NANOSCALE NICKEL-TITANIUM SHAPE MEMORY ALLOYS THIN FILMS
FABRICATED BY USING BIASED TARGET ION BEAM DEPOSITION

A Dissertation in
Engineering Science and Mechanics
by
Huilong Hou

© 2015 Huilong Hou

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

December 2015
The dissertation of Huilong Hou was reviewed and approved* by the following:

Reginald F. Hamilton  
Assistant Professor of Engineering Science and Mechanics  
Dissertation Advisor  
Chair of Committee

Mark W. Horn  
Professor of Engineering Science and Mechanics

Aman Haque  
Professor of Mechanical Engineering and Graduate Faculty of Engineering Science and Mechanics

Long-Qing Chen  
Distinguished Professor of Materials Science and Engineering, Engineering Science and Mechanics, and Mathematics

Jerzy Ruzyllo  
Distinguished Professor of Electrical Engineering and Professor of Materials Science and Engineering

Judith A. Todd  
P. B. Breneman Chair and Professor of Engineering Science and Mechanics  
Head of the Department of Engineering Science and Mechanics

*Signatures are on file in the Graduate School
Shape memory alloys offer the highest work output per unit volume among smart materials and have both high actuation stress and large recoverable strain. Miniaturization of materials and devices requires shape memory actuation which is uncompromised at a small scale. However, size effects need to be understood in order to scale shape memory actuation with the minimum size critical to device design. Controlling material quality and properties is essential in fabrication of shape memory alloys into nanometer regime. This work demonstrates a novel fabrication technique, biased target ion beam deposition (BTIBD), which uses additional adatom energy in order to fabricate high-quality nickel-titanium (NiTi) alloys thin films with nanometer thickness. These fabricated ultrathin NiTi films provide insight into the size scale dependence of shape memory functionality at nanoscale regime.

BTIBD provides additional adatom energy to the growing film in order to fundamentally tailor the film growth mode for quality and properties. An independent ion beam source is customized in BTIBD to provide low-energy ions (tens of eV) during growth of films on substrates. Pure Ti and pure Ni targets are co-sputtering in BTIBD to fabricate NiTi thin films. The prepared NiTi films are continuous, and the thickness ranges from several tens to a few hundreds nanometers. The composition is controllable over the range of Ni-rich (>50.5 at% Ni), near-equiaxial, and Ti-rich (<49.5 at% Ni). The film surfaces are consistently ultra-smooth — twice as smooth as conventional NiTi thin films fabricated by magnetron sputtering — over all the composition ranges and over wide surface areas. The substrate/film interface is smooth and the interfacial diffusion is a minimal portion of the film thickness.

Crystallographic phases and grain size in BTIBD NiTi films with thickness on the order of 100 nm are tunable via heat treatment. The as-deposited BTIBD films are amorphous. A pure B2 phase (without other microstructural phases) is achieved via low-energy ion beam preheating
of the film. Coexistence of B2 and B19' phases are formed by post-deposition annealing, and the grain size increases in diameter as the annealing temperature increases. NiTi thin films prepared by BTIBD are absent of columnar-void morphology at the surface and produce a large grain size, in contrast to the columnar-void prevalence and small grain size in magnetron sputtered films. It is postulated that columnar-void morphology is imposing constraints on crystallization for formation of limited grain size. Thermally-induced phase transformations occur to the ultrathin BTIBD films and are observed using temperature-dependent thin film stress measurements. The thermal hysteresis in these films is considerably smaller (up to 50 %) than that in magnetron sputtered films.

Free-standing NiTi alloy 1D nanowires are machined from the NiTi alloy thin films by using nanoskiving. Results are also shown for focused ion beam 1D micropillars, 2D thin sheet with nanometer thickness, and 2D micro-double shear specimen as additional objects to investigate geometric/microstructural size effect. Nanoskiving combines deposition of thin films with thin sectioning to generate nanowires. NiTi nanowires herein are generated under extreme conditions of alloy composition and sectioning orientation. The mechanism of nanoskiving on NiTi alloy is postulated, and supported by microstructure characterization. The preliminary findings demonstrate — for the first time — the feasibility of nanoskiving of metallic alloys.
# TABLE OF CONTENTS

List of Figures .................................................................................................................. vii

List of Tables ................................................................................................................... xiv

Acknowledgements .......................................................................................................... xv

Chapter 1 Introduction ..................................................................................................... 1

  § 1.1 Functionality, applications, and size miniaturization of shape memory alloys ....... 1
  § 1.2 Problem statement and proposed research .......................................................... 5

Chapter 2 Fundamentals .................................................................................................. 6

  PREVIEW ....................................................................................................................... 6
  § 2.1 Shape memory behaviors and martensitic transformation .................................... 6
  § 2.2 Size effects at small scale ..................................................................................... 9
    § 2.2.1 Characteristic dimensions of martensite ......................................................... 10
    § 2.2.2 Geometric size effect and constraints to martensitic transformation ........... 11
    § 2.2.3 Grain size effect and transformation criteria of energy barriers ................. 14
  § 2.3 Thin films and nanofabrication ............................................................................ 18
    § 2.3.1 Nucleation, growth, and coalescence of thin films ....................................... 18
    § 2.3.2 Structure zone model ...................................................................................... 19
    § 2.3.3 Ion bombardment to facilitate film formation ............................................... 21
    § 2.3.4 Correlation of microstructure morphology to stress-temperature behaviors in thin films ................................................................. 23

Chapter 3 Fabrication and characterization methods ...................................................... 28

  PREVIEW ....................................................................................................................... 28
  § 3.1 Fabrication of 2D thin films with nanometer thickness ......................................... 28
    § 3.1.1 Biased target ion beam deposition (BTIBD) .................................................. 30
    § 3.1.2 Magnetron sputtering deposition .................................................................. 33
  § 3.2 Characterization ................................................................................................... 37
    § 3.2.1 Composition determination — inductively coupled plasma atomic emission spectroscopy ............................................................... 37
    § 3.2.2 Microstructural analysis and energy-filtering map — transmission electron microscopy ............................................................................. 38
    § 3.2.3 Surface analysis — atomic force microscopy ............................................... 40
    § 3.2.4 Crystal structure analysis — x-ray diffraction ............................................ 41
    § 3.2.5 Heat treatment — post deposition rapid thermal annealing and transmission electron microscopy in-situ heating .................... 41
    § 3.2.6 Thermally-induced behaviors in substrate-attached thin films — substrate curvature measurement with temperature capability ...... 42
Chapter 4 Results and discussions ................................................................. 46

PREVIEW ............................................................................................................. 46
§ 4.1 NiTi thin films fabricated by BTIBD co-sputtering from elemental Ni and Ti targets ................................................................. 46
§ 4.2 Structure and interfacial analysis of nanoscale NiTi thin films fabricated by BTIBD ................................................................. 56
§ 4.3 Crystallization and microstructural development of nanoscale NiTi thin films fabricated by BTIBD ................................................................. 63
  § 4.3.1 Influence of surface morphology on crystallization and microstructural development ................................................................. 64
  § 4.3.2 Effect of rapid thermal annealing on the crystal structure and grain size ... 76
§ 4.4 Thermally-induced shape memory behaviors of nanoscale NiTi thin films fabricated by BTIBD ................................................................. 83

Chapter 5 Preliminary results for future work on top-down nanomachining/ nanofabrication ................................................................. 94

PREVIEW ............................................................................................................. 94
§ 5.1 1D nanowires with nanometer cross section machined using nanoskiving ................................................................. 94
  § 5.1.1 Methodology ............................................................................................ 95
  § 5.1.2 Feasibility of nanoskiving on NiTi nanowires ........................................ 104
§ 5.2 1D micropillars fabricated using focused ion beam ......................................................... 113
  § 5.2.1 Methodology ............................................................................................ 113
  § 5.2.2 Nanoindentation ...................................................................................... 118
§ 5.3 2D thin sheet with nanometer thickness fabricated using focused ion beam ............ 120
  § 5.3.1 Methodology ............................................................................................ 120
  § 5.3.2 Microstructure characterization ................................................................ 121
§ 5.4 2D double shear specimen fabricated using focused ion beam ......................... 128

Chapter 6 Summary and conclusions ................................................................ 131

§ 6.1 Conclusions .............................................................................................. 131
§ 6.2 Contributions ............................................................................................ 132
§ 6.3 Future directions ....................................................................................... 133

References ......................................................................................................... 137

Appendix Nontechnical abstract ...................................................................... 147
LIST OF FIGURES

Figure 1-1. Chart on the work output per unit volume of various materials for actuation. NiTi shape memory alloys (SMAs) exhibits the largest work output per unit volume. Adapted from [11]..........................2

Figure 1-2. (A.1) and (A.2) Photograph of Boeing chevron capable of variable geometry. Shape memory alloys are embedded inside to bend or straighten the chevron in order to regulate the exhaust gases flow and reduce engine noise. The shape memory effect is utilized. Taken from [4]. (B.1) and (B.2) Scanning electron microscope images of a microcage actuated by shape memory alloys to capture a small polymer ball. NiTi alloys thin films are incorporated into the fingers to utilize two way shape memory effect. Taken from [14].................................3

Figure 1-3. (A) Stress-strain curves of the same Cu-Al-Ni composition at bulk (black dot), micrometer (blue dot) and sub-micrometer (red dot) scale. Taken from [4]. (B) Plot of stress hysteresis versus sample diameter. Regimes of Volume, Surface, and Starvation dominate at different length scale. Adapted from [13]...............................4

Figure 2-1. Schematics of stress-temperature phase diagram for shape memory alloys. See text for description of symbols. Adapted from [4,12].................................7

Figure 2-2. (A) Schematics of differential scanning calorimetry curve to show the determination of the four martensitic transformation temperatures. (B) Sketch of martensite start temperature, $M_s$, as a function of the Ni concentration for NiTi alloys. $M_s$ is nearly constant in Ti-rich region. As the Ni concentration increase from 49.8 at%, $M_s$ decreases in near-equiatomic and Ni-rich regions. Adapted from [12,18].................................9

Figure 2-3. a) Sketch of martensite plates and austenite in one grain of a polycrystalline shape memory alloy. Space between martensite plates, $S$, width of a martensite plate, $W$, and location of grain boundary, $IGB$, and austenite/martensite interface, $IAM$, are delineated. $IAM$ can also be called habit plane. (b) Sketch of twin-related variants arrangement within a martensite plate. The width of martensite variant 1 and martensite variant 2 is $d_1$, and $d_2$, respectively. The periodicity of variants is $\lambda = d_1 + d_2$. Between martensite variant 1 and 2 is twinning boundary, $ITW$. (c) Zoomed-up view on morphology of martensite variants near the habit plane. $\theta$ is the shape parameter at microstructural level..........................11

Figure 2-4. (A) Schematic of thermal cycling under constant loading. (B) Schematic of isothermal uniaxial testing for shape memory alloys showing the transformation stress. The transformation temperatures under constant loading can be identified. Adapted from [12].................................12

Figure 2-5. (A) Stress-temperature curves of NiTi thin films with different thickness. Taken from [32]. (B) Uniaxial compression stress-strain curve of bulk single crystal and of Cu-Al-Ni pillar. Adapted from [33].................................13
Figure 2-6. (A) Schematic of generating three types of martensite variants via BCC-BCT Bain deformation. (B) Assembly of martensite variants into twinned microstructure. The austenite-martensite interface is a straight plane. (C) Sketch of the energy contribution from twinned microstructure in the total transformation barrier. (D) Crossover of calculated energy barrier as a function of decreasing grain size. Below a critical size ~70 nm, single laminate of twinned martensite is favorable for low energy barrier while herringbone morphology has minimum energy barrier above the critical size and thus is favorable. (A) and (B) are adapted from [51]. (C) and (D) are taken from [30,49].

Figure 2-7. Schematic of growth mode in thin films. (A) Frank-van der Merwe mode with the characteristics of layer by layer. (B) Volmer-Weber mode with three dimensional islands. (C) Stranski-Krastanov mode with the feature of layer plus three dimensional islands. Letter a denotes the distance between surface sites. Taken from [53].

Figure 2-8. Schematic of the four basic structure zones in thin films via the view of cross section. The homologous temperature increases along the direction Z1 \(\rightarrow\) ZT \(\rightarrow\) Z2 \(\rightarrow\) Z3. Taken from [53].

Figure 2-9. Schematic of structure zone model as a function of pressure and \(T_h\). Taken from [55].

Figure 2-10. Schematic of bombarding ions on the surface atoms showing the inducing effects. (a) Removal of absorbed impurity atoms; (b) lateral displacement due to enhanced surface diffusion; (c) surface vacancy formed by sputtering a film atom out upward; (d) surface vacancy created by moving a film atom to an adatom position; knock-on implantation of (e) an impurity atoms and (f) a film atom; (g) void filled by the deposited atoms with enhanced surface mobility; (h) void filled by forward sputtering the suspended atoms; (i) breakup of three dimensional nucleus. Taken from [53].

Figure 2-11. Schematic of stress-temperature curve for a thin film constrained on a substrate. The black represents martensite, light gray stands for austenite, and dark gray is for the substrate. Taken from [60].

Figure 2-12. Schematic of microstructural development during phase transformations of a thin film under uniaxial stress. Phase-front velocity vector \(v\) is (A) perpendicular and (B) parallel to the normal of the substrate. Taken from [61].

Figure 2-13. Schematic of cross-section strain distribution of a thin film with finite width at the condition of (A) tensile stress and (B) compressive stress. The arrows indicate the distribution direction of strain from small to large values (including the negative sign). Adapted from [62].

Figure 3-1. Illustration of co-sputtering system configuration for the biased target ion beam deposition technique.
Figure 3-2. Schematic of Kurt J. Lesker magnetron sputtering system. Atoms which are knocked out from targets by accelerated inert gas ions are deposited on the substrate to form a thin film.

Figure 3-3. Schematic diagram of the SiN membrane chip. The chip fits exactly into the TEM hole and can be used for multifaceted characterization.

Figure 3-4. (A) Schematic of the shape of a thin film constrained on a substrate. (B) The shape of the thin film when an external force is applied to render the film/substrate interface stress-free. (C) The shape of the thin film separated from the substrate. The applied force is equivalent to the reaction in the substrate-constrained condition. Adapted from [62].

Figure 4-1. TEM image showing a BTIBD Ni-rich NiTi thin film in the as-deposited state at room temperature. The inset is a diffraction pattern which does not reflect crystallinity.

Figure 4-2. Roughness measurements ($Z_{\text{Range}}$ = peak-to-valley, $R_a$ = average roughness, and RMS = root mean squared) as a function of the at% Ni concentration in NiTi for films fabricated using BTIBD and magnetron sputtering (MS).

Figure 4-3. A BTIBD Ni-rich Ni$_{60.2}$Ti$_{39.8}$ (at%) thin film in the as-deposited state at room temperature: (a) TEM image with diffraction pattern illustrating that the film is amorphous; (b) surface topography measurements from AFM analysis; (c) cross-section profiles from (b).

Figure 4-4. An as-deposited Ni-rich Ni$_{55.7}$Ti$_{44.3}$ (at%) thin film made by magnetron sputtering at room temperature: (a) TEM image with diffraction pattern illustrating that the film is amorphous, (b) surface topography measurements from AFM analysis; (c) cross-section profiles from (b).

Figure 4-5. A magnetron sputtered Ni-rich Ni$_{55.7}$Ti$_{44.3}$ (at%) thin film as-deposited at room temperature: (a) TEM image showing features that are not evident in Figure 4-4 (a); (b) Energy-filtering TEM thickness map contrast which is complementary to (a); (c) thickness profile across the region within dashed boundary in (b).

Figure 4-6. Bright-field TEM images (a-c) and corresponding diffraction patterns (d-f) showing austenite (A) and martensite (M) for BTIBD films of Ni$_{28.0}$Ti$_{72.0}$, Ni$_{49.7}$Ti$_{50.3}$ and Ni$_{51.7}$Ti$_{48.3}$ (at%) after heat treatment. The grain size in (b) is larger than (a) which is larger than (c). Indexing diffraction patterns B19’ is present in (a-c) while only (a) and (c) have B2. For clarity, Si$_3$Ni$_4$ and Ti$_2$N are listed in Table 4-1 instead of being indexed in diffraction patterns.

Figure 4-7. (a) TEM bright field micrograph with the diffraction pattern inset and (b) AFM image of the NiTi film surface.

