density of states (pDOS) with 100% of carbon sites occupied (middle). The partial density of states (pDOS) with 70% of carbon occupancy (right). \(E_F\) marks the Fermi level in the density of states (fixed at 0 eV). \(P_{\text{gap}}\) denotes the location of the pseudogap, a minimum in the DOS that occurs between bonding and non-bonding/anti-bonding states. \(\dagger\) indicates the position of new energy states generated due to carbon vacancies.

A partial density of states (pDOS) analysis (Figure 4.10, center) was performed for the stoichiometric composition in order to determine which orbitals contributed most strongly to the bonding and anti-bonding states. The carbon 2p orbital and metal d orbitals contributed strongly to the density of states below the pseudogap, with peaks around -3 eV. The overlapping metal d and carbon p orbitals are indicative of the strong covalent bonding that gave rise to the high hardness in the near-stoichiometric (HfNbTaTiZr)C\textsubscript{x} film. The previously mentioned anti-bonding and non-bonding states, located above the psuedogap, are dominated almost entirely by metal d orbitals.

The density of states of compositions with a substantial fraction of carbon vacancies revealed new states between the pseudogap and Fermi level (denoted by \(\dagger\)). The density of the newly developed states intensified rapidly as the carbon vacancy concentration increased from 10 to 50% (Figure 4.10, left). The partial density of states (pDOS) analysis for (HfNbTaTiZr)C\textsubscript{x} with a carbon vacancy concentration of 30% is presented in Figure 4.10 (right). The carbon 2p orbital’s contribution to the density of states did not change substantially, despite the large increase in carbon vacancies. Conversely, the metal d orbitals contributed strongly to the new metallic states located between the pseudogap and Fermi level.
An evaluation of the electronic structure of TaC and WC by Medvedeva & Ivanovskii found that a carbon vacancy concentration of 12.5% introduced new energy states from the metal orbitals both above and below the Fermi level. The densities of states plotted in Figure 4.10 indicate that the introduction of carbon vacancies in high entropy carbides produced similar behavior, as the DOS also changed both above and below the Fermi level.

Closer analysis of the complete DOS plot (Figure 4.10, left) reveals that the pseudogap position (separating bonding and non/anti-bonding states) monotonically shifts to lower energies as carbon vacancies are added to the structure. Additionally, the hybridized pseudo-valence band (around -3 eV) narrows sharply and decreases in intensity as the carbon concentration decreases. Therefore, the introduction of carbon vacancies reduces the number of covalent bonds and replaces them with new metallic states in the chemically disordered structure. Unfortunately, these new metallic states cannot fully compensate for the lost covalent bonds, leading to the linear softening trend with an increase in carbon vacancy concentration.

### 4.5 Conclusions

This study focused on the synthesis and properties of the high entropy carbide, (HfNbTaTiZr)\(C_x\), as a function of carbon stoichiometry. Thin films were synthesized over a broad range of carbon stoichiometries using reactive RF magnetron sputtering. The resulting films exhibited structural transitions from metallic, to carbide, and finally carbide-carbon nanocomposite structures, simply by changing the methane flow during the deposition.

The highest hardness of 24 ± 3 GPa was obtained from a near-stoichiometric (HfNbTaTiZr)\(C\) film. Ab-initio calculations revealed that this result was dominated by the covalent bonding in the crystal, with microstructure playing a negligible role in the properties of the stoichiometric film. However, a modest increase in methane flow lowered the hardness to ~10 GPa due to the formation of a two-phase microstructure. The precipitation of poorly crystalline excess carbon weakened the grain boundaries of the columnar carbide film, facilitating easy fracture. Further increases in methane flow led to the formation of a carbide-carbon nanocomposite with increased hardness, albeit less than the near-stoichiometric carbide.

Anion vacancies clustered in stacking faults, similar to the Group VB carbides, despite the chemically disordered and distorted high entropy metal sublattice. The presence of anion vacancies in the high entropy crystal introduces new occupied metallic states that inadequately compensate for the lost strong covalent bonds, resulting in a reduced hardness. Overall, carbon substoichiometry appears to cause similar changes in the bonding, microstructure, and properties of high entropy carbides and binary carbides.
4.6 Acknowledgements

Abinash Kumar, Xi Chen, and James LeBeau were responsible for all of the transmission electron microscopy (TEM) work in this chapter.
Chapter 5
Refining the High Entropy Carbide Sputtering Process

5.1 Introduction

The reactive RF magnetron sputtering process used in the prior chapter provided insight into some of the characteristics of sputter deposited high entropy carbides including the formation of carbon vacancy stacking faults and strongly textured / highly crystalline growth. Samples made with conventional sputtering techniques also proved valuable for the study of thermal transport in highly disordered (metal lattice) and defective (carbon lattice) crystalline materials systems. However, this approach posed significant limitations, as stoichiometric films could only be deposited in a very narrow process window. When excess carbon did precipitate, it occurred suddenly, creating a large discontinuity in the otherwise linear carbon stoichiometry – methane flow rate trend. The rapid, unpredictable onset of carbon precipitation makes the synthesis and study of stoichiometric films even more challenging.

It was critical to improve the carbide deposition technique before exploring other high entropy compositions. The deposition process needed to be capable of predictably controlling the carbon stoichiometry of the films in order to facilitate reliable comparisons between high entropy compositions. Furthermore, a more forgiving processing window was desired to enable facile deposition of stoichiometric films without excess carbon. Achieving this control required the consideration of many facets of the deposition process including the supply and control of reactive gasses, the energetics of the deposition process, and accurately maintaining the metal flux despite target erosion and poisoning.

Experiments were designed to investigate how several factors impacted the carbon stoichiometry and processing window of sputter deposited high entropy carbide films. The complex interplay between inert and reactive gas flow rates, flow ratios, and partial pressures during the magnetron sputtering process was examined to understand which gas conditions play the strongest role in film stoichiometry. Tunable high energy ion bombardment was investigated as a means to influence the growth of carbide films in lieu of conventional temperature and pressure based approaches. Finally, the carbide processing window was examined under the combined influence of precisely regulated metal fluxes, high ionization fractions, and energetic bombardment during high power impulse magnetron sputtering (HiPIMS).
5.2 Regulating the Methane to Carbide Reaction

Reactive sputtering processes involve a delicate balance of sputtered and gaseous components. The metal flux is dictated by the applied power (and regulation mode), sputtering gas pressure, and sputter yield of the target surface. Meanwhile, the molecular flux of the reactive gas (into the chamber) is predominately controlled by the mass flow rate, while the reaction rate is dictated by the partial pressure of reactant. The reactive gas can also influence the metal flux by forming compounds with reduced sputter yields on the target surface. Transition metal carbides exacerbate these challenges due to the extreme range of stoichiometries that can form, from nearly metallic MC$_{0.25}$ to MC+$C_n$ nanocomposites (where n can exceed 100).

In principle, the partial pressure of the reactive gas controls the stoichiometry of the final film. A higher partial pressure of reactive gas results in more metal-reactant interactions and the formation of a compound with a higher fraction of reactant. Reactions between the sputtered film, target, and reactive gas give rise to the reactive sputtering hysteresis described in Section 2.3.2.

In Chapter 4, (HfNbTaTiZr)C$_x$ films were sputtered with a range of methane flows at a fixed total pressure of 5 mT, finding a narrow stoichiometric processing window at 2.75 sccm of methane. A further 0.07 sccm increase in the methane flow resulted in the precipitation of ~20% excess carbon. Flow rate was used as the primary carbon stoichiometry control for the prior work; however, flow rate was not the only variable that changed between samples. Increased methane flow rates also caused increases in the methane partial pressure, methane to argon flow ratio, and methane to argon partial pressure ratio. Furthermore, the argon partial pressure was reduced as a consequence of the fixed total pressure.

Since the prior films were deposited at a fixed total pressure, the changes in carbon stoichiometry could have been dictated by any of these variables:

1. The partial pressure of methane determines interaction rate between the reactive gas and film, based on the monolayer formation time.
2. The flow of methane dictates the rate that new methane molecules are added to the system. The turbomolecular pump and growing metal film deplete the atmosphere of methane.
3. The partial pressure of argon determines the sputtering rate, bombardment energetics, and target poisoning rate at a given power.
4. The partial pressure ratio of argon and methane can change the composition of the plasma and the poisoning of the target surface.
5. The flow ratio of argon and methane can dictate the partial pressure ratio in the chamber when operating in certain gas flow / pumping speed regimes.

While all of these variables are capable of influencing the outcome of the deposition, their impact (or lack thereof) depends on the exact processing conditions and equipment being used. For instance, at low flow rates the consumption of reactant by the film can significantly reduce the partial pressure, whereas
the consumption becomes insignificant at high flow rates.\textsuperscript{260–262} However, the definition of low or high flow rate depends on the rate at which the metal can consume reactive gas. This, in turn, is a function of sputtering rate, the surface area of the metal film, velocity of the gas, and sticking coefficient.\textsuperscript{260} Therefore, changes in nearly any detail including chamber design, target to substrate distance, target size, magnetron configuration, and pumping characteristics, among others, can all influence the point where the system transitions between low and high gas flow regimes modes or metallic and poisoned reactive sputtering modes.\textsuperscript{174,256–259,261}

Understanding the methane to carbide reaction required characterization of the interplay between gas flows, partial pressures, the deposition system, and the processes used in this work. Partial pressures, flows, and ratios needed to be decoupled in order to understand the relative influences on the process regime in this system. Unfortunately, it is not possible to fully isolate any one of these variables due to the inexorably linked nature of partial pressures, flow rates, and pumping speeds.

Instead, experiments were designed to limit the number of simultaneously changing variables in order to glean information about the deposition process. All of these experiments were tested by magnetron sputtering (HfNbTaTiZr)\textsubscript{C} with 200 W of RF power onto a 500 °C c-plane sapphire substrate, as these parameters allowed the data from the prior chapter to serve a basis for comparison. In all cases, the target was presputtered in argon for 5 minutes and the argon/methane mixture for 2 minutes before depositing for 8 minutes. This produced films which were 90 ± 15 nm thick (depending on conditions).

### 5.2.1 Decoupling Methane and Argon Partial Pressure

The films studied in Chapter 4 were deposited with a fixed total pressure of 5 mT. While this approach has seen use in reactive processes, it does have some disadvantages.\textsuperscript{263,264} Under total pressure control, any increases in reactive gas partial pressure (from increased flow) coincides with a decrease in the argon partial pressure. The increase in reactant partial pressure will further poison the target and decrease the sputter yield. Simultaneously, the reduced argon partial pressure can result in a decrease in the sputtering rate.\textsuperscript{256–259} The decline in sputtering rate reduces the consumption of reactive gas, increasing the reactive gas partial pressure further.

In essence, the fixed pressure approach can create a positive feedback loop that produces a much larger partial pressure change than expected from a given change in reactive gas flow rate. Furthermore, the reduction in inert gas partial pressure can influence deposition energetics and microstructural development.\textsuperscript{192,193} Regulating the argon partial pressure with the gate valve, while allowing the total pressure to vary, enables both gas partial pressures to be adjusted independently with flow rate, avoiding these drawbacks. This approach is often used in the reactive sputter deposition of a wide range of materials.\textsuperscript{166,201,262}

As such, the first experiment investigated the difference between a deposition at fixed total deposition pressure (5 mT) and one at a fixed argon partial pressure (5 mT). The gas flow rates of 20 sccm of argon
and 2.75 sccm of methane were kept constant for both depositions. These flows were selected because they produced the stoichiometric sample with the highest hardness in the prior chapter. The sample deposited with a $P_{Ar}$ of 5 mT had a total pressure of 6.2 mT.

X-ray diffraction (XRD) patterns from (HfNbTaTiZr)C$_x$ samples sputtered with a $P_{Ar}$ and $P_{total}$ of 5 mT are plotted in Figure 5.1. Both samples were predominantly \{1 1 1\} textured, with some secondary orientations present in the sample deposited at $P_{total} = 5$ mT. These results are in contrast to the 2.75 sccm of CH$_4$ film in Figure 4.1, which exhibited polycrystalline texture. Instead, these XRD patterns more closely match the samples deposited with 2.82–2.92 sccm of CH$_4$ in Chapter 4. The film deposited with 5 mT of argon was ~10% thicker, implying that the increased argon partial pressure (although unquantified) led to a higher deposition rate. Furthermore, the \{1 1 1\} XRD peak was over 70% more intense, suggesting that the increase in argon partial pressure improved the crystallinity of the film.

Micrographs of the films are shown in Figure 5.2. Both films had similar triangular grained microstructures, reflecting the strong \{1 1 1\} texturing of the films. The microstructure was slightly more

Figure 5.1: X-ray diffraction patterns from (HfNbTaTiZr)$_x$ films deposited with a total pressure (bottom, red) or argon partial pressure (top, black) of 5 mT. Both films were deposited with 20 sccm of Ar and 2.75 sccm of CH$_4$. RS denotes peaks which correspond to the rocksalt carbide crystal structure. X-ray artifacts and secondary wavelengths (Cu$_{k\beta}$, W$_{L\alpha}$) are denoted by ♦.
Figure 5.2: Scanning electron micrographs of (HfNbTaTiZr)$_x$ films deposited with a total pressure (left) or argon partial pressure (right) of 5 mT. Both films were deposited with 20 sccm of Ar and 2.75 sccm of CH$_4$.

well-defined for the sample deposited with 5 mT of argon, which may be a consequence of the higher texture and crystallinity of that sample. As with the XRD patterns, these micrographs most closely resembled the micrograph of the 2.92 sccm of CH$_4$ sample in Figure 4.4.

X-ray photoelectron spectroscopy indicated that the sample sputtered with a total pressure of 5 mT had approximately 15% more total carbon than the sample sputtered with $P_{\text{Ar}} = 5$ mT. This is most likely consequence of the greater metal flux associated with the higher argon pressure. However, both samples exhibited a fraction of excess carbon ($\sim C_{0.15-0.2}$) similar to that of the 2.92-3 sccm samples in Chapter 4.

The strong resemblance between the 2.92 sccm sample in Chapter 4 and the samples deposited with 2.75 sccm of methane in this chapter is believed to be related to the erosion of the HfNbTaTiZr target and the corresponding changes in plasma energetics and deposition rate. The films in Chapter 4 were deposited at rates an average of 25% higher than the samples in this section despite operating at the same power. The increased metal flux in Chapter 4 would result in decreased carburization for a given methane flow / partial pressure, as was evidenced by the contrast between these samples and the samples in Chapter 4. Counterintuitively, the methane flow only had to be reduced by $\sim 6\%$ to compensate for the $\sim 25\%$ reduction in metal flux between Chapters 4 and 5. This discrepancy is explored further in the following sections, using the 5 mT argon partial pressure sample as a basis for comparison.
5.2.2 Exploring the Role of Sputtering Gas Partial Pressure

Variations in the partial pressure of the sputtering gas can affect the sputtering rate of the metal target and the metal composition of the resulting film due to changes in gas phase scattering.\textsuperscript{256–259} The prior section demonstrated than an increase in the argon partial pressure raised the metal deposition rate and lowered the carbon content of the film. However, the increase in argon partial pressure was not quantified, just inferred from the increase of total pressure from 5 to 6.2 mT.

A series of films were synthesized in order to determine how significantly the argon partial pressure influences the final film. In order to do so the gate valve was throttled for an argon partial pressure of 5 mT with a flow of 20 sccm. Without adjusting the gate valve, films were sputtered at three different argon partial pressures (controlled by argon flow) while maintaining a fixed methane flow and partial pressure as listed in Table 5.1.

The film deposited at the lowest argon pressure was approximately 20% thinner than both the 5 and 10 mT samples. While low pressures limit gas phase scattering and increase the transmission coefficient\textsuperscript{(I)} the increased bombardment energy can decrease the sticking coefficient of the elements, reducing the overall deposition rate.\textsuperscript{256} Furthermore, the power supply was operated in constant power mode, thus reductions in sputtering gas pressure led to higher voltages and lower currents. This increase in voltage can reduce the sputtering efficiency (atoms sputtered / watt) of the plasma, although it is dependent on the particular gas-target-pressure combination.\textsuperscript{256,257,259,265} Finally, the reduced sputtering rate of the target could have increased the target poisoning, further decreasing the sputter yield and rate.\textsuperscript{164} Conversely, the 10 mT film had a similar thickness to the film deposited at the intermediate pressure.

All three films crystallized in a highly \{1 1 1\} textured rocksalt structure as shown in Figure 5.3. The peak of the sample deposited at the highest pressure was broader and shifted to higher angles than the other films, indicative of a lower carbon content. The low pressure film (2.5 mT) diffracted twice as strongly as the 5 mT sample and began to develop a Cu\textsubscript{Kβ} peak at 30.8° (2θ) despite being thinner. This increase in diffraction could be attributed to increased atomic bombardment and/or a change in carbon stoichiometry that enhanced the crystalline quality of the film (see data of Chapter 4).\textsuperscript{192,193}

Table 5.1: Flow rates and partial pressures used to study the impact of sputtering gas flow rate and partial pressure on the carburization of (HfNbTaTiZr)\textsubscript{C\textsubscript{x}} films.

<table>
<thead>
<tr>
<th>Ar flow (sccm)</th>
<th>CH\textsubscript{4} flow (sccm)</th>
<th>Ar partial pressure (mT)</th>
<th>Combined CH\textsubscript{4} + H\textsubscript{2} partial pressure (mT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>2.75</td>
<td>2.5</td>
<td>1.2</td>
</tr>
<tr>
<td>20</td>
<td>2.75</td>
<td>5.0</td>
<td>1.2</td>
</tr>
<tr>
<td>40</td>
<td>2.75</td>
<td>10.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>

\textsuperscript{(I)} The transmission coefficient is a measure of the fraction of sputtered atoms that reach the substrate.\textsuperscript{256}

69
Figure 5.3: X-ray diffraction patterns from (HfNbTaTiZr)C<sub>x</sub> films deposited with 2.5 (bottom, red), 5 (middle, black), and 10 (top, blue) mT of argon while maintaining a fixed methane flow (2.75 sccm) and partial pressure (1.2 mT). RS denotes peaks which correspond to the rocksalt carbide crystal structure. X-ray artifacts and secondary wavelengths (Cu<sub>Kβ</sub>, W<sub>Lα</sub>) are denoted by †.

Analysis of x-ray photoelectron spectra found no significant difference in the carbon stoichiometry of the 2.5 and 5 mT samples; however, the carbon content of the 10 mT sample was approximately 25% lower than the other samples. These data suggest that the increase in peak intensity of the 2.5 mT sample can be ascribed to increased atomic bombardment, as described in the literature.\textsuperscript{192,193}

The decreased carbon content of the 10 mT sample could be attributed a number of factors including an increase in the deposition rate of the metal, reduced reactive ion implantation in the target, and increased gas phase scattering. While the thickness of the 10 mT film was similar to the 5 mT sample, the lower carbon content and smaller lattice parameter indicate a greater density of metal atoms, and thus an increased metal flux at the higher argon pressure. Increases in sputtering gas pressure can also lead to decreased reactive ion implantation induced target poisoning.\textsuperscript{263,266} This mechanism may have reduced the carbon stoichiometry of the surface layer of the target, improving the sputter yield and reducing the carbon content in the film. Finally, the increased pressure would have resulted in increased gas phase scattering. While the film is not substantially thicker than the 5 mT film, the number of atoms sputtered...
off of the target could be significantly higher, albeit not coalescing on the substrate. However, these scattered metal atoms would react with methane, acting as a getter pump and reducing the amount of methane available for incorporation into the film.\(^{260}\)

While depositions at low argon partial pressures (<5 mT) do provide energetic benefits, the reduction of pressure is not without its consequences, including increased target poisoning and reduced plasma density. Conversely, an increased argon pressure will produce a higher plasma density which can facilitate the growth of stoichiometric films carbide films.\(^{19}\) An increase in pressure will have ramifications for the mean free path of the sputtered species; however, the deposition distance in this system is relatively short (~75 mm), limiting scattering.\(^{257}\) For the carbide system, the benefits of increased plasma density and reduced target poisoning at increased argon pressures (5–10 mT) outweigh the energetic benefits of low pressures. Furthermore, the energetics of the deposition can be controlled through other means, as will be discussed in Section 5.3.

### 5.2.3 Determining the Flow Rate and Gas Consumption Regime

A methane flow rate of 2.75 sccm was found to yield highly \{1 1 1\} textured (HfNbTaTiZr)\(_x\) films; however, it remained unknown what molar fraction of the methane gas was consumed during the sputtering process. Was the methane flow into the chamber sufficiently high that it could be considered an infinite source of methane molecules, or was the metal flux consuming a significant fraction of the reactive gas?\(^{261}\) With a constant gas flow ratio, the partial pressures of argon and methane (with no plasma) can be kept constant across a broad range of flow magnitudes by throttling the gate valve. If the fraction of methane consumed by the metal film is small, then there should be a critical flow rate where the reactive gas pumping speed of the film becomes insignificant relative to the physical pump. At this point, further increases in the flow rate will not impact the partial pressure or carbon stoichiometry.\(^{\text{(II)}}\)

A series of films were synthesized using a fixed 20:2.75 Ar:CH\(_4\) flow ratio with an 8 fold change in flow rate in order to test which flow regime the process was in. The argon partial pressure was fixed at 5 mT by throttling the gate valve before the turbomolecular pump during the argon presputtering step. The flow rates and partial pressures from this study are listed in Table 5.2. The combined partial pressure of methane and hydrogen gas was derived from the total pressure and argon partial pressure (5 mT). The 8 fold change in flow magnitude resulted in a 4.4 fold change in P\(_{\text{CH}_4+\text{H}_2}\) despite a fixed P\(_{\text{Ar}}\) of 5 mT.\(^{\text{(III)}}\)

X-ray diffraction patterns of the (HfNbTaTiZr)\(_x\) samples deposited as a function of increasing argon and methane flow magnitude are shown in Figure 5.4. The XRD patterns indicate that the films grew significantly differently, despite maintaining a fixed Ar/CH\(_4\) flow ratio. The film with the lowest flow ratio exhibited broad peaks, implying that this film was grown in extremely carbon deficient (metal-like) conditions. The \{1 1 1\} peak of the 10:1.38 film was located at a higher angle than the 20:2.75 film which

\(^{\text{(II)}}\) This would require the flow ratio to be constant and the gate valve to be throttled to maintain a fixed argon partial pressure.