Figure 4-8. (a) TEM bright-field micrograph with two lines delineating the interface between the film and substrate. (b) Diffraction pattern with a white bracket that highlights the directionality of diffraction spots. (c) Dark-field micrograph.
corresponding to the red-circled diffraction spot in b). High resolution TEM images in (d) and (e) show the boxed regions in (c). .................................................................60

Figure 4-9. Plot of diffusion layer thickness to film thickness ratio versus film thickness. The references for square and triangle markers are listed beside the plot; the substrate is listed first and followed by the deposition method and heat treatment method. The circle marker is the measurement on BTIBD film. ...........................................61

Figure 4-10. (a), (d), (g), TEM diffraction patterns and (b), (e), (h), (c), (f), (i), bright field micrographs for magnetron sputtered thin films during in-situ heating in the TEM. The high resolution images (f) and (i) correspond to the boxed regions in (e) and (h). The arrow in (e) marks a formed crystal. In (f), the open arrows point at the location of channels spanned by crystals. The diffraction pattern in (g) includes the indexed B2 pattern superposed at the top-right corners. ........................................67

Figure 4-11. (a), (d), (g), TEM diffraction patterns and (b), (e), (h), (c), (f), (i), bright field micrographs for thin films prepared by BTIBD during in-situ heating in the TEM. The high resolution images (f) and (i) correspond to the boxed regions in (e) and (h). In (e), (f) and (h), the yellow circles mark the formed crystals. .........................68

Figure 4-12. TEM bright field micrographs before (a), (b), (c) and after (d), (e), (f) in-situ TEM heating of magnetron sputtered NiTi films. The open arrows in (d)–(f) mark the original location of channels prior to merging of the islands. Note that the 55.7 at% Ni has the same composition but larger thickness compared to the magnetron sputtered film in Figure 4-10.................................................................69

Figure 4-13. TEM bright field micrograph (a), (b), (c), (d) before and (e), (f), (g), (h) after ex-situ RTA heat treatment of NiTi films prepared by BTIBD. The yellow circles in (e) and (f) highlight the locations of large grains.................................................................70

Figure 4-14. AFM images of as-deposited NiTi films prepared by (a), (b) magnetron sputtering in contrast to (c), (d) BTIBD prior to heat treatment. The small arrow in (a) points at one rod-shaped column on the surface of magnetron sputtered film. For clarity, the scale bar of contour is placed at the center and applies for (a)–(d)..............71

Figure 4-15. (a) STEM image of a magnetron sputtered NiTi thin film before heat treatment, and (b) energy-dispersive x-ray spectroscopy profile on selected areas of site A and site B in (a). In (a), site A is on one rod-shaped column and site B is on one void. The operation conditions on site A and site B are the same. .........................73

Figure 4-16. X-ray diffraction pattern of (A) Ti-49.7 at% Ni films, (B) Ti-50.3 at% Ni films, (C) Ti-50.8 at% Ni films after RTA heat treatment at conditions of 465 ºC, 10 min; 490 ºC, 10 min; 515 ºC, 10 min; 540 ºC, 10 min.................................78

Figure 4-17. AFM images of Ti-49.7 at% Ni, Ti-50.3 at% Ni and Ti-50.8 at% Ni thin films after heat treatment. The scale bar of contour is placed at the bottom and applies for (a)–(l).................................................................80
Figure 4-18. Summary of surface roughness after heat treatment in RTA. The dash line are superposed to delineate the trend of roughness change. The red regime are the Rq value of as-deposited films measured in previous work. [19,111] ........................................82

Figure 4-19. (A) Schematic of temperature-dependent thermal stress during heating and cooling. (B) Stress-temperature curve of a Ti-49.7 at% Ni thin film with 65 nm thickness prepared by BTIBD. ..................................................................................................................85

Figure 4-20. (A) Sketch of stress-temperature curve when there is phase transformations taking place during heating and cooling. Four transformation temperatures under stress, $T_{MS}$, $T_{MF}$, $T_{AS}$, $T_{AF}$, and the thermal hysteresis, $H$, can be identified. (B) Sketch of stress-temperature curve when the temperature-dependent thermal stress is combined with phase transformations. Phase transformations occur in the middle range of the temperature. (C) Experimental stress-temperature curve of a Ti-50.3 at% Ni thin film, 800 nm after the heat treatment 600 °C, 10 min + 450 °C, 10 min. ..........................................................86

Figure 4-21. Schematic of two-stage phase transformations, from austenite to R-phase, R-phase to martensite, in the plot of stress versus temperature. (B) Experimental stress-temperature behavior of a Ti-49.7 at% Ni thin film exhibiting two-stage phase transformations.................................................................88

Figure 4-22. Stress-temperature curve showing the change of stress level after one thermal cycle is completed. (A) Ti-51.7 at% Ni, 800 nm and (B) A Ti-49.7 at% Ni thin film, 800 nm under the heat treatment 600 °C, 10 min + 450 °C, 10 min; (C) A Ti-49.7 at% Ni thin film, 800 nm under the heat treatment 500 °C, 10 min.................90

Figure 4-23. (A) Two cycles of stress-temperature behavior of a Ti-49.7 at% Ni thin film, 800 nm under the heat treatment 600 °C, 10 min + 450 °C, 10 min. The second cycle starts from and fully recovers to the increased stress level after the first cycle......91

Figure 4-24. Stress-temperature behavior of a Ti-50.3 at% Ni thin film, 800 nm under the heat treatment 600 °C, 10 min + 450 °C, 10 min. The behavior of the first cycle is identical to the fourth one, indicating the stability of the phase transformations in the NiTi thin film prepared by BTIBD. .................................................................................................92

Figure 5-1. Schematic illustration of nanoskiving. Three steps can independently control the nanowire dimensions. In Step A, the NiTi thin film is deposited with precisely-controlled composition and thickness, followed by embedding and cutting into a strip in Step B. In Step C, the nanowire is generated by sectioning the strip. ...............96

Figure 5-2. Photograph of an ultramicrotome (A) and zoomed-in view (B) of the sample and knife setup. .....................................................................................................................................98

Figure 5-3. Images of mounting, slicing and collecting in the process of generating slabs. (A) shape of trimmed block, (B) mounting the trimmed block to the ultramicrotome, (C) alignment of knife with respect to the block, (D) serial slicing of the block into slabs, (E) separating and grouping the generated slabs, and (F) collecting the slabs of interest by using a TEM grid........................................................................................................101
Figure 5-4. Illustration of film-based description on sectioning direction. (A) Parallel sectioning: longitudinal dimension of the thin film parallel to direction of sectioning; compressive cutting forces parallel to the film/epoxy interface. (B) Perpendicular sectioning: direction of sectioning perpendicular to longitudinal dimension of the thin film but parallel to lateral dimension; compressive cutting forces perpendicular to the interface.

Figure 5-5. High resolution TEM micrograph of the as-deposited NiTi thin film. The yellow lines delineate two representative nanograins in amorphous matrix of the thin film.

Figure 5-6. SEM images (A), (B), (C), and TEM image (D) of a representative NiTi nanowire acquired from parallel sectioning in nanoskiving. (A), (B) and (C) are images captured in the process of transferring from a honeycomb TEM grid to a V-shape TEM grid. Residual epoxy are discernible along the nanowire probably due to incomplete etching. (D) is TEM micrograph of the zoom-up regions within the box in (C); the wire is smooth on one side (contacted with NaCl substrate) and rough (top of sputter-deposited film) on the other side.

Figure 5-7. SEM images of multiple nanowires produced from parallel sectioning, as supplementary to the nanowire in Figure 5-6. (A) is the image of TEM grid hosting the nanowires. (B.1–B.2) are the images captured during the FIB transferring of a second nanowire. (B.3-B.5) are the images of three intact nanowires in the grid. Each yellow line delineates the length of one nanowire. (C.1–C.3) are images of the fragmented nanowires. The green lines delineate the length.

Figure 5-8. Energy-filtering TEM images of NiTi nanowires. Elemental map of Ni (A) and Ti (B), thickness map (C), and profile (D) of thickness map within the dashed boundary in (C). The halo-like layer at bottom-side of nanowire in (C) is probably due to the residual NaCl after dissolution. The inserted direction coordinates, thickness (T), length (L), and width (W), correspond to Step C in Figure 5-1: lower left applies to (A–C) and the other only applies to (D).

Figure 5-9. Schematic of two sectioning mechanisms: shearing (A) and cracking (B); adapted from [155,174,176]. In (A), the abruptness in the neutral axis locates the region of intense shearing in the slab. In (B), the knife cleaves the slabs by initiating and propagating the crack; cleaved slab has the neutral axis curved gradually.

Figure 5-10. (A) Schematic of sectioning procedure, adapted from [179]. Free body diagram of (B) the sectioning knife and (C) the slab in sectioning.

Figure 5-11. Schematic of two displacement modes in fracture mechanics. A) Mode I, tensile opening. B) Mode II, in-plane sliding. Adapted from [180].

Figure 5-12. Schematic illustration of concentric milling to fabricate a pillar. Milling circles with decreasing diameters are made step by step on the bulk sample until the desired pillar diameter is achieved.
Figure 5-13. SEM images (A)–(E) during concentric milling. In (E), a hole with the diameter larger than that of the pillar is surrounding the pillar. .......................................................... 115

Figure 5-14. Schematic illustration of ion lathing. One milling box is made for rotational lathing surrounding the pillar. Lathing rotation with small increment is required for smoothening the surface of the pillar. .................................................................................. 117

Figure 5-15. SEM images (A)–(H) during ion lathing. A Fiducial Mark with diameter smaller than that of the desired pillar is made to collimate the lathing after each rotation. (I) shows the shape of final pillar made by ion lathing. .................................................. 118

Figure 5-16. SEM image of micropillars fabricated by (A.1) concentric milling and (B.1) ion lathing, and the corresponding compression load vs depth curve in (A.2) and (B.2). Note (A.1) from Figure 5-13 and (A.2) from Figure 5-15 are placed here for the sake of comparison. .......................................................... 119

Figure 5-17. Photograph of (A) NiTi bulk materials and (B) fabricated thin sheet by using focused ion beam. .............................................................................................................. 121

Figure 5-18. DSC thermo-grams of Ti-50.8 at% Ni bulk materials. For clarity, the tangential to the side of each peak is to intersect with the horizontal line to identify the transformation temperatures. ........................................................................... 123

Figure 5-19. (A) Bright-field TEM image of grain morphology in thin sheet prepared by focused ion beam. (B) Dark-field TEM image of the boxed part in (A). (C) Zoomed-in view on the three regions circled in (A). ........................................................................ 124

Figure 5-20. Chart on grain size and thickness in the three regions. The ratio of grain size to the thickness are inserted for each region. .................................................................................. 125

Figure 5-21. Diffraction patterns of the three regions during in-situ TEM cooling. Scale bar, 5 1/nm. The indexing superposed to (A) and (B) also apply for (C)–(I). ................. 126

Figure 5-22. (A) Schematic diagram of grain size and thickness in the thin sheet, and (B) illustration showing the effect of thickness and grain size on transformation temperature ................................................................. 128

Figure 5-23. (A) Schematic of micro-double shear test setup. The dimensions of sheared specimen are optimized for measurable shear strain and for minimizing unwanted bending stress. (B) Side view and (C) top view of SEM images on the micro-double shear specimen fabricated by focused ion beam. .................................................. 129
LIST OF TABLES

Table 3-1. Calibration of BTIBD on the relation between power ratio and composition, and on deposition rate. ........................................................................................................................................32

Table 3-2. Calibration of magnetron sputtering on the relation between power ratio and composition, and on deposition rate........................................................................................................................................36

Table 4-1. Summary of heat treatment parameters and the resulting crystallographic phase in three NiTi films........................................................................................................................................53

Table 4-2. Heat treatment parameters and sample details of NiTi thin films. .................................65

Table 4-3. Summary of BTIBD film condition, heat treatment and substrate. .................................84

Table 4-4. Values of transformation temperature and hysteresis in the Ti-49.7 at% Ni BTIBD thin film........................................................................................................................................89

Table 5-1. Parameters of sectioning the strips by using ultramicrotome. ........................................100
ACKNOWLEDGEMENTS

Learning is a lifelong journey. Within the journey, Doctor of Philosophy (Ph.D.)
graduate study in The Pennsylvania State University is the section made possible with financial
assistance from funding agencies and with intellectual and technical guidance from experts. This
work was funded by Materials Research Institute, The Pennsylvania State University under the
startup funding, and by National Science Foundation under Grant No. CMMI 1335283 and
1538354. The author would first thank his advisor, Professor Reginald F. Hamilton. His research
philosophy of framing research in fundamental and logical manners has taught the author how to
effectively conduct advanced research. His writing principle — Be critical of your writing; use
simple words and write explicitly — has helped the author grow in professional writing which
produced scientific publications worthy of international attention. His first question as well as
advice — How to teach yourself — has continually sparked the author’s inner reflection and has
gradually transformed the way of thinking and acting, which will be instrumental to the author for
independently conducting future research. The author would also like to thank Professor Mark
W. Horn and Professor Robert M. Rioux. Professor Horn has provided access to the experimental
equipment in his group for deposition and characterization of thin films. In addition, discussion
with Professor Horn on growth mechanism and analysis of thin films has extremely matured the
author’s knowledge in the field of thin films. Professor Rioux introduced the author to the
subject of nanoskiving — a novel technique for fabrication of nanowires — and provided
beneficial suggestions on the utilization of nanoskiving.

The author would like to thank the other three committee members for providing
invaluable suggestions on study and communication. Professor Jerzy Rzylllo’s course,
Manufacturing Methods in Microelectronics, taught the author the standardized microfabrication
and characterization techniques in micro-technology. Discussion with Professor Rzylllo has
expanded the author’s knowledge on the potential applications of shape memory alloys in microelectronics. Professor Aman Haque is thanked for providing technical suggestions on testing — using as simple techniques as possible to obtain the needed information — to streamline the testing protocol. Professor Long-Qing Chen is gratefully thanked for providing suggestions — slow down and speak clearly — to benefit the author in team collaboration and future job searching.

The author would also like to thank the technical support from Materials Research Institute, and the Huck Institutes of the Life Sciences, The Pennsylvania State University. Trevor Clark and Ke Wang at Materials Characterization Laboratory of Materials Research Institute, are both thanked for training the author on the use of transmission electron microscope and for the assistance with the data interpretation. The author thanks Bill Drawl and Guy Lavell at Nanofabrication Laboratory of Materials Research Institute, for help on deposition techniques (by Bill) and on etching techniques (by Guy). Missy Hazen at Microscopy and Cytometry Facility of the Huck Institutes of the Life Sciences is thanked for the demonstration and assistance on the utilization of ultramicrotomy including embedding, curing, trimming and sectioning.

The author would also thank the Department of Engineering Science and Mechanics for providing the well-established infrastructure and the in-depth mechanics courses to enable rapid access to the high-level research. The author’s labmates are thanked for hands-on help, discussion and comments. The author’s friends are thanked for accompanying, encouragement, and support to make the author’s graduate study a memorable one.

The author would lastly like to thank his family for insightful love and unconditional support. More than ten years ago, the author’s parents provided him the strong belief and motivation that acquiring higher education is important for him, and that attending the university is the effective pathway to elicit his untapped potential and to realize his inner value. Unconditional support, both financial and emotional, invariably drives the author to move
forward from learning barriers and to enhance the competitive advantages. Inspiring the author to learn fast and be positive in life, his young sister, Huiyue Hou, always amazes the author by her ability of rapid solution-seeking and of maintaining confidence on everything. Finally, the author’s wife, Ye Yun, is thanked for providing the continual trust and never-ending belief that the togetherness distance of heart to heart is infinitely shorter than the thousands of miles apart in physical distance, and that both of our strenuous learning journey will never cease to increasingly broaden our mutual outlook on life and world.
“Realize that your objective in research is to formulate and test hypotheses, to draw conclusions from these tests, and to teach these conclusions to others. Your objective is not to ‘collect data.’”

—George M. Whitesides
Chapter 1

Introduction

§ 1.1 Functionality, applications, and size miniaturization of shape memory alloys

Shape memory alloys (SMAs) are a class of functional materials. The alloys are able to “remember” the original form (shape or size) after thermal-mechanical deformation at high stress level (over 500 MPa)[1] and large recoverable strains (up to 10 %)[2]. In addition, the work output per unit volume in shape memory alloys is the highest among the smart materials used for actuation, as shown in Figure 1-1. Applications utilizing the shape memory functionality span the fields of aerospace,[3,4] automobiles,[5] robotics,[6] and biomedical tools[7,8]. Figure 1-2(A.1) and (A.2) show that shape memory alloy beams are incorporated to bend or straighten a Boeing variable geometry chevron. The nickel-titanium (NiTi) class of shape memory alloys are the most commonly investigated shape memory material and readily employed in commercial applications.[4]

Micro- and nano-electromechanical systems (MEMS/NEMS) is a world-wide market worthy of one hundred billion dollars that can benefit from technological development of miniaturized functional materials.[9] NiTi shape memory alloys with their high work output density (about $10^7$ J m$^{-3}$) are a candidate material.[10] Furthermore, the inherent slow thermal response can be overcome upon miniaturization due to the small thermal mass and large surface-area-to-volume ratio.[11] Figure 1-2(B.1) and (B.2) show a microcage utilizing the shape memory effect via thermal cycling of a NiTi alloys thin film with 800 nm thickness to capture a polymer microsphere.
Figure 1-1. Chart on the work output per unit volume of various materials for actuation. NiTi shape memory alloys (SMAs) exhibit the largest work output per unit volume. Adapted from [11].

As dimensions of materials become small during the course of miniaturization, shape memory alloys have been shown to exhibit size dependent thermal-mechanical behaviors. A recent study shows that at the scale of bulk, micrometer and sub-micrometer, the transformation stress and the recoverable strain in the shape memory alloys with the same composition differ as in Figure 1-3(A). Both the transformation stress at sub-micrometer scale and the recoverable strain at micrometer scale are higher than that of bulk. In particular, the hysteresis magnitudes as the areas of stress-strain loop are larger at micrometer and sub-micrometer scale than that of bulk. From a practical point of view, a large hysteresis in shape memory alloys is suitable for damping applications while a narrow hysteresis is desirable for fast response. Figure 1-3(B) shows the proposed physical mechanisms at different scales for the size dependent hysteresis.[12,13]
Figure 1-2. (A.1) and (A.2) Photograph of Boeing chevron capable of variable geometry. Shape memory alloys are embedded inside to bend or straighten the chevron in order to regulate the exhaust gases flow and reduce engine noise. The shape memory effect is utilized. Taken from [4]. (B.1) and (B.2) Scanning electron microscope images of a microcage actuated by shape memory alloys to capture a small polymer ball. NiTi alloys thin films are incorporated into the fingers to utilize two way shape memory effect. Taken from [14].

The hysteresis is due to energy dissipation with a considerable portion by frictional resistance against transformation interface. Friction work is generated by the interface motion during transformation and is related to the density of obstacles or defects. When the size is large, the inherent volumetric density of obstacles or defects imposes nearly no effect, as seen in the Volume regime of Figure 1-3(B). As the size decreases, the obstacles at free surface act as the pinning points against the transformation interface and increasingly dominate, leading to the effect of increasing hysteresis as in Surface regime of Figure 1-3(B). Further size reduction to the Starvation regime will cause the starvation of nucleation sites or obstacles: The hysteresis
increase by enlarging the ratio of surface to volumetric obstacles is offset and gradually overshadowed by the decreasing probability of interacting with obstacles. A comprehensive understanding on the size-scale dependence of thermal-mechanical behaviors and mechanisms is required and critical to the successful and reliable design of potential micro/nano devices that utilizes small-scale shape memory alloys.

Figure 1-3. (A) Stress-strain curves of the same Cu-Al-Ni composition at bulk (black dot), micrometer (blue dot) and sub-micrometer (red dot) scale. Taken from [4]. (B) Plot of stress hysteresis versus sample diameter. Regimes of Volume, Surface, and Starvation dominate at different length scale. Adapted from [13].

Fabrication and characterization of small-scale shape memory alloys is the first step to miniaturization for MEMS/NEMS applications. Although NiTi thin films fabricated by magnetron sputtering are being extensively studied at the micrometer scale, there is a shortage of work at the nanometer scale. Specifically, there is limited research on microstructure tailoring of NiTi thin films with nanometer thickness, and even less research on the quality control from atomic level on the surface and the interface of these films. The importance is manifested in reported work at micrometer scale that there is a strong influence of microstructure, and film quality on the microscopic transformation and shape memory behaviors. For example, the
surface smoothness of Cu-Zn-Al alloy microwires impose inverse effect on hysteresis in that the smoother the microwire surface is, the less the surface obstacles are, the less the energy dissipations by encountering the surface obstacles are, and the smaller the hysteresis will be.\textsuperscript{[15]} For further miniaturization, nanowire is a mean to investigate the size effect on microscopic transformation and macroscopic deformation of shape memory alloys with a nanometer cross section. To date, there is virtually no fabrication work on NiTi nanowires.

\textbf{§ 1.2 Problem statement and proposed research}

The current proposed research investigates a state-of-the-art thin film deposition technique — biased target ion beam deposition (BTIBD). BTIBD is a recent advancement in the sputter deposition technique, and is capable of readily controlling the energy of depositing atoms via a low-energy ion beam. The control of adatom mobility and coalescence can tailor the film growth mechanism. The purpose of this research is to assess the BTIBD of NiTi thin films with nanometer thickness.

Fabrication of NiTi thin films will require to establish a relation between composition and power ratio to enable the precise control on binary elemental concentration. Heat treatment will be utilized to crystallize the as-deposited thin films and tailor their microstructures. Characterization will require the investigation of the surface, interface, grain morphology, and crystal structure. The spatial resolution of elemental and thickness distribution mapping will be reported. The thermally-induced shape memory phase transformation will be characterized by tracking the evolution of film stress during temperature cycling. A recently developed nanofabrication technique, nanoskiving, will be utilized on NiTi alloys thin films to generate nanowires. The feasibility of nanoskiving on NiTi alloys will lay the groundwork for fabrication of one-dimensional shape memory alloys.
Chapter 2
Fundamentals

PREVIEW

At the beginning of the chapter, the thermo-mechanical behaviors and the underlying mechanism, martensitic transformation, in shape memory alloys are presented. Influences of alloy composition on martensitic transformation temperature are discussed. The characteristic dimensions of martensite, the geometric size effect and the grain size effect at a small scale are summarized from the literature. Subsequently, the formation mechanism of thin films and the structure zone model are described, and the following section presents the effect of ion-assisted bombardment on film growth. Finally, the correlation between microstructural morphology and thermally-induced behaviors in thin films is discussed.

§ 2.1 Shape memory behaviors and martensitic transformation

Shape memory alloys exhibit a shape memory effect and superelasticity.[4,16] The shape memory effect refers to a phenomena in which a “remembered” shape is recovered when heated. Superelasticity is the ability to deform to large strains reversibly, with energy dissipation as heat. The underlying mechanism is the martensitic phase transformation between two crystallographic phases, austenite (the high temperature cubic phase) and martensite (the low temperature phase with lower symmetry).
To describe the martensitic transformation, four characteristic transformation temperatures are defined: $M_s$, $M_f$, $A_s$, $A_f$, as shown in Figure 2-1. The first two indicate the starting and finishing transformation temperature from austenite to martensite and the last two represent the starting and finishing transformation temperature from martensite to austenite. Upon cooling without stress, the austenite transforms into twinned martensite and no shape changes occur. If below $M_f$ a load is applied, the twinned martensite will change into detwinned martensite; shape change takes place and remains after unloading. If heating until above $A_f$, the detwinned martensite will directly return to the austenite and the deformed shape will macroscopically recover to the original shape. The above describes shape memory effect how to “remember” the original shape. In the case that a constant load is applied during cooling, the four transformation temperature will increase accordingly. Under the applied load, the martensitic starting and finishing temperature are $T_{M_s}, T_{M_f}$, meanwhile the austenitic starting and finishing temperature $T_{A_s}, T_{A_f}$, as shown on the horizontal dash line in Figure 2-1.

![Figure 2-1. Schematics of stress-temperature phase diagram for shape memory alloys. See text for description of symbols. Adapted from [4,12].](image-url)
Superelasticity will take place when the temperature is above $A_f$ and the load is increasingly applied. Similar to the four transformation temperatures, there are four transformation stresses in this case, $\sigma_{As}$, $\sigma_{Af}$, $\sigma_{Ms}$ and $\sigma_{Mf}$. Here $\sigma_{As}$, $\sigma_{Af}$ stand for austenitic starting and finishing transformation stress, respectively while $\sigma_{Ms}$ and $\sigma_{Mf}$ respresent martensitic starting and finishing transformation stress. When the load increases above $\sigma_{Mf}$, the initial austenite will change into detwinned martensite with macroscopic deformation. Upon unloading, the detwinned martensite will transform into austenite and the deformation disappears. The corresponding loading path can be shown in vertical dash line in Figure 2-1.

Alloy composition imposes a strong influence on the martensitic transformation temperatures; even a 0.1 at% difference in composition can result in up to 10 °C variation in the transformation temperatures.[17,18] For each composition, the transformation temperatures can be determined by differential scanning calorimetry based on the principle that the release/absorption of latent heat during the martensitic transformation is compensated by supplying heat energy in order to maintain the constant cooling/heating rate. The typical plot from differential scanning calorimetry to determine the four transformation temperatures $M_s$, $M_f$, $A_s$, $A_f$ is shown in Figure 2-2(A). The dependence of $M_s$ on the Ni concentration in binary NiTi alloys is shown in Figure 2-2(B). The compositions can be divided into three regions: Ni-rich (>50.5 at% Ni), near-equiaatomic (in between 49.5 at% Ni and 50.5 at% Ni), and Ti-rich (<49.5 at% Ni).[19,20] In the Ti-rich region, two phases of NiTi and Ti$_3$Ni exist; $M_s$ is nearly independent of the Ni concentration. In the near-equiaatomic region, one single phase, NiTi is present, and as the Ni concentration increases above 49.8 at%, the transformation temperature will decrease. Two phases of NiTi and Ni$_4$Ti$_3$ exist in the Ni-rich region. The transformation temperature in the Ni-rich region decreases as the Ni concentration increases. Thus, adjusting the
Ni concentration in the binary NiTi alloys is a means to tailor the martensitic transformation temperatures. In fabrication of small-scale NiTi alloys, care should be given to the precise control of composition.

Figure 2-2. (A) Schematics of differential scanning calorimetry curve to show the determination of the four martensitic transformation temperatures. (B) Sketch of martensite start temperature, $M_s$, as a function of the Ni concentration for NiTi alloys. $M_s$ is nearly constant in Ti-rich region. As the Ni concentration increase from 49.8 at%, $M_s$ decreases in near-equiaatomic and Ni-rich regions. Adapted from [12,18].

§ 2.2 Size effects at small scale

Size effects arise when characteristic dimensions associated with the mechanics of a phenomenon interact with the parametric size.[21,22] Martensitic transformation exhibits size dependent effects when a geometric size such as the thickness of the thin film or the grain size are approaching the scale of the characteristic dimensions associated with martensite.
§ 2.2.1 Characteristic dimensions of martensite

Martensitic transformation is accompanied by shear of the original austenite lattice, and twinning is the lattice invariant shear in shape memory alloys to generate twin-related martensite. [12,17] Since austenite has high symmetry, multiple martensite with the same crystal structure but different orientation can be formed, and referred to as variants. Hierarchically, a martensite variant is the smallest unit, and two twin-related variants constitute a correspondence variant pair (CVP); CVPs stack up to form the martensite plate; multiple plates arrange within one grain. The spatial distribution of martensite plates in a grain and the martensite variants within a martensite plate are schematically shown in the Figure 2-3. Such a hierarchical structure of martensite has been proposed to describe the evolving twin morphology at austenite-martensite interface.[23-25] Furthermore, thermo-mechanical behaviors of a single crystal/grain have been demonstrated highly sensitive to the spatial distribution of martensite plates, and microstructural arrangement inside the martensite plates.[26] Therefore, the characteristic dimensions of martensite can be associated with martensite plates and martensite variants. Specifically, the characteristic parameter metrics can include the following: 1) width, \( W \), and spacing, \( S \), of martensite plates, and 2) width, \( d_1 \), \( d_2 \), and periodicity, \( \lambda \), of martensite variants within a martensite plate.
Figure 2-3. a) Sketch of martensite plates and austenite in one grain of a polycrystalline shape memory alloy. Space between martensite plates, \( S \), width of a martensite plate, \( W \), and location of grain boundary, \( I_{GB} \), and austenite/martensite interface, \( I_{AM} \), are delineated. \( I_{AM} \) can also be called habit plane. (b) Sketch of twin-related variants arrangement within a martensite plate. The width of martensite variant 1 and martensite variant 2 is \( d_1 \) and \( d_2 \), respectively. The periodicity of variants is \( \lambda = d_1 + d_2 \). Between martensite variant 1 and 2 is twinning boundary, \( I_{TW} \). (c) Zoomed-up view on morphology of martensite variants near the habit plane. \( \theta \) is the shape parameter at microstructural level.

§ 2.2.2 Geometric size effect and constraints to martensitic transformation

Thin films with one dimension at a small scale is under extensive study. The metric to gauge the geometric size effect can be derived from the two standard thermo-mechanical tests: isothermal uniaxial testing, and thermal cycling under constant loading. The typical plot of isothermal uniaxial testing, as sketched in Figure 2-4(A), has four transformation stress, \( \sigma_{AS} \), \( \sigma_{AF} \), \( \sigma_{MS} \) and \( \sigma_{MF} \). The transformation temperatures \( T_{MS}, T_{MF}, T_{AS}, T_{AF} \), during thermal cycling under constant loading is shown in Figure 2-4(B).
As the thickness of thin films decreases, literature results have shown a decreased transformation temperature [27-29], a reduced thermal hysteresis [28], increased film stress [29], and suppression of the martensitic transformation below 100 nm [30]. The constraints from the free surface and the substrate/film interface affect the lattice distortion within thin films during martensitic transformation. The ratio of the inter-diffusion layer and the surface oxide layer to the film thickness become large when the film thickness is below 1 μm [31,32]. The large ratio will lead to increasing resistive forces to oppose the lattice distortion and twinning deformation mechanisms. The resistive forces becomes so large that when the film thickness is below certain value, the martensitic transformation is fully suppressed, as seen in the curve of the 48-nm film in Figure 2-5(A).

Another shape memory alloy object under extensive study with regard to a geometric size effect are pillars with the diameter at small scale. As the diameter of pillars decreases, the uniaxial test results show increased forward critical stress [33-35], lowered reverse recovery stress, [33,34], change of selection rule of martensite variants [34,36], enhanced hysteresis
dissipation [12,33,35,37,38], extended fatigue lifetime [37,39], and the absence of superelastic strain below 200 nm [40]. The mechanically constrained thermal cycling on wires with decreasing diameters has been demonstrated. Uniaxial test result on a Cu-Al-Ni alloy pillar, 500 nm in diameter is shown in Figure 2-5(B). The uniaxial compression on the pillar shows significantly enhanced hysteresis as opposed to the bulk materials. The suggested physical mechanism is the following: The free surface is imposing the constraints on the martensite variants. Scarcity of nucleation sites of martensite in smaller, smooth single-crystal pillars lead to the higher forward critical stress, similar to dislocation starvation for increasing yield strength.[41] Moreover, martensite variants can span the entire pillars with smaller diameter to reach the free surface in order to release the stored elastic strain energy [9,42]. The release will reduce the driving force of promoting the reverse transformation from austenite to martensite. Furthermore, the variants reaching to the free surface will become stabilized; a low value of stress is required to initiate the reverse transformation.

Figure 2-5. (A) Stress-temperature curves of NiTi thin films with different thickness. Taken from [32]. (B) Uniaxial compression stress-strain curve of bulk single crystal and of Cu-Al-Ni pillar. Adapted from [33].
§ 2.2.3 Grain size effect and transformation criteria of energy barriers

In addition to the geometric size, microstructural size will also impose an effect on martensitic transformation. When the grain size is reduced to nanoscale regime by mechanical methods such as severe plastic deformation [43-46], unusual transformation properties arise compared to coarse grain materials. Martensitic transformation temperatures decrease as the grain size decreases, and martensitic transformation is completely suppressed at grains less than 50 nm. The self-accommodated herringbone morphology of martensite in large grains has switched into a single martensite variant as the grain size reduces below 100 nm. The observed grain size effect is associated with transformation criteria of energy barriers.

Based on the analysis of Gibbs free energy on the microregion with volume $V_{in}$ and surface area $O_{in}$,[47,48] the necessary condition for the onset of transformation from austenite to martensite is only when the transformation barrier is overcome by the thermodynamic driving force which is consisting of chemical driving force and mechanical driving forces. The chemical driving force comes from the difference of chemical free energy between austenite to martensite; the mechanical driving forces are the mechanical work arising from the transformation strain in the presence of external and internal stress. In thermally-induced martensitic transformation, the mechanical driving forces are neglected, and thus the criteria of onset of transformation can be written as follows [30,48-50]:

$$\Delta \varphi_{chem}(T) = E_b, \quad (2-1)$$

where $\Delta \varphi_{chem}(T)$ is chemical driving force, and $E_b$ is transformation barrier. Specifically, $E_b$ is consisting of surface-related energy contribution, volume-related energy contribution and work of friction, and mathematically can be written as follows:[48]

$$E_b = (\Gamma_{in} + \Sigma_s + \Gamma_{tw}) \frac{O_{in}}{V_{in}} + F_c + U_v \frac{1}{V_{in}}, \quad (2-2)$$
where $\Gamma_{in}$ is interfacial energy at twin interface, $\Gamma_{Tw}$ is twin strain energy, $\Sigma_s$ is the change of interfacial energy of surface area $O_{in}$ upon transformation, $V_{in}$ is the volume of microregion, $F_c$ is the work of friction, $U'_v = U_v \frac{1}{V_{in}}$ is volume-related energy. $(\Gamma_{in} + \Sigma_s + \Gamma_{Tw}) \frac{O_{in}}{V_{in}}$ is surface energy, and $F_c + U_v \frac{1}{V_{in}}$ is the total volume energy.

To understand the physical interfaces related to surface energy, as an example, the transformation from body centered cubic (BCC) unit cell to body centered tetragonal (BCT) martensite variants is shown in Figure 2-6(A). The assembled morphology of twin-related martensite variants and the austenite-martensite interface are in Figure 2-6(B). Upon Bain strain of extending in one direction and contracting in the others, there are three martensite variants with three possible extending directions. The variants can assemble in pair to form the twin-related microstructure which is in contact with the austenite-martensite interface. Figure 2-6(C) shows the interfaces related to the energy terms in equation (2-2).
Figure 2-6. (A) Schematic of generating three types of martensite variants via BCC-BCT Bain deformation. (B) Assembly of martensite variants into twinned microstructure. The austenite-martensite interface is a straight plane. (C) Sketch of the energy contribution from twinned microstructure in the total transformation barrier. (D) Crossover of calculated energy barrier as a function of decreasing grain size. Below a critical size ~70 nm, single laminate of twinned martensite is favorable for low energy barrier while herringbone morphology has minimum energy barrier above the critical size and thus is favorable. (A) and (B) are adapted from [51]. (C) and (D) are taken from [30,49].
From calculation, components of surface energy have different scaling behaviors. Twin strain energy has the following scaling behavior with grain size:

\[ (\Gamma_{Tw} O_{in}/V_{in}) \propto (d/\delta), \] (2-3)

where \( d \) is the half length of austenite-martensite interface at the end of one twin, \( \delta \) is the grain size. On the other hand, twin interfacial energy has the following scaling behavior:

\[ \Gamma_{in} O_{in}/V_{in} = (\Sigma_{Tw}/d)/unit\ of\ transformed\ volume, \] (2-4)

By minimizing \( E_b \), the optimum width of the twins, \( d_{opt} \), has the following relation to the grain size:

\[ d_{opt}(\delta) \propto \delta^{1/2}, \] (2-5)

Optimum width of the twins is thus decreasing with the decreasing grain size. It was shown that with \( d_{opt} \), twin strain energy is equal to the interfacial energy at twin interface per unit of transformed volume, i.e. \( \Gamma_{Tw} = \Gamma_{in} = \Gamma \). From (2-3) and (2-5), \( \Gamma \) is inverse function of square root of grains size, \( \delta \),

\[ \Gamma \propto \delta^{-1/2}, \] (2-6)

Thus, contributions from twin-related energy to total energy barrier, \( E_b \), can strongly increase as the grain size decrease. It is predicted that the morphology with minimum \( E_b \) is always favorable. Calculation in Figure 2-6(D) shows that when grains size is 50 nm, single laminate of twined martensite possess lower energy barrier than the herring-bone morphology, and thus the single laminate is favorable which is supported by the experimental observation.[49] For the grain size of 100 nm, transformation energy barrier is lower in the herring-bone morphology than that of single laminate; herringbone morphology becomes favorable and is also observed in experiments.[49] Morphology of martensite which is depending on grain size can thus be explained by the transformation criteria of energy barriers.
§ 2.3 Thin films and nanofabrication

§ 2.3.1 Nucleation, growth, and coalescence of thin films

The sequential event of nucleation, growth and coalescence leads to a continuous thin film.[52,53] During the nucleation, depositing atoms accumulate into nuclei with a diameter, $r$. At growth stage, the nuclei grow with increasing diameter as the deposition proceeds. When the diameter of nuclei reach the critical diameter, $r^*$, the nuclei will grow spontaneously and coalesce with each other until a continuous film is formed.

![Figure 2-7](image)

Figure 2-7. Schematic of growth mode in thin films. (A) Frank-van der Merwe mode with the characteristics of layer by layer. (B) Volmer-Weber mode with three dimensional islands. (C) Stranski-Krastanov mode with the feature of layer plus three dimensional islands. Letter $a$ denotes the distance between surface sites. Taken from [53].