\(^{\text{(III)}}\) Note that the highest flow sample was deposited at 40:5.4 rather than the intended 40:5.5 Ar:CH\(_4\) ratio. This error resulted in a 2% change in the flow ratio relative to the other samples, but it did not interfere with the conclusions of this section.
Table 5.2: Flow rates and partial pressures used to study the impact of flow rate magnitude (at fixed flow ratio) on the carburization of (HfNbTaTiZr)C_x films.

<table>
<thead>
<tr>
<th>Ar flow (sccm)</th>
<th>CH_4 flow (sccm)</th>
<th>Ar partial pressure (mT)</th>
<th>Combined CH_4 + H_2 partial pressure (mT)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.69</td>
<td>5</td>
<td>0.5</td>
</tr>
<tr>
<td>10</td>
<td>1.38</td>
<td>5</td>
<td>0.6</td>
</tr>
<tr>
<td>20</td>
<td>2.75</td>
<td>5</td>
<td>1.2</td>
</tr>
<tr>
<td>40</td>
<td>5.40</td>
<td>5</td>
<td>2.2</td>
</tr>
</tbody>
</table>

Figure 5.4: X-ray diffraction patterns from (HfNbTaTiZr)C_x films deposited across an 8 fold change in flow magnitude (doubling with each successive trace from bottom to top) while maintaining a fixed 20:2.75 Ar/CH_4 flow ratio and argon partial pressure (5 mT). RS denotes peaks which correspond to the rocksalt carbide crystal structure. X-ray artifacts and secondary wavelengths (Cu_Kβ, W_Lα) are denoted by ♦.
served as the basis for comparison. This behavior indicates that, while the carbide structure had formed, it was still quite carbon deficient. Finally, the XRD pattern of the sample deposited with the highest flow rates corresponded relatively closely to the standard sample.

The carbon stoichiometry of the films was measured using X-ray photoelectron spectroscopy to glean information about the impacts of flow magnitude on film stoichiometry. The film with the lowest flow ratio had a stoichiometry around MC$^{0.3}$ which aligns closely with the observation of metallic character in the x-ray diffraction patterns. A doubling of the gas flow rates only resulted in a modest increase to a stoichiometry near MC$^{0.5}$. The stoichiometries of these low flow rate samples were close to those of samples deposited with similar (0.5 and 1.5 sccm) methane flow rates in Chapter 4. The increase from 20:2.75 to 40:5.4 was accompanied by a doubling of excess carbon from $\sim$15 to 30 at. % (metals basis), resulting in a carbon stoichiometry near that of the 5.5 sccm sample in Chapter 4.

This experiment demonstrated that the magnitude of gas flows can cause significant changes in the carburization of the final carbide film. The system was clearly operating in a regime where the consumption of methane by the growing film was a significant contributor to the total methane pumping speed, as evidenced by the reduced partial pressure during the deposition of the low flow samples. The increased partial pressure during the deposition of the high flow sample was likely a consequence of the large amount of hydrogen which is produced from the methane and pumped away slowly by the turbomolecular pump.$^{209}$

Unlike the reactive deposition of oxides or nitrides, the carbide film's ability to uptake carbon is never satiated. As a result, increases in gas flow continue to increase the carbon stoichiometry of the film well past stoichiometry. Given this characteristic, the flux of methane molecules (as controlled by the flow rate) must be closely matched to the flux of metal atoms sputtered off of the target. However, it is important to note that the 8 fold change in flow rate was accompanied by a 4.4 fold change in the partial pressure of reactive gasses (CH$_4$ and H$_2$). Thus, the relative contributions of methane partial pressure and flow needed to be established.

### 5.2.4 Understanding the Contribution of Methane Flow

The outcomes of the prior section indicated that the combined effect of reactive gas flow magnitude and partial pressure can have significant impacts on the resulting film. In order to isolate the contribution of methane flow, the reactive gas partial pressure must remain fixed across several depositions. Decoupling these variables can be accomplished by varying the methane to argon flow ratio from sample to sample.

Films were deposited with argon flows of 10, 20, and 40 sccm. The argon pressure was throttled to 5 mT during the 5 minute argon presputtering step. Throughout the 2 minute argon/methane presputtering step, the flow rate of methane was gradually increased until the combined partial pressure of the reactive gasses reached 1.2 mT (i.e. 6.2 mT total pressure). The resulting methane flow rates are listed with other gas parameters in Table 5.3.
The X-ray diffraction patterns from this series of films are plotted in Figure 5.5. All three films were highly \{1 1 1\} textured with some secondary orientations in the 40:3.6 film, albeit near the noise floor. The peaks of the medium and high flow samples were sharper than the low flow sample, suggesting higher crystallinity in these samples. Meanwhile, the peaks of the low flow sample were shifted to slightly higher angles, indicating a lower lattice carbon content than the other samples.

The microstructure of these films was examined with scanning electron microscopy. A representative micrograph from each sample is displayed in Figure 5.6. The medium and high flow samples had similar triangular grained microstructures; although, the highest flow sample had a greater concentration of anomalously large grains. Conversely, the low flow sample had an equiaxed microstructure which closely resembled the microstructures of samples deposited with 1.5 to 2.5 sccm of methane in Chapter 4. This coincides with the compositional analysis that indicated the low flow rate film had \(\sim\) 20% less carbon than the films deposited at higher flow rates, which had similar stoichiometries.

The films of this section were deposited with fixed partial pressures of argon and reactive gasses. A consistent sputtering rate and metal flux between the three sets of gas flows was facilitated by the fixed argon partial pressure. In theory, the carburization of the growing film was governed by the interaction rate with the gas, which was dictated by the partial pressure of reactive gas.\(^{266}\) This suggests that there should have been no difference between any of these films as they should have the same metal and reactant fluxes.

However, there were clearly microstructural, crystallographic, and compositional differences between the films. This discrepancy can be explained by a combination of the pressure measurement technique and gas pumping mechanics. First, the reactive gas partial pressure was determined from the total pressure and argon partial pressure, as measured by a convection enhanced Pirani gauge. This gauge cannot discriminate between gas types; as a result, it was limited to measuring the sum of \(P_{\text{CH}_4}\) and \(P_{\text{H}_2}\), which was kept at a constant 1.2 mT. However, the partial pressure ratio \(P_{\text{CH}_4}/P_{\text{H}_2}\) may have changed between depositions, resulting in a lower \(P_{\text{CH}_4}\) for the low flow deposition.

Gas pumping mechanics can justify this hypothesis. The gas load (mass flow pumping rate) of a pump (Q) is defined as the product of the volumetric pumping speed (S) and the partial pressure of the gas of interest (P), as defined in Equation (5.1).
Figure 5.5: X-ray diffraction patterns from (HfNbTaTiZr)C\textsubscript{x} films deposited with fixed argon (5 mT) and reactive gas (1.2 mT) partial pressures arranged as a function of increasing gas flow (bottom to top). RS denotes peaks which correspond to the rocksalt carbide crystal structure. X-ray artifacts and secondary wavelengths (Cu\textsubscript{K\beta}, W\textsubscript{L\alpha}) are denoted by †.

Figure 5.6: Scanning electron micrographs of (HfNbTaTiZr)\textsubscript{x} films deposited with fixed argon (5 mT) and reactive gas (1.2 mT) partial pressures arranged as a function of increasing gas flow (left to right).
The pumping speed ($S_m$) of the sputtered metal getter pump is a function of the area ($A$), velocity of gas ($v$), sticking coefficient ($s$), and a geometric constant (Equation (5.2)). The pumping speed of the metal film can be treated as a constant, as none of these variables changed between depositions.

$$S_m = \frac{Avs}{4}$$

(5.2)

The gas load of a getter pump ($Q_m$) is a function of the metal atom supply rate ($\lambda_m$), specific volume of the gas ($V_{CH_4}$), number of gas molecules consumed by each metal atom ($n$), and Avogadro’s number ($N_A$) by Equation (7.5).

$$Q_m = \frac{\lambda_m V_{CH_4} n}{N_A}$$

(5.3)

The metal flux of the films was roughly constant, as all films had similar deposition rates. The films deposited at the lowest flow rate had a lower stoichiometry (by $\sim$20%), and thus a lower $n$ than the other samples, which indicates a lower gas load. However, the pumping speed of the getter pump was a fixed value, as none of the variables in Equation (5.2) changed between the deposits. Thus, the only way to lower the gas load of the metal getter pump was to lower the partial pressure of methane, as demonstrated by Equation (5.1).

Unfortunately, while a Pirani gauge could measure reactive gas partial pressure during oxide or nitride depositions, it is unsuitable for carbide depositions due to the production of $H_2$ gas. The samples at higher flow rates were quite similar, suggesting that the total partial pressure technique could be valid at high gas flow rates. At these flows, the film may not consume enough methane to substantially change the methane to hydrogen partial pressure ratio with modest changes in the methane flow rate. However, this would not be a reliable approach, as the Pirani gauge would not be able to distinguish when the methane to hydrogen partial pressure ratio began to change. As a result, there could be unpredictable or discontinuous changes in carbon content as a function of the total reactive gas partial pressure, due to underlying changes in the methane partial pressure.

### 5.2.5 Refining the Gas Control Approach

The information gleaned from the prior set of experiments presents a few routes to improve the selection of gas flows and pressures during the high entropy carbide deposition process. Operating under a fixed argon pressure increases the stability and predictability of the metal flux and stops the positive feedback loop between methane flow, argon partial pressure, and sputtering rate. Section 5.2.2 demonstrated that while lower argon pressures do provide energetic advantages, they also sacrifice deposition rate...
and plasma density. Higher pressures (5–10 mT) increase plasma densities and reduce target poisoning, improving carbon stoichiometry control; meanwhile, the low deposition energetics can be compensated for with other techniques.

Sections 5.2.3 and 5.2.4 demonstrated that the growing film can consume a significant fraction of the methane introduced into the chamber, reducing the methane partial pressure. This limitation can be overcome by operating under very high gas flow rates, as pioneered by Serikawa & Okamoto. At high flows, the consumption of reactant by the growing film becomes negligible, and the partial pressure of the reactive gas scales linearly, rather than hysteretically, with the flow rate of reactive gas.160–163

Typically, this involves inert gas flows in excess of 100 sccm with reactive gas flows on the order of 20-50 sccm. The required volumetric pumping speed for a deposition with 150 sccm of total gas flow and a 5 mT process pressure can be calculated from the process pressure \( P_p \) and flow rate \( \dot{m} \) of gas as demonstrated in Equation (5.4). The pump used in this work has a maximum pumping speed of 240 L/s neglecting any restrictions in conductance, such as the gate valve. A pump with several times the capacity and an exponentially higher price would be necessary to implement this approach. Additionally, new high capacity mass flow controllers and potentially a new chamber with a larger flange for the larger pump would be necessary. This approach is seldom used for these reasons.160,163

\[
m \frac{P_{atm}}{P_p} = 150 \text{sccm} \left( \frac{760 \text{Torr}}{5 \times 10^{-3} \text{Torr}} \right) \left( \frac{1 \text{L}}{10^3 \text{cm}^3} \right) \left( \frac{1 \text{min}}{60 \text{s}} \right) = 380 \text{L/s} \quad (5.4)
\]

Section 5.2.4 demonstrated that monitoring the partial pressure of methane could be a useful metric; however, it must be possible to measure the methane partial pressure, rather than the sum of contributions from methane, hydrogen, and other hydrocarbons.167 Optical emission spectroscopy is often used to infer the partial pressure of reactive gas from the decrease in optical emission from the target material, but the opaque carbide films would quickly coat any unshuttered viewport in the system, preventing continuous process monitoring. An alternative method involves the use of a mass spectrometer to directly measure the partial pressure of the reactive gas. In order to implement this approach, a rapidly scanning, high pressure residual gas analyzer is needed. While commercially available, they are quite costly, the maximum pressure of 8 mT does not leave much overhead, pressures are prone to drift over time, and the instrument can be affected by sputtered material.161

The best approach, considering the expense and challenges of the high flow and partial pressure techniques, is operating at a fixed argon partial pressure (5–10 mT) and carefully controlling the flow rate of methane. Increases in the flow rate of methane will produce a linear increase in the partial pressure when a plasma isn’t lit. Upon igniting the plasma and sputtering, the film will begin consuming methane based on the pumping speed and partial pressure of methane until the \( P_{\text{CH}_4} \) is reduced to a steady state condition. This steady state condition will be a function of the metal flux (ability to consume methane) and the methane flow rate. While this should produce relatively linear behavior up until the metal film is saturated with carbon, it will be dependent on maintaining a consistent metal flux.
5.3 Influence of Tunable Deposition Energetics on Carbide Film Growth

5.3.1 Microstructural Trends in Physical Vapor Deposited Films

For over half a century, the selection of thin film growth conditions has been guided, in part, by structure zone diagrams. The earliest diagrams were developed from trends observed in evaporated films by Movchan & Demchishin. These diagrams were only a function of the homologous temperature \( T_h \), a normalization of the deposition temperature by the film's melting point (both temperatures in Kelvin). Depositions below 0.3\( T_h \) rapidly quench the arriving atoms, limiting rearrangement and producing fine grained films. An increase to the range of 0.3–0.5\( T_h \) lowers the quench rate sufficiently for surface atoms to diffuse, resulting in columnar films with increased density. Bulk diffusion becomes significant when the deposition temperature exceeds half of the melting point, recrystallizing the film into a dense, three dimensional microstructure.

Unfortunately, many of the compositions of interest in this work have extreme melting points. For instance, the constituents of \((\text{HfNbTaTiZr})_x\) have an average melting point of \( \sim 3600 \, ^\circ\text{C} \). A substrate temperature in excess of \( \sim 900 \, ^\circ\text{C} \) would be required to achieve a homologous temperature over 0.3 and encourage surface diffusion on the growing film. The chamber in this work can heat the substrate \( \sim 900 \, ^\circ\text{C} \) by operating the element at its maximum working temperature of 1200 \( ^\circ\text{C} \); however, depositions at these extreme temperatures are impaired by substrate reactions. Silicon carbide and silicon substrates form silicides with metal constituents, sapphire can oxidize the Group IVB elements, and refractory metal (W, Ta, Mo) foils will diffuse into the films. Consequently, increasing the deposition temperature is not a very tractable approach to influence the microstructure of high entropy carbide films.

Once magnetron sputtering was widely adopted, researchers quickly found that single variable (homologous temperature) structure zone models were no longer sufficient to explain processing trends. Sputtering produced neutral and ionic species with significantly higher kinetic energies than evaporated species. The combination of kinetic energy from incident sputtered atoms and thermal energy from the substrate dictated the microstructure of sputtered films. Eventually, Thornton published a structure zone diagram that used homologous temperature and argon pressure (an analog for kinetic energy). At low pressures, sputtered species make it to the substrate with no collisions, retaining enough energy to encourage adatom rearrangement on the surface of the film. Conversely, at higher pressures, sputtered atoms collide with the inert gas before reaching the substrate, dissipating energy. The microstructure of carbide films could be improved by reducing argon pressure to avoid gas phase scattering. However, as established in Section 5.2, the argon pressure also can strongly influence the film stoichiometry through changes in target poisoning and plasma density.

Subsequently, researchers have found other means to control the energy of incident atomic and ionic species independently of process pressure. Messier et al. replaced the argon pressure axis with an ion energy axis, controlling the ion energy with the floating potential of the substrate. Researchers
have continued to modulate the ion energy with several approaches, most commonly choosing to apply bias to the substrate or use ion assisted deposition sources.\textsuperscript{158,172,173} As a result, Anders published a new structure zone model which presented microstructural trends as a function of a generalized temperature (a combination of the homologous temperature and thermalization of the heat of condensation) and a normalized kinetic energy (addressing atomic displacement and heating effects from kinetic energy).\textsuperscript{173}

High power impulse magnetron sputtering (HiPIMS) can produce high fractions of ionized species, facilitated by the extreme plasma densities of the HiPIMS discharge.\textsuperscript{168,173} Many researchers have taken advantage of this characteristic, increasing the energy of these ions with substrate bias during or after the HiPIMS pulse.\textsuperscript{173,271,272} However, unlike conventional sputtering, HiPIMS operates at very low duty cycles (often less than 5\%) which leaves the magnetron and target under no bias for much of the deposition process.\textsuperscript{168} Instead of leaving the target floating after the HiPIMS pulse, the target can be positively biased, precisely adding energy to the ionic species.\textsuperscript{182,273} The benefits of incorporating this positive pulse — known as bipolar HiPIMS — have been demonstrated predominately with elemental carbon and metal films.\textsuperscript{180–182,274–276}

5.3.2 Impact of High Energy Ion Bombardment During Sputtering of Carbide Films

High energy ion bombardment via B-HiPIMS is a promising strategy to modify the microstructure of high entropy carbide films, while avoiding the shortcomings of thermal or pressure based approaches. However, it is uncertain how the high energy bombardment will affect the metal and carbon stoichiometries of the resulting film. There are very few reports on reactive bipolar HiPIMS, with most focusing on hard nitrides. Viloan \textit{et al.} reactively sputtered TiN with B-HiPIMS, finding an increase in compressive stress, hardness, and film density with increasing positive pulse voltage, but they did not report any titanium to nitrogen ratios.\textsuperscript{186} Batková \textit{et al.} compared CrN films deposited with bipolar HiPIMS or HiPIMS with substrate bias, finding that B-HiPIMS changed the residual stress of the films with no change in the Cr:N ratio.\textsuperscript{185} As of this time there don't appear to be any publications describing bipolar HiPIMS deposition of films with multiple metal constituents. With high enough ion energies, it may be possible to preferentially resputter the growing film, depleting it of some metal species.\textsuperscript{173,237}

The HiPIMS supplies used in this work support bipolar HiPIMS with delays as low as 4\,µs between negative and positive pulses, and a positive pulse voltage as high as 200\,V. (HfNbTaTiZr)\textsubscript{C\text{x}} films were deposited with positive pulse voltages ranging from 20 to 150 volts in order to study the impacts of ionic bombardment energy on the growth of high entropy carbide films. Following the work of Keraudy \textit{et al.}, this should produce ion populations with ion energies ranging 20–300\,eV (based on 1+ and 2+ ionic species).\textsuperscript{182} The depositions were voltage (on the DC supply) and power (on the HiPIMS supply) regulated to produce consistent fluxes and target bombardment energetics across all films. The pulsing frequency on the HiPIMS supply was allowed to vary in order to maintain a fixed power. All parameters used during the depositions are found in Tables 5.4 and 5.5.
Table 5.4: Source conditions used to deposit (HfNbTaTiZr)Cₓ films with a range of ionic bombardment energies

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage (-V)</td>
<td>700</td>
</tr>
<tr>
<td>Frequency (Hz)</td>
<td>350–380</td>
</tr>
<tr>
<td>Maximum power (W)</td>
<td>250</td>
</tr>
<tr>
<td>Pulse width (µs)</td>
<td>75</td>
</tr>
<tr>
<td>Pulse current limit (A)</td>
<td>25</td>
</tr>
<tr>
<td>Positive pulse delay (µs)</td>
<td>4</td>
</tr>
<tr>
<td>Positive pulse length (µs)</td>
<td>400</td>
</tr>
<tr>
<td>Positive pulse voltage (+V)</td>
<td>20–150</td>
</tr>
</tbody>
</table>

Table 5.5: Chamber conditions and sputtering durations used to deposit (HfNbTaTiZr)Cₓ films with a range of ionic bombardment energies

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar Flow (sccm)</td>
<td>20</td>
</tr>
<tr>
<td>Ar pressure (mTorr)</td>
<td>7.5</td>
</tr>
<tr>
<td>Methane flow (sccm)</td>
<td>3.0</td>
</tr>
<tr>
<td>Total pressure (mTorr)</td>
<td>9.1 ± 0.1</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>500</td>
</tr>
<tr>
<td>Presputter times (s)</td>
<td>300 (Ar)</td>
</tr>
<tr>
<td>Sputter time (s)</td>
<td>120 (Ar &amp; CH₄)</td>
</tr>
<tr>
<td></td>
<td>1600 (~0.5 µm)</td>
</tr>
</tbody>
</table>

Figure 5.7: X-ray diffraction patterns from (HfNbTaTiZr)Cₓ films deposited using bipolar HiPIMS. Patterns are arranged as a function of increasing kick voltage from 20 V (bottom, red) to 150 V (top, light blue). RS denotes peaks which correspond to the rocksalt carbide crystal structure. X-ray artifacts and secondary wavelengths (CuKβ, WLa) are denoted by ♠.
X-ray diffraction patterns from (HfNbTaTiZr)C_x films deposited with 20, 50, 100, and 150 volt positive pulses are plotted by voltage in Figure 5.7. All films crystallized in a phase pure rocksalt structure irrespective of the positive pulse voltage and ion energy. However, the texture of the films did change as a consequence of the high energy bombardment. The film deposited with a 20 volt positive pulse was mostly \{1 1 1\} textured, but had a strong presence of \{2 0 0\}, \{2 2 0\}, and \{3 1 1\} oriented grains. An increase to 50 volts resulted in the disappearance of these secondary orientations, producing nearly perfect \{1 1 1\} texture to the detection limits of the instrument. Further increases in ion energy lead to the return of secondary orientations, this time favoring the \{3 1 1\}, with smaller contributions from the \{2 2 0\} and \{2 0 0\} than the sample deposited with a 20 volt positive pulse. These changes in orientation suggest that 50 eV ionic bombardment may drive the system towards the ion-assisted epitaxial growth and preferentially textured nanocrystalline regimes of Anders's structure zone diagram.