Experimental observations have led to three growth modes of thin films which are shown in Figure 2-7.[52-54] The three modes can be described by using the concept of surface energy,
\( \gamma \). Suppose that thin films are depositing on a substrate of different species, it is necessary to consider the free surface energy of films, \( \gamma_f \), free surface energy of the substrate, \( \gamma_s \), and substrate-film interface energy, \( \gamma_i \). When \( \gamma_f + \gamma_i < \gamma_s \), i.e. the film spreads across the substrate, atomic growth layer by layer occur, as the Frank-van der Merwe mode in Figure 2-7(A). When \( \gamma_f + \gamma_i > \gamma_s \), there is insufficient substrate bonding to spread across the substrate. Instead, three dimensional islands are formed, as the Volmer-Weber mode in Figure 2-7(B). The Stranski-Krastanov mode shown in Figure 2-7(C), involves the change from layer mode to the island mode after the first one or two monolayers. The energy situation is \( \gamma_f + \gamma_i < \gamma_s \). The Frank-van der Merwe mode is only observed in a limited number of substrate-film combinations.[53] Volmer-Weber mode is often observed in metals on insulators.[54] Stranski-Krastanov mode is associated with epitaxy.[53]

\[ \text{§ 2.3.2 Structure zone model} \]

The structural development of thin films changes with thermal motion. The thermal motion scales with the ratio of input temperature \( T \) to the melting temperature \( T_m \) of thin films, referred to as “homologous” temperature, \( T_h \), i.e. \( T_h = T/T_m \).[53] In case of in-situ heating the substrate during film growth, the input temperature is the temperature of a substrate. As for post-deposition annealing, the temperature is applied to both film and substrate. In addition to the temperature, additional energy delivered to the free surface during film growth will change the film structure as well. Generally, four zone structures are identified in terms of different structural morphologies. These zone structures as shown in Figure 2-8 are the basis of structure zone model.[52]
Zone structure 1, denoted as Z1, is due to shadowing effects which involves limited adatom mobility. Zone structure 2 abbreviated as Z2, is the result of surface diffusion-controlled growth. Z3, as short for zone structure 3, is induced by dominating lattice diffusion. Specifically, zone structure 1 occurs when $T_h < 0.3$ where there is negligible surface diffusion. The structural characteristics are the columns with tens of nanometers in diameter separated by voided boundaries. The columns are typically amorphous or have poor crystallinity. In thick films, arrays of cones with wide voids will superpose on the structure of columns, and will terminate as domes at film surface, as shown in Figure 2-8. Transitional zone structure denoted as ZT also takes place when $T_h < 0.3$. Compared to Z1, the structural characteristics of ZT has no voids or domes. ZT is typically induced by energy-enhanced processes. Z2 exist when $T_h > 0.3$ where surface diffusion dominates. Structurally, columns have dense grain boundaries, and the diameter of columns increases with $T_h$. In case of crystalline films, grains within the films are usually faced at the film surface. In case of amorphous films, the boundaries between columns are planes of reduced bonding instead of crystalline planes. Z3 occurs when $T_h > 0.5$ where the large bulk of film is annealed. The structures are the equiaxed recrystallized grains. Film surfaces are typically smooth.
The observations on the four structure zones have been generalized into a structure zone model which is a function of $T_h$. Moreover, for sputtered films, argon pressure is imposing influence. For example, at low pressure, the ZT is broad compared to that in high pressure. Pressure, however, seems have limited influence at elevated $T_h$.[56] The structure zone model as a function of $T_h$ and pressure is shown in Figure 2-9.

§ 2.3.3 Ion bombardment to facilitate film formation

Ion bombardment on the free surface of growing films is an effective way to influence the energy of depositing atoms and thus modifies the properties of thin films.[52] Ion beam assisted processes are designed to provide independent control of ions toward the substrate. However, without the aid of an independent ion beam, controlling the ions via the plasma is limited because the energy, flux, direction of incident ions within the plasma are beyond control.[52] Characteristics of independent ion beams typically includes low-energy spread (~10
eV), excellent collimation with slight divergence angle, and small flux of bombarding ions on the substrate compared to that of depositing atoms. Furthermore, the background gas is quite low (~10 e-4 Torr).

Figure 2-10. Schematic of bombarding ions on the surface atoms showing the inducing effects. a) Removal of absorbed impurity atoms; (b) lateral displacement due to enhanced surface diffusion; (c) surface vacancy formed by sputtering a film atom out upward; (d) surface vacancy created by moving a film atom to an adatom position; knock-on implantation of (e) an impurity atoms and (f) a film atom; (g) void filled by the deposited atoms with enhanced surface mobility; (h) void filled by forward sputtering the suspended atoms; (i) breakup of three dimensional nucleus. Taken from [53].

The key feature of ion bombardment is efficient energy transfer from ions to the individual atoms which is most efficient when the ion mass is on the same order as the mass of atoms.[53] The energy transfer allows the ions to move atoms around which is the core reason of ion bombardment effect on film structure and properties. There are four types of effects: surface effects, ion implantation, bulk atomic displacement and sputtering, the occurrence of which effect depends on the energy of ions. In the energy window from several eV to a few tens of eV, the surface effects take place, and will be specifically introduced here in order to illustrate how the bombarding ions move the surface atoms around. The other three types can be referred to the textbook by Smith.[53]
The surface effect of ions bombarding the surface atoms is sketched in Figure 2-10.[53] Lateral displacement occurs due to the enhanced surface diffusion caused by the ion bombardment. The displacement will depend on the excess energy brought to the adatom by the ions. Voids can be filled by the mobilized atoms with enhanced surface mobility as in (g) or by forward sputtering the suspended atoms in (h). Furthermore, the surface topography can be smoothened by breaking up the three dimensional nucleus as in (i). Sputtering can cause the generation of vacancy as in (c) and (d). The other effects are associated with the adsorbates. The impurity atoms on surface can be desorbed as in (a), thus ion-bombardment can be a useful way to clean the impurity from the substrate prior to film deposition. Ion bombardment can knock on the impurity atoms as in (e) or the surface atoms in (f) into the bulk. Among the effects, lateral displacement, breakup of 3D nucleus, and ion-enhanced surface mobility will likely contribute to the smoothening of film surface and the enhancement of film density.

§ 2.3.4 Correlation of microstructure morphology to stress-temperature behaviors in thin films

The thin films deposited on substrates are typically under stress. The film stress $\sigma_f$ in the substrate-attached condition consists of three contributions: 1) thermal stress $\sigma_{th}$, due to the difference of coefficients of thermal expansion between film and substrate causing a mismatch upon thermal cycling,[57] 2) intrinsic stress $\sigma_{in}$, formed during deposition at the as-deposited temperature, depending on the deposition conditions (deposition rate, substrate temperature, deposition method, defects, as well as the purity of the deposited film), the lattice mismatch between film and substrate, and/or degree of stress relaxation from substrate,[57-59] and 3) transformation stress $\sigma_t$, resulting from phase transformations. Mathematically, $\sigma_f$ is expressed as follows:
\[ \sigma_f = \sigma_{tn} + \sigma_{th} + \sigma_t, \quad (2-7) \]

On the other hand, if temperature changes, the strain between film and substrate at a temperature, \( T \), can be calculated with respect to a reference temperature \( T_R \) where the stress between film and substrate is zero.[60] If the film and the substrate was separated as shown in Figure 2-11, the mutual constraints between film and substrate would not exist. At \( T \) below \( T_R \), the strain of the substrate, \( \varepsilon_s \), due to thermal contraction can be expressed as follows:

\[ \varepsilon_s = \alpha_s (T - T_R), \quad (2-8) \]

where \( \alpha_s \) is the coefficients of thermal expansion of the substrate. Similarly, the strain of the film, \( \varepsilon_f' \), due to thermal contraction can be expressed. In addition, the film may transform at \( T \), and thus an additional term due to phase transformations need to be incorporated, as follows:

\[ \varepsilon_f' = \alpha_f (T - T_R) + \varepsilon_t (\xi), \quad (2-9) \]

where \( \alpha_f \) is the coefficients of thermal expansion of the film, and \( \xi \) is the fraction of martensite.

If the separated film and substrate are combined, the strain of film in the substrate-attached condition can be calculated by subtracting the strain of the substrate from that of the film, expressed as follows:

\[ \varepsilon_f = \varepsilon_f' - \varepsilon_s = \alpha_f (T - T_R) + \varepsilon_t (\xi) - \alpha_s (T - T_R) = (\alpha_f - \alpha_s) (T - T_R) + \varepsilon_t (\xi). \quad (2-10) \]

To simplify the expression, let \( \varepsilon_T = (\alpha_f - \alpha_s) (T - T_R) \). The expression of film strain in the substrate-attached condition becomes the following:

\[ \varepsilon_f = \varepsilon_T + \varepsilon_t (\xi). \quad (2-11) \]

The above derivation rules out the stress relaxation due to plastic deformation during temperature changes. Of note is that reference temperature, \( T_R \), will be affected by the deposition conditions which may bring immobile dislocations, and that in the scenario of epitaxial films, neither movement nor generation of misfit dislocations take place during temperature change.
Microstructure morphology of a thin film constrained on a substrate can be correlated to the stress as well as the associated strain as shown in Figure 2-11.

Figure 2-11. Schematic of stress-temperature curve for a thin film constrained on a substrate. The black represents martensite, light gray stands for austenite, and dark gray is for the substrate. Taken from [60].

Microstructural morphology of thin films are hypothesized to correlate to, instead of overall stress in the film, the gradient of stress in the through-thickness direction.[61] The through-thickness stress is assumed uniform if the microstructure is macroscopically homogeneous during phase transformations. The morphology would be homogenous distribution of isolated, equiaxed islands of martensite in the austenite matrix. The islands expand with the velocity of austenite/martensite interface perpendicular to the normal of the substrate, as the Figure 2-12(A). A partitioning of through-thickness stress would occur if the velocity of
austenite/martensite interface is along the normal to the substrate, as in Figure 2-12(B). The martensite, in this case, is a continuous sheet; the expanding of the sheet would lead to the macroscopic stress gradient due to the high stiffness in austenite and low stiffness in martensite. The proposed morphology is hypothetical, and still needs experimental validation.

Figure 2-12. Schematic of microstructural development during phase transformations of a thin film under uniaxial stress. Phase-front velocity vector \( v \) is (A) perpendicular and (B) parallel to the normal of the substrate. Taken from [61].

When thin films are patterned into fine line shapes or deposited directly on line substrates, the width of thin films is finite and comparable to the film thickness. For example, the 1 \( \mu \)m thickness metal interconnect line in memory chip typically has 1 \( \mu \)m width.[53] The gradient of film stress throughout the thickness is intensified. The stress at the outer surface is zero because the surface is free of any constraints. However, at the film/substrate interface the stress is large and imposed by the constraining substrate. The stress gradient will lead to non-uniform deformation of thin films throughout the thickness; the strain distribution of film under
tensile stress and compressive stress is sketched in Figure 2-13(A), and Figure 2-13(B), respectively. At the two lower corners of thin films, the strain under tensile stress is the largest while the strain is smallest (in terms of value plus negative sign) under compressive stress. Meanwhile, there is a stress concentration at the two corners compared to the stress-free at the outer surface and to the stress imposed by the substrate at the film/substrate interface. The stress concentration may have detrimental effect leading to adherence failure. [53]

![Figure 2-13](image)

Figure 2-13. Schematic of cross-section strain distribution of a thin film with finite width at the condition of (A) tensile stress and (B) compressive stress. The arrows indicate the distribution direction of strain from small to large values (including the negative sign). Adapted from [62].
Chapter 3
Fabrication and characterization methods

PREVIEW

Experimental methods related to the fabrication and characterization of shape memory alloys thin films are discussed. A conventional technique — magnetron sputtering deposition — was used to deposit NiTi thin films as the benchmark to compare to the thin films fabricated by a novel technique — biased target ion beam deposition. Characterization was achieved by a variety of techniques for analysis on composition, microstructural morphology, surface topography, and crystal structure. Fundamental principles of each technique are introduced, and afterwards the parameters used in the current work for each technique are stated. Heat treatment of the deposited NiTi thin films was conducted by rapid thermal annealing and transmission electron microscopy in-situ heating. A wafer curvature measurement apparatus equipped with a temperature stage was used to determine the film stress as a function of temperature.

§ 3.1 Fabrication of 2D thin films with nanometer thickness

Although thin films are three dimensional, two dimensional (2D) shorthand is used to emphasize the two dimensions are much larger than the other, and similar shorthand for 1D nanowire, 1D pillar, 2D thin sheet, and 2D double shear specimen. A historical overview of 2D shape memory alloys thin films follows: In 1990, shape memory alloys thin films with micrometer thickness were first reported.[63] The shape memory effect was demonstrated on
NiTi thin films prepared by magnetron sputtering. For integration into a small-scale system, shape memory alloys are attractive in the form of thin films.[64] From 1990 on, progress has been increasingly made on the deposition parameters for optimum properties, microstructure control via heat treatment, and transformation properties by thermal-mechanical characterization. Research on pushing shape memory alloys from micrometer scale toward the nanometer scale has been ongoing since 2004. Producing nano-grains in bulk materials via severe plastic deformation,[30,43-46,49] reducing the geometric size such as the diameter of pillars into nanoscale regime,[9,33,40,65-70] depositing thin films with sub-micrometer thickness,[28,31,32,71-73] and introducing local nanoscale defects via doping [74-77] are the fabrication manifestations of advancing to the nanometer scale.

Shape memory alloy thin films with nanometer thickness were, by following the tradition of micrometer deposition, deposited using magnetron sputtering and first reported in 2004 to investigate crystallization and microstructure development.[78] The progress on nanometer thickness films was limited to films made by magnetron sputtering. The preliminary studies investigated the measurement of kinetic parameters such as nucleation rate and growth rate [79-83], the influence of thickness on occurrence and suppression of phase transformations [28,32,71,84], the heterostructures of coupling to ferroelectric materials such as lead zirconate titanate [85-88], and multilayers such as alternative NiTi layers and W layers [89]. As a recent advancement of deposition technique, biased target ion beam deposition (BTIBD) was conceptualized and designed for thin films with sub-micrometer thickness. The first demonstration of the technique was the deposition of Cu thin films with hundreds of nanometers thickness in 2000.[90,91] Since then, BTIBD has been used for an increasing variety of materials such as vanadium dioxide[92-96], diamond-like carbon[97-100], nickel-incorporated hydrogenated carbon[101,102], and nickel oxide and molybdenum oxide [103]. Alloy thin films were first reported to be deposited by BTIBD in 2012.[104] A BTIBD system (4Wave Cluster
Sputter, 4Wave Inc.) was brought to The Pennsylvania State University in 2011 for deposition of high-quality thin films at the nanoscale regime. Compared to magnetron sputtering which has been used more than twenty years, BTIBD has only been in the field of alloy thin films for less than three years, and there are no reports in literature of using BTIBD on shape memory alloys yet.

§ 3.1.1 Biased target ion beam deposition (BTIBD)

BTIBD allows differential biasing of each target, combines ion beam deposition and sputter deposition, and offers low-pressure operation to produce high-quality ultrathin films.\[93,105,106\] A schematic of the BTIBD system is shown in Figure 3-1. BTIBD utilizes a high-ion-density, low-energy ion beam as a remote plasma source. A low-energy end-Hall (or closed-drift Hall) type ion source, typically lower than 25 eV, creates the plasma used by negatively biased targets. A stable plasma must be maintained in the hollow cathode. The hollow cathode (HC) generates electrons and ejects electrons to the end-Hall ion source, rendering the plasma at the end-Hall constantly stable. Targets, orthogonal to the source and substrate, are then pulse-DC biased. The bias on target is used to accelerate the low-energy Ar ions for sputtering of the target atoms. Each target bias can be modulated differently by controlling the pulsed width and period. The sputtered target atoms then deposit onto the substrate to which the low-energy Ar ions can also be directed. The independent control of the target bias and the ion beam source allow controlling adatom energy (for high and low adatom energy process capabilities) on the growing film and thus tune the properties of the deposited film. The BTIBD technique enables decoupling adatom energy and deposition rate, separation of target and substrate plasma, and directing the flux while providing low-energy ion bombardment.
at low processing pressure (~$10^{-4}$ Torr) versus $\sim 10^{-3}$ Torr in the conventional sputtering systems. The substrate stage was rotated during deposition in order to achieve compositional uniformity.

![Diagram of co-sputtering system configuration for the biased target ion beam deposition technique.](image)

Figure 3-1. Illustration of co-sputtering system configuration for the biased target ion beam deposition technique.

BTIBD has produced films with highly uniform thickness (within 3% across 4 inch wafer),[95] less “overspill” contamination,[99,107] and less interlayer mixing (in multilayers).[107,108] The thin films produced by BTIBD maintain high-quality even on the order of a few tens of Angstroms;[91] the demanding quality at the very thin level is challenging for magnetron sputtering which is more suitable to deposit thicker films.[91,109] BTIBD is advantageous for the fabrication of ultra-thin, ultra-smooth films.
Table 3-1. Calibration of BTIBD on the relation between power ratio and composition, and on deposition rate.

<table>
<thead>
<tr>
<th>Power configuration *</th>
<th>Composition (at% Ni)</th>
<th>Deposition time (s)</th>
<th>Thickness (nm)</th>
<th>Deposition rate (Å/s)</th>
<th>Ni concentration for as-deposited thin films</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 : 1</td>
<td>74.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.4 : 1</td>
<td>64.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.45 : 1</td>
<td>62.5</td>
<td></td>
<td>120.2</td>
<td>0.8</td>
<td>Ni-rich</td>
</tr>
<tr>
<td>0.5 : 1</td>
<td>60.2</td>
<td></td>
<td>114.5</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>0.6 : 1</td>
<td>54.6</td>
<td></td>
<td>105.3</td>
<td>0.7</td>
<td></td>
</tr>
<tr>
<td>0.65 : 1</td>
<td>51.7</td>
<td></td>
<td>101.3</td>
<td>0.675</td>
<td></td>
</tr>
<tr>
<td>0.67 : 1</td>
<td>50.8</td>
<td></td>
<td>101.2</td>
<td>0.674</td>
<td>Near-equialemic</td>
</tr>
<tr>
<td>0.68 : 1</td>
<td>50.3</td>
<td></td>
<td>102.1</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>0.69 : 1</td>
<td>49.7</td>
<td></td>
<td>103</td>
<td>0.686</td>
<td></td>
</tr>
<tr>
<td>0.7 : 1</td>
<td>48.6</td>
<td></td>
<td></td>
<td></td>
<td>Ti-rich</td>
</tr>
<tr>
<td>0.8 : 1</td>
<td>40.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.9 : 1</td>
<td>28</td>
<td></td>
<td>79.6</td>
<td>0.531</td>
<td></td>
</tr>
</tbody>
</table>

* Pulsed width over pulse period in target of Ni : Ti, e.g. 40/100 : 100/100 denoted as 0.4:1

NiTi thin film depositions using a BTIBD system (4Wave Cluster Sputter, 4Wave Inc.) were performed in the Pennsylvania State University Nanofabrication Facilities. The BTIBD operational pressure parameter was set to 6.5×10^-4 Torr, and Ar flow rate in ion source and HC were 60 and 10 sccm, respectively. The base pressure was 1.3×10^-7 Torr. Using the ion source, pre-cleaning was conducted firstly on targets for 600 s and subsequently on substrate for 600 s. Prior to actual deposition, a seasoning procedure of the targets was conducted, with the same deposition parameter as the actual deposition set for 120 s. To correlate the power ratio with the binary elemental concentration, the power applied to the Ti target was incrementally varied while keeping the power unchanged on the Ni target for calibration. The deposition rate was calibrated by measuring the thickness achieved within a given time in order to control the film thickness based on the deposition time. The calibration of the relation between power ratio and composition and the relation between time and thickness is shown in Table 3-1. The rotating speed of the substrate stage was 20 rpm. Note the current BTIBD system is configured with three
targets and individual control on the power of each target can be achieved for each target. Potentially, alloys films with up to three elements or multilayers thin films[110] can be deposited. High temperature stage is not part of this BTIBD system. However, irradiation by the ion beam source can raise the temperature of substrate prior to the deposition and the resulting temperature can be up to 120 °C.[111]

Three types of substrates were used in each deposition: electron transparent SiN chips for direct microstructure characterization, Kapton tapes for composition measurements, and a photoresist-masked silicon piece for thickness measurements. After LOR A5 and SPR 3012 photoresist on silicon piece were routinely spun and exposed, the NiTi films were deposited on the patterned silicon piece in one run. By stripping the removable resist on silicon piece, well-defined steps with different heights of NiTi films were generated and were for thickness measurements. The details of the SiN chips and Kapton tape as the substrates can be found the characterization sections.

§ 3.1.2 Magnetron sputtering deposition

Magnetron sputtering is, to date, the most widely used film technology to deposit shape memory alloys thin films,[11,112-114] The primary reasons are its high deposition rate and the ability for controlling alloy concentration. [52,114] The main application range is for micrometer thickness films. [91,109] There are three major components in the process of magnetron sputtering: 1) striking of plasma to generate ions (such as $Ar^+$) and electrons from sputtering inert gas (such as Argon), 2) sputtering of targets to eject target atoms, and 3) deposition of target atoms onto substrate. The plasma is sustained by ionization in which new free electrons are supplied to ionize more Ar atoms. A typical ionization is the following:[52]

$$e^- + Ar \rightarrow Ar^+ + 2e^-.$$ (3-1)
The multiplication of new free electrons ensure the continuous generation of plasma as well as $Ar^+$. The atoms are ejected from targets by impacting the generated $Ar^+$ to the targets. In order to provide sufficient amount of sputtering gas atoms to strike plasma, a minimum pressure must be maintained. The relation between amount of gas atoms and pressure is the ideal gas equation:

$$PV = nRT,$$

(3-2)

where $P$ is pressure, $V$ is volume, $n$ is number of moles, $R$ is ideal gas constant, and $T$ is temperature. The amount of sputtering gas atoms is proportional to the pressure. In order to maintain efficient momentum transfer in each sputtering of target, the atomic weight of sputtering gas should be close to, if not heavier than, that of the target. In the path of depositing on the substrate, the sputtered atoms can be scattered by the background sputtering gas atoms once or twice at a pressure of $10^{-4}$ Torr, and about 50-100 times at $5 \times 10^{-3}$ Torr. One or two scattering collision can reduce adatom energy to 5-20 V while 50-100 times reduces the adatom energy down to about 0.1 V. [90,93,100,105] Thus, the lower background gas pressure will lead to less scattering collisions which bring about a higher adatom energy for the depositing features and often results in a dense film and a smooth surface.
NiTi alloys thin films were deposited using a magnetron sputtering system (Combinatorial Materials Science Series, Kurt J. Lesker Company) located at the Nanofabrication Laboratory of The Pennsylvania State University. The setup for magnetron co-sputtering Ni and Ti is schematically depicted in Figure 3-2. Calibrating operational parameters was conducted to maintain a stable plasma, to minimize the materials sputtered from vacuum chamber, to provide sufficient energy to generate electrons, and to keep enough current in target for high deposition rate. A Ni target and a Ti target were in two guns and directed toward the substrate; the deposition is a co-sputtering scenario. The power applied to the Ni target and the Ti target controlled the deposition rate of each target. The composition of films can be adjusted by varying the deposition rate of each target atoms which is controlled by the applied target power. The Ti target was powered by the allowable maximum of 200 Watts in order to achieve maximum deposition rate. The Ni target power could be varied up to 300 Watts, but here was varied from 75 to 155 Watts since the typical deposition rate of Ni is three times that of Ti. The calibration of
deposition with preset power values was performed. The calibration results on the composition adjustment and co-sputtering deposition rate are shown in Table 3-2. Substrate bias was set 100 Watts radio frequency (RF) for pre-cleaning 600 s. With the parameters set to the same value as the actual deposition, a seasoning procedure of the targets was conducted for 120 s before the actual deposition. The operational pressure parameters were then set at the value of 3.65×10⁻³ Torr, and the Ar flow was set at 19.4 sccm. The working distance between the guns and Si substrate was 8 inches and remained unchanged during the entire series of deposition. The substrate was placed inside the chamber facing downward, and was rotated at 20 rpm. The heat by preheating and post-annealing on the as-deposited thin films is detailed in Section 4.3.

### Table 3-2. Calibration of magnetron sputtering on the relation between power ratio and composition, and on deposition rate.

<table>
<thead>
<tr>
<th>Power configuration *</th>
<th>Composition (at% Ni)</th>
<th>Deposition time (s)</th>
<th>Thickness (nm)</th>
<th>Deposition rate (Å/s)</th>
<th>Ni concentration for as-deposited thin films</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 : 90</td>
<td>75.9</td>
<td>600</td>
<td>72</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td>155 : 195</td>
<td>70</td>
<td>3600</td>
<td>430</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>120 : 195</td>
<td>61.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>110 : 195</td>
<td>60.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>105 : 195</td>
<td>55.7</td>
<td>300</td>
<td>30</td>
<td>1</td>
<td>Ni-rich</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1200</td>
<td>120</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>200</td>
<td>30</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>95 : 195</td>
<td>52</td>
<td>600</td>
<td>60</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>85 : 195</td>
<td>47.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>75 : 195</td>
<td>42.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Target power of Ni (RF) versus Ti (DC), unit in Watts
§ 3.2 Characterization

§ 3.2.1 Composition determination — inductively coupled plasma atomic emission spectroscopy

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) has the highest accuracy in measuring the composition of NiTi alloys thin films, down to 0.5 at% [20], in contrast to 1 at% accuracy in methods using incident beams such as energy dispersive x-ray spectroscopy, and wavelength dispersive x-ray spectroscopy.[20] The basic principle of ICP-AES is the following: After electrons in the materials receive energy from high energy sources, these electrons will be excited to high energy level. After these electrons return to the ground states, characteristic wavelengths of radiation will be emitted. Measuring the emitted wavelengths can determine which element is present within the sample; comparing the intensity of the wavelength to that of known standards gives the absolute concentration of different elements in the sample.

The composition of NiTi films was determined by using ICP-AES (5300 DV, PerkinElmer Inc.) with detect limit of Ti 0.002 µg/mL and Ni 0.006 µg/mL which is located in Materials Characterization Laboratory, The Pennsylvania State University. Kapton tape (10 mm by 5 mm area) was used as the substrate in each deposition for the composition measurements. A mixed acid of HF: HNO₃: H₂O was formed with volume ratio of 1: 1: 20 to dissolve the NiTi film. The absolute mass value for Ti and Ni was determined quantitatively. The weight percent of Ti versus Ni can be calculated by dividing the mass of Ti by that of Ni. The mass of Ti divided by atomic mass of Ti and the divided mass of Ni by atomic mass of Ni gives the atomic percent. Note due to destructive nature of dissolving thin films, Kapton tape, which was not dissolvable to the etchant of dissolving films, were chosen for composition measurement.
## 3.2.2 Microstructural analysis and energy-filtering map — transmission electron microscopy

Electron transparent SiN chips were used as the substrates for direct microstructure characterization. SiN chips were purchased from Ted Pella, Inc.. Each chip consisted of a SiN membrane (~30 nm thick) on top of a Silicon frame (~50 micron thick) which had a hollow center (250 by 250 micron square) to expose the SiN membrane. The SiN membrane was amorphous, and underwent a pre-cleaning with ions for 600 s prior to the actual deposition. The chips were circular with 3 mm diameters in order to precisely fit into the circular mounting hole of the TEM holder. The layout is illustrated in Figure 3-3. The thickness of the as-deposited NiTi film was directly ready for plan-view TEM analysis on the ultrathin SiN. The direct deposition and in-situ characterization circumvents conventional TEM sample preparation, such as polishing and ion milling which could introduce artificial information into the sample. Using a SiN chip enables the real time monitoring of microstructural development associated with crystallization.[78-80]

Energy-filtering TEM (EFTEM) is a nanoanalytical technique for elemental mapping, that is, a two-dimensional distribution of a specific element [115]. EFTEM is based on the electron energy-loss spectroscopy (EELS) which is the analysis of the energy distribution of electrons passing through and inelastically interacting with the specimen. By selecting a narrow energy window on the EELS spectrum, the features associated with the selected window will be monitored over the broad area of the specimen. A relative thickness map can be captured by using log-ratio method:[116] the relative thickness is defined as \( t/\lambda \), where \( t \) is absolute thickness, and \( \lambda \) is the total electron inelastic mean free path.
Figure 3-3. Schematic diagram of the SiN membrane chip. The chip fits exactly into the TEM hole and can be used for multifaceted characterization.

In the current work, EELS and EFTEM were conducted with STEM mode on 200 kV JEOL 2010 LaB6 equipped with a Gatan Imaging Filter (GIF) and a 1024×1024 CCD camera. Digital Micrograph Software was used to acquire the EEL spectra and EFTEM images. The chemical composition and the distribution of each element can be measured in EFTEM images: The signal intensity distribution of each element can be related to the concentration within the specimen. High-resolution transmission electron microscopy (HRTEM) micrographs of fine microstructure were captured in a JEOL 2010 LaB6 TEM with accelerating voltage 200 kV, operating at α-selector = 1, spot size = 1, and smallest objective aperture. The crystal structure
and grain morphology of NiTi thin films were analyzed in a JEOL EM-2010F TEM operating at 200 kV.

§ 3.2.3 Surface analysis — atomic force microscopy

The atomic force microscope is designed to measure local material properties such as height, friction and magnetism by using a sharp tip. The close-range forces between the tip and material surface deflect the cantilever of the tip. A laser beam, which is originally incident to the flat top of the cantilever, will change direction affected by the deflected cantilever. A position-sensitive photo-detector is able to track the changes of the reflected beam. A feedback loop is used to maintain the distance between the tip and the material surface constant so that any height variations on material surface will deflect the cantilever. The resulting changes in the reflected beam are captured so that topographic map of the material surface can be generated.[117]

The surface morphology data was collected on an atomic force microscope (AFM, Dimension Icon, Bruker Corporation) in PeakForce tapping mode using SCANASYST-AIR probes. The probes consisted of a SiN cantilever and a Si probe. The probe had 5 nm nominal tip radius, and 0.4 N/m nominal spring constant. Images were collected at 1 μm by 1 μm with PeakForce setpoints in the 0.5–1.0 nN range and scan speeds 0.25–0.75 Hz. A 128 by 128 line image was first captured with fast scanning speed in order to position the area of interest and to verify the area was free of contamination. 512 by 512 line images were then captured for high-resolution analysis. Offline analysis was performed with Nanoscope Analysis version 1.40. All displayed images had the Z color scale set to a range of −6 nm to 6 nm for consistent comparison.
§ 3.2.4 Crystal structure analysis — x-ray diffraction

Diffraction effects arise when the electromagnetic radiation interacts with the periodic structures which have the length scale comparable to the wavelength of the radiation. The distance between atoms of crystalline materials is 0.15 ~ 0.4 nm, corresponding to the wavelength of x-ray in electromagnetic spectrum. Thus, when the crystalline materials are exposed to x-ray, constructive and destructive interference occurs, manifested as diffraction peaks.[118]

The crystal structure of the heat treated thin films was examined in grazing incident x-ray diffraction (GIXRD). GIXRD uses small incident angles for the incoming x-ray beam and the penetration into a substrate is limited which is suitable for study on surface or layers. GIXRD was conducted in an instrument (X’Pert MPD, PANalytical) with a Cu Kα1 x-ray source (λKα = 1.5418 Å). The x-ray diffraction patterns were collected between 20 and 80 two-theta ranges. The step size was set as 0.02°, and the holding time for each step was 0.5 s.

§ 3.2.5 Heat treatment — post deposition rapid thermal annealing and transmission electron microscopy in-situ heating

Rapid thermal anneal (RTA) is a thermal process with ramp rate typically 20-200 °C/sec. The annealing temperature ranges from 200 to 1250 °C. The capability of increasing to high temperature in a short time is advantageous for minimization of total thermal energy. The minimized thermal energy is required to constrain dopant diffusion, particularly in semiconductor fabrication. The diffusion becomes an issue in conventional furnace annealing where the ramping rate is slow and annealing time is long.

Post deposition heat treatment was conducted in a RTA furnace produced by Allwin21 Corporation. The annealing process consisted of three steps: 1) pre-purge with Ar inert gas for 6 min, 2) ramp to the target temperature which was maintained for the desired duration, and 3)
post-purge with Ar inert gas for 12 min, and naturally cool down. The pre-purge and post-purge were used to maintain the vacuum environment and prevent oxidation. The ramp time was 30 s. Two-stage annealing can be used so that at the end of the first stage of annealing, instead of naturally cooling down, an additional temperature for a certain duration was conducted, and then cooled down. The two-stage annealing can control the microstructure of thin films by nucleating the amorphous films at high temperature, and then promoting grain growth at low temperature.

Transmission electron microscopy in-situ heating was performed using a double tilt heating holder (Gatan 652 Cryo, Gatan Inc.). The heating holder is a type of furnace allowing the observation of the microstructural phase transformations, nucleation, and growth at elevated temperatures. The furnace was made of tantalum, and had low mass, high temperature strength as well as resistance to solid state welding. The low mass allows the furnace the fast response to the heater current. The specimen was clamped to the tantalum furnace in order to ensure the sufficient thermal contact. The temperature was controlled through the heat generated by the current supplied by the controller. The generated heat was conducted to the specimen located at the tip of conductor rod. The maximum operating temperature was 1000 °C, and the ramp rate was manually controlled by increasing the rate of the applied current. The ramp rate of heating was roughly 30 °C/min. The temperature was monitored by using calibrated silicon diode which has a sensitive and linear response to temperature. Bright-field images and diffraction patterns were captured at the predefined value after no drifting occurred to the specimen.

§ 3.2.6 Thermally-induced behaviors in substrate-attached thin films — substrate curvature measurement with temperature capability

For a thin film deposited on a substrate, phase transformations (in addition to thermal expansion, intrinsic defects/boundaries) within the thin film will cause changes to the film stress
which is externally reflected in substrate curvature. A sketch of the curvature is shown in Figure 3-4(A). In Figure 3-4(B), an external force is applied to the film to negate the reaction from the substrate, rendering the film/substrate interface stress-free. After the film is ideally separated from the substrate, all of the forces applied to the film are shown in Figure 3-4(C). After the substrate reaction on the film is determined by measuring the substrate curvature, the film force can be determined by equaling the reaction from substrate. Since the substrate curvature is a function of temperature, film force will be temperature-dependent, and thus by monitoring the temperature at which significant changes occur to the film force, one can accordingly determine the phase transformation temperature and thermal hysteresis. Note that film force has physical dimension of force/length, and thus can be converted to film stress by dividing by the film thickness.

The relation between film stress and substrate curvature is expressed in Stoney's equation: [32,62]

\[ \sigma_f = M_s t_s^2 / (6t_f R), \]

(3-3)

where \( \sigma_f \) is film stress, \( t_f \) is film thickness, \( t_s \) is substrate thickness, \( M_s \) is biaxial modulus of a substrate (a constant specific to a substrate), and \( R \) is radius of curvature in the substrate. Since the substrate before deposition is generally not flat, it is necessary to measure the radius of curvature in substrate prior to and after deposition, and thus \( R \) can be calculated in the following equation:

\[ R = R_1 R_2 / (R_1 - R_2), \]

(3-4)

where \( R_1 \) and \( R_2 \) are radius of curvature in the substrate before and after deposition, respectively.
Figure 3-4. (A) Schematic of the shape of a thin film constrained on a substrate. (B) The shape of the thin film when an external force is applied to render the film/substrate interface stress-free. (C) The shape of the thin film separated from the substrate. The applied force is equivalent to the reaction in the substrate-constrained condition. Adapted from [62].