Closer inspection of the \{1 1 1\} peak presents some additional ramifications of increased ionic bombardment energy. The position of the peak shifted to lower angles with a pulse voltage in excess of 50 V, indicating the development tensile stresses out-of-plane and compressive stresses in-plane (Table 5.6). The highest energy condition (150 V) strained the film out-of-plane by 1.41% relative to the 20 volt film. Assuming an elastic modulus of 300 GPa, this change in strain represents a greater than 4 GPa change in the out-of-plane residual stress of the film. This demonstrates that the energy and momentum imparted by high energy ions is sufficient to influence the stress state of systems with strong bonding and a large degree of chemical disorder. Similar behavior has been observed in bipolar HiPIMS deposited metal and nitride films.

The high energy ionic bombardment also influenced the crystalline quality of the (HfNbTaTiZr)C_x films. A moderate ion energy (50 V pulse) decreased the full width at half maximum of the \{1 1 1\} peak by 25% while higher energies resulted in a broadening of the peak. This characteristic, combined with changes in texture, implies that modest ion bombardment energies encourage surface rearrangement of the growing carbide film, favoring a uniform lattice parameter and growth of the \{1 1 1\} grains. Conversely, high energy bombardment appears to damage the crystalline structure of the film, producing broader and less intense diffraction peaks as well as encouraging the nucleation of grains in other orientations (Table 5.6).

The microstructures of the films were also affected by the high energy ion irradiation produced by bipolar HiPIMS. Representative scanning electron micrographs from each sample are shown in Figure 5.8. The sample deposited with the lowest energy had a substantial fraction of small, faceted grains interspersed throughout a relatively equiaxed matrix. A modest increase in ion energy from 20 to 50 eV produced a smoother, more equiaxed, and homogeneous surface microstructure, with far fewer small faceted grains. Further increases in deposition energy retained the low concentration of faceted grain but increased the roughness and contrast of grain boundaries. This suggests that positive pulses in excess of 50 V provide sufficient energy to begin ion etching the film.

\[^{[5]}\] There is a miniscule feature present at the \{2 2 0\} position, barely surpassing the noise floor.
Table 5.6: Interplanar spacing, integrated intensity, and full width at half maximum measured from the \{1 1 1\} peak of the X-ray diffraction patterns plotted in Figure 5.7 Out-of-plane strain (positive is tensile) and relative intensity are calculated with respect to the sample deposited with a 20 V positive pulse.

<table>
<thead>
<tr>
<th>Positive pulse voltage (V)</th>
<th>d-spacing {1 1 1} (Å)</th>
<th>Strain relative to 20 V (%)</th>
<th>Integrated intensity (10^5 cps-degrees)</th>
<th>Intensity relative to 20 V (%)</th>
<th>FWHM (degrees)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2.600</td>
<td>0.00</td>
<td>1.56</td>
<td>0</td>
<td>0.387</td>
</tr>
<tr>
<td>50</td>
<td>2.599</td>
<td>−0.04</td>
<td>3.88</td>
<td>+149</td>
<td>0.288</td>
</tr>
<tr>
<td>100</td>
<td>2.617</td>
<td>+0.69</td>
<td>2.08</td>
<td>+33</td>
<td>0.453</td>
</tr>
<tr>
<td>150</td>
<td>2.636</td>
<td>+1.41</td>
<td>2.09</td>
<td>+34</td>
<td>0.663</td>
</tr>
</tbody>
</table>

Figure 5.8: Scanning electron micrographs of (HfNbTaTiZr)_x films deposited using bipolar HiPIMS with a range of positive pulse voltages from 20 (upper left) to 150 (lower right) volts.
Further evidence of etching was manifested in the thickness of the resulting films, as measured by SEM using cleaved cross sections. The film deposited with a 20 V pulse reached the intended thickness of 0.5 µm based on a calibration film deposited at the same conditions. However, films deposited with higher positive pulse voltages (50–150 volts) were approximately 15% thinner than the sample deposited with 20 V. This indicates that substantial etching, occurs somewhere between 20 and 50 V, before many of the positive effects are observed at 50 V. A similar decrease in deposition rate has been observed in copper films deposited with bipolar HiPIMS; however, others reported an increased deposition rate with similar conditions.\textsuperscript{180,181}

Curiously, no substantial difference in etch rate is observed between 50 and 150 V despite a significant change in the surface microstructure and crystal structure. However, high energy ion bombardment has been demonstrated to produce porosity in many materials systems via collision cascades and noble gas implantation.\textsuperscript{190,277,280,281} Furthermore, bombardment could also produce hydrogen gas bubbles from the residual hydrogen in the film, left over from the reactive sputtering process.\textsuperscript{15,189,201} Large compressive residual stresses (Table 5.6) in ion irradiated films have been attributed to the implantation of argon gas in the film.\textsuperscript{277} High pulse voltages may have reduced the film density in addition to the thickness, but further investigation is necessary to draw any conclusions. Nevertheless, given the deleterious effects of high energy bombardment on the microstructure and crystal quality, the positive pulse shouldn’t exceed 50 volts for the deposition of high entropy carbide films.

There is precedent for the preferential resputtering of species during high energy ion irradiation.\textsuperscript{237,282–284} The composition of the films was measured by X-ray photoelectron spectroscopy after etching away the top 20 nm with the in-situ 3 keV Ar\textsuperscript{+} beam. Despite the broad range of crystallographic characteristics, stress states, microstructures, roughnesses, and thicknesses, no significant changes in the metal ratio or carbon content were observed as a function of ion bombardment energy. This may be a consequence of the dilute concentration of light metals (which preferentially resputter more readily) in a heavy metal rich matrix and the high enthalpy of formation of the transition metal carbides.\textsuperscript{284,285(VI)}

Although bipolar HiPIMS provides a pressure and temperature independent means to influence the microstructure of high entropy carbide films, it is not without its drawbacks. Modest positive pulse voltages can significantly improve the crystal quality, texture, and surface roughness of the films with only a slight reduction in deposition rate. However, the magnitude of the positive pulse voltage (and thus ion energy) requires judicious selection. The overzealous use of high ion energies can roughen films, lower crystallinity, randomize crystallographic orientations, and produce porosity, all of which can have a deleterious impact on the properties of the film.\textsuperscript{173,277,281}

\textsuperscript{[VI]}While carbon is the lightest, it has a very low sputter yield due to its extremely low mass.\textsuperscript{286}
5.4 Prospect of Expanding the Stoichiometric Process Window with High Power Impulse Magnetron Sputtering (HiPIMS)

5.4.1 Precedent for the HiPIMS Deposition of Transition Metal Carbides

High power impulse magnetron sputtering (HiPIMS) is frequently used to synthesize hard, low friction, wear resistant coatings including diamond-like carbon, carbides, and nitrides.\textsuperscript{19,174,287} The high ionization fractions can increase the reactivity of the gas and improve the density, hardness, and other properties of interest.\textsuperscript{19,287} Additionally, HiPIMS drives materials towards equilibrium with high energy ion bombardment, which should encourage full carburization of carbide films before the precipitation of excess carbon.\textsuperscript{19,173}

There are numerous publications on the HiPIMS deposition of transition metal carbide based coatings for tribological applications. However, most of these researchers are focused on maximizing hardness and minimizing the coefficients of friction. As such, they primarily operate in the carbon rich nanocrystalline-MC/amorphous-C:H regime of the reactive process space.\textsuperscript{189,203,244,249} Conversely, reports on the HiPIMS deposition of near-stoichiometric carbide films are sparse, despite promising results.\textsuperscript{19,201}

Samuelsson \textit{et al.} reported on the reactive HiPIMS deposition of TiC and TiC-C nanocomposites. At low acetylene (C\textsubscript{2}H\textsubscript{2}) flows, they found that the carbon to titanium ratios of the DC and HiPIMS deposited samples were nearly identical. As the flow of reactive gas increased, the C/Ti ratio of the DC sputtered samples continued to increase at an accelerating rate. Conversely, the C/Ti ratio of the HiPIMS samples began to plateau as the acetylene flow continued to increase, reaching TiC\textsubscript{0.94} before precipitation. The researchers attributed this, in part, to the broader transition region between metallic and poisoned modes in reactive HiPIMS processes.\textsuperscript{187,201} They also suggested that the high ion bombardment may have favored the stoichiometric carbide phase while physically and chemically etching excess carbon out of the film.\textsuperscript{201} Furthermore, bipolar HiPIMS provides an avenue to both enhance and tune the energy of this bombardment.

Jiang \textit{et al.} used an optical emission spectrometer (OES) feedback-loop to control their HiPIMS titanium carbide deposition process, observing a transition window similar to Samuelsson \textit{et al.}.\textsuperscript{201,288} However, Chang & Yang did not report a plateau in carbon stoichiometry when depositing tungsten carbide with HiPIMS.\textsuperscript{289} It is unknown which factors are responsible for the presence of the transition window. It could be a consequence of the fact that tungsten carbide cannot have as much carbon as titanium carbide in the rocksalt structure, or perhaps excess carbon is more difficult to etch from tungsten carbide.\textsuperscript{19,201} Alternatively, it could be system configuration dependent, as alluded to by Jansson & Lewin in their review of the sputter deposition of carbides.\textsuperscript{19} Nevertheless, the results of Samuelsson \textit{et al.} and Jiang \textit{et al.} are promising enough to warrant further investigation, particularly with a high entropy system.
5.4.2 Sputtered Flux Stability During HiPIMS

Reactive gas flow control was determined to be the best approach for controlling the carbon content of high entropy carbide films in Section 5.2.5. This was chosen given the configuration of the system as it stands but came with the caveat that the metal flux needed to be as predictable and stable as possible. There are two main mechanisms which can lead to changes in target flux: erosion of the target over time and target poisoning during the deposition process.\textsuperscript{173,290}

The output of HiPIMS supplies can be regulated in multiple ways including time-averaged power or current, peak voltage, peak current, frequency, or combinations of some of these variables. In all of the publications mentioned above, the HiPIMS supply was operated with both a fixed time-averaged power and frequency.\textsuperscript{201,288,289} Regulating the time-averaged power protects the target and cathode from thermal damage by compensating for any unexpected runaway of the plasma upon the addition of a reactive gas. The formation of compounds on the target surface (poisoning) can substantially increase the power due to changes in secondary electron emission yield.\textsuperscript{174} Additionally, the HiPIMS pulse frequency can impact the hysteresis of reactive processes due to changes in the time available between pulses for gas to refill the space in front of the target and poison it.\textsuperscript{174,287} Consequently, operating at a fixed frequency will result in consistent hysteretic behavior during the deposition process. However, this power and frequency regulation scheme is susceptible to changing sputtering rates, and thus metal fluxes, throughout the target lifetime.

Magnetron sputtering, as used in this work, traps electrons in helical paths above the surface of the target, resulting in increased gas collisions and ionization.\textsuperscript{174} This confinement occurs where the magnetic field lines are parallel to the target surface, creating a region of higher plasma density. The higher plasma density leads to more extreme target erosion in this region, creating the characteristic "racetrack" of magnetron sputtering.\textsuperscript{158,174,290}

As the target erodes and the racetrack becomes deeper, the target surface gets closer to the magnets underneath it. This results in an increase in the magnetic field (33% for 4.7 mm of erosion in the case of Madsen et al.) and further confinement of the plasma.\textsuperscript{291} This increased confinement improves the efficiency of the plasma and changes its I-V response, reducing the voltage and increasing the current required to maintain a given power.\textsuperscript{291,292} This change in the balance of voltage and current can result in changes in the rate efficiency (metal flux / watt) of the sputtering process.

The sputtering rate ($\Phi$, atoms/second) is the product of the ion current ($I_i$), and sputtering yield ($Y$) which in turn is a function of the voltage (i.e. $Y(V)$) as shown in Equation (5.5). The sputtering yield ($Y(V)$) can be replaced with the sputtering yield efficiency ($Y(V)/V$ or $\eta(V)$) multiplied by the voltage ($V$) to create Equation (5.6).

\begin{align*}
\Phi &= Y(V)I_i \quad \text{(5.5)} \\
\Phi &= \eta(V)V I_i \quad \text{(5.6)}
\end{align*}
The power (P) applied to the system (Equation (5.7)) is the product of the voltage (V) and the sum of currents from arriving ions and escaping secondary electrons \(I_i + I_{SE}\).\(^{173}\) The secondary electron current is proportional to the effective secondary ion emission yield \(Y_{SE,\text{eff}}\) which accounts for the finite probability emitted secondary electrons escape and don't return to the target surface (Equation (5.8)).

\[
P = V (I_i + I_{SE}) \tag{5.7}
\]

\[
I_{SE} = I_i (Y_{SE,\text{eff}}) \tag{5.8}
\]

These equations can be used to solve for the ion current in terms of power, voltage, and secondary electron yield in Equation (5.10). Then, Equation (5.10) can be substituted into Equation (5.6), producing Equation (5.11).

\[
P = V I_i (1 + Y_{SE,\text{eff}}) \tag{5.9}
\]

\[
I_i = \frac{P}{V (1 + Y_{SE,\text{eff}})} \tag{5.10}
\]

\[
\Phi = \eta(V) \frac{P}{1 + Y_{SE,\text{eff}}} \tag{5.11}
\]

In power regulation mode, the power is by definition a constant. The secondary electron emission yield of clean metal surfaces is relatively constant across the range of ion energies used for sputtering (0.5–1 kV).\(^{293}\) Therefore, under these conditions, the flux is proportional to the sputtering yield efficiency of the target \(\Phi \propto \eta(V)\), which is a function of the voltage. Keller & Simmons reported a peak in the sputtering efficiency (atoms/keV-ion) at ~500 eV dropping rapidly at lower voltages and slowly at higher voltages.\(^{256}\) The reduction in voltage associated with target erosion under fixed power conditions would result in a change in the sputter yield efficiency of the plasma, and subsequently a change in the deposition rate. Depending on the voltage regime, minor changes in the secondary electron yield could change the balance of ion current to electron current, also producing changes in the sputtering rate.\(^{293}\)

Conversely, in a system where power and voltage are fixed, the total current is also fixed. The constant voltage results in a consistent secondary electron emission yield which means the ratio of electron to ion current remains a constant.\(^{(VII)}\) The fixed ion current produces a consistent ionic bombardment rate, while the fixed voltage produces a constant bombardment energy. The result is a consistent flux of sputtered metal atoms from the target; however, the role of target poisoning must also be considered.

Audronis & Bellido-Gonzalez reported that the chromium sputtering rate took over 120 seconds to stabilize during flow controlled CrC depositions, demonstrating the gradual equilibration of target poisoning. Additionally, they observed significant hysteresis in the chromium optical emission as a function of acetylene flow, making it challenging to relate gas flow and metal flux.\(^{294}\) Others have

\(^{(VII)}\)In principle, the higher magnetic field (due to proximity to the magnets) could result in a change in the escape probability and affect secondary electron emission yield.
reported the presence of target poisoning, hysteresis, and reduced deposition rates, despite observing broad transition windows while depositing TiC.\textsuperscript{201,288}

Compounds which form on the surface of the target during poisoning have a different secondary electron and sputter yield than the metal, causing changes in the current and voltage necessary to sustain the plasma at a given power.\textsuperscript{174,266} In the case of reactively sputtered carbides, the current decreases and the voltage increases to maintain a fixed power.\textsuperscript{198}

Compounds typically have stronger bonds than the metal atoms within the target, resulting in a lower sputter yield on the target surface and thus a decreased deposition rate.\textsuperscript{174} The increase in target voltage will increase the energy of the ions but diminish their bombardment rate (ion current). Unfortunately, as described above, an increase in ion energy does not always increase the sputter yield efficiency.\textsuperscript{256} Thus, the reduction in deposition rate from the reduced sputter yield of the compound can be exacerbated by an increase in target voltage and coinciding decrease in both the sputter yield efficiency and ion current when operating under constant power conditions.

Historically, there was no way to simultaneously regulate power and voltage, as they were inexorably linked by the I-V characteristics of the plasma; however, HiPIMS can overcome this limitation. While the instantaneous power, voltage, and current are all linked by the I-V characteristics of the plasma, the time-averaged power, voltage, and current are also linked by the frequency of operation. Using HiPIMS, the time-averaged power, voltage, and current can all be operated at fixed values by running a PID loop on the pulse frequency. The fixed voltage will provide a more consistent sputtering yield and the fixed current produces a more consistent bombardment rate when compared to a system where voltage and current are variable.

As mentioned earlier, the HiPIMS pulsing frequency can play a role in the hysteresis of reactive processes. Many researchers operate at or below 500 Hz, where a small change in frequency leads to a substantial (in magnitude) change in the period between pulses, relative to the gas refill time and poisoning rates.\textsuperscript{\textsuperscript{(VIII)}} However, this effect can be alleviated by operating at a higher frequency, such that the gas has less time to refill and poison the target between pulses.\textsuperscript{174,287}

\subsection*{5.4.3 Reactive Bipolar HiPIMS of High Entropy Transition Metal Carbides}

In order to test the benefits of HiPIMS, (HfNbTaTiZr)\textsubscript{C\textsubscript{x}} films were deposited as a function of methane content. In accordance with the results of Section 5.2, all films were deposited with 7.5 mT of argon and a methane flow dependent total pressure. Based on the theory of the prior section, the depositions used both power and voltage regulation in order to keep a more consistent flux. This regulation mode resulted in frequencies between 1100–1300 Hz over the course of the various depositions. The remaining experimental parameters can be found in Tables \ref{tab:5.7} and \ref{tab:5.8}.

\begin{footnote}\textsuperscript{(VIII)}At typical sputtering pressures (10 mTorr), the gas refill time is estimated to be around 100 µs with poisoning occurring after the gas refills.\textsuperscript{207,295}\end{footnote}
The crystallographic structure of the films was characterized using X-ray diffraction, producing the patterns plotted in Figure 5.9. At the lowest methane flows (1–1.3 sccm) the films exhibited broad, extremely carbon deficient rocksalt peaks, similar to those observed in Chapter 4. Upon increasing to 1.5 sccm, the film peaks began to sharpen, and the films exhibited preferred \{111\} texture, unlike the films of the prior chapter, which still had polycrystalline texture. The peak size and shape remained consistent up until 1.9 sccm, although the peak did shift towards lower angles (0.25° in 2θ). Between 1.5 and 1.9 sccm the out-of-plane \{111\} d-spacing increased by approximately 0.67%, indicating increased carburization. A further increase to 2.0 sccm of methane produced a significant increase in the diffraction signal intensity as well as an additional 0.09° shift to lower angles, corresponding to a 0.27% increase in the out-of-plane d_{111}. Further increases beyond 2.0 sccm began to develop secondary orientations, most notably \{220\} and \{420\}. The precipitation of these secondary orientations coincided with a reduction and broadening of the \{111\} peak. Finally, at the highest methane flow (2.8 sccm) the \{111\} peak intensity and sharpness increased substantially, although the film still exhibited secondary orientations. This flow rate coincided closely with the 2.82 sccm flow rate that resulted in carbon precipitation and epitaxial growth in the prior chapter.

Raman spectroscopy was used to determine when excess carbon began to precipitate out of the HiPIMS deposited (HfNbTaTiZr)C_x films. The resulting Raman spectra are presented in Figure 5.10, with the carbon D (1350 cm^{-1}, defect induced breathing mode) and G (1580 cm^{-1}, sp^2 bonding) peak locations labeled.\(^\text{212}\) The Raman spectra were quite uniform from 1.0 to 2.0 sccm of methane flow, showing no signs of the D or G modes from excess carbon. Upon increasing the methane flow to 2.1 sccm, a small signature of the D and G modes was present; however, it was quite low in intensity relative to the noise floor. The film deposited with 2.3 sccm of methane produced a high intensity feature spanning the locations of both the D and G peaks, indicating the precipitation of substantial excess carbon. The change in Raman signal intensity between the 2.0 and 2.3 sccm samples closely matched the change observed between the 2.75 and 2.82 sccm samples in Chapter 4. This suggests that bipolar
Figure 5.9: X-ray diffraction patterns from (HfNbTaTiZr)C\textsubscript{x} films deposited at a range of methane flows using HiPIMS. Patterns are arranged as a function of increasing methane flow from 1.0 sccm (bottom, light red) to 2.8 sccm (top, light blue). RS denotes peaks which correspond to the rocksalt carbide crystal structure. X-ray artifacts and secondary wavelengths (Cu\textsubscript{K\beta}, W\textsubscript{L\alpha}) are denoted by ♦.
HiPIMS can hinder the precipitation of excess carbon in high entropy carbide films. Based on the Raman data alone, HiPIMS deposited films required four times the methane flow increase to transition from a near stoichiometric film (2.0 sccm) to a film with substantial carbon precipitation (2.3 sccm) when compared to RF magnetron sputtered counterparts.

Finally, the microstructures of the bipolar HiPIMS deposited (HfNbTaTiZr)\(_x\) films were characterized using scanning electron microscopy. Micrographs for a subset of the samples are shown in Figure 5.11. The films deposited with less than 1.8 sccm of methane were very smooth, revealing very little surface structure, even with a low energy (1 keV) monochromatic electron beam, suggesting that HiPIMS may produce smoother films than RF sputtering. As the methane flow increased above 1.8 sccm, the film surface became slightly rougher, albeit retaining fairly equiaxed grain morphologies. The microstructure of these samples (1.8–1.9 sccm) is reminiscent of the samples deposited with 1.5–2.5 sccm of methane in Figure 4.4.