A stress-temperature measurement was conducted in Flexus (FLX-2320, Tencor Instruments). The temperature range in Flexus was 25 °C to 500 °C, and the heating rate can be up to 30 °C/min. The film stress at a target temperature was obtained by measuring the curvature of substrate before and after the film was deposited. In the stress-temperature plot, the slope due to thermal expansion is typically a straight line; any temperature point at which there is a distinct slope deviation from the straight line is associated with phase transformations. In order to accelerate the measurement of tens of samples, one substrate from the substrate groups was measured the same number of times prior to deposition as the amount of substrates. The measured pre-curvature values were saved. The post-curvature of each substrate with different film conditions (such as different thickness, different composition, or different heat treatment) was measured and superposed to each value of the pre-curvature. The film stress at each substrate can be thus obtained by using the equation (3-3) and (3-4). Note that compared to the
methodology of measuring the same substrate before and after film deposition, the superposition of the post-curvature of each substrate with different films to the pre-curvature values of one substrate will only affect the absolute stress value, but not the stress change interval and the phase transformation temperature. Since the stress change interval and the transformation temperature, rather than the actual film stress, are of interest in phase transformations, the superposition methodology was utilized throughout the research.
Chapter 4

Results and discussions

PREVIEW

Energy of depositing atoms from elemental Ni and Ti targets is controlled by biased target ion beam deposition in order to prepare high-quality NiTi thin films. The prepared films range the thickness from tens to hundreds of nanometers, and span the composition from Ni-rich, near equiatomic NiTi, to Ti-rich. Due to enhanced adatom energy, the surface topography, interfacial features, and crystallization behaviors of NiTi thin films fabricated by biased target ion beam deposition highly differ from the benchmark films prepared by magnetron sputtering. Biased target ion beam deposition produces NiTi thin films with small hysteresis phase transformations in contrast to those in magnetron sputtered films.

§ 4.1 NiTi thin films fabricated by BTIBD co-sputtering from elemental Ni and Ti targets

Shape memory alloys thin films are of great interest\cite{28,32,71-73,78,82,84,119} because of the highest work output density (about $10^7$ J m$^{-3}$)\cite{11} with high actuation stress (over 500 MPa)\cite{1} and large recoverable strains (up to 10 \%)\cite{2} among the smart materials families (Electromagnetic, thermos-pneumatic, Electrostatic, etc.)\cite{11}. Advancing miniaturization to nanoelectromechanical systems requires the fabrication of nanoscale shape memory alloys and the characterization of properties at the nanoscale\cite{9,30,120,121}. Deposition of high-quality nanoscale thickness thin films is an essential step. To date, magnetron sputtering is the most
commonly used film technology to deposit shape memory alloys thin films with micrometer thickness.[11,112-114] When nanoscale thickness films were deposited and tested by the stress-temperature method[32,114] and by resistivity-temperature method,[28,71] a critical thickness (~100 nm) became apparent, below which there was no shape memory response.[28,32,71] The shape memory response was prohibited most likely due to, in addition to the constraint from free surface and substrate-film interface,[31,32,71] the difficulty in the repeated, precise control of composition[82,113] and in atomically tailoring the film growth.[19,52] BTIBD, a recently-developed film technology,[19,90,91,93,111] is well-suited for atomically engineered thin films given its wide range of processing pressures, ability to control adatom energy, and remarkable repeatability and uniformity.

NiTi alloys films with thicknesses on the order of 100 nm are co-sputtered from separate Ni and Ti targets utilizing BTIBD technique. Co-sputtering enables the fabrication of NiTi thin films with Ni-rich, near-equiaatomic, and Ti-rich compositions. Near-equiaatomic ranges from 49.5 to 50.5 at% Ni based on [20], and the Ni-rich and Ti-rich regions are assigned outside that range. For preparing NiTi alloys thin films, the importance of controlling the alloy composition is reflected in Figure 2-2(B): The ordinate axis is the temperature at which the thermal-induced martensitic transformation (TIMT) starts (referred to as $M_s$), and within a very small range of compositions, 0.1 at% Ni change can facilitate a 10 °C change in $M_s$. Since the TIMT is the foundation of shape memory behaviors for practical application, such a large change in $M_s$ will deteriorate the shape memory performance and even result in an uncontrolled status. Therefore, the operating parameters in BTIBD are systematically adjusted for precisely tuning the alloy composition as well as deposition rate. Additionally, in this section, the BTIBD films (nearly 150-nm thick) are compared to a control group of films deposited by magnetron sputtering. The morphological observations in TEM, composition measurements in ICP-AES, and surface roughness measurements from AFM are reported. Heat treatment is able to crystalline the as-
deposited amorphous films and is utilized to crystallize BTIBD NiTi films. Grain morphology of the B2 and B19’ crystal structures after heat treatment are demonstrated. The coexistence of B2 and B19’, after heat treatment of as-deposited NiTi films, confirms the potential for phase transformations, and thus shape memory behaviors. Without optimizing the operating parameters, BTIBD yields high-quality NiTi films at the ultrathin level.

Figure 4-1. TEM image showing a BTIBD Ni-rich NiTi thin film in the as-deposited state at room temperature. The inset is a diffraction pattern which does not reflect crystallinity.

A TEM image of Ni-rich Ni<sub>60.2</sub> Ti<sub>39.8</sub> (at%) thin film prepared using BTIBD is shown in Figure 4-1. The inset diffraction pattern shows diffuse rings that indicate the film is amorphous. It is well known that as-deposited NiTi films are amorphous [20,78,82]. The image is gray and featureless similar to previously reported observations for amorphous NiTi thin films [78,82]. The observation that as-deposited BTIBD films at room temperature are amorphous is consistent with the amorphous nature in as-deposited films prepared by magnetron sputtering.
The surface topography is measured using AFM. Three characteristic roughness metrics are peak-to-valley roughness ($Z_{\text{Range}}$), average roughness ($R_a$), and root mean squared (RMS). Measurements are plotted as a function of the Ni concentration in the NiTi thin film in Figure 4-2. The average roughness and RMS are very close in Figure 4-2. There is a miniscule increase with increasing Ni content. The peak-to-valley roughness also displays a miniscule variation though the magnitude is more substantial relative to the other measures. By all three metrics, as-deposited NiTi films prepared by BTIBD are less rough than magnetron sputtered films. $R_a$ and RMS of BTIBD films are consistently less than 0.3 nm over a large composition range from 28 to 74.6 at%.
Figure 4-3. A BTIBD Ni-rich Ni$_{60.2}$Ti$_{39.8}$ (at%) thin film in the as-deposited state at room temperature: (a) TEM image with diffraction pattern illustrating that the film is amorphous; (b) surface topography measurements from AFM analysis; (c) cross-section profiles from (b).

Figure 4-3 shows TEM and AFM analysis for the Ni$_{60.2}$Ti$_{39.8}$ (at%) thin film prepared by BTIBD. Figure 4-3(a) is a higher magnification of Figure 4-1, and shows diffuse ring in the inset and featureless microstructure in bright-field image, indicating the film is amorphous. The AFM image is shown in Figure 4-3(b). The $Z_{Range}$ height was measured along three different cross sections as shown in Figure 4-3(c). Along each section, the average $Z_{Range}$ is less than 0.6 nm. Similarly the Ti-rich Ti$_{79.2}$Ni$_{20.8}$ and near-equatomic Ti$_{51.4}$Ni$_{48.6}$ thin films fabricated in BTIBD are amorphous and uniformly ultra-smooth, with the $Z_{Range} < 0.6$ nm.

Figure 4-4. An as-deposited Ni-rich Ni$_{55.7}$Ti$_{44.3}$ (at%) thin film made by magnetron sputtering at room temperature: (a) TEM image with diffraction pattern illustrating that the film is amorphous, (b) surface topography measurements from AFM analysis; (c) cross-section profiles from (b).
As a comparison to Figure 4-3, Figure 4-4 shows the TEM and AFM analysis for a Ni-rich Ni_{55.7}Ti_{44.3} (at%) thin film. The diffraction pattern, as well as the featureless surface in Figure 4-4(a), corroborate the film is amorphous. Along cross sections of the AFM topography in Figure 4-4(b), the $Z_{Range}$ height is much larger than those for the BTIBD film in Figure 4-3.

From Figure 4-2, the roughness measurements of magnetron sputtered thin films are highly composition-dependent with respect to BTIBD films. When the magnetron sputtered film is viewed at a high magnification in TEM, Figure 4-5(a) exhibits striking features.

Figure 4-5. A magnetron sputtered Ni-rich Ni_{55.7}Ti_{44.3} (at%) thin film as-deposited at room temperature: (a) TEM image showing features that are not evident in Figure 4-4 (a); (b) Energy-filtering TEM thickness map contrast which is complementary to (a); (c) thickness profile across the region within dashed boundary in (b).

EFTEM of the region corresponding to Figure 4-5(b) provides the local normalized thickness ($t/\lambda$) map via the log-ratio method [116,122], where $t$ is the absolute thicknesses and $\lambda$ is the inelastic mean free path. The $t/\lambda$ map for Figure 4-5(b) is demonstrated in Figure 4-5(c). The dark area in Figure 4-5(a) allows less beam through to be recorded so that in thickness map it is bright. The white channels in Figure 4-5(a) correspond to the dark lines in thickness map. Non-uniform contrasts illustrate that the thickness of the dark area and that of the channels is not the same. The logarithm of the integral of the entire spectrum is divided by the integrated intensity of zero-loss peak. Since the film was deposited in a rotated condition and
thus a uniform composition, $\lambda$ is constant, and $t/\lambda$ gives the profile of thickness distribution. The thickness profile of one selected area, marked as dashed rectangle in Figure 4-5(b), is shown in Figure 4-5(c). The results suggest that the densest materials are in the island areas. Relative to the island areas, the channels are considered unfilled.

Growth of NiTi thin films prepared by BTIBD and magnetron sputtering can be classified in the Volmer-Weber (VW) model, which is common when metals are deposited on SiO$_2$ and grown near room temperature [54]. Physical vapor deposition (PVD) involves the condensation of vaporized component of materials on the surface of substrates under vacuum. The stages of thin film growth in PVD are nucleation, growth, and coalescence [54]. The deposition of thin solid film commences with a nucleation stage and clusters of atoms form islands on the surface of substrates. A growth stage follows as deposition continues, in which islands take on impinging atoms and grow as nuclei until they reach a sub-critical size. A coalescence then starts in order to reduce surface area: Small islands coalesce and agglomeration facilitates the formation of large islands until a continuous film is deposited.

Agglomeration is related to surface mobility of the absorbed species, and increasing the surface mobility of adatom facilitates the agglomeration. For the ultrathin films prepared by magnetron sputtering, unfilled channels separate a network of islands, rather than the islands coalescing to form a continuous film. The unfilled channels appear white in TEM images, which are not obvious for the ultrathin BTIBD NiTi films. (Compare Figure 4-3(a) and Figure 4-5(a)). Hylton et al. specified that two advantages of BTIBD are control of adatom energies and a large range of process pressures [90]. The findings from the microstructural comparison confirm that BTIBD enables adatom surface mobility (and thus mass transfer) of co-sputtered Ni and Ti atoms such that coalescence during deposition of NiTi films is enhanced. Of note is that neither the BTIBD nor the magnetron deposition parameters were intentionally optimized to minimize or eliminate unfilled channels. When using magnetron sputtering, the microstructural
heterogeneities were consistently observed. Moreover, the surface roughness of magnetron sputtered films is composition dependent but BTIBD films are consistently smooth; with the correlation of the channels to surface roughness, the results clearly suggest that BTIBD inherently enhances coalescence. Thus, BTIBD is advantageous for the deposition of ultrathin smooth NiTi films at different compositions.

The underlying mechanism of shape memory behaviors is martensitic transformation, the transformation between two crystallographic phases, B2 phase and B19' phase, in the case of NiTi based SMAs. Since the BTIBD NiTi films deposited at room temperature did not show any crystallographic phase evidenced by the diffuse ring in the diffraction pattern of Figure 4-1, Figure 4-3, and Figure 4-4 and crystalline films are required for the shape memory behaviors, the films were subjected to heat treatments in order to achieve crystallization. The heat treatment parameters are listed in Table 4-1.

Table 4-1. Summary of heat treatment parameters and the resulting crystallographic phase in three NiTi films.

<table>
<thead>
<tr>
<th>Composition (at% Ni)</th>
<th>Heat treatment</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>28.0</td>
<td>450 °C for 1 min, then 500 °C for 5 min</td>
<td>B2, B19', Ti2Ni</td>
</tr>
<tr>
<td>49.7</td>
<td>450 °C 1 min, then 500 °C for 5 min</td>
<td>B19', Ti2Ni</td>
</tr>
<tr>
<td>51.7</td>
<td>450 °C 1 min, 500 °C 5 min, 500 °C 3 min, and then 515 °C for 3 min</td>
<td>B2, B19'</td>
</tr>
</tbody>
</table>

Figure 4-6 presents TEM analysis on grain morphology (a-c) and crystal structure (d-f) of Ni28.0Ti72.0, Ni49.7Ti50.3 and Ni51.7Ti48.3 (at%) thin films after the heat treatment. Bright-field images in Figure 4-6(a-c) shows all three films are crystallized with different grain size. Qualitatively, Ni49.7Ti50.3 film in (b) has the largest grains, about ~200 nm, and grains of 120 nm are in Ni28.0Ti72.0 film while Ni51.7Ti48.3 film produced the smallest grains among the three films, roughly 70 nm. Diffraction patterns in (d-f), after overlapping with theoretical patterns of B2,
and B19', are demonstrating that B19' are present in all three films. Of note is that Ni_{49.7}Ti_{50.3} has only B19' phase without B2 compared to both phases existing in Ni_{28.0}Ti_{72.0} and Ni_{51.7}Ti_{48.3}. The rationale for observed grains size and crystal structure is related to composition-sensitive nature of NiTi, reflected in Figure 2-2(A).

![Bright-field TEM images](image)

Figure 4-6. Bright-field TEM images (a-c) and corresponding diffraction patterns (d-f) showing austenite (A) and martensite (M) for BTIBD films of Ni_{28.0}Ti_{72.0}, Ni_{49.7}Ti_{50.3} and Ni_{51.7}Ti_{48.3} (at%) after heat treatment. The grain size in (b) is larger than (a) which is larger than (c). Indexing diffraction patterns B19' is present in (a-c) while only (a) and (c) have B2. For clarity, Si_{3}Ni_{4} and Ti_{2}N are listed in Table 4-1 instead of being indexed in diffraction patterns.

As in Figure 2-2(B), transformation temperature of Ni_{49.7}Ti_{50.3} is about 320 K which is higher than room temperature (294 K), probably leading to complete transformation from B2 to B19. This complete transformation explains the existence of only the B19' phase at room temperature in Ni_{49.7}Ti_{50.3}. Also based on Figure 2-2(B), Ni_{28.0}Ti_{72.0} film will have a similar
transformation temperature to Ni$_{49.7}$Ti$_{50.3}$, and thus should have only the B19’ phase at room temperature. However, both B2 and B19’ phases are present in Ni$_{28.0}$Ti$_{72.0}$ film. The coexistence can be explained by the grains size effect on transformation temperature reported in [30,44]. The smaller grains in the Ni$_{28.0}$Ti$_{72.0}$ film of Figure 4-6(a), compared to the Ni$_{28.0}$Ti$_{72.0}$ film in Figure 4-6(b), will facilitate an increase in the transformation barrier. As more driving force from thermo-mechanical energy is required to initiate the transformation, the transformation temperature will decrease to provide the additional energy by undercooling. With the lowered transformation temperature, the Ni$_{28.0}$Ti$_{72.0}$ film undergoes an incomplete transformation at room temperature. The preceding argument cannot explain the coexistence of B2 and B19’ phases in the Ni$_{51.7}$Ti$_{48.3}$ alloy film based on Ni-rich composition. The coexisting phases in Ni$_{51.7}$Ti$_{48.3}$ are attributed to the additional high temperature heat treatments which probably lead to increased stress. The stress may facilitate the formation of B19’ in B2 matrix.

In summary, the potential of co-sputtering Ni and Ti using BTIBD to deposit NiTi films that are a few 100 nanometers thickness is demonstrated. BTIBD is capable of producing a range of compositions and microstructures in the NiTi films. For both BTIBD and magnetron sputtering, operational parameters were adjusted with the aim of controlling composition and deposition rate. Adjusting certain magnetron process parameters could possibly improve the quality of thin films: biasing the substrate and/or varying the temperatures of substrate and target to affect adatom mobility [19]. However, BTIBD is shown to readily enable composition control and low-energy bombardment, and to consistently yield high-quality ultrathin NiTi films at a large range of compositions. The films are uniform at the nanoscale without additional adjustments on operating parameter in BTIBD.

The as-deposited BTIBD NiTi films are amorphous. After heat treatment, crystallographic phases, B2 phase and B19’ phase are obtained. These two phases are prerequisites for martensitic transformation in NiTi. The existence of B2 and B19’ phases exhibits
potential for phase transformations, and thus shape memory behaviors in 100 nm BTIBD NiTi thin films. For conventional fabrication of NiTi thin films via magnetron sputtering, size effects are expected when the film thickness is below 0.5 µm and/or the grain size is between 50 and 100 nm [18, 20]. The high-quality thin films prepared by BTIBD will enable unparalleled insight into size effect and composition effects on the shape memory capacity of NiTi films.

§ 4.2 Structure and interfacial analysis of nanoscale NiTi thin films fabricated by BTIBD

To date, magnetron sputtering is widely used for deposition of NiTi shape memory alloys thin films.[114,123,124] During the MT between B2 phase and B19’ phase in NiTi thin films, resistive forces to the lattice distortion and twinning deformation mechanisms arise from the substrate/film interfacial diffusion layer and the surface oxidation layer.[31,32,125] Oxygen contamination is inherently curtailed at higher vacuum, as less residual oxygen is present to react with titanium atoms.[20] Diffusion at the substrate/film interface typically results from heat treatments that are necessary to crystallize the otherwise amorphous as-deposited NiTi alloys films.[20,32] For a film that exhibits shape memory functionality, those layers will make up a small ratio of the overall thickness and the MT can occur within a volume ratio of the thin film material unaffected by resistive forces. The interfacial diffusion layer has been reported as 120 nm in a crystalline NiTi film with 4 micron thickness,[126] and 10 nm in a 234-nm-thick film.[71] Despite the disparity in film thickness, the respective layer thickness-to-film thickness ratios are ~3 % and ~4.3 % and the MT was reported for both films. As film thickness decreases to values below 100 nm, the diffusion layer thickness can account for over 15% of the film thickness; such a ratio can impose a pronounced constraint to the extent that the MT is suppressed.[32,71] An ideal preparation method for ultrathin (thickness on the order of 10 nm)
NiTi films that exhibit MT will minimize oxidation while minimizing the ratio of diffusion layer thickness to film thickness.

Biased target ion beam deposition (BTIBD), a deposition method able to produce high-quality ultrathin films,[93,105,106] was employed. BTIBD has been demonstrated the potential of preparing NiTi thin films with precise control of composition (down to 0.5 at.%), broad composition range (from 28 to 74.6 at.%), smooth surfaces (less than 0.3 nm roughness), and crystallographic structure of B2 and B19' for thin films with 100 nm thickness.[19] BTIBD has independent control on target bias and on ion beam source to control adatom mobility on the surface of growing film to achieve the tailoring on surface and interface. This system has a low base pressure (< 10⁻⁷ Torr) and lower processing pressure (~10⁻⁴ Torr) compared to conventional sputtering (>10⁻³ Torr), thus minimizing oxygen contamination.[105]

The current section details the interfacial information and structure of a 65-nm-thick NiTi film prepared by BTIBD. The minimum thickness of magnetron sputtered NiTi films that exhibit the MT is reportedly around 100 nm.[32,71] Below that critical thickness, the resistance forces can become severe and suppress the MT.[29,31,32,71] The ratio of diffusional layer thickness to film thickness is assessed and the existence of the B2 structure in a sub-100-nm BTIBD film is reported. The accompanying surface roughness was examined using AFM analysis to confirm consistency with the previously reported 100-nm-thick film. The grain size and morphology, crystal structure, and film/substrate interface were characterized using TEM analysis. High-resolution TEM has the advantage of profiling the interfacial thickness variation along lateral variation compared to the commonly employed pointwise thickness profiling in x-ray photoelectron spectroscopy (XPS),[32,127] or in secondary ion mass spectrometry (SIMS).[124]

Surface views in Figure 4-7 show the crystal structure and surface morphology. The inset diffraction pattern in Figure 4-7(a) consists of sharp diffraction rings. The rings stem from the diffraction of numerous grains with different orientations and confirm that the film is
polycrystalline. The white and black areas in the bright-field TEM image of Figure 4-7(a) correspond to differently oriented grains. The average grain size is about 15 nm, which was determined using the average grain intercept (AGI) method. The crystallographic plane indices are superposed in the diffraction pattern and are identified as B2, which is the parent phase in the MT underlying shape memory behaviors. Pure B2 phase without other micro-constituents can allow for microstructure control with heat treatment and maximize the material undergoing the MT and thus optimize the achievable shape memory strains.[17,113]

The current films are crystalline in the as-deposited condition, whereas, the as-deposited films were amorphous in our previous work.[19] Compared to our previous work, the duration for low-energy ion beam pre-cleaning of the substrate in this work is twice as long. The threshold crystallization activation energy of NiTi film was reported as 475.6 kJ/mol.[79] The prolonged pre-cleaning likely elevated the energy of the deposited film into thermal activated regime for crystallization.

The surface morphology of the current 65 nm NiTi film is shown in Figure 4-7(b). In the 1 by 1 \( \mu \text{m} \) scanning area, the nearly uniform color underscores that the Z values are spatially equal. The surface roughness, root mean square (RMS) value equals 0.357 nm. The value is comparable to that for the 100 nm BTIBD NiTi film (RMS=0.229 nm) in preceding section. The results support that BTIBD promotes a smooth surface for ultrathin films. This observation substantiates that low-energy ion beam can smoothen the surface of the crystalline film. Unfilled channels that can roughen the film surface may not develop when BTIBD is employed, as the technique can facilitate moving the irregularly arranged atoms and thus fill the channels.[19,90]
Figure 4-7. (a) TEM bright field micrograph with the diffraction pattern inset and (b) AFM image of the NiTi film surface.

Cross-sectional views of the NiTi film are shown in Figure 4-8 and Figure 4-8(c) and the corresponding diffraction patterns in Figure 4-8(b) confirm grain morphology. From the left to the right in Figure 4-8(a), non-uniform contrasts are evident along the film. The contrasts alternate between bright areas and dark areas. In Figure 4-8(b), the diffraction pattern on the cross section of the thin film shows discrete spots with faint rings. The bracketed diffraction spots are aligned in a directional manner. Directionality underscores that the cross-section grains exhibit preferential orientation. To further scrutinize the structure, the dark-field image is shown.
in Figure 4-8(c). The image corresponds to the red-circled spot in Figure 4-8(b), which is investigated because it likely corresponds to numerous grains with the same diffracting conditions so that they accumulate into that large spot. The bright areas in the dark-field image are those diffracting grains, which appear aligned along the film thickness direction.

Figure 4-8. (a) TEM bright-field micrograph with two lines delineating the interface between the film and substrate. (b) Diffraction pattern with a white bracket that highlights the directionality of diffraction spots. (c) Dark-field micrograph corresponding to the red-circled diffraction spot in b). High resolution TEM images in (d) and (e) show the boxed regions in (c).

In the high-resolution image of Figure 4-8(d), yellow lines outline several oriented grains. Those grains are roughly 2 nm in width and 5 ~ 10 nm in length. The larger length dimension compared to the width resembles the fibrous structure.[55,56] From the top view in Figure 4-7(a), the grains are ~15 nm in size and larger than the cross-section size 5 ~ 10 nm and the proportions resemble the “domed” top description of fibrous grains.[55,56,128] The appearance is consistent with the characteristics in Zone T of Thornton structure-zone model.[55,56]

Two white lines in Figure 4-8(a), (c) and (e) delineate the interface between SiN and the NiTi film. The thickness of the inter-diffusion interface layer is estimated around 2.5 nm by
measuring the distance between the two lines. Temperatures greater than 500 °C and annealing time up to several hours can significantly accelerate the inter-diffusion. Furthermore, it can be affected by the film intrinsic stress, which critically depends on the mismatch between SiN/NiTi film.[20] The thin interface in this study supports the prolonged pre-cleaning as an alternative pre-heating with lower temperature 80 ~ 120 °C and shorter duration <1 hour albeit the mismatch-induced stress can still play a role. In addition to facilitating the minimal interface, the pre-heating brings about the formation of B2 structure without other unwanted microstructural phases.

Figure 4-9. Plot of diffusion layer thickness to film thickness ratio versus film thickness. The references for square and triangle markers are listed beside the plot; the substrate is listed first and followed by the deposition method and heat treatment method. The circle marker is the measurement on BTIBD film.

Figure 4-9 shows the relation between film thickness and ratio of diffusion layer thickness to film thickness for available data in literature and the current work. Reportedly 100 nm is the threshold and NiTi thin films should be above it in order to exhibit the MT.[32,71] The
black vertical dashed line represents that threshold. Triangle markers represent the film
thicknesses above the threshold value that exhibit the MT. As stated earlier, the ratio of diffusion
layer to film thickness should be kept below a certain limit in order to facilitate the MT.[71,126]
Consistent with that understanding, a limit ratio, is identified roughly 0.05, by a horizontal dashed
line in Figure 4-9. The region below the limit is highlighted in yellow. A single data point for a
film thickness that is close to BTIBD film is included and its ratio is much higher than BTIBD
film. MT is not reported in that film which may be due to the high ratio. The ratio of diffusion
layer to film thickness in BTIBD film is below the limit of the yellow region, even though the
film thickness (65 nm) is smaller than the threshold (100 nm).

The authors acknowledge that different substrates can affect the thickness of the diffusion
layer. A recent work showed that the diffusion layer of a NiTi film sputtered onto a SiN substrate
(140 nm) was largest compared to the layer (120 nm) on a Si substrate, as well as the layer (30
nm) on a SiO₂ substrate.[126,127] However, for the SiN substrate used for BTIBD film, a
miniscule diffusion layer (2.5 nm) is measured, which attribute to the nature of the BTIBD
technique.

In summary, the surface and cross-sectional morphology of 65 nm NiTi thin films
prepared by BTIBD exhibited smoothness and continuity, i.e. without holes. BTIBD employs a
low-energy ion beam source, high vacuum base pressure and low processing pressure. Moreover,
the technique allows for controlling the adatom energy over a wide range to modify film quality.
Consistent with the work on 100-nm-thick NiTi films, the observation suggests that BTIBD films
remain continuous and dense down to 65 nm, which is distinct from the features of islands and
channels (representing a lack of material) reported in magnetron sputtered films.[19] The B2
crystal structure, the essential phase for MT, occurs in the as-deposited film with minimal
interfacial diffusion, presumably due to the ion beam preheating of the substrate. The B2
structure is pure, i.e. not mixed with other unwanted microstructural phases, without the use of
high-temperature post-deposition annealing. The pure B2 structure should enable the tailoring of microstructure and maximization of the shape memory strains related to the film being predominantly B2 at the onset of MT. A regime is identified for the ratio of minimal interfacial diffusion to film thickness, for which the MT readily occurs for film thicknesses above the threshold, 100 nm. Despite the current 65 nm films being below that thickness threshold, the ratio is within the aforementioned regime, thereby providing potential to further advance the minimum thickness of thin films that exhibit MT.

§ 4.3 Crystallization and microstructural development of nanoscale NiTi thin films fabricated by BTIBD

Crystallization heat treatment is necessary to produce the B2 atomic crystal structure for the crystallographically reversible martensitic phase transformation that results in shape memory behaviors.[11,113,114] As-deposited NiTi thin films are typically amorphous and do not exhibit shape memory behaviors.[114,123] Crystallization of the as-deposited films is essential to tailoring the microstructure such as grain size, and to avoiding unwanted microstructures such as deformation-induced defects.[44,129-135] Crystallization is typically accomplished by post-deposition annealing.[114] To date, there is only one systematic study of magnetron sputtered films (~200 nm thick) during post-annealing.[79-82] Furthermore, in bulk materials, a critical grain size of 50 nm has been reported to significantly increase the energy barrier of martensitic transformation, which suppressed shape memory behaviors.[30,48] The preceding sections on BTIBD films reported preliminary microstructure characterization showing grain sizes nearly three times the critical size in film thicknesses on the order of 100 nm.[19] Understanding the crystallization of high-quality nanoscale thickness films fabricated using BTIBD will provide a
basis to tailor the microstructure evolution for furthering shape memory functionality into the nanoscale.

§ 4.3.1 Influence of surface morphology on crystallization and microstructural development

BTIBD has been demonstrated capable of producing nanoscale thickness NiTi thin films with the following features: a broad range of compositions, ultra-smooth surface, minimal diffusional interface, and transformable crystal phases.\[19,111\] Furthermore, the thin films produced by BTIBD maintain high-quality even on the order of a few tens of Angstroms;\[91\] the demanding quality at the ultrathin level is challenging for magnetron sputtering which is suitable to deposit thick films.\[91,109\]

This section investigates the crystallization and the microstructural development of nanoscale thickness NiTi thin films fabricated by BTIBD. \textit{In-situ} TEM is used to monitor the development of grain morphology and crystal structure. The \textit{in-situ} monitoring is augmented by \textit{ex-situ} post-deposition heating on as-deposited films in the composition range from Ti-rich to Ni-rich. The surface morphology is examined using an AFM in order to expound on the microstructure characterization. The local film density is examined using scanning transmission electron microscopy (STEM) and energy dispersive x-ray spectroscopy (EDS). The results for films fabricated using BTIBD are compared to those for films fabricated using magnetron sputtering.

For crystallization, the as-deposited NiTi thin films were heat treated either \textit{in-situ} (using the TEM heating holder) or \textit{ex-situ} (using post-deposition RTA, Allwin21 Corp.). The heat treatment and sample details are shown in Table 4-2. The samples are grouped according to the Ni concentration: Ni-poor/Ti-rich, near-equatomic, and Ni-rich composition.\[19\] The heating
parameters were chosen based on the reported parameters [82,131] and the attempted parameters in preliminary tests.[19] The parameters were maintained for each sample until the sample had completed the crystallization. Note that the time and temperatures differed due to samples having different compositions and fabrication methods.

Table 4-2. Heat treatment parameters and sample details of NiTi thin films.

<table>
<thead>
<tr>
<th>Fabrication technique</th>
<th>Heat treatment Apparatus</th>
<th>Composition (at% Ni)</th>
<th>Thickness (nm)</th>
<th>Heat treatment Temperature (°C) and time (min)</th>
<th>Figures showing micrographs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnetron sputtering</td>
<td>TEM</td>
<td>42.2</td>
<td>30</td>
<td>490 °C 50 min, then 500 °C 17 min, to 520 °C 15 min, to 550 °C 23 min, to 610 °C 29 min, to 650 °C 28 min, to 700 °C 10 min</td>
<td>Figure 4-12. (a), (d)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>52</td>
<td>60</td>
<td>490 °C 5 min, then 500 °C 32 min</td>
<td>Figure 4-12. (b), (e)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>55.7</td>
<td>30</td>
<td>450 °C 40 min</td>
<td>Figure 4-10. (a)–(i)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>120</td>
<td>500 °C 30 min</td>
<td>Figure 4-12. (c), (f)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>49.7</td>
<td>99.7</td>
<td>450 °C 1 min, then 500 °C 5 min</td>
<td>Figure 4-13. (a), (e)</td>
</tr>
<tr>
<td>BTIBD</td>
<td>RTA</td>
<td>51.7</td>
<td>101.3</td>
<td>450 °C 1 min, 500 °C 5 min, 500 °C 3 min, and then 515 °C 3 min</td>
<td>Figure 4-13. (b), (f)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>54.6</td>
<td>105.3</td>
<td>450 °C 1 min, then 500 °C 5 min</td>
<td>Figure 4-13. (c), (g)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>62.5</td>
<td>120.2</td>
<td>450 °C 1 min, then 500 °C 5 min</td>
<td>Figure 4-13. (d), (h)</td>
</tr>
<tr>
<td></td>
<td>TEM</td>
<td>60.2</td>
<td>114.5</td>
<td>450 °C 10 min, then 500 °C 50 min</td>
<td>Figure 4-11. (a)–(i)</td>
</tr>
</tbody>
</table>

TEM images show the initiation and evolution of crystallization during in-situ heat treatment of films that were fabricated using magnetron sputtering (Figure 4-10(a)–(i)) and using BTIBD (Figure 4-11(a)–(i)). The composition of the BTIBD film and the magnetron sputtered film are Ni-rich, in general. In the magnetron sputtered film, diffraction patterns obtained before
heating in Figure 4-10(a) show diffuse rings that indicate the as-deposited film is amorphous. During heating, the appearance of sharp and clear rings in Figure 4-10(d) indicates the formation of crystals. After heating, well-defined rings become obvious in Figure 4-10(g); indexing confirms that the crystal structure is B2. As for microstructure, the TEM image in Figure 4-10(b) appears featureless and the high magnification image in Figure 4-10(c) reveals a network of large gray, circular regions surrounded by white boundaries. The gray regions are defined as “islands” and the white boundaries as “channels” in preceding sections.[19] Crystals appear during heating, marked with a solid arrow in Figure 4-10(e). In Figure 4-10(f), crystals span channels and seem to merge islands as pointed out by open arrows. The crystals are about 8 nm in diameter. After heating, it is evident in Figure 4-10(h) and Figure 4-10(i) that the crystal size increases modestly to ~10 nm in diameter. Note that white boundaries are faintly visible during and after heating.

The diffraction pattern in Figure 4-11(a) is for the film fabricated using BTIBD before heating and the diffuse rings within the pattern indicate an amorphous film. The heat treatment (450 °C, 10 min) for BTIBD film in Figure 4-11(d)–(f) is the same as that for magnetron sputtered film in Figure 4-10(d)–(f). For BTIBD films, however, diffraction spots are apparent in the diffuse rings in Figure 4-11(d). After heating, discrete diffraction spots exist in Figure 4-11(g). The spots belong to the diffraction ring pattern for the B2 crystal structure. The appearance of discrete diffraction spots underscores that large crystals, which have crystallographic planes of the same orientation, can form in BTIBD films. The BTIBD film is featureless in both low (Figure 4-11(b)) and high (Figure 4-11(c)) magnification TEM images, in stark contrast to the magnetron sputtered film. Heat treatment produces giant, compared to magnetron sputtered film (see Figure 4-10(e)), crystals that are more than 100 nm in diameter as circled in yellow in Figure 4-11(e). Also, small crystals circled in yellow in Figure 4-11(f) have ~5 nm in diameter. Upon visual inspection for a qualitative comparison with Figure 4-10(f), the
amount of crystals increases for the BTIBD film. After heating in Figure 4-11(h) and Figure 4-11(i), the amount of giant crystals, with a size larger than 200 nm, noticeably increases; one example crystal is circled in yellow in Figure 4-11(h). In general, the crystal sizes are on the order of 50 nm in diameter.

Figure 4-10. (a), (d), (g), TEM diffraction patterns and (b), (e), (h), (c), (f), (i), bright field micrographs for magnetron sputtered thin films during in-situ heating in the TEM. The high resolution images (f) and (i) correspond to the boxed regions in (e) and (h). The arrow in (e) marks a formed crystal. In (f), the open arrows point at the location of channels spanned by crystals. The diffraction pattern in (g) includes the indexed B2 pattern superposed at the top-right corners.
The microstructure for the *ex-situ* (i.e. post-deposition RTA) heat treatment of Ni-poor (42.2 at% Ni) and Ni-rich (52 at% Ni and 55.7 at% Ni) magnetron sputtered films (Figure 4-12) are contrasted with BTIBD films (Figure 4-13) having near-equiaatomic (49.7 at% Ni) and Ni-rich (51.7 at% Ni, 54.6 at% Ni, and 62.5 at% Ni) composition. As for all the magnetron sputtered films in the as-deposited condition in Figure 4-12(a)–(c), a network of channels surround island regions. The findings illustrate that channels and islands are ubiquitous for magnetron sputtered films, which we attribute to limited adatom mobility playing an important role for the nanoscale thickness film deposition. The images after heating in Figure 4-12(d)–(f) reveal that the merging
of islands prevails, marked with open arrows. In Figure 4-13(a)–(d), all the as-deposited BTIBD films are featureless in comparison with magnetron sputtered films. After heat treatment, crystals are formed in Figure 4-13(e)–(h). On average, the size of crystals in the BTIBD films (>50 nm) is larger than that (10 ~ 20 nm) in the magnetron sputtered films. Among the BTIBD films, the near-equiaxial composition (49.7 at% Ni) has the largest crystals, ~100 nm as circled in Figure 4-13(e), and the crystal size remains roughly 60 nm in slightly Ni-rich (51.7 at% Ni) film.