**Figure 5.10:** Raman spectra of (HfNbTaTiZr)\(_x\) films deposited with HiPIMS, plotted as a function of methane flow. D and G correspond to the locations of the D and G Raman modes of excess carbon in the system. Spectra are linearly offset for clarity.
Figure 5.11: Scanning electron micrographs of (HfNbTaTiZr)C_x films deposited with HiPIMS, arranged as a function of methane flow.
The sample deposited with 2 sccm of methane was substantially smoother than the samples deposited with similar flow rates. This sample also exhibited a substantially higher XRD peak intensity and sharpness (Figure 5.9). The reduced surface roughness may be a consequence of the improved crystallographic quality and texture of this material, providing a more uniform microstructure with fewer grain boundaries. Further increases in methane flow beyond this point produced films with a higher roughness. The nucleation of secondary orientations in these films (Figure 5.9) produced irregularly shaped grains which protrude from the relatively equiaxed underlying surface of presumably \{111\} grains. Finally, at the highest methane flow (2.8 sccm), the film developed the familiar triangular microstructure and sharp \{111\} peak found in many of the carbon rich (2.82–3.5 sccm methane) samples synthesized in the prior chapter, suggesting significant carbon precipitation.

5.4.4 Influence of Bipolar HiPIMS on Sputtered Transition Metal Carbides

(HfNbTaTiZr)\(_x\) films deposited with bipolar HiPIMS show significant improvements relative to RF sputtered counterparts in Chapter 4. While some very slight changes in texture were observed as a function of methane flow, the crystallographic characteristics of the films were significantly more uniform than the RF sputtered films, which exhibited broad changes in texture, peak width, and peak position. The microstructure of the films (below the onset of carbon precipitation) was also very consistent, with only modest changes in roughness.

The crystallographic and microstructural uniformity are likely a consequence of the increased high energy ionic bombardment from the 20 V bipolar pulse. The additional energy increases adatom mobility and encourages the growth of existing \{111\} grains, rather than the nucleation of secondary orientations. Furthermore, the bombardment drives the system towards equilibrium, adding energy to surface atoms so they can diffuse towards more stable sites which reduce the roughness and thus surface energy.\(^{173}\)

The bipolar pulse was lower in this section than the prior section (20 V vs. 50 V); however, the pulse length was decreased 47% and the frequency was increased 3-4fold. Although the energy per ion is lower with a 20 V pulse, the bombardment occurred more frequently (on a time and film thickness basis). High energy ions can penetrate deeper into the film, causing more significant collision cascades and atomic rearrangement beneath the film surface; however, this comes with the risk of ion irradiation damage and implantation. Conversely, low energy bombardment will only affect the top few monolayers of the film. Nevertheless, low energy bombardment can still provide positive effects as long as it occurs frequently enough, before layers of the film are buried beyond its influence.

The change in Raman signal intensity between the 2.0 and 2.3 sccm HiPIMS samples closely matches the change observed between the 2.75 and 2.82 sccm RF samples in Chapter 4. This suggests that bipolar HiPIMS can hinder the precipitation of excess carbon in high entropy carbide films, potentially requiring a four times larger methane flow change to transition from a near stoichiometric film (2.0 sccm) to a
film with substantial carbon precipitation (2.3 sccm). However, this finding needs to be confirmed and quantified with additional techniques and in other high entropy compositions.

The Raman spectra of 2.3 sccm HiPIMS sample closely matched the spectra of the same 2.82 sccm RF sputtered sample. This implies that there is a similar quantity of excess carbon in the pair of films. In the RF magnetron sputtered samples, this Raman signal intensity also corresponded with the development of the triangular microstructure. Conversely, in the HiPIMS deposited films, the transition to a triangular microstructure occurred with somewhere between 2.3 and 2.8 sccm of methane, after the onset of excess carbon by Raman.

The precipitation of free carbon is known to limit grain growth in sputtered carbide films, but this wasn't observed in the HiPIMS film deposited with 2.3 sccm of methane. However, the penetration depth of visible light into metallic transition metal carbides is rather low, limiting the depth at which the Raman spectra is collected. As a result, the measured Raman spectra may not be fully representative of the entire film thickness. In the case of the RF sputtered sample (2.82 sccm), excess carbon is apparently present throughout the entire sample (Chapter 4) hindering the mechanical properties of the film. Conversely, in the HiPIMS deposited sample (2.3 sccm) this may not be the case.

The reduction of excess carbon in HiPIMS deposited films has been attributed to a combination of preferential physical and chemical ion etching of the free carbon present in the film. If this is the case, then HiPIMS doesn't fully prevent the formation of excess carbon, it just removes excess carbon after it has formed. As a result, there may not have been adequate time for the excess carbon to be etched from the surface layers of the film, leaving an adequate amount for Raman to detect. Conversely, the underlying layers would have experienced a longer period of ion bombardment, which may have etched away enough of the excess carbon to eliminate its effects on the microstructure. Eventually, once the methane flow reaches some critical value, the etching rate will no longer sufficient to remove all of the free carbon before it is buried too deeply in the film to be removed.

The high plasma density, ionization fraction, and bombardment afforded by bipolar HiPIMS appear to substantially improve the carbide sputtering process. The resulting films were more uniform in crystallographic texture and microstructure than RF counterparts. High bombardment energies led to significantly smoother films than those deposited by RF sputtering. Furthermore, the onset of free carbon precipitation was both delayed and more gradual than what was observed in RF deposited films. HiPIMS enables the decoupling of deposition energetics and fluxes, allowing flux to be maintained without influencing the energetics of the sputtering process. As a result, the combined voltage and power regulation approach produced predictable shifts in lattice parameter as a function of methane flow and provided a more consistent metal flux despite target wear and poisoning.
5.5 Conclusions

This chapter explored several ways to improve the quality, uniformity, and reproducibility of sputter deposited high entropy carbide films. While partial pressure control of methane would be the optimal gas control strategy, it is difficult and expensive to implement. However, the flow-controlled process can be improved by carefully regulating the metal and gas fluxes. Operating under a fixed argon partial pressure and flow rate produces a more uniform sputtering rate than the fixed total pressure approach. Similarly, voltage and power regulated high power impulse magnetron sputtering (HiPIMS) depositions produce a more consistent metal flux over the target lifetime due to fixed sputtering energetics and ion currents. The combination of these factors produces a much more consistent deposition rate and predictable stoichiometry trends as a function of methane flow rate. The increased plasma density, ionization, and bombardment from HiPIMS produced (HfNbTaTiZr)C_x films with reduced roughness, delayed carbon precipitation, and greater microstructural and crystallographic consistency than radio frequency magnetron sputtered films. Finally, the decoupling of deposition energetics and rates during HiPIMS provided a foundation for the development of novel deposition techniques, as will be discussed in the following chapters.
Chapter 6

Asynchronously Patterned Pulsed Sputtering (APPS): A Novel Co-Cputtering Technique

6.1 Preface

The contents of this chapter are intended for publication as follows:

Trent Borman, Mohammed Delower Hossain & Jon-Paul Maria. Asynchronously Patterned Pulsed Sputtering (APPS): A Novel Co-Sputtering Technique
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802

6.2 Introduction

Controlling the composition of multicomponent thin films is critical for a broad range of materials systems including metals, oxides, nitrides, and carbides. Multicomponent thin films are often deposited from a single alloy or compound target (i.e. TiW, Pb(ZrTi)O₃ (PZT), etc.). While this approach is suitable for many materials systems, it is not without its limitations. Alloy or compound targets restrict depositions to a single stoichiometry, while many materials systems have several compositions of interest, such as the numerous stoichiometries of PZT or (AlSc)N. Furthermore, resputtering or gas-phase scattering can cause uncorrectable deviations from target stoichiometry. Co-sputtering avoids these limitations by sputtering from multiple targets, enabling the flux of each species to be controlled independently. Unfortunately, compositional trends are often non-linear, and control over deposition energetics must be sacrificed to adjust flux. With conventional sputtering techniques (RF or DC, Figure 6.1(a)), any change in the flux necessitates a change of the energetics. Sputtering at a higher voltage (more energetic bombardment of the target) will also result in a higher power, current, and flux. High power impulse magnetron sputtering (HiPIMS) provides a means to decouple the deposition energetics from the flux. In HiPIMS, short
Figure 6.1: Schematic representation of applied voltage as a function of time for (a) DC sputtering, (b) HiPIMS operating at different rates leading to variable degrees of overlap, (c) HiPIMS operating at the same rate leading to no overlap but restricting energetic control (narrower pulse width), and (d) APPS leading to no overlap and independent energetic and flux control.

(typically < 100 µs) pulses at 100s of volts are applied to the target at relatively low duty cycle (< 5 %).\cite{174} The energetics and instantaneous current of the plasma are predominately controlled by the voltage and pulse width, while the time-averaged flux is controlled by the frequency of the pulses, making HiPIMS an ideal candidate for co-sputtering.\cite{168,174,287,305}

Co-sputtering with HiPIMS generally presents two control options: run at independent frequencies or lock the frequencies of the two sources together (master/slave configuration). In the first case, the deposition flux and energetics remain decoupled; the voltage, pulse width and frequency are freely changed on each supply. However, pulsing at different frequencies will result in the overlap of some pulses, while other pulses will occur at separate times (as seen in Figure 6.1(b)). This periodic overlap can lead to scattering in the intersecting plasmas as well as plasma characteristics which are not consistent from pulse to pulse. This could be particularly problematic when reactively depositing materials where one source may preferentially consume the reactive gas, depriving the other source of reactant.
The second approach involves operating both sources at the same frequency (Figure 6.1(c)) using the sync ports on the HiPIMS supplies. In this configuration, the plasma characteristics will be the same for every pulse; pulses will always have the same interaction, or lack thereof, dictated by the phase shift between pulses. However, now the flux can only be controlled by the voltage or pulse width, as the frequency is fixed. This returns to the limitation faced by conventional (RF or DC) sputtering: the inseparable coupling of flux and plasma energetics.

This report describes the development and use of asynchronously patterned pulsed sputtering (APPS — Figure 6.1(d)). This technique retains the decoupled flux and energetic characteristics afforded by HiPIMS while avoiding the plasma interactions present in most co-sputtering methodologies. APPS consists of two independent HiPIMS supplies, operating at voltages and pulse widths optimized for the given targets. Both supplies operate at the same control frequency (CF), as in Figure 6.1(c); however, one of the sources skips a fraction of these pulses in a given pattern, resulting in Figure 6.1(d). The flux of source A is controlled by changing the control frequency, while the flux of source B is controlled by the fraction of skipped pulses. Asynchronous HiPIMS pulses prevent any plasma interactions, while the pattern of pulses and skips controls the flux ratio while maintaining fixed energetics.

6.3 Design

The experimental setup (Figure 6.2) consisted of two DC sputtering power supplies (Advanced Energy MDX 5K) supplying a constant voltage to two HiPIMS power supplies (Starfire Industries IMPULSETM 2-2). The HiPIMS supplies were connected to a pair of 2” magnetron sputtering sources (Kurt J. Lesker Torus® Mag KeeperTM) installed in a custom designed spherical HV chamber (Kurt J. Lesker) with a base pressure of $10^{-8}$ Torr.

The HiPIMS supplies need to be capable of operating with a patterned pulsing scheme in order to successfully perform an APPS deposition. Arbitrary waveforms were generated as .csv files using the Python script found in Appendix B. These waveforms provided the 100$\mu$s pulse width 5 V TTL logic necessary to trigger the HiPIMS supplies used in this work. The arbitrary waveforms were supplied to the sync-in ports of the HiPIMS power supplies by an arbitrary waveform generator (AWG — Rigol DG1022Z), with the necessary 180° phase shift applied by the AWG. The pulse sequencing and output voltage/current traces for each HiPIMS unit were monitored via oscilloscopes (Rigol DS1054Z).

6.4 Operation and Application to NbW

Deposition parameters were optimized for the individual targets prior to the deposition of the multi-component film. The HiPIMS parameters (pulse width, voltage, current limit, and positive pulse voltage and time) were optimized for each source material. Additionally, deposition pressures and temperatures which facilitated the formation of dense, high-quality films of both components were determined.
Finally, a maximum frequency ($f_{\text{max}}$) was chosen for each source to prevent the power from reaching levels that could cause target cracking, bond failure, or cathode damage during the APPS depositions. The NbW system was synthesized in order to demonstrate the efficacy of asynchronously patterned pulsed sputtering (APPS). Niobium and tungsten form a BCC solid solution across the entire compositional range, enabling a wide range of stoichiometries to be tested. Additionally, the refractory nature of the constituents makes the energetics of HiPIMS attractive for densification. All films were sputtered from elemental Nb (99.95% ex. Ta, Kurt J. Lesker) and W (99.95%, Kurt J. Lesker) targets onto epi-polished c-plane sapphire substrates.

Pulse widths were selected such that the sputter pulse stopped at peak current, before the advent of gas rarefaction. After a 4 μs delay, a 100 μs 20 V positive pulse was applied to the cathode. The positive pulse provided additional adatom energy for densification and quenched the plasma rapidly, instead of allowing a gradual decay of voltage on the magnetron. Maximum frequencies were chosen so the power did not rise above ~250 W for tungsten and ~350 W for niobium. Targets were presputtered for 5 minutes to clean target surfaces, getter residual oxygen, and allow target temperatures to begin to equilibrate before the film deposition.

The thickness, density, and roughness of the metal film and native oxide (if present) were quantified with X-ray reflectivity (XRR — Malvern Panalytical Empyrean). The Bragg-Brentano incident optic was equipped with a 1/8° divergence slit, 2 mm mask, and 1/2° anti-scatter slit. The reflected beam passed through a 1/32° slit (programmable anti-scatter slit in follow mode) before being measured by a PIXcel detector operated in receiving slit mode (1 channel, 55 μm). Data were collected with a step size of 0.005° and a net count time of 0.5 s per step. Spectra were fit using the X’Pert Reflectivity software package to determine the thickness, density, and roughness of the layers.
The parameters in Tables 6.1 and 6.2 were found to yield dense and smooth Nb and W films with minimal native oxide via XRR. Films were deposited 100–110 nm thick in order to calculate fluxes. The pulse rates listed are also the maximum frequencies \( f_{\text{max}} \) for each source.

The calibration films were used to calculate the flux of metal atoms per HiPIMS pulse. The pulse flux (atoms / area-pulse) is calculated with Equation (6.1), where \( \Phi_i \) is the pulse flux (atoms of species \( i / \text{Å}^2 \)-pulse), \( d \) is the thickness (Å), \( n \) is the number of atoms of \( i \) per formula unit, \( f \) is the pulse rate (Hz), \( t \) is the deposition time (seconds), and \( V \) is the volume per formula unit (Å³).

\[
\Phi_i = \frac{d n_i}{f t V} \quad (6.1)
\]

For metal films with a native oxide, the metal atom pulse fluxes from the metal and oxide layers were independently calculated and added together to yield a total metal atom pulse flux. The volume per formula unit was derived from the unit cell volume and \( Z \) since the calibration films were 100% dense (verified by XRR). Alternatively, the measured density and molecular weight could be used to calculate volume per formula unit. The pulse fluxes from the calibration Nb and W films are listed in Table 6.3. The tungsten film was fit with a thin oxide layer which accounted for approximately 0.4% of the total tungsten atom flux.

Next, the dose for the APPS deposited film (\( Q_i \), atoms of species \( i / \text{Å}^2 \)) was calculated as a function of the desired thickness (\( d_t \), 100 nm in this work), the theoretical volume per formula unit (\( V_t \), from literature or Vegard’s law), and the subscript from the desired chemical formula (\( m_i \)), as shown in Equation (6.2). The quantity of pulses for each source (\( P_i \)) was calculated from the respective pulse flux (\( \Phi_i \)) and dose (\( Q_i \)) using Equation (6.3).

\[
Q_i = \frac{d_t m_i}{V_t} \quad (6.2)
\]

\[
P_i = \frac{Q_i}{\Phi_i} \quad (6.3)
\]
Table 6.3: Calculation of metal pulse flux for Nb and W films. Volume per formula unit of Nb and W determined from International Center for Diffraction Data (ICDD) PDF cards.\textsuperscript{306,307} The volume per formula unit of WO$_3$ was derived from the density and molar mass.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Nb</th>
<th>W</th>
<th>WO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Volume per f.u. (Å$^3$)</td>
<td>104.0</td>
<td>109.9</td>
<td>1.6</td>
</tr>
<tr>
<td>Calibration dose ($Q_{cal,i}$) (metal atoms / Å$^2$)</td>
<td>17.97</td>
<td>15.78</td>
<td>53.76</td>
</tr>
<tr>
<td>Total pulses</td>
<td>648000</td>
<td>960000</td>
<td>960000</td>
</tr>
<tr>
<td>Pulse flux ($\Phi_i$) (metal atoms / Å$^2$-pulse)</td>
<td>8.93 × 10$^{-5}$</td>
<td>Total W: 7.29 × 10$^{-5}$</td>
<td></td>
</tr>
</tbody>
</table>

Table 6.4: Sample order, intended composition, theoretical volume (Vegard’s law) per formula unit, total dose for 100 nm, and pulse quantities for NbW alloys.

<table>
<thead>
<tr>
<th>Sample order</th>
<th>Intended Nb/W ratio</th>
<th>Theoretical V / f.u. (V$_t$, Å$^3$)</th>
<th>Total dose (Q) (atoms / Å$^2$)</th>
<th>Nb pulses ($\times 10^5$)</th>
<th>W pulses ($\times 10^5$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50/50</td>
<td>16.9</td>
<td>59.3</td>
<td>3.32</td>
<td>4.07</td>
</tr>
<tr>
<td>2</td>
<td>30/70</td>
<td>16.4</td>
<td>60.8</td>
<td>2.04</td>
<td>5.84</td>
</tr>
<tr>
<td>3</td>
<td>70/30</td>
<td>17.3</td>
<td>57.8</td>
<td>4.53</td>
<td>2.38</td>
</tr>
<tr>
<td>4</td>
<td>90/10</td>
<td>17.7</td>
<td>56.3</td>
<td>5.68</td>
<td>0.77</td>
</tr>
<tr>
<td>5</td>
<td>20/80</td>
<td>16.2</td>
<td>61.7</td>
<td>1.38</td>
<td>6.77</td>
</tr>
<tr>
<td>6</td>
<td>10/90</td>
<td>16.0</td>
<td>62.5</td>
<td>0.70</td>
<td>7.22</td>
</tr>
<tr>
<td>7</td>
<td>80/20</td>
<td>17.5</td>
<td>57.0</td>
<td>5.11</td>
<td>1.57</td>
</tr>
<tr>
<td>8</td>
<td>40/60</td>
<td>16.7</td>
<td>60.0</td>
<td>2.69</td>
<td>4.94</td>
</tr>
<tr>
<td>9</td>
<td>60/40</td>
<td>17.1</td>
<td>58.5</td>
<td>3.93</td>
<td>3.21</td>
</tr>
</tbody>
</table>

\[
P_i = \frac{Q_i}{\Phi_i}
\] (6.3)

The theoretical volumes per formula unit, total doses ($Q_{\text{Nb}}+Q_{\text{W}}$), and pulse quantities for Nb and W films spanning 10-90 at. % Nb are tabulated in Table 6.4. With the exception of the 50/50 sample, the sample order was randomly generated to randomize the impacts of any changes in pulse flux over the course of the sample deposition process.

During an APPS deposition, the source with more pulses will pulse at the control frequency (CF) while the other will skip some subset of pulses. The control frequency was typically set to the maximum frequency of the source operating at the CF ($f_{\text{Max,CF}}$). However, it was necessary to verify that time-averaged pulse rate of the patterned source ($r_P$) would not exceed its maximum frequency ($f_{\text{Max,P}}$) and thus power limit. Using the pulse quantities ($P_P$ and $P_{\text{CF}}$) and the maximum frequency ($f_{\text{Max,CF}}$), it was possible to determine the pulse rate of the patterned source with Equation (6.4).
The control frequency (CF) was determined using the relations in Equation (6.5). In the first case, the thermal limits of the patterned source won’t be exceeded if \( CF = f_{\text{Max,CF}} \). In the second case, the power limitations of the patterned source restrict the control frequency to a value derived from the maximum frequency of the patterned source and the pulse ratio.

\[
CF = \begin{cases} 
  f_{\text{Max,CF}} & \text{if } r_p < f_{\text{Max,P}} \\
  \frac{P_{\text{CF}}}{P_p} f_{\text{Max,P}} & \text{if } r_p > f_{\text{Max,P}}
\end{cases}
\]  

(6.5)

The control frequency and pulse rates for all of the samples in this work are found in Table 6.5. It is noted that the only time that CF did not equal \( f_{\text{Max,CF}} \) was the 50/50 case. For this sample, the 1350 Hz maximum frequency for Nb resulted in a CF of 1654 Hz. Additionally, an estimate of the time for a 100 nm film was calculated by taking the pulse quantity from Table 6.4 and dividing by the respective pulse rate in Table 6.5.

The length (L) of the pulse train for the AWG was determined using the ratio of pulses from each source. The pulse ratio \( P_{\text{CF}}/P_p \) was rounded to 3 significant digits and multiplied by 100, yielding the length of the pulse train, L. The number of pulses was 100 (by virtue of the pulse ratio n:1 being multiplied by 100) and the number of skips was \( L - 100 \). The pulses, skips, and length were divided by the greatest common denominator (if applicable) to yield the reduced quantities shown in Table 6.6.

The pulses and skips were put into a pattern by hand in a relatively even pattern. One methodology is as follows: with a ratio of 9 pulses to 26 skips, a pattern may not immediately be intuitive, but by

<table>
<thead>
<tr>
<th>Sample order</th>
<th>Intended Nb/W ratio</th>
<th>Control freq. (Hz)</th>
<th>Nb pulse rate (Hz)</th>
<th>W pulse rate (Hz)</th>
<th>Deposition time (s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50/50</td>
<td>1654</td>
<td>1350</td>
<td>1654</td>
<td>246</td>
</tr>
<tr>
<td>2</td>
<td>30/70</td>
<td>2000</td>
<td>700</td>
<td>2000</td>
<td>292</td>
</tr>
<tr>
<td>3</td>
<td>70/30</td>
<td>1350</td>
<td>1350</td>
<td>709</td>
<td>335</td>
</tr>
<tr>
<td>4</td>
<td>90/10</td>
<td>1350</td>
<td>1350</td>
<td>184</td>
<td>421</td>
</tr>
<tr>
<td>5</td>
<td>20/80</td>
<td>2000</td>
<td>408</td>
<td>2000</td>
<td>338</td>
</tr>
<tr>
<td>6</td>
<td>10/90</td>
<td>2000</td>
<td>181</td>
<td>2000</td>
<td>386</td>
</tr>
<tr>
<td>7</td>
<td>80/20</td>
<td>1350</td>
<td>1350</td>
<td>414</td>
<td>378</td>
</tr>
<tr>
<td>8</td>
<td>40/60</td>
<td>2000</td>
<td>1088</td>
<td>2000</td>
<td>247</td>
</tr>
<tr>
<td>9</td>
<td>60/40</td>
<td>1350</td>
<td>1350</td>
<td>1103</td>
<td>291</td>
</tr>
</tbody>
</table>

Table 6.5: Control frequency and pulse rates (rounded to 1 Hz) of each target based on intended composition. The deposition time is determined from the pulses (Table 6.4) divided by pulse rate.
Table 6.6: The patterned species, pulse ratio, pulse train length, and quantity of pulses and skips used to deposit NbW films with APPS. The pulse train length, pulses, and skips have already been divided by the greatest common denominator.

<table>
<thead>
<tr>
<th>Sample order</th>
<th>Intended Nb/W ratio</th>
<th>Patterned species</th>
<th>Pulse ratio</th>
<th>Pulse train length (L)</th>
<th>Pulses</th>
<th>Skips</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50/50 Nb</td>
<td>1.225</td>
<td>123</td>
<td>100</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>30/70 Nb</td>
<td>2.859</td>
<td>143</td>
<td>50</td>
<td>93</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>70/30 W</td>
<td>1.904</td>
<td>19</td>
<td>10</td>
<td>9</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>90/10 W</td>
<td>7.345</td>
<td>367</td>
<td>50</td>
<td>317</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>20/80 Nb</td>
<td>4.901</td>
<td>49</td>
<td>10</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>10/90 Nb</td>
<td>11.028</td>
<td>11</td>
<td>1</td>
<td>10</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>80/20 W</td>
<td>3.264</td>
<td>163</td>
<td>50</td>
<td>113</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>40/60 Nb</td>
<td>1.838</td>
<td>46</td>
<td>25</td>
<td>21</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>60/40 W</td>
<td>1.224</td>
<td>61</td>
<td>50</td>
<td>11</td>
<td></td>
</tr>
</tbody>
</table>

Adding or subtracting a constant to the skips, another greatest common denominator can be formed. For instance, 9 and 27 (s+1) are both divisible by 9. Now the ratio is 1 pulse and 3 skips, bearing in mind there is an extra skipped pulse that must be accounted for. This 1:3 sequence can be repeated 8 times followed by a 1:2 sequence, preserving the ratio of 9 pulses to 26 skips. Mathematical optimization of the patterns may be possible; however, considering that ~1000 pulses are needed for a single monolayer, it is unlikely fully optimized patterns would yield any measurable difference. The patterns used for the samples in this work are found in Table 6.7. The pattern syntax necessary for the Python script can be found in Appendix B.

Once the .csv waveform files were generated and loaded, a phase shift of \( \frac{180°}{\text{pulse-train length}} \) was applied using the arbitrary waveform generator. This caused the patterned pulses to be 180° out of phase with the unpatterned source, preventing interference. For additional sources, the spacing would be reduced, i.e. 120° for 3 or 90° for 4 sources.

The source that pulses at the control frequency was also driven by an arbitrary waveform. The 100 ns resolution of the arbitrary waveform rounds the period associated with a given input, thus causing a minute frequency shift from the input value. For instance, 750 Hz has a period of 1333.3 μs that rounds to 1333 μs, yielding a frequency of 750.019 Hz. This small difference in frequency would cause a changing phase shift during the deposition but was avoided by generating a waveform with L pulses in a row (Python input: [L,0]) for the unpatterned source.
Table 6.7: Pulse and skip patterns used for each composition in this work. The patterns are structured as \( n[p,s,p,s,\cdots] \) where \( n \) (if present) is the number of times to repeat the portion in brackets, \( p \) is the number of pulses in a row, and \( s \) is the number of skipped pulses in a row. Asterisks between \( n \) and opening brackets, and commas after closing brackets are required for the Python script but omitted for clarity.

<table>
<thead>
<tr>
<th>Sample order</th>
<th>Intended Nb/W ratio</th>
<th>Pattern</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>50/50</td>
<td>11[3,1,3,1,2,1] 4[3,1]</td>
</tr>
<tr>
<td>2</td>
<td>30/70</td>
<td>9[1,2][1,1] 8[1,2] 2[1,1] 9[1,2][1,1] 8[1,2] 2[1,1] 9[1,2][1,1]</td>
</tr>
<tr>
<td>3</td>
<td>70/30</td>
<td>9[1,1][1,0]</td>
</tr>
<tr>
<td>4</td>
<td>90/10</td>
<td>8[1,6,1,7,1,6,1,7,1,6] 10[1,6][0,1]</td>
</tr>
<tr>
<td>5</td>
<td>20/80</td>
<td>9[1,4][1,3]</td>
</tr>
<tr>
<td>6</td>
<td>10/90</td>
<td>[1,10]</td>
</tr>
<tr>
<td>7</td>
<td>80/20</td>
<td>7[1,2,1,2,1,2,1,2,1,3] 3[1,2,1,3,1,2,1,3,1,2]</td>
</tr>
<tr>
<td>8</td>
<td>40/60</td>
<td>4[2,1,1,1,1,1,1,1,1,1,1] 5[1,1]</td>
</tr>
<tr>
<td>9</td>
<td>60/40</td>
<td>10[5,1][0,1]</td>
</tr>
</tbody>
</table>

6.5 Results

Films ranging from 10 at. % to 90 at. % Nb were deposited on epi-polished c-plane sapphire substrates using the pulse patterns and parameters found in the prior section. X-ray diffraction (XRD — Malvern Panalytical Empyrean) patterns were collected with a Bragg-Brentano\(^{\text{HD}}\) incident optic and a PIXcel\(^{\text{3D}}\) detector. The x-ray beam passed through a 1/4° divergence slit, 1° anti-scatter slit, and 10 mm mask on the incident side before diffracting through a 1/2° anti-scatter slit mounted to the detector. Data were collected in scanning line mode with a step size of 0.0263° and a net count time of 72 s per step.

The resulting diffraction patterns are plotted in order of composition in Figure 6.3. All films were found to form a single BCC phase to the detection limits of the diffraction system. As the fraction of niobium was increased, the lattice parameter steadily shifted to lower angles, an indication of the ~4.5% larger lattice parameter of Nb. It is noted that the 90% sample peaks shifted to higher angles relative to the 80% Nb peak. The exact origin of this is unknown but it does not appear to be related to the chemical composition of the film, as will be discussed later. The \{1 1 0\} peak remained sharp and intense despite broad changes in stoichiometry and deposition power. Some texture changes were observed as a function of stoichiometry, but the \{1 1 0\} peak was not substantially impacted by these variations.

The niobium to tungsten ratio was measured with energy dispersive spectroscopy (EDS — Oxford X-Max\(^{\text{N}}\) 80 mm\(^2\)) on a field emission scanning electron microscope (FESEM — Thermo Fisher Scientific Verios G4 UC). A 10 keV, 3.2 nA beam was rastered across a ~0.1 mm\(^2\) area with the immersion lens in EDX mode to limit the impact of backscattered electrons. Spectra were collected for 120 s of live time.
yielding a total of 5-6 million counts. Atomic percentages were extracted and normalized in the Aztec software package.

The atomic percent niobium and film density (by XRR) are plotted as a function of the intended niobium content in Figure 6.4. Films were found to be within a few percent of the intended stoichiometry across the entire compositional range. Film densities followed the rule of mixtures; deviations from the linear trend mirrored those observed in the EDS spectra, reflecting the higher density of tungsten.
Figure 6.4: Experimental niobium concentration (blue, left) and film density (red, right) of APPS deposited NbW films as a function of intended niobium concentration. Linear regression coefficients are listed and plotted for both datasets.

While some error (averaging $-2.0 \pm 1.3$ at. % Nb) was observed relative to predictions, it is important to consider the level of calibration necessary to obtain such results. Only two deposition rate checks (one per target) were used to produce samples across the entire compositional range. While no significant trend in error was observed with sample order, changes in deposition rate per pulse due to target erosion could cause compositions to drift through the sample series. Furthermore, it was necessary to vary the power applied to the targets by 7 to 11 fold to achieve the compositional range tested in this work. The variations in target temperature resulting from this broad range of powers could lead to deviations in the sputter yield and pulse flux. Finally, the 20 V positive pulse may have caused preferential resputtering, leading to deviations in film stoichiometry.

The true benefits of APPS are apparent when compared to conventional co-sputtering techniques. Spanning an entire phase diagram with conventional sputtering techniques would also require a 10 fold change in power across the composition range. These large power changes would have significant impacts on the energetics of deposition and the resulting film quality. This could result in a need for recalibrations at the extremes in order to ensure dense, smooth, and highly crystalline films. Additionally, the compositional trends associated with conventional co-sputtering are often highly nonlinear. Conversely, APPS produced films that were dense, smooth (averaging 1 nm by XRR), and highly crystalline.
across the entire compositional range despite these broad changes in power. The separation of flux (power) from energetics (voltage/pulse width) during APPS results in predictable compositional trends while maintaining high film quality across the entire compositional spectrum.

Although the initial results of APPS make it a compelling choice for compositional exploration, there is room for improvement. For more precise compositional control, a quartz crystal monitor (QCM) could be utilized to quickly recalibrate the pulse fluxes, enabling the user to make minor adjustments to the APPS waveform immediately before each deposition. Eventually, APPS could be implemented into a fully automated system that would calibrate fluxes on a QCM, generate the APPS patterns, and supply the waveforms directly to the HiPIMS units based on a user’s desired thickness and composition.

In principle there is nothing to prevent the application of APPS to reactive depositions of oxides, nitrides and more. Reactive APPS will require some additional considerations, most importantly the role of target poisoning. Changes in reactive gas flow may alter the pulse flux due to target poisoning and hysteretic effects. Additionally, the consumption of the reactive gas by each source must be considered. It is anticipated that a weighted sum of the calibration gas flows and will be necessary in order to provide enough reactant for the metal fluxes of both sources.

6.6 Conclusions

Asynchronously patterned pulsed sputtering (APPS) is a new technique that enables co-sputtering of films across a broad range of compositions with minimal calibration. The pulsed nature of HiPIMS enables independent flux and energetic control, while the asynchronous pattern prevents the overlap of any sputter pulses. The APPS process provides a linear relationship between flux, pulse rate, and power, resulting in more predictable compositional trends than conventional co-sputtering. Using APPS, NbW films ranging from 10 to 90 at. % Nb were deposited within a few percent of predicted values using a single deposition rate calibration from each source. All films were found to be dense, smooth, and highly crystalline across the entire compositional range due to the consistent plasma energetics during APPS. Asynchronously patterned pulsed sputtering shows tremendous promise for the exploration of multicomponent systems.
Chapter 7

Exploring the (NbW)C System with Reactive Asynchronously Patterned Pulsed Sputtering

7.1 Preface

The contents of this chapter are intended for inclusion in a manuscript as follows:

Trent Borman,* Mohammed Delower Hossain,* & Jon-Paul Maria. Exploring the (NbW)C System with Reactive Asynchronously Patterned Pulsed Sputtering
Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA 16802
* Denotes equal contribution

7.2 Introduction

Ultra-high temperature ceramics (UHTCs) are promising structural materials for extreme environments. The mixed covalent, metallic, and ionic bonding results in a unique combination of properties including high melting points, hardness, stiffness, and low chemical reactivity. Unfortunately, many UHTCs still exhibit the low fracture toughness and thermal shock resistance observed in many ceramic materials.\(^1\)

Tests of UHTCs in simulated or real atmospheric reentry conditions often result in thermomechanical failure.\(^1\) For instance, half of the specimens fractured during the NASA/USAF SHARP-B2 atmospheric reentry test of HfB\(_2\) and ZrB\(_2\) based composites. These thermal gradient induced fractures were attributed to diboride agglomerations in the composite structure.\(^{15,16}\) Similarly, the Italian Aerospace Research Center (CIRA) tested hypersonic reentry of the UHTC tipped SHARK capsule. Post-flight analysis found that the sharp tip of the UHTC fractured during the middle of the flight and the remaining portion of the tip fractured radially into 3 segments. These failures were ascribed to defects from machining or ground testing prior to the flights, as most cracks originated from a machined hole.\(^{311}\)
Hypersonic vehicles could face catastrophic failure if UHTC leading edges fracture during a flight plan; thus, many researchers are focused on improving the fracture toughness of UHTCs. One common strategy is continuous fiber reinforcement, typically taking the form of a $\text{MB}_2\text{-SiC}_f$ composite material. Fabrication of these composites requires development of reactive melt, chemical vapor, powder, or polymer infiltration processes to deposit UHTC materials between the woven SiC fibers. Others strive to increase fracture toughness by engineering the composition of the UHTC itself. This is most commonly approached by increasing the valence electron concentration (VEC) of the UHTC.

The VEC is the weighted average number of valence electrons from each metal species plus each non-metal species. For example, the VECs of TiC, $\text{Ti}_{0.5}\text{W}_{0.5}\text{C}$, WC are 8, 9, and 10 respectively. The number of covalent bonds increases as the valence electron concentration rises to 8. Metallic nonbonding and antibonding states begin to populate once the valence electron concentration surpasses 8. Metallic and covalent states that resist shear deformation continue to populate until a VEC of ~8.4. Eventually, other phases such as hexagonal WC form, reducing the quantity of antibonding states.

High valence electron concentrations have been associated with an increase in the toughness of rocksalt UHTC ceramics. Sangiovanni et al. reported enhanced toughness in ordered $\text{Ti}_x\text{M}_{1-x}\text{N}$ ($\text{M}=\text{Mo}$ and W) modeled by density functional theory. They found that charge was less localized around Mo and W, producing a stronger covalent character in the bonds with nitrogen. Additionally, charge spread towards second nearest neighbors, an indication that $d(t_{2g})$ antibonding states were occupied by the extra valence electrons.

Upon shear deformation, the distance between second nearest neighbors reduces, strengthening the $\sigma^*$ bonds between metals. The $\sigma^*$ bonds favor shear deformation, lowering the shear modulus and increasing the metallicity of the material. Simultaneously, the additional electrons from Mo or W increase the electron density and bulk modulus of the material. This large reduction in shear modulus (G), coupled with a modest increase in bulk modulus (B), lowers the Pugh modulus (G/B) below 0.5. Pugh empirically determined that G/B can be used as a predictor of ductility; materials with a Pugh modulus below 0.5 are ductile while those above are brittle. Researchers have demonstrated reduced Pugh moduli in a number of other materials systems including Ta(CN), (TiMo)C, (TiW)C, (VMo)C, (VMo)N, (VW)C, and (VW)N.

Anion vacancies can further enhance the toughness and stability of the rocksalt carbide or nitride structure. Kindlund et al. demonstrated that $\text{V}_{0.5}\text{Mo}_{0.5}\text{N}_x$ alloys exhibit increased toughness with the addition of nitrogen vacancies; films with 45% of nitrogen sites vacant were approximately 50% harder while maintaining a similar Pugh modulus. Crystal-orbital overlap population analysis indicated that the addition of nitrogen vacancies strengthened the covalent metal-nitrogen bonds while maintaining the metal-metal bonds responsible for ductility. Others have reported that anion vacancies can increase d-d bonding and reduce the shear modulus, increasing the toughness of the material. Finally, anion vacancies can provide a means to stabilize thermodynamically and mechanically unstable (i.e. shear modulus < 0) phases, such as cubic WC or WN.
Studies of these phenomena usually rely on *ab-initio* techniques, such as density functional theory. However, some researchers add an experimental component, typically synthesizing materials by magnetron sputtering. In this work, asynchronously patterned pulsed sputtering (APPS) will be applied to the synthesis of ternary carbides. Combining APPS with reactive sputtering enables the synthesis of ternary carbides with controlled metal and carbon stoichiometries.

While these thin film studies are of great scientific value, they can have limited utility for engineering applications that require monolithic UHTC components. (NbW)C was chosen for this work based on the broad compositional range of the rocksalt phase at 1700 °C, suggesting that it may be possible to synthesize and quench in bulk form. Reactive APPS provides an experimental approach to rapidly screen the Nb-W-C and other M-M-C systems for tough compositions. With this knowledge, researchers can determine if bulk synthesis of the tough ternary ceramic compositions is tractable.

### 7.3 Experimental Details

Niobium tungsten carbide films were synthesized with reactive asynchronously patterned pulsed sputtering (R-APPS). The equipment, setup, and operation of APPS is thoroughly described in Chapter 6. This work builds upon the core APPS technique by adding a reactive gas to explore a ternary system.

First, processes to reactively sputter NbC and WC from elemental Nb (99.95% ex. Ta, Kurt J. Lesker) and W (99.95%, Kurt J. Lesker) targets were developed. Optimization of methane flow was critical during this step; the deposition should maximize carbon content while minimizing carbon precipitation. Prior work (Chapters 4 and 5) demonstrated that changes in the \{1 1 1\} peak and film density can indicate the onset of carbon precipitation. As carbon content increases, the \{1 1 1\} will shift to lower angles and plateau; simultaneously, the film density will hover around the theoretical density. A precipitous drop in film density or a further shift to lower angles are indications that excess carbon has precipitated. This method was sufficient for this work because (NbW)C films were synthesized with a range of methane flows around these calibrations.

The remaining process variables (Tables 7.1 and 7.2) were chosen based on prior work and conditions in the literature. Films were deposited on epi-polished c-plane sapphire substrates as they provide a favorable template for \{1 1 1\} rocksalt structure growth. HiPIMS pulse widths were limited to avoid the effects of gas rarefaction; The depletion of sputtering and reactive gasses from the vicinity of the target would be accompanied by a significant drop in current and plasma density. This drop in plasma density could lead to more carbon precipitation in WC rich films due to the limited solubility of C in rocksalt WC. A 20 V, 100 µs positive pulse (limited to 20A) was applied to the cathode 4 µs after the sputter pulse. This positive pulse provided additional adatom energy to densify the growing film and discourage the precipitation of excess carbon.

Pulsing frequencies were chosen to limit the power during the carbide deposition to ~210 W and ~350 W on the tungsten and niobium sources respectively. Targets were presputtered in argon to clean
Table 7.1: Source parameters and methane flows for NbC and WC flux calibration film depositions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NbC</th>
<th>WC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voltage (-V)</td>
<td>700</td>
<td>700</td>
</tr>
<tr>
<td>Frequency (Hz)</td>
<td>750</td>
<td>2000</td>
</tr>
<tr>
<td>Pulse width (µs)</td>
<td>28</td>
<td>25</td>
</tr>
<tr>
<td>Pulse current limit (A)</td>
<td>60</td>
<td>25</td>
</tr>
<tr>
<td>Positive pulse delay (µs)</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Positive pulse length (µs)</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>Positive pulse voltage (+V)</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Methane flow (sccm)</td>
<td>2.8</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Table 7.2: Chamber conditions and sputtering durations for NbC and WC flux calibration film depositions

<table>
<thead>
<tr>
<th>Parameter</th>
<th>NbC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ar flow (sccm)</td>
<td>20</td>
</tr>
<tr>
<td>Ar pressure (mT)</td>
<td>5</td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>500</td>
</tr>
<tr>
<td>Presputter times (s)</td>
<td>120 (Ar)</td>
</tr>
<tr>
<td></td>
<td>120 (Ar &amp; CH₄)</td>
</tr>
<tr>
<td>Sputter time (s)</td>
<td>300</td>
</tr>
</tbody>
</table>

target surfaces followed by Ar/CH₄ to equilibrate the reactive process prior to film deposition. The pressure was set to 5 mT during the argon presputtering step and allowed to increase when methane flow started. This kept the partial pressure of the sputtering gas constant across all samples, avoiding changes in flux associated with variations in P_{Ar}.

The pulse flux calculations for NbC and WC involved additional considerations relative to metal films. First, rocksalt WC_{1-x} is a non-equilibrium phase, thus the lattice parameter is relatively uncharacterized.³²³,³²⁴ Additionally, the presence of excess carbon is not accounted for with the unit cell volume based approach used in Chapter 6. To circumvent these factors, a molar mass–density approach was used to calculate the pulse flux in this work. The mass of carbon (12) is much smaller than Nb (92.92) and W (183.8), so carbon stoichiometry will have a limited impact on the molar mass (which was assumed to be stoichiometric). However, carbon precipitation was reflected by a rapid decrease in the mass density of the system. Quantification of carbon stoichiometry could have made the calculations more accurate, but that level of accuracy was not deemed necessary for the goals of this work.

The density and thickness of the calibration films were measured by X-ray reflectivity (XRR — Malvern Panalytical Empyrean). The incident beam was shaped by a Bragg-Brentano HD incident optic equipped with a 1/8° divergence slit, 2 mm mask, and 1/2° anti-scatter slit. The reflected signal was measured on a PIXcel³D detector operating in receiving slit mode (55 µm) with a matching 55 µm anti-scatter slit. Data were collected in steps of 0.005° with a count time of 0.5 seconds, and fit using X’Pert Reflectivity to determine the density, thickness, and roughness.

The metal atom dose of the calibration samples (Q_{cal}) was calculated from the thickness (d), mass density (ρ), Avagadro’s number (Nₐ), and molar mass (M) of each film using Equation (7.1). The dose was divided by the total number of pulses (ft) to yield a pulse flux (Φ) for each metal species i, using the relationship in Equation (7.2).
\[
Q_{cal,i} = \frac{d_i \rho_i N_A}{M_i} 
\]

(7.1)

\[
\Phi_i = \frac{Q_{cal,i}}{f t} 
\]

(7.2)

The calibrations in Table 7.3 were used to deposit five 300 nm thick films of \((\text{Nb}_{0.5}\text{W}_{0.5})\text{C}_x\) with varying carbon stoichiometries. The pulse fluxes for both species increased around 3% after these 5 depositions; thus, re-calibrations were performed prior to both the \((\text{Nb}_{0.7}\text{W}_{0.3})\text{C}_x\) and \((\text{Nb}_{0.3}\text{W}_{0.7})\text{C}_x\) sample series. The increase in pulse flux and power from target erosion resulted in a decrease in the carbon stoichiometry of the calibration films. This was compensated for by reducing the frequency until the power returned to \(~210\) W and \(~350\) W on the tungsten and niobium sources respectively. The resulting films had deposition rates, densities, and XRD patterns similar to the first calibration films while maintaining the same gas flow. The modified frequencies and pulse fluxes used for the \((\text{Nb}_{0.7}\text{W}_{0.3})\text{C}_x\) and \((\text{Nb}_{0.3}\text{W}_{0.7})\text{C}_x\) films are listed in Table 7.4.

The calculation of the APPS parameters followed the procedure in Chapter 6. The pulse ratios and time were derived from the desired metal stoichiometry and thickness using the pulse fluxes in Tables 7.3 and 7.4. Films were grown with an intended thickness of 300 nm to facilitate mechanical property measurements using nanoindentation. Table 7.5 provides all of the processing conditions for the metal fluxes but does not address the reactive gas flow.

The reactive gas flow was determined by considering the reactive gas pumping rates during the deposition process. Reactive gas is consumed by a number of mechanisms during a deposition including reactions with the target surface, gettering by the film (both on the substrate and the walls of the chamber), and removal by the turbomolecular pump.\(^{261}\) Gas load is the mass flow pumping rate of reactive gas \((Q)\); it is defined as the product of the volumetric pumping speed \((S)\) of the pumps and the partial pressure of reactive gas \((P_{\text{CH}_4})\) in Equation (7.3).\(^{260}\) This can further be broken down into the contributions from the turbomolecular pump \((p)\), and the metal \((m)\) in Equation (7.4).

| Table 7.3: Calculation of metal atom pulse fluxes used to deposit \((\text{Nb}_{0.5}\text{W}_{0.5})\text{C}_x\) films with R-APPS. |
|-------------------------------------------------|--|--|
| Thickness (nm) | NbC | WC |
| Molar mass (g/mol) | 104.9 | 195.8 |
| Mass density (g/cm\(^3\)) | 7.51 | 16.24 |
| Calibration dose \((Q_{cal,i})\) (metal atoms / Å\(^2\)) | 38.2 | 32.5 |
| Total pulses | 225000 | 600000 |
| Pulse flux \((\Phi_i)\) (metal atoms / Å\(^2\)-pulse) | \(1.70 \times 10^{-4}\) | \(5.42 \times 10^{-5}\) |
Table 7.4: Calculation of metal atom pulse fluxes used to deposit (Nb<sub>0.7</sub>W<sub>0.3</sub>)C<sub>x</sub> and (Nb<sub>0.3</sub>W<sub>0.7</sub>)C<sub>x</sub> films with R-APPS.

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>(Nb&lt;sub&gt;0.7&lt;/sub&gt;W&lt;sub&gt;0.3&lt;/sub&gt;)C&lt;sub&gt;x&lt;/sub&gt;</th>
<th>(Nb&lt;sub&gt;0.3&lt;/sub&gt;W&lt;sub&gt;0.7&lt;/sub&gt;)C&lt;sub&gt;x&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NbC</td>
<td>WC</td>
</tr>
<tr>
<td>Frequency (Hz)</td>
<td>725</td>
<td>1975</td>
</tr>
<tr>
<td>Mass density (g/cm&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>7.55</td>
<td>16.19</td>
</tr>
<tr>
<td>Calibration dose (Q&lt;sub&gt;_{cal,i}&lt;/sub&gt;) (metal atoms / Å&lt;sup&gt;2&lt;/sup&gt;)</td>
<td>38.1</td>
<td>33.3</td>
</tr>
<tr>
<td>Total pulses</td>
<td>217500</td>
<td>592500</td>
</tr>
<tr>
<td>Pulse flux (Φ&lt;sub&gt;i&lt;/sub&gt;) (metal atoms / Å&lt;sup&gt;2&lt;/sup&gt;-pulse)</td>
<td>1.75 × 10&lt;sup&gt;-4&lt;/sup&gt;</td>
<td>5.62 × 10&lt;sup&gt;-5&lt;/sup&gt;</td>
</tr>
</tbody>
</table>

Table 7.5: APPS pulsing parameters used to deposit (Nb<sub>y</sub>W<sub>1-y</sub>)C<sub>x</sub> films, listed in order of deposition. The tungsten source always operates at the control frequency and niobium is always the patterned source.

<table>
<thead>
<tr>
<th>Nb/W ratio</th>
<th>Nb pulse rate (Hz)</th>
<th>W pulse rate (Hz)</th>
<th>Time (s)</th>
<th>Pulse ratio (W/Nb)</th>
<th>Pulse train length</th>
<th>Pulses</th>
<th>Skips</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50</td>
<td>639</td>
<td>2000</td>
<td>674</td>
<td>3.132</td>
<td>313</td>
<td>100</td>
<td>213</td>
</tr>
<tr>
<td>70/30</td>
<td>724</td>
<td>970</td>
<td>781</td>
<td>1.338</td>
<td>67</td>
<td>50</td>
<td>17</td>
</tr>
<tr>
<td>30/70</td>
<td>259</td>
<td>1925</td>
<td>964</td>
<td>7.423</td>
<td>371</td>
<td>50</td>
<td>321</td>
</tr>
</tbody>
</table>

\[
Q = SP_{CH_4} \quad (7.3)
\]
\[
Q = (S_p + S_m)P_{CH_4} \quad (7.4)
\]

The turbomolecular pump was located behind a gate valve that was used as a throttle to vary the conductance and net pumping speed of the pump. However, all films were deposited with the valve throttled so P<sub>Ar</sub> was 5 mT; thus, the conductance and pumping speed of the turbomolecular pump were fixed across all of the depositions. As such, the gas load of the turbomolecular pump was governed solely by the partial pressure of the reactive gas (P<sub>CH_4</sub>).\(^{260}\)

Unlike most pumps, a metal getter pump is consumed as it pumps gas. Metal atoms pump the reactive gas by forming compounds with it. If the metal begins to saturate with reactant, then the pumping speed (S<sub>m</sub>) declines. The maximum gas load (Q<sub>m</sub>) of a getter pump is related to the supply rate of new metal atoms (λ<sub>m</sub>), specific volume of the gas (V<sub>CH_4</sub>), number of gas molecules consumed by each metal atom (n), and Avogadro’s number (N<sub>A</sub>) by Equation (7.5). The pumping speed (S<sub>m</sub>) of a getter pump (Equation (7.6)) is the product of the area (A), sticking coefficient (s), velocity of the gas (v), and a geometric constant. Finally, Equation (7.7) was derived from Equations (7.3), (7.5), and (7.6).\(^{260}\)
\[ Q_m = \frac{\lambda_m V_{CH_4} n}{N_A} \]  
\[ S_m = \frac{A s v}{4} \]  
\[ \frac{\lambda_m V_{CH_4} n}{N_A} = \frac{A s v P_{CH_4}}{4} \]  

Cancellation of all constants\(^{(I)}\) resulted in Equation (7.8).\(^{(II)}\) This was simplified further because the arrival rate of metal species \((\lambda_m)\) is proportional to the product of the pulse flux \((\Phi_m)\) and the frequency of operation \((f)\), while \(n\) is the carbon stoichiometry \((x)\) in \(MC_x\), resulting in Equation (7.9). If the carbon stoichiometry remained consistent between calibration and R-APPS depositions, then \(x\) must also be a constant. Finally, control over the metal ratio required the assumption that the metal pulse flux did not change with variations in reactive gas flow. Safi reported that the deposition rate should be relatively insensitive to reactive gas flow in the poisoned regime, supporting this assumption.\(^{161}\) Removal of these constants indicated that any change in the frequency between calibration and R-APPS depositions should be accompanied by a proportional change in the partial pressure of reactive gas (Equation (7.10)).

\[ \lambda_m n \propto P_{CH_4} \]  
\[ \Phi_m f x \propto P_{CH_4} \]  
\[ f \propto P_{CH_4} \]

The pumping speeds of the turbomolecular and getter pumps were constant; thus, an increase in partial pressure resulted in a proportional increase in gas load (Equation (7.3)). At a fixed carbon stoichiometry, each metal consumed an amount of reactive gas proportional to its frequency. Therefore, the total methane flow was a frequency weighted sum of the methane flows required for each metal species. Equation (7.12) defines the total R-APPS mass flow rate \((\dot{m}_{R,T})\) of methane as a function of the calibration and R-APPS frequencies \((f_{C,m} \text{ and } f_{R,m})\) and calibration flow rates \((\dot{m}_{C,m})\) for each metal species. The R-APPS mass flow rates for each metal ratio are listed in Table 7.6.

\[ \dot{m}_{R,T} = \dot{m}_{R,Nb} + \dot{m}_{R,W} \]  
\[ \dot{m}_{R,T} = \frac{f_{R,Nb}}{f_{C,Nb}} m_{C,Nb} + \frac{f_{R,W}}{f_{C,W}} m_{C,W} \]

With the pulsing parameters and R-APPS mass flow rates determined, it was possible to synthesize \((Nb_{y}W_{1-y})C_x\) films with R-APPS. Films were deposited with 80 to 120% of the total R-APPS mass flow rate \((\dot{m}_{R,T})\) in 10% increments in order to study the impacts of carbon stoichiometry. The resulting data are presented as a function of metal ratio and percentage of the total R-APPS mass flow rate \((\dot{m}_{R,T})\).

\(^{(I)}\) Area, gas velocity, sticking coefficient, specific volume of the gas, Avogadro’s number, and geometric constants.  
\(^{(II)}\) This assumed that regions of the getter pump were not saturated with carbon. This was based on the facts that there was minimal (if any) excess carbon in the calibration films, and the chamber walls contributed substantially to the pump's size.
Table 7.6: Frequency ratios and R-APPS methane mass flow rates for the (Nb<sub>y</sub>W<sub>1-y</sub>)C<sub>x</sub> films deposited in this work.

<table>
<thead>
<tr>
<th>Nb/W ratio</th>
<th>Nb f&lt;sub&gt;A&lt;/sub&gt;/f&lt;sub&gt;C&lt;/sub&gt;</th>
<th>W f&lt;sub&gt;A&lt;/sub&gt;/f&lt;sub&gt;C&lt;/sub&gt;</th>
<th>m&lt;sub&gt;R,Nb&lt;/sub&gt;(sccm)</th>
<th>m&lt;sub&gt;R,W&lt;/sub&gt;(sccm)</th>
<th>m&lt;sub&gt;R,T&lt;/sub&gt;(sccm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50/50</td>
<td>0.852</td>
<td>1.000</td>
<td>2.38</td>
<td>2.5</td>
<td>4.88</td>
</tr>
<tr>
<td>70/30</td>
<td>0.999</td>
<td>0.491</td>
<td>2.80</td>
<td>1.23</td>
<td>4.03</td>
</tr>
<tr>
<td>30/70</td>
<td>0.375</td>
<td>1.000</td>
<td>1.05</td>
<td>2.5</td>
<td>3.55</td>
</tr>
</tbody>
</table>

7.4 Results and Discussion

The metal ratio of the films was quantified in atomic percent (metals basis) by energy dispersive spectroscopy (EDS — Oxford Instruments Ultim Max 100) with a field-emission scanning electron microscope (FESEM — Thermo Fisher Scientific Apreo S). A 3.2 nA beam at 10 keV was rastered across regions of the film for 60 s of live time. Spectra were taken in two locations on each sample and found to be within 0.3 at. % (metals basis) of each other once normalized. The average Nb content is presented in Figure 7.1 as a function of the intended Nb percentage, and the percentage of the total R-APPS mass flow rate.

Figure 7.1: Concentration of niobium (metals basis) as a function of the percentage of total APPS mass flow rate. The three traces represent samples with intended Nb concentrations of 30% (red, bottom), 50% (blue, middle), and 70% (blue, top).
Table 7.7: Linear regression coefficients for the dependence of atomic percent Nb on the percentage of flux normalized methane flow. The right most column is the mean measured W percentage.

<table>
<thead>
<tr>
<th>Nb/W Ratio</th>
<th>Slope</th>
<th>Intercept</th>
<th>r²</th>
<th>Mean W (at. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>70/30</td>
<td>0.033 ± 0.005</td>
<td>64.0 ± 0.5</td>
<td>0.94</td>
<td>32.7</td>
</tr>
<tr>
<td>50/50</td>
<td>0.050 ± 0.009</td>
<td>43.8 ± 1.0</td>
<td>0.90</td>
<td>51.2</td>
</tr>
<tr>
<td>30/70</td>
<td>0.071 ± 0.038</td>
<td>22.6 ± 3.9</td>
<td>0.54</td>
<td>70.3</td>
</tr>
</tbody>
</table>

All films were found to be within 3.3 at. % of the intended Nb composition. The films at 70 at. % Nb had the greatest error (averaging -2.7 at. %) while those at 30 at. % Nb had the greatest variability (ranging from -2.1 at. % +1.9 at. %). There was no significant trend correlating to the order of deposition; the 5 films for each Nb/W ratio were deposited in the order 100%, 110%, 90%, 120%, 80% at R,T. However, there was a slight positive slope in niobium content as a function of the percentage of at R,T.

The linear regression coefficients for each of the three traces in Figure 7.1 are listed in Table 7.7. The slope of each trace was found be approximately 1/1000th of the mean tungsten concentration (at. %). This is likely a consequence of the difference in deposition characteristics of reactively sputtered NbC and WC. Tungsten carbide can be more challenging to sputter as it often grows in a non-equilibrium phase that is difficult to fully carburize.

This difficulty is further evidenced by the carbide Ellingham diagram. While NbC has a Gibb's formation energy of −130 kJ/mol, W₂C only has a formation energy of −30 kJ/mol at 500 °C. Other researchers have found that hexagonal WC exhibits a similar formation energy to W₂C. Furthermore, the Ellingham diagram allows for the determination of the partial pressure ratio $P_{\text{CH}_4}/P_{\text{H}_2}$ that will thermodynamically favor the equilibrium formation of each of these phases. Shatynski’s Ellingham diagram indicates that the boundaries for NbC and W₂C formation are $3 \times 10^{-9}$ and $2 \times 10^{-2} P_{\text{CH}_4}/P_{\text{H}_2}$, respectively, at 500 °C. Metastable stoichiometric cubic WC has a positive formation energy which will lead to a $P_{\text{CH}_4}/P_{\text{H}_2}$ ratio exceeding 1 at 500 °C.

The partial pressure ratio for NbC suggests that it should always be fully carburized under these deposition conditions. While the decomposition of methane does produce hydrogen gas in a 2:1 ratio, fresh methane is continuously added to the chamber. The total partial pressure of CH₄ and H₂ was on the order of 1–2.5 mT. It is unlikely that the metal getter pump could consume methane gas fast enough to reduce the $P_{\text{CH}_4}/P_{\text{H}_2}$ below $3 \times 10^{-9}$ while methane was being added to the chamber. Carbon deficient Nb films can be deposited by sputter deposition, but this is a kinetic limitation not a thermodynamic one. A high niobium deposition rate or low methane impingement rate can result in sub-stoichiometric material being buried by new material before it can fully carburize.

The total pressure rise upon introduction of methane is between 1–2.5 mT. It is unknown what the balance of methane and hydrogen were in that pressure rise.
Conversely, hexagonal tungsten carbide falls into a range where it may or may not be fully carburized. With a $P_{\text{CH}_4}/P_{\text{H}_2}$ ratio around 0.02, it is possible that there may be enough methane depletion in the chamber ($P_{\text{CH}_4} \sim 10^{-5}$ Torr) for tungsten carbide to be thermodynamically unstable. While changes in methane flow should only affect the kinetics of NbC deposition, the thermodynamics and kinetics of WC deposition are both susceptible to changing $P_{\text{CH}_4}$.

Changes in thermodynamic stability could affect the poisoning of the W target surface. As methane flow changes, different phases and stoichiometries may form on the target surface, each with different sputtering characteristics. As carbon is added, the additional covalent bonds and changes in crystal structure should lower the sputter yield and change the Nb/W ratio of the film.\(^{200}\) This is supported by the fact that films with higher tungsten fractions were more susceptible to changes in methane flow, as indicated by the slopes in Table 7.7.

The phase purity, texture, and crystallinity of the films were assessed with Bragg-Brentano X-ray Diffraction (XRD — Malvern Panalytical Empyrean). X-ray diffraction patterns were collected using a Bragg-Brentano\(^{\text{HD}}\) incident optic configured with a \(1/8^\circ\) divergence slit, \(1/2^\circ\) anti-scatter slit, and 2 mm mask. The diffracted beam passed through a \(1/4^\circ\) anti-scatter slit before being collected by the PIXcel\(^{\text{3D}}\) detector. Data were collected in scanning line mode with a step size of 0.0525° and a net count time of 59 s per step.

X-ray diffraction patterns are presented in Figure 7.2, grouped by niobium content. All compositions formed a rocksalt carbide structure with no evidence of hexagonal WC or W\(_2\)C phases. Films had polycrystalline texture, albeit showing a preference for \{1 1 1\} texture that tended to increase with methane flow. This behavior is similar to that seen in Chapter 4; however, the films never transitioned to the epitaxial structure observed with carbon precipitation in (HfNbTaTiZr)C. At the highest methane flows, the peaks of the 30 and 50 at. % Nb samples began to decrease in intensity and sharpness, a possible indication of a nanocomposite structure.\(^{19,201}\)

Increases in the niobium concentration also increased the \{1 1 1\} texturing and \{1 1 1\} peak sharpness. WC is unstable in the rocksalt phase and tends to form nanocrystalline films, leading to diffuse peaks and polycrystalline texture.\(^{19,326}\) As the amount of WC decreased, the rocksalt structure became more favorable, resulting in improved crystal quality. The \{1 1 1\} shifted to lower angles with increasing niobium content due to the larger lattice parameter of NbC. However, changes in methane flow had little effect, suggesting all films had enough carbon to prop the rocksalt lattice up to a fixed lattice parameter.

Field emission scanning electron microscopy (FESEM — Thermo Fisher Scientific Verios G4 UC) was used to investigate the microstructure of the films. Micrographs from all of the films are presented in Figure 7.3, arranged by Nb/W ratio and percent of the R-APPS mass flow. At low methane flows (80% of $\dot{m}_{\text{R,T}}$), the grain size and morphology are relatively similar across all Nb/W ratios. As the methane flow increases (90-100% of $\dot{m}_{\text{R,T}}$) the microstructures begin to diverge. The fraction of grains with a triangular morphology increased with niobium content at a methane flow of 100% of $\dot{m}_{\text{R,T}}$. This reflects the higher fraction of \{1 1 1\} texture in niobium rich films. The grains of the 30 at. % Nb samples grew in
Figure 7.2: X-ray diffraction patterns of (Nb$_y$W$_{1-y}$)C$_x$ films deposited with reactive APPS. Patterns are clustered into 3 groups of 5 by intended niobium content: 30% (red, bottom), 50% (black, middle), and 70% (blue, top). Within each of these groups of 5, the patterns are stacked in order of increasing methane flow: 80% of the total APPS mass flow rate (bottom, lightest) to 120% (top, darkest) in steps of 10%. RS denotes peaks which correspond to the rocksalt carbide crystal structure. X-ray artifacts and secondary wavelengths (Cu$_{K\beta}$, W$_{L\alpha}$) are denoted by ♦.
size relative to the lower methane flows, while those of the other Nb/W ratios show little change in this flow rate regime.

Further increases to 110% of $\dot{m}_{R,T}$ caused a rapid decrease in the grain size of the 30Nb/70W film, forming a nanocomposite structure as seen in Chapter 4. The grains of the 50/50 film became slightly less defined, while the triangular grain population increased in the 70% Nb film at this methane flow. At the highest methane flow, the grain size of the 30% Nb film continued to reduce and the 50% Nb sample began to form a nanocomposite. Conversely, the triangular grains persisted in the 70 at. % Nb sample at the highest methane flow, avoiding nanocomposite formation.

Nanocomposites form more readily with an increased fraction of tungsten. This is likely a consequence of the stoichiometry limitations of the cubic WC$_{1-x}$ structure.\textsuperscript{19,23} As the fraction of tungsten is increased in the rocksalt structure, the maximum thermodynamically stable carbon stoichiometry should decrease. The R-APPS methane flow did compensate for the changing Nb/W ratio with a rule of mixtures approach, but the maximum carburization of (NbW)C may not have followed the same linear trend. Additionally, the tungsten flux decreased with increasing methane flow, reducing the total amount of metal available to react with the carbon.

Nevertheless, the similarities between the films leave them well suited for studies of toughness in the (NbW)C system as a function of both metal ratio and carbon content. The films are phase pure and similarly textured by XRD, eliminating the impacts of anisotropy or precipitation hardening. Additionally, the small and similar grain sizes allow the nanoindenter to probe a comparable number of grains and grain boundaries in all films. The nanocomposite films may show different mechanical properties due to carbon precipitation, but they make up only 20% of the total samples.

R-APPS exhibits many of the same benefits as APPS including linear compositional control and consistent film characteristics (density, roughness, crystallinity) across broad compositional ranges. However, it also exhibits some of the same challenges, most notably compositional deviations due to small changes in the pulse flux as a function of target wear, temperature, or frequency. Additionally, R-APPS adds an additional complication: the dependence of pulse flux on reactive gas flow. This behavior may be even more problematic for targets which are insulating when poisoned, such as reactively sputtered oxides.

At this juncture, there is approximately 2-3 at. % (metals basis) error in the metal ratio during an APPS or R-APPS deposition. This error level may be above the acceptable limit for materials where the stoichiometries of interest are well established and narrow, such as for perovskites or other line compounds. However, this does not preclude R-APPS from being applied to other materials systems where accuracy demands may be reduced, such as the (NbW)C system. APPS and reactive APPS are both new and emerging techniques with untapped potential. Further developments, such as in-situ target calibrations, will present many opportunities to improve the process and reduce the compositional error.
<table>
<thead>
<tr>
<th>Percent of $m_{A,T}$</th>
<th>Intended Metal Stoichiometry</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 / 70</td>
<td>At.% Nb / At.% W</td>
</tr>
<tr>
<td>50 / 50</td>
<td>80</td>
</tr>
<tr>
<td>70 / 30</td>
<td>90</td>
</tr>
<tr>
<td>80</td>
<td>100</td>
</tr>
<tr>
<td>90</td>
<td>110</td>
</tr>
<tr>
<td>100</td>
<td>120</td>
</tr>
</tbody>
</table>

**Figure 7.3:** SEM micrographs of $(Nb_{y}W_{1-y})C_{x}$ films deposited with reactive APPS arranged by increasing niobium content (left to right) and percentage of total APPS mass flow rate ($m_{R,T}$, top to bottom).
7.5 Conclusions

Reactive asynchronously patterned pulsed sputtering (R-APPS) builds upon the APPS technique to reactively deposit ternary materials. As with APPS, metal fluxes can be controlled predictably and linearly by changing the pulsing ratio. The reactive gas flow is determined simply by a frequency weighted average of the calibration gas flows, resulting in the R-APPS mass flow rate. The R-APPS process was applied to the (NbW)C system to study the impacts of Nb/W ratio and carbon content on crystal structure, microstructure, and mechanical properties. Films were found to be within 3.3 at. % Nb (metals basis) of the intended Nb/W ratio across all samples despite a ±20% change in methane flow. The niobium fraction did increase modestly with methane flow as a consequence of increased poisoning of the tungsten target. However, all films produced similar x-ray diffraction patterns with modest changes in microstructure across broad stoichiometry ranges. Reactive APPS provides a new method to explore reactively sputtered multicomponent systems for novel properties and applications.
8.1 Conclusions

8.1.1 Microstructure-Stoichiometry-Property Relations in High Entropy Carbide Films

The first section of this dissertation focused on understanding the links between microstructure, stoichiometry, and functional properties of a high entropy carbide. While (HfNbTaTiZr)C and related compositions have received great research interest, the impacts of carbon sub-stoichiometry have not been investigated.\textsuperscript{7,10,22,143,144,327} In Chapter 4, (HfNbTaTiZr)C\textsubscript{x} films were examined as a function of the methane flow rate used during the sputter deposition process. This facilitated an understanding of how the sputter deposition of high entropy carbides compares to low entropy counterparts and provided insight into the effects of carbon vacancies in high entropy carbides.\textsuperscript{19,21}

A HfNbTaTiZr target was RF magnetron sputtered with methane flow rates between 0.5 and 5.5 sccm, resulting in carbide films that spanned a compositional range from \(~\text{MC}_{0.2}\) to \(~\text{MC}_{1+C_{0.5}}\). Films transitioned from metallic, to carbide, and finally carbide-carbon nanocomposites as carbon was added to the system. A stoichiometric carbide (with no excess carbon) was synthesized with 2.75 sccm of methane before the rapid onset of carbon precipitation in a film deposited with 2.82 sccm of methane. This narrow process window is similar to the window observed in binary counterparts, such as TiC.\textsuperscript{19,201}

Transmission electron microscopy analysis revealed that the a carbon deficient sample (~7% carbon vacancies) had a substantial number of stacking faults and twin boundaries. This indicated that the carbon vacancies may still favor clustering in planes, even in a chemically disordered, high entropy crystal.\textsuperscript{103,104,109,240} Electron energy loss spectroscopy (EELS) and energy dispersive spectroscopy (EDS) showed that the metal cations were evenly distributed throughout the film, except for a slight enrichment of titanium at some grain boundaries. A poorly crystalline carbon phase precipitated out at the grain boundaries of films that had excess carbon in the Raman and XPS spectra.

The mechanical properties of the (HfNbTaTiZr)C\textsubscript{x} films were measured via nanoindentation. The hardness of films linearly increased to a peak of 24 \(\pm\) 3 GPa at the near-stoichiometric composition. This
value is relatively close to the rule of mixtures from the binary constituents (~25 GPa), although it is lower than reports for the same composition in bulk form (32 ± 2 GPa).\textsuperscript{7,103,105} The precipitation of excess carbon promptly decreased the hardness by nearly 60% to 10.5 ± 1.5 GPa; however, further additions of excess carbon (between C\textsubscript{0.4} and C\textsubscript{0.5}) form a carbide-carbon nanocomposite with an increased hardness of 15.5 ± 1.0 GPa.

Ab-initio calculations validated the experimental hardness measurements. At low stoichiometries, the bonding had significantly more metallic character, leading to hardness values which depended on plastic flow and dislocation motion throughout the crystal. The hardness of stoichiometric films was dominated by the bond strength and breaking of the M-C covalent bonds. Superstoichiometric films were dominated by microstructural effects, softening with trace amounts of excess carbon and hardening when a nanocomposite structure formed. Overall, the experimentally observed and theoretically predicted carbon stoichiometry trends in the high entropy carbide films closely mirrored the trends of binary carbide counterparts.

\subsection{8.1.2 Refining the High Entropy Carbide Deposition Process}

The radio frequency magnetron sputtering approach used in Chapter 4 was a valuable foray in the deposition of thin film high entropy carbides. The samples led to valuable insight about the behavior of carbon and carbon vacancies in a high entropy carbide structure; however, the technique had some significant limitations. While films could be deposited over a broad compositional range, the synthesis of stoichiometric films with no excess carbon proved incredibly challenging.

As a result, a number of experiments were undertaken in order to understand the factors that contributed to the final film stoichiometry and the narrow process window. Several aspects were identified as warranting investigation: improving the metal flux stability, consistency, and linearity of the reactive gas control approach, methods to drive the system towards equilibrium, and hindering the precipitation of excess carbon.\textsuperscript{19} Gas flows and pressures, energetic bombardment, and alternate sputtering techniques were all explored as possible strategies to improve these factors.

In Chapter 4, the total pressure in the chamber was kept fixed across the entire methane flow regime. Any increase in methane flow required a coinciding decrease in argon partial pressure, which changed the plasma density, target poisoning rate, and metal flux. Avoiding these factors required operating at a fixed argon partial pressure and a methane-flow dependent total pressure. Low argon partial pressures were shown to provide benefits through enhanced energetics; however, a low $P_{\text{Ar}}$ reduced the deposition rate and increased target poisoning. As such, a modest (5–10 mT) and constant argon partial pressure was determined to provide the most consistent metal flux and plasma characteristics.

Improving the control of the reactive gas required identifying which gas consumption regime the deposition process was operating in. A study of flow magnitude (fixed ratio) demonstrated that the growing carbide film consumed a significant fraction of the methane introduced into the chamber.
In this regime, the partial pressure of reactive gas is most indicative of the resulting film composition. Unfortunately, the deposition system, as configured, could only measure the combined partial pressure of hydrogen and methane, which was not sufficient to control stoichiometry. Controlling carbon stoichiometry with methane flow remained the best strategy given the configuration and capabilities of the system. However, the reliability of this technique is contingent on maintaining a fixed metal flux.

The fixed argon partial pressure and temperature restrictions (due to substrate reactions) limited the ways that the system could be driven towards equilibrium (away from carbon precipitation). Energy was added to growing films by controlled ion bombardment during bipolar HiPIMS depositions. Modest bombardment produced smoother films with enhanced crystallinity; however, high energy bombardment (over 100 eV), began to show detrimental effects, such as increased surface roughness.

Finally, high power impulse magnetron sputtering (HiPIMS) was explored as a means to increase plasma density, regulate the metal flux, and hinder the precipitation of excess carbon. Films deposited over a range of methane flow rates with bipolar HiPIMS were significantly smoother and more uniform in microstructure and crystallography than RF sputtered counterparts. Power and voltage regulation led to more consistent metal fluxes and deposition rates than RF sputtering, despite changes in methane content and target erosion. The processing window between near-stoichiometric carbide films and excess carbon precipitation was broadened, with carbon precipitation occurring more slowly.

8.1.3 Development of Novel Pulsed Co-Sputtering Techniques

The latter half of this dissertation focused on the development of new pulsed co-sputtering techniques for the deposition of multicomponent thin films. Earlier work found that the decoupling of energetics and flux afforded by high power impulse magnetron sputtering (HiPIMS) were beneficial for a number of materials systems. Asynchronously patterned pulsed sputtering (APPS) was developed to harness this decoupled characteristic in order to deposit multicomponent thin films with accurate chemistry and consistent film quality across broad compositional ranges.

With conventional sputtering, sputtering flux and energetics are inseparably coupled. Spanning a broad compositional range with co-sputtering involves 10-fold changes in power, often sacrificing film quality for stoichiometric control. Additionally, the relationship between power and flux is often non-linear, resulting in tedious calibrations.

The energetics of HiPIMS are controlled by the pulse width, sputter voltage, and positive pulse voltage. While these parameters will affect the flux per pulse, the time-averaged flux can be adjusted via the pulsing frequency with no impact on the energetics. However, conventional HiPIMS co-sputtering techniques have their drawbacks. One approach involves operates the two sources at independent frequencies, but this leads to pulse overlaps and plasma interactions between targets. The alternative approach operates both sources at the same frequency; however, flux must now be controlled with voltage or pulse width, impacting energetics.
Asynchronously patterned pulsed sputtering (APPS) provides a way to keep the time-averaged flux decoupled from energetics while preventing any pulse overlaps and plasma interactions. An arbitrary waveform generator triggers one source at a fixed frequency, while triggering the other source in a pattern of pulses and skips at the same frequency. Operating the patterned and unpatterned sources at the same frequency with a 180° phase shift prevents plasma overlaps. The composition can be controlled linearly by changing the pulse to skip ratio of the patterned source.

The niobium-tungsten metal system was used to prove the concept of APPS with a simple, non-reactive process. Films ranging from 10 to 90 at.% Nb were deposited from one deposition rate calibration per source. Films were an average of $-2.0 \pm 1.3$ at. % Nb away from the anticipated composition over the entire range. Additionally, the films showed similar XRD patterns, with narrow \{1 1 0\} BCC peaks, and low surface roughnesses (averaging 1.1 $\pm$ 0.6% of the thickness via XRR) across the entire compositional range, despite a 7 to 11 fold change in power on each cathode.

Reactive asynchronously patterned pulsed sputtering (R-APPS) was used to deposit films from the (NbW)C ternary system by adding carbon with a CH$_4$ plasma. Switching to a reactive process required determination of the proper reactive gas flow rate for the R-APPS process. A mathematical treatment of the various pumping contributions was used to determine that the flow rate during an R-APPS deposition should be a frequency weighted sum of the calibration gas flow rates.

Niobium-tungsten carbide films were deposited with 30/70, 50/50, and 70/30 Nb/W ratios at a range of methane flow rates. All films were within an average of 1.7 $\pm$ 1 at. % Nb (metals basis) of the intended composition despite a $\pm$20% change in methane flow from the frequency weighted sum. Tungsten rich films were found to form weaker XRD peaks and transition to nanocomposites at lower methane flows than niobium rich films. Additionally, films became richer in Nb with increasing methane flow at a rate proportional to the tungsten content of the film. Reactive-APPS was demonstrated as a viable technique for the exploration of reactively deposited ternary systems. It enabled the rapid deposition of a broad range of (NbW)C compositions to facilitate the search for ductile UHTC compositions.

The development of APPS showed great promise for both metallic and reactively deposited systems. It provided predictable and accurate compositional trends with significantly less calibration than conventional co-sputtering while maintaining high film quality. While the initial results were encouraging, there are several opportunities to improve APPS that will be discussed in the following section. These developments have the potential to both streamline the APPS technique as well as improve the accuracy for more compositionally sensitive systems.
8.2 Future Work

8.2.1 Advancing Asynchronously Patterned Pulsed Sputtering

Asynchronously patterned pulsed sputtering (APPS) and its reactive counterpart (R-APPS) were developed and tested in Chapters 6 and 7. The results of these initial tests were promising, with predictable compositional trends and consistent film quality across broad ranges of stoichiometry. However, compositions were not as accurate as desired (ideally < 1 at.%), and the need to continuously recalibrate the deposition rates as targets wear can prove cumbersome. There are a number of ways in which the APPS process could be improved, both in refining the workflow of the technique as well as improving the understanding of the process.

Film thicknesses were measured ex-situ using X-ray reflectivity in the prior chapters, while this approach is reliable it does have some shortcomings. The ex-situ nature of XRR makes calibrations quite time-consuming; each rate measurement involves mounting, loading, heating, depositing, cooling, and measuring a sample. This process takes somewhere between 30–60 minutes to complete depending on the deposition temperature and availability of equipment. While the thickness accuracy of XRR is excellent (~1 Å or ~0.1% on most calibration films), it only provides a measure of the average deposition rate over the calibration cycle.

APPS operates on the assumption that the pulse flux is a constant throughout the entire deposition process; however, this might not be the case. The power on the tungsten magnetron operating at fixed conditions was found to change over the course of over 30 minutes. This was believed to be a consequence of the target temperature reaching equilibrium between the 250 W load on the target surface and the 12.5°C water cooled hearth on the backside. In order to study the impacts of this phenomenon on deposition rate, a series of tungsten samples were deposited with presputtering times ranging from 60 to 1800 seconds. By the end of the depositions the target was operating for a total of 550 to 2280 seconds, resulting in a 4 fold change in the thermal equilibration time.

The metal, oxide, and equivalent metal thicknesses are presented with the corresponding deposition rate in Table 8.1. The thicknesses were measured with X-ray reflectivity; thus, the deposition rate is time-averaged over the entire deposition (~480 s). Increasing the presputtering time from 60 to 300 seconds resulted in a 4.7% increase in the average deposition rate while a further extension to 1800 seconds provided an additional 3% increase. This suggests that the changes in the frequency (and thus power) or deposition time between calibration and APPS depositions could cause compositional error.

Measurements of instantaneous deposition rate as a function of sputtering time could be made using an in-situ quartz crystal monitor (QCM), providing multiple benefits for both accuracy and efficiency. Pulse fluxes could be calibrated from this in-situ rate measurement, reducing the calibration time substantially relative to the ex-situ X-ray reflectivity approach. Additionally, rapid calibrations before every sample would alleviate most error from target erosion. While calibrations before every sample are
Table 8.1: Tungsten deposition rate as a function of pre-sputtering time following deposition conditions in Chapter 6. The volume per formula unit of W is $\sim 30\%$ that of WO$_3$. The equivalent thickness (of metal) is calculated as $d_W + 0.3d_{WO_3}$.

<table>
<thead>
<tr>
<th>Presputter time (s)</th>
<th>Total sputter time (s)</th>
<th>Metal thickness (nm)</th>
<th>Oxide thickness (nm)</th>
<th>Equivalent thickness (nm)</th>
<th>Deposition rate (nm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>550</td>
<td>93.5</td>
<td>0.6</td>
<td>93.7</td>
<td>0.191</td>
</tr>
<tr>
<td>300</td>
<td>780</td>
<td>95.5</td>
<td>1.6</td>
<td>96.0</td>
<td>0.200</td>
</tr>
<tr>
<td>1800</td>
<td>2280</td>
<td>98.7</td>
<td>0.0</td>
<td>98.7</td>
<td>0.206</td>
</tr>
</tbody>
</table>

possible with ex-situ techniques, each APPS sample would take three times longer to synthesize due to the two calibration samples.

Another benefit of in-situ calibration before each deposition would be the ability to easily compensate for pulse flux changes as a function of frequency / power. In Chapter 6, the pulse flux was only measured at one frequency (2000 Hz for W), despite the APPS frequency varying by a factor of 10. As a consequence, the pulse flux was assumed to be the same at both 25 watts / 25 Hz, and 250 W / 2000 Hz. As demonstrated in Table 8.1, the thermal state of the target can play a role in the deposition rate of the system; thus, it would be ideal to calibrate the pulse flux at frequencies near the final APPS parameters.

This could be implemented by using the prior set of pulse flux calibrations to generate preliminary APPS parameters for the next sample. These preliminary parameters would be used to measure an updated pulse flux. The APPS parameters would then be recalculated with this new flux measurement, compensating for the impacts of target erosion or power on the pulse flux. With this approach, one might initially calculate an APPS frequency of 0.1f, calibrate in-situ at 0.1f, and find they need to deposit at 0.09f to compensate for target erosion and power-dependent pulse flux changes. This is in contrast to calibrating at 1f and depositing at 0.1f while assuming the pulse flux doesn’t change, as in Chapter 6.

In this dissertation the Python script was only used for the generation of the arbitrary waveforms; the remainder of the necessary calculations, from pulse fluxes to pulse ratios, were performed in a spreadsheet. The Python script could be expanded to include this functionality by allowing input of the calibration parameters and desired film characteristics and outputting the necessary APPS parameters. An additional point of streamlining would involve developing an algorithm to automatically generate the APPS patterns from a given pulse ratio.

The impacts of pattern uniformity on the final outcome of the film should be investigated before development of a patterning algorithm. Given that a monolayer is on the order of 1000 pulses, there may be no significant difference between a complex pattern and no pattern at all (i.e. all pulses in row followed by all skips). However, cross-contamination from the neighboring targets during these idle periods could impact the stoichiometry. Additionally, the fluctuations in target surface temperature from numerous high power pulses in a row followed by a long idle period could also impact the composition.
The addition of in-situ calibration, using a quartz crystal monitor (QCM), would make it possible to fully automate the APPS process. A deposition system would accept inputs of desired composition, thickness, and other deposition parameters (maximum power, temperature, pressure, HiPIMS parameters, etc.). Pulse fluxes would be measured using the QCM, APPS parameters and waveforms generated by the script, and patterned trigger signals supplied to the HiPIMS units with no user intervention. The user would likely be involved in the process optimization of the individual constituents, however all APPS depositions could occur automatically based on these parameters.

8.2.2 Investigating Tough Carbonitrides

The toughness and ductility of rocksalt carbides and nitrides increases with the valence electron concentration.\textsuperscript{315,317} Additionally, anion vacancies play a substantial role in the phase stability and mechanical properties of the material.\textsuperscript{103,321,322} In Chapter 7, the reactive asynchronously patterned pulsed sputtering (R-APPS) process was applied to the (NbW)C system to produce samples for a study of the mechanical properties and structural stability as a function of the Nb/W ratio and carbon (vacancy) stoichiometry. In this case, WC provided a high valence electron concentration while NbC served to increase the stability of the rocksalt structure. Alloying with high VEC metals (Mo or W) on the cation site is not the only way to increase the VEC; alternatively, one can occupy anion sites with other species, such as nitrogen or oxygen. Additional anions provide another degree of freedom that can be leveraged to develop tough, stable rocksalt UHTC materials.

Adding oxygen presents a significant challenge as most of the Group IVB and VB transition metals will readily oxidize, making it difficult to precisely control oxygen content. Additionally, the vastly different structures of transition metal carbides and oxides will lead to a low solubility limit.\textsuperscript{115} Nitrogen, by comparison, is a much more appealing alloying addition. The Group IVB nitrides all crystallize in a rocksalt structure, while the Group VB nitrides form rocksalt (V) or hexagonal structures (Nb and Ta). However, as with MoC and WC, the higher symmetry cubic NbN and TaN phases will form at elevated temperatures (1160–1700 °C).\textsuperscript{23,318} Similarly, MoN and WN prefer hexagonal nitride phases, although the rocksalt structure becomes stable at modest temperatures (290–380 °C) with significant (30-50%) nitrogen vacancy concentrations.\textsuperscript{23,322}

Alloying carbides with nitrides follows the same philosophy as alloying low and high VEC carbides; the lower VEC component stabilizes the rocksalt structure while the higher VEC constituent reduces the Pugh modulus. While many researchers have investigated ternary carbides and nitrides,\textsuperscript{229,317,319–321,328,329} relatively few have studied the toughness of carbonitride counterparts.\textsuperscript{315,318,330,331} Furthermore, there are few, if any, reports on the mechanical properties of high VEC quaternary or quinary carbonitrides (i.e. 2-3 metals, carbon, and nitrogen).

This dissertation has laid a foundation for the synthesis of carbonitrides using reactive sputtering techniques. High-entropy or ternary carbonitrides can be synthesized using the findings that are
encompassed in Chapters 4, 5, and 7. Transitioning from a reactive carbide to carbonitride process requires the addition of nitrogen gas as a reactant and an understanding of the relative affinities for carburization and nitridization. While excess nitrogen won’t precipitate in the film, it could cause the precipitation of excess carbon by occupying too many anion sites. This will likely lead to a complex balancing process to control the carbon to nitrogen ratio while mitigating the precipitation of excess carbon. The advantages of the high plasma density and energy afforded by HiPIMS may once again prove useful for the deposition of carbonitrides.19

Reactive APPS can also enable the synthesis of carbonitrides by sputtering from metal and graphite targets in an Ar/N₂ atmosphere, alleviating the need to balance two reactive gasses. The metal/carbon ratio can be accurately controlled using the R-APPS process described in Chapter 7 while nitrogen can be incorporated from the gas phase. This should alleviate some of the difficulties with controlling a pair of simultaneous reactive processes. One limitation of this process is the slow sputtering rate of carbon; carbon has a low atomic mass which results in a low sputter yield with Ar⁺.286 However this can be remediated by sputtering in an Ar/Ne gas mixture, using the lower mass of Ne to increase the carbon sputter yield.286 Neon will also raise the average hot-electron temperature, increasing the fraction of ionized carbon. A large ionized carbon population enables high-yield self-sputtering and energetic ionic bombardment of the growing film.305,332 One possible limitation of this process is the loss of hydrogen ion assisted etching of excess carbon; however, resputtering from high energy carbon or neon ions may remediate this.201,208

8.2.3 Exploring High Power Pulsed Radio Frequency (RF) Magnetron Sputtering

High power impulse magnetron sputtering (HiPIMS) has been applied to a broad range of materials including metals, carbides, diamond-like carbon, and oxides.158,168,174,287 At its core, HiPIMS is a direct current based sputtering technique and requires a conductive sputtering target. While this does not preclude the reactive deposition of some insulating materials, such as Al₂O₃, TiO₂, and AlN, it does limit the scope of tractable compositions.174,287

Consider, for instance, the prototypical perovskite oxides: BaTiO₃ and SrTiO₃. These oxides, if sputtered, are typically deposited from ceramic targets in an Ar or Ar/O₂ atmosphere using RF power.333 HiPIMS deposition of these insulating perovskites would require appropriate metallic targets, either Ba/Sr and Ti elemental targets or a (Ba/Sr)/Ti composite target. The alkaline earth metals are highly reactive with water and air making them challenging to handle and use while maintaining purity. Furthermore, barium and strontium are completely immiscible with titanium, preventing the formation of an alloy target which may be less reactive.23 HiPIMS deposition of BaTiO₃ and SrTiO₃ is impractical due to these target limitations.

Additionally, transition metal borides and diborides are of interest for ultra-hard, wear resistant materials.316,334 Typically, diboride films are sputtered from diboride targets, or a combination of metal
and diboride targets. There are very few reports on reactive sputtering of borides, as most boron containing gasses, such as diborane ($\text{B}_2\text{H}_6$), are pyrophoric. Boron can be sputtered from elemental targets, although it has a low sputter yield like carbon; however, this can be overcome with the use of neon gas as described in Section 8.2.2. Unlike carbon, boron is an excellent insulator which means it cannot be used with conventional HiPIMS.

It would be beneficial to achieve the high plasma densities, ionization fractions, and reactivity of a HiPIMS plasma when sputtering from insulating targets. The key differences between conventional DC magnetron sputtering and HiPIMS are the increased peak power density and decreased duty cycle of the latter (Figure 2.12). The high ionization fractions, plasma densities, and other HiPIMS phenomena are consequences of the higher voltages and instantaneous currents afforded by the lower duty cycle. In principle, high voltage/current radio frequency power could also lead to HiPIMS like behavior. There are some reports in the literature on the use of pulsed RF power to deposit thin films of $\text{Al}_2\text{O}_3$ and $\text{V}_2\text{O}_5$. However, these reports use modest duty cycles (~50%) with relatively low power densities rather than the high power densities necessary for HiPIMS-like behavior. Others have studied the plasma characteristics and utility of pulsed RF for time-of-flight mass spectroscopy techniques. There are a number of patents by semiconductor equipment manufacturers alluding to high power pulsed RF sputtering, although publications on the outcomes of this technique are difficult to find. Nevertheless, the following text will describe some of the requirements and possible challenges of implementing this technique.

First and foremost, it is necessary to create pulsed RF power so that the duty cycle can be controlled. One rudimentary method involves use of the common exciter (CEX) input on the back of most RF power supplies. Rather than amplifying the internal 13.56 MHz crystal oscillator, an external 13.56 MHz waveform can be supplied to the CEX connection. An arbitrary waveform generator could provide a pulsed (low voltage) RF signal at a given duty cycle and pulse width, which is then amplified by the power supply to the voltages necessary for sputtering. A more refined approach requires power supplies (such as the Advanced Energy RFX-600) which pulse from a trigger pin located on the rear of the supply. In this case, an arbitrary waveform generator can provide a square wave with the requisite duty cycle, pulse width, and trigger voltage.

The most elegant solution involves power supplies with built in pulsing functionality through the user interface. For instance, the Kurt J. Lesker R301 RF supplies used in this work support a 0-100% duty cycle with a 50 µs minimum pulse width. This would enable 50 µs pulses at frequencies ranging from 20 Hz to 20 kHz. Other models from the same original equipment manufacturer (Seren Industrial Power Systems) allow for pulse widths as low as 10 µs. This shorter pulse width falls closely in line with the lower end of HiPIMS pulse widths in this work and the literature.

Now that the duty cycle can be controlled, the next requirement is increasing the instantaneous (peak) power density. With DC HiPIMS this is relatively simple: a large high voltage capacitor bank (510 µF for the Starfire IMPULSE 2-2 used in this work) is separated from the sputter magnetron by a
low resistance solid-state switch. A DC power supply slowly charges up the capacitor bank while the switch briefly lets 100s of amps flow into the plasma. There is no equivalent item that can be used to store RF energy like a capacitor can store DC energy; as a result, the peak power will be limited to the maximum power of the RF power supply.

This can be compensated for by purchasing larger RF power supplies; however, the pricing of large RF power supplies does not scale nearly as favorably as their DC and HiPIMS counterparts. For instance, a 1.5 kW DC power supply and a 2 kW average / 400 kW peak power HiPIMS module costs the same as a 2 kW RF power supply and matching network. The 2 kW peak power would be better matched to a 1 inch magnetron than the 2 inch cathodes used in this work. Achieving power densities similar to HiPIMS on a 2 inch magnetron would require vastly larger (>10 kW) and more expensive RF power supplies and matching networks.

One significant challenge with pulsed RF power will be managing the rapidly changing impedance as the plasma ignites, ramps up, reaches steady state, and extinguishes during every single pulse; each of these stages will have a different load impedance. In conventional RF sputtering these are typically ignored as the system rapidly reaches steady state and a stable impedance. However, with pulsed RF sputtering, the ignition and ramp stages comprise a significant amount of the operational time of plasma. As a result, the characteristics of these stages will need to be considered in order to lower the reflected power and develop a stable process. Researchers have investigated techniques to compensate for these impedance changes including frequency modulation, superposition of low power continuous wave RF and high power pulsed RF, ramped power outputs, and rapid feedback loops for the ignition and ramp stages. While high power pulsed radio frequency magnetron sputtering poses many challenges, the benefits it could impart to the deposition processes of insulating materials could be unparalleled.
Appendix A

Supplementary Data for the Properties of RF Sputtered (HfNbTaTiZr)C\(_x\)

A.1 Quantifying Stoichiometry of the Carbide Films

The metal composition of the carbide thin films was verified with electron probe microanalysis (EPMA). X-ray spectra were measured using a Cameca SX Five EPMA with a focused 20 kV, 100 nA electron beam. Twenty data points were collected on the sample, probing ~1.2 \(\mu\)m of the sample thickness. Peaks with over 101.5% or less than 98.5% total stoichiometry were discarded, the remainder were averaged. The analysis (Table A.1) indicated that each metal was within 2 at.% of the target stoichiometry.

The carbon stoichiometry and ratio of bonded to excess carbon was determined with x-ray photoelectron spectroscopy. The surfaces of the thin films were presputtered to remove oxidation products (from the Group IVB metals) and adventitious carbon from the environment. Accurate measurement of excess carbon in the film requires the removal of adventitious carbon, as both contribute to the carbon-carbon bonding peak. Unfortunately, bonded carbon can also be preferentially sputtered from the film during this presputtering step, affecting the carbon to metal stoichiometry.

Commercially available, stoichiometric TaC (Alfa Aesar, 4017818) and TiC (Alfa Aesar, 1214409) powders were analyzed before and after presputtering to determine the magnitude of preferential carbon sputtering from the carbide structure. The metal to carbon ratios before and after presputtering can be found in Table A.2. The carbide phase of the as received powders was found to be at or nearly stoichiometric after accounting for the contributions of adventitious carbon and surface oxides to the spectra. A significant reduction (25-26 at.%) in the measured carbon stoichiometry was observed after presputtering both titanium and tantalum carbide.

The results of Table A.2 were used to estimate the true carbon stoichiometries of the carbide films. The estimated carbon stoichiometries plotted in Figure 4.3 were calculated as follows:

1. The as received to pre-sputtered carbon stoichiometry ratios of TaC and TiC were 1.33 and 1.32 respectively.
Table A.1: Metal stoichiometry of the sample deposited with 2.5 sccm of methane, as determined by electron probe microanalysis.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hafnium</td>
<td>18.2 ± 0.4</td>
</tr>
<tr>
<td>Niobium</td>
<td>22.8 ± 0.4</td>
</tr>
<tr>
<td>Tantalum</td>
<td>21.4 ± 0.4</td>
</tr>
<tr>
<td>Titanium</td>
<td>18.5 ± 0.4</td>
</tr>
<tr>
<td>Zirconium</td>
<td>19.1 ± 0.5</td>
</tr>
</tbody>
</table>

Table A.2: Metal to bonded carbon stoichiometry of commercially available TaC and TiC powders before and after 3 keV Ar⁺ presputtering.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Ta:C</th>
<th>Ti:C</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-received</td>
<td>1:0.96</td>
<td>1:1</td>
</tr>
<tr>
<td>Presputtered</td>
<td>1:0.72</td>
<td>1:0.76</td>
</tr>
</tbody>
</table>

2. Based on the commercially available powders, multiplying the measured carbon stoichiometry by 1.325 should yield an estimate of the intended carbon stoichiometry.

3. This factor of 1.325 was applied to all samples. Estimated bonded carbon contents in excess of 1:1 were rounded down to 1:1.

A.2 Verifying the Precipitation of Excess Carbon

The presence and nature of the excess carbon precipitation in the films was examined with Raman spectroscopy. The Raman spectra collected from the films studied in Chapter 4 are plotted in Figure A.1. The onset of the carbon D (1350 cm⁻¹, defect induced breathing mode) and G (1565 cm⁻¹, sp² bonding) modes in the sample deposited with 2.82 sccm of methane coincides with the onset of excess carbon in the XPS spectra (Figure 4.2).²¹²,²¹³ The presence of the G mode indicates a substantial amount of sp² bonding character, while the D mode suggests the structure has a large degree of defects and is poorly crystalline.

A.3 Changes in Cross-Sectional Microstructure

Figure A.2 shows the contrast between a columnar, epitaxial carbide sample grown with 3.0 sccm of methane, and a carbide-carbon nanocomposite grown with 5.5 sccm of methane. The epitaxial carbides grew with clear columnar grains, extending from the substrate interface to the surface of the film, where they formed a three-sided pyramid. Conversely, the nanocomposite samples formed a very fine grained microstructure with no clear growth trends.
Figure A.1: Raman spectra for (HfNbTaTiZr)Cₓ films plotted as a function of the methane flow rate. D and G correspond to the locations of the D and G Raman modes of excess carbon in the system. Spectra are linearly offset for clarity.

Figure A.2: SEM cross-sectional micrographs of (HfNbTaTiZr)Cₓ samples deposited with 3.0 and 5.5 sccm of methane.
Appendix B

Python Script for Generation of APPS Waveforms

```python
# Begin user inputs
filename='waveforms/Example.csv' # Filename to save in waveforms subdirectory
freq=2000 # Control frequency
patternin=[[6,1],[0,1]] # Input pattern in format [n*[p,s],n*[p,s],...] # End user inputs

# Create empty variables
pattern=[] # For the 1D pattern
patternforgraph=[] # For plotting the wave pattern at the end
outputdata=[] # Data to save to the .csv

# Reflow into the 1D Pattern
def flatten(patterninput): # Recursive pattern flattening scheme
    if isinstance(patterninput, list): # If the input is a list
        for part in patterninput: # For each part in that list
            yield from flatten(part) # Flatten the part
    else: # If the part is not a list (i.e. a single number)
        yield patterninput # Yield the value
pattern=list(flatten(patternin)) # Pattern is the result of flattening the input pattern

# Calculate periods and number of data points (1 microsecond per point)
period=round(10000000/freq) # Calculates period in microseconds (inverse of frequency).
points=sum(pattern)*period # Calculates total number of datapoints period times sum of pulses and skips
```
# Make the list that will be put into the csv
for p in range(len(pattern)):  # For each item in the pattern...
    if pattern[p] == 0:  # If item is zero...
        pass  # Don't do anything
    elif (p % 2 == 0):  # If the point index is an even number (pulses)...  
        for i in range(0,pattern[p]):  # Repeat for the number of pulses at this index...
            outputdata.extend(["",5]*1000)  # Write 100 points as 5V (100 microseconds)
            outputdata.extend(["",0]*(period-1000))  # Write remainder of period as as 0 volts
            patternforgraph.append(1)  # Add a pulse to the graph
    elif (p % 2 == 1):  # If the point index is an odd number (skips)...
        for v in range(0,pattern[p]):  # Repeat for the number of skips at this index...
            outputdata.extend(["",0]*(period))  # Entire period as as 0 volts
            patternforgraph.append(0)  # Add a skip to the graph

print("The length of the pulse train", sum(pattern))  # Prints out sum total of pulses and skips
print("The number of pulses", sum(pattern[:2]))  # Prints out number of pulses
print("The number of skipped pulses", sum(pattern[1::2]))  # Prints out number of skipped pulses
print("The Pattern:",pattern)  # Prints out the 1D pattern

# Import csv, create and open file
import csv  # Import csv module
with open(filename, mode='w+', newline='') as file:  # Define file name
    preamblewrite=csv.writer(file, delimiter=":")  # Define delimiter for preamble (colon :)
    wavewrite=csv.writer(file, delimiter="", quoting=csv.QUOTE_NONE)  # Define delimiter for the waveform (comma ,)

    # Write the preamble that the AWG expects
    preamblewrite.writerows([['RIGOL','DG1','CSV DATA FILE'],  # Header
        ['TYPE','Arb'],  # Arbitrary waveform
        ['AMP','10.0000 Vpp'],  # 10 V peak to peak
        ['PERIOD','1.00E-7 S'],  # 1 microsecond per point
        ['Dots',points],  # Number of datapoints in the file
        ['MODE','STEP'],  # Directly step between points with no interpolation
        ['Sample Rate','10000000.000000'],  # Sample at 1 million points per second (1 microsecond)
        ['AWG N','0'],
        ['x,y[V]']])  # Y is in Volts
# Write the waveform
```
wavewrite.writerows(outputdata)  # Export the previously made variable to csv
```
```
outputdata = None  # Dump the variable from memory
```
```
# Plotting for visual confirmation
```
import matplotlib.pyplot as plt  # Import plotting module
```
```
plt.figure(figsize=(15,5))  # Make figure size larger
```
```
plt.plot(patternforgraph, drawstyle='steps-mid', linestyle='-', linewidth=1)  # Plot thin stepfunction lines
```
```
plt.plot(patternforgraph, 'ro', markersize=4)  # Plot small markers overlaid
```
```
Examples of input pattern formats are as follows:
```
[6,1] → [6 pulses, 1 skip]
```
```
5*[6,1] → [6 pulses, 1 skip] repeated 5 times
```
```
[6,0] → [6 pulses]
```
```
[0,2] → [2 skips]
```
```
These blocks can be combined in the primary square brackets to create more complex patterns. As an example, patternin=[5*[6,1],[0,1]] would be [6 pulses, 1 skip] repeated 5 times followed by an extra skip. This could also be written as [4*[6,1],[6,2]], or [[6,1,6,1,6,1,6,1,6,2]], Patterns can also be nested in multiple levels, for instance [6,1,6,1,6,2,6,1,6,2,6,1] is equivalent to both [2*[6,1],[6,2],2*[6,1],[6,2],[6,1]] and [2*[2*[6,1],[6,2]],[6,1]].
References


8. Shen, W. J., Tsai, M. H., Tsai, K. Y., Juan, C. C., Tsai, C. W., Yeh, J. W. & Chang, Y. S. Superior oxidation resistance of (Al_{0.34}Cr_{0.22}Nb_{0.11}Si_{0.11}Ti_{0.22})_{50}N_{50} high-entropy nitride. *Journal of The Electrochemical Society* **160**, C531–C535 (2013).


10. Yan, X., Constantin, L., Lu, Y., Silvain, J. F. J.-F., Nastasi, M. & Cui, B. (Hf_{0.2}Zr_{0.2}Ta_{0.2}Nb_{0.2}Ti_{0.2})C high-entropy ceramics with low thermal conductivity. *Journal of the American Ceramic Society* **101**, 4486–4491 (2018).


31. Percy, J. *Que cette manière de voir soit exacte ou non, il est certain que l’acier dur et l’acier doux
diffèrent essentiellement quant au mode d’existence du carbone dans la masse* in *Traité complet de
métałlurgie* 304 (Librairie Polytechnique de Noblet et Baudry, Paris/Liége, 1867).
(1885).
Sciences* **100**, 450–452 (1885).
35. Abel, F. *Research committee on the hardening, etc., of steel: final report on experiments bearing
upon the question of the condition in which carbon exists in steel*. *Proceedings of the Institution
41. Moissan, H. *Volatilisation of zirconia and silica at a high temperature and their reduction by
43. Moissan, H. *Preparation of certain refractory metals in the electric furnace – tungsten, molybde-
(1896).
(1865).
51. Hägg, G. *Eigenschaften der phasen von übergangselementen in binären systemen mit bor,


151. Gild, J., Braun, J., Kaufmann, K., Marin, E., Harrington, T., Hopkins, P., Vecchio, K. & Luo, J. A high-entropy silicide: (Mo0.2Nb0.2Ta0.2Ti0.2W0.2)Si2. *Journal of Materiomics* (2019).


224. Wang, Y.-P., Gan, G.-Y., Wang, W., Yang, Y. & Tan, B.-Y. Ab-initio prediction of mechanical and electronic properties of ultrahigh temperature high-entropy ceramics (Hf_{0.2}Zr_{0.2}Ta_{0.2}Mo_{0.2}Ti_{0.2})B_2 (M = Nb, Mo, Cr). *Phys. Status Solidi B*, 1800011 (2018).


Vita

Trent M. Borman

Trent Mitchell Borman was born in Bismarck, North Dakota on September 2nd, 1992 to Karen and Todd Borman. His stay in Bismarck was short lived, with a brief move to Iowa and several years in Washington state before his family settled in Minnesota for the majority of his childhood. During his time at Eden Prairie High School he played the cello and helped lead FIRST Robotics Competition (FRC) team #2502. His involvement in robotics was critical in steering him towards an education and career in materials engineering.

After graduating high school in 2011, he attended Iowa State University for Materials Engineering, graduating summa cum laude as the Materials Science and Engineering outstanding senior in 6 semesters. During his time at Iowa State, Trent worked as a teaching assistant for labs and a peer mentor for incoming undergraduate materials engineering students. In his free time, he was a mentor for FRC team #3928 (operating out of the materials science and engineering building) and participated in countless Materials Advantage outreach events (serving as outreach co-chair his second year).

In the summer after his first year at ISU he moved west of the Mississippi River for the first time, participating in a National Science Foundation sponsored Research Experience for Undergraduates (REU) at North Carolina State University. During this program he worked in Jon-Paul Maria's lab (for the first time) on Ti-Sn based alloys for reactive solar cell metallization. The following summer he returned to Jon-Paul (JP) Maria's lab (round two), researching ferroelectric hafnia and synthesizing some of the first high entropy oxides.

After these wonderful research experiences with JP, Trent instead chose to work for JP's Ph.D. advisor Susan Trolier-McKinstry at Penn State University for his graduate studies. During his time in the STM group he spent many hours in the cleanroom sol-gel depositing lead zirconate titanate (PZT) thin films. Sol-gel deposition and user facilities didn't fully satisfy his yearning for an instrumentation and process engineering oriented Ph.D. experience. As a result, he finished a master's degree on PZT with in the Fall of 2016 and returned to Jon-Paul Maria's group (third time's a charm?) at North Carolina State University.

A few months later he received a departmental email on his Penn State account (and numerous text messages) about Dr. Maria's faculty interview at Penn State. At the end of 2017 the Maria group moved, and Trent returned to Penn State, working in the renovated Steidle building this time. Trent graduated as the "first Penn State-er" student of the Maria Group and remained on the east coast after graduation. He believes his time at Penn State may now be over, but nobody knows what the future might hold; after all, he thought the same thing once before.