Figure 4-12. TEM bright field micrographs before (a), (b), (c) and after (d), (e), (f) in-situ TEM heating of magnetron sputtered NiTi films. The open arrows in (d)–(f) mark the original location of channels prior to merging of the islands. Note that the 55.7 at% Ni has the same composition but larger thickness compared to the magnetron sputtered film in Figure 4-10.

For the Ni-rich films fabricated using BTIBD, comparing microstructural development after heating in Figure 4-11 and Figure 4-13 enables assessment of the influence of the heat treatment method. The results for the in-situ TEM heat treatment of the film with 60.2 at% Ni concentration are shown in Figure 4-11(h) and 1(i). The results for the ex-situ RTA of films with 54.6 and 62.5 at% Ni concentrations are shown in Figure 4-13(g) and Figure 4-13(h). The microstructures exhibit similar crystal sizes on the order of 10 nanometers in diameter, and thus
heat treatment method appears inconsequential to assessing the BTIBD technique. Consequently, we believe that the differential heat treatment methods in Figure 4-11 (in-situ) and Figure 4-13 (ex-situ) do not detract from the comparative analysis in the preceding paragraphs.

Figure 4-13. TEM bright field micrograph (a), (b), (c), (d) before and (e), (f), (g), (h) after ex-situ RTA heat treatment of NiTi films prepared by BTIBD. The yellow circles in (e) and (f) highlight the locations of large grains.

Examining the surface topography of the as-deposited BTIBD films versus magnetron sputtered films provides the basis for contrasting crystallization morphologies that arise during and after heat treatment. Figure 4-14 shows the surface topography, prior to heat treatment, for magnetron sputtered films with Ni-poor (42.2 at% Ni) and Ni-rich (55.7 at% Ni) compositions (top row) versus BTIBD films with near-equiaxial (49.7 at% Ni) and Ni-rich (60.2 at% Ni) compositions (lower row). In magnetron sputtered films, large amounts of islands appear as rod-shaped columns,[52] as pointed out by the arrow in Figure 4-14(a). The low height regions are considered as the channels.[52] The Ti-rich film (42.2 at% Ni) in Figure 4-14(a) has higher
columns (and hence the darker contour on the color scale) than Ni-rich (55.7 at% Ni) film in Figure 4-14(b). The columnar-channel microstructure is prevalent for magnetron sputtered films, and will be referred to as columnar-void, which is consistent with fundamental descriptions.[52] In BTIBD films, tiny height differences are apparent throughout the film plane for the near-equiatomic (49.7 at% Ni in Figure 4-14(c)) and Ni-rich (60.2 at% Ni in Figure 4-14(d)). Both BTIBD films exhibit unsubstantial height variations, compared to the films fabricated using magnetron sputtering. The differential as-deposited film morphology inherent to each technique likely influence the energy required for crystallization.

Figure 4-14. AFM images of as-deposited NiTi films prepared by (a), (b) magnetron sputtering in contrast to (c), (d) BTIBD prior to heat treatment. The small arrow in (a) points at one rod-shaped column on the surface of magnetron sputtered film. For clarity, the scale bar of contour is placed at the center and applies for (a)–(d).
The columnar-void microstructure can be attributed to limited adatom mobility when magnetron sputtering is used. The limited adatom mobility facilitates shadowing of the unoccupied surface sites from the depositing atoms, referred to as the self-shadowing effect.[52,53] Recent microstructure studies on thick (0.5–1 micron) NiTi alloys films fabricated using substrate-bias assisted magnetron sputtering displayed reduced roughness.[136] It was suggested that increasing adatom mobility can greatly reduce the columnar-void morphology.

In order to elucidate the material elements and their relative amounts within column versus void regions, EDS analysis was conducted on the as-deposited sputtered film as shown in Figure 4-15. The STEM image in Figure 4-15(a) shows that rod-shaped columns are bright and the voids are dark. Although the profile view of columns in Figure 4-15(a) resembles crystallographic grains, the structure is amorphous (see Figure 4-10(a)). In Figure 4-15(b), the EDS analysis on one rod-shaped column at site A and on one void at site B provide a qualitative means to assess the total volume of materials excited by the STEM probe with the same collection time 60 s. The peak positions of each element in site A is consistent with those in site B, indicating that there is no difference in the type of material elements. The counts, i.e. signal strength, however, are different, meaning large volumes of material in columns compared to voids. The rod-shaped columns and surrounding voids, respectively, have been attributed to higher density materials and to lower density materials. Based on fundamental understandings,[52] for a magnetron sputtered film it is expected that the EDS signal from a void should be lower than that from the rod-shaped column. The difference in height between rod-shaped columns and surrounding voids is due to the different amount of elements. In addition, the large amount of elements in column versus small amount in void confirms the non-uniform surface distribution of atoms which is associated with the limited adatom mobility in magnetron sputtered film. Note that the presence of Carbon (abbreviated as C) is attributed to the ambient environment, and that Oxygen (abbreviated as O) is present due to high affinity of Ti to
oxygen[137]; since the signal of O is considerably small compared to Ni and Ti, it is likely that a thin layer of TiO$_2$ is formed.

The rod-shape columns morphology and the amount of atoms in the columns can contribute to the grain formation. The differential grain size in BTIBD films vs magnetron sputtered films are inherently due to the different techniques BTIBD vs magnetron sputtering. Admittedly, the different thickness and heat treatment protocols can affect the grain size; however, the following observations suggest that the dominant factor influencing grain size is the nucleation barrier associated with the different smoothness (or film morphology) for BTIBD vs magnetron sputtering: Compared to the magnetron sputtered film in Figure 4-10, the magnetron sputtered film with the same composition but larger thickness (120 nm) in Figure 4-12 underwent higher temperature treatment, and still gave rise to the grain size on the same order as in Figure 4-12(c) and Figure 4-12(f). Moreover, for different composition, 42.2 at% Ni in Figure 4-12(a) and (d), and 52 at% in Figure 4-12(b) and (e), the same order of grain size has been observed, albeit different temperature and/or time. Despite the different composition, thickness, heat
treatment in magnetron sputtered films, the results show unanimously the same order of small grain size. Note in micrometer thickness films, it has been reported that as the heat treatment temperatures increase the grain sizes grow to large dimensions.[50] However, for film thicknesses below 200 nm, as temperature increases, nucleation is favored over growth so that within the same area, there will be the more nuclei and thus the grain sizes are constrained. Thus at higher temperatures, smaller grain sizes are reported and at lower temperatures, larger grain sizes were observed.[82] It is reasonable to assume that the source of the grain size differential is the nucleation dominating for the thin film thickness on the order of 100 nm.

BTIBD films are postulated conducive to crystallizing large grains. The observations that large grains were formed in BTIBD films evidenced by the discrete spot in Figure 4-11(a) and the circled grains in Figure 4-11 and Figure 4-13 in contrast to small grains in magnetron sputtered films underscore the consequences of utilizing magnetron sputtering to fabricate nanoscale thickness films. The columnar-void morphology in magnetron sputtered films may present a large energy barrier for crystallization from the amorphous state based on the following rationale.[53] Rod-shaped columns should exhibit small radii of curvature. Relative to a smooth surface, the amount of free convex surface atoms, i.e., atoms on the convex surface that are free and unbounded to the bulk, can increase significantly. Consequently, the surface tension, which is due to the force required to support the film per unit width, should be increased.[53] An analogy is drawn between nucleation of grains in the amorphous, solid phase of nanoscale thickness NiTi alloys films to nucleation of thin film nuclei from physical vapor deposition. The energy barrier to the film nucleation from the vapor is a cubic function of surface tension,[53]

\[
\Delta G^* = \left(\frac{16}{3}\right)\pi \gamma_f^3 / \left[\left(\frac{RT}{V_{mc}}\right)\ln\left(\frac{p}{p_v}\right)\right]^2 , \tag{4-1}
\]

where \( \Delta G^* \) is energy barrier to nucleation, \( \gamma_f \) is surface tension of film free surface, \( V_{mc} \) is molar volume of the condensate, \( T \) is temperature, \( R \) is gas constant, \( p_v \) is saturation vapor
pressure, and $p$ is pressure above $p_v$. Likewise, the energy barrier for nucleation of grains from the amorphous film can be a cubic function of surface tension. The rod-shaped columns are prevalent in the magnetron sputtered films and absent for the BTIBD films, and thus the magnetron sputtered films should have significantly higher surface tension and energy barrier than BTIBD films. We believe that the disparity between magnetron sputtering and BTIBD is exacerbated for the nanoscale thickness films because the height differentials between the columns and the voids are drastic and prevail over a large fraction of material surface so that free surface will considerably increase. A large part of the thermal energy input via heat treatment temperatures and time is likely spent to overcome the high energy barrier for nucleation in magnetron sputtered films. Presumably, the remaining fraction of the energy is insufficient to grow grains to a substantial size. On the other hand, in the smooth BTIBD films, low energy barrier for nucleation utilizes a small part of thermal energy, thereby allowing sufficient energy to facilitate the formation of large grains in the ultra-thin films.

In summary, BTIBD produces ultra-thin NiTi films without the columnar-void surface topography observed for thin films fabricated using magnetron sputtering. BTIBD adds independent control of low-energy ion flux toward the growing film, which increases the adatom mobility of deposited atoms.[53] The increased mobility results in smooth surfaces for as-deposited films and the smoothening is composition-independent. In sputtering, mobility of deposited atoms is limited resulting in columnar-void surface. The as-deposited films, from both BTIBD and magnetron sputtering, are amorphous. For the magnetron sputtered films, grain formation occurs by merging arrays of columns. The columnar-void morphology is postulated to impose a relatively large energy barrier for crystallization so that small grains (~10 nm), which exhibit the B2 crystal structure, are present by comparison with BTIBD films. The BTIBD is promising for fabricating nanoscale thickness NiTi alloys thin films as crystallization heat
treatments produce large grains (>100 nm) with the B2 crystal structure which are the prerequisite for the shape memory mechanism.

§ 4.3.2 Effect of rapid thermal annealing on the crystal structure and grain size

Rapid thermal annealing (RTA) has a high ramp rate (up to 200 °C/sec) and short annealing time (less than 15 min). The short time annealing is desired for the nanometer-thick films since the diffusion between film and substrate becomes severe with the increasing annealing time and the increasing volume of film/substrate diffusion will oppose the lattice distortion during martensitic transformation within thin films. [31,32,71] As an alternative to a sputtering chamber or furnace (up to hours), RTA was recently utilized to crystallize the micrometer-thick sputtered films in order to exhibit shape memory response.[138-144] In preceding sections, BTIBD is demonstrated to fabricate nanometer-thick high-quality films with ultra-smooth surface. However, there is no work to this date about the feasibility of RTA on NiTi films with nanometer thickness prepared by BTIBD. The feasibility of RTA on BTIBD films will provide a pathway to accelerate the heat treatment on tailoring of microstructure to further advance shape memory functionality into nanoscale.

In this section, RTA is conducted on NiTi films (~100 nm thickness) prepared by BTIBD. The near-equiaxomic, and Ni-rich films are deposited and undergo the heat treatment in RTA. Four groups of heat treatment with different temperatures but unchanged time are conducted. The crystal structure of the heat treated films are examined in grazing incident x-ray diffraction (GIXRD), followed by the study of surface morphology in atomic force microscopy (AFM).

Figure 4-16(A) shows x-ray diffraction pattern of Ti-49.7 at% Ni thin films. The phases are identified by searching and matching the detected peaks to the databases of international
center for diffraction data (ICDD), and national institute of standards and technology (NIST). Austenite B2 with lattice constants (2.9980, 2.9980, 2.9980, (Å) <90.00°, 90.00°, 90.00°>) are present, accompanying by Ti$_2$Ni, referred to as precipices, with lattice constants (11.2780, 11.2780, 11.2780 (Å) <90.00°, 90.00°, 90.00°>). As the heating temperature increases while the time remains constant, the main peak of B2 at two-theta 43° becomes predominantly sharp. Meanwhile, the peak of Ti$_2$Ni at two-theta 41° appears noticeable. The sharpness can be quantitatively described by virtue of full width at half maximum (FWHM) after the instrumental line broadening is subtracted. The relation between FWHM and microstructural crystallite size is given by the Scherrer equation,[145]

$$G_{size} = \frac{K\lambda}{\beta \cos(\theta)}, \quad (4-2)$$

where $G_{size}$ is the mean size of crystallites, $\lambda$ is x-ray wavelength, $K$ is dimensionless shape factor with a typical value 0.9, $\beta$ is FWHM denoted as $\Delta 2\theta$ with unit in Radian, and $\theta$ is Bragg angle. Since $\lambda$ is constant for an instrument, crystallite size will be in inverse proportion of FWHM if $\theta$ is given. In other words, the larger the crystallites are, the sharper the peaks are. Thus, as heating temperature increases from 490 °C to 540 °C, the increasingly sharp peaks of B2 at two-theta 43° and Ti$_2$Ni at 2-theta 41° indicate the crystallites of B2 and of Ti$_2$Ni are growing into large size. Fractions of phases are associated with the relative intensity between peaks because the scattering power for all atoms in unit cell contribute to the intensity, and the more atoms of the same type will make the intensity stronger. The increasingly noticeable Ti$_2$Ni peak at 2-theta 41°, with respect to B2 peak at 2-theta 43° suggests the increasing fraction of Ti$_2$Ni in the materials. Note that heat treatment at 490 °C, 10 min produces no crystallized film because of broad B2 peak and absence of Ti$_2$Ni.
Figure 4-16. X-ray diffraction pattern of (A) Ti-49.7 at% Ni films, (B) Ti-50.3 at% Ni films, (C) Ti-50.8 at% Ni films after RTA heat treatment at conditions of 465 °C, 10 min; 490 °C, 10 min; 515 °C, 10 min; 540 °C, 10 min.

The x-ray diffraction pattern of Ti-50.3 at% Ni thin films in Figure 4-16(B) shows a third phase, Ni₄Ti₃ with lattice constants (11.2400, 11.2400, 5.0770 Å) <90.00°, 90.00°, 120.00°> in addition to the B2 and Ti₂Ni. The FWHM of B2 at two-theta 43° in the Ti-50.3 at% Ni thin films is roughly 2°, and much smaller than that (5°) in Ti-49.7 at% Ni film as in Figure 4-16(A). The
smaller FWHM indicates larger crystallite size. With the increasing temperature, crystallite size of B2 and Ti$_2$Ni become large. The increasing intensity of B2 peak at 2-theta 43° with respect to the peak intensity of Ti$_2$Ni at 2-theta 41° suggests the B2 phase occupies the increasing fraction of the materials compared to Ti$_2$Ni, being opposite to the trend in Figure 4-16(A). Ni$_4$Ti$_3$ phase, however, is most noticeable at 490 °C with the primary diffraction angle at 40.9° and 44°, and becomes indistinguishable in other three heating conditions. The crystallization temperature, similar to that in the Ti-49.7 at% Ni thin films in Figure 4-16(A), is between 465 °C and 490 °C since the film is amorphous at 465 °C evidenced by broad B2 peak, and the film becomes crystallized at 490 °C with coexistence of B2, Ni$_4$Ti$_3$ and Ti$_2$Ni crystalline phases.

The B2, Ni$_4$Ti$_3$ and Ti$_2$Ni phases also coexist in Figure 4-16(C) for Ti-50.8 at% Ni thin films. The Ni$_4$Ti$_3$ is present in all crystallized films at temperature 490 °C and above, in contrast to the nonexistence in Ti-49.7 at% Ni film and presence in only one heat treatment condition in Ti-50.3 at% Ni film. The difference can be attributed to the Ni concentration which plays an important role in the NiTi alloys, as reflected in Figure 2-2(B). Sharp peaks with small FWHM similar to that in Ti-50.3 at% Ni thin films indicates the presence of large crystallites size in Ti-50.8 at% Ni thin films. The B2 phase possesses the dominating fraction since B2 at 2-theta 43° has much higher peaks than those of Ni$_4$Ti$_3$ and Ti$_2$Ni. The crystallization temperature in Ti-50.8 at% Ni thin films is in between 465 and 490 °C as well, consistent with that in Ti-49.7 at% Ni, and Ti-50.3 at% Ni thin films. Of note is that at 490 °C in Figure 4-16(C), Ni$_4$Ti$_3$ has large intensity, even higher than the primary B2 peak, which is a disparity from the other three heat treatments.
Figure 4-17. AFM images of Ti-49.7 at% Ni, Ti-50.3 at% Ni and Ti-50.8 at% Ni thin films after heat treatment. The scale bar of contour is placed at the bottom and applies for (a)–(f).

In order to examine the relation between crystalline phases and surface morphology, crystallized thin films at each heat treatment condition are characterized in AFM. For the Ti-49.7 at% Ni thin films, the surface after a 10 min heat treatment at 465 °C has slight blue and yellow contrast as in Figure 4-17(a), indicating slight height variation through the film plane. At 490 °C, just above the crystallization temperature, blue strips (about 1 μm long) appear, and the
distribution is nonhomogeneous, as shown in Figure 4-17(b). At even higher temperatures as in
Figure 4-17(c) and Figure 4-17(d), contrast between blue and yellow portions are not
distinguishable under the current scale bar, meaning the height variations are tiny. Similar trends
are followed by the Ti-50.3 at% Ni and Ti-50.8 at% Ni thin films: At 465 °C below the
crystallization temperature as in Figure 4-17(e) and Figure 4-17(i), a small amount of blue and
yellow contrast, i.e. small surface variation are found. Upon crystallization, long strips appears
for both Ti-50.8 at% Ni in Figure 4-17(f) and Ti-50.3 at% Ni in Figure 4-17(j). At a temperature
relatively higher than crystallization temperature in Figure 4-17(g), (h), (k) and (l), nearly one
color exists corresponding to the zero value in scale bar, meaning the surface is even smoother
than that before crystallization in Figure 4-17(e) and Figure 4-17(i).

Quantitatively, surface roughness metric, $R_q$, is used to describe the qualitative
observations in Figure 4-17 and the results are summarized in Figure 4-18. After a 10 min heat
treatment at 465 °C, $R_q$ increases for all the thin films of three compositions compared to the
surface roughness of as-deposited films. 49.7 at% Ni has higher roughness than the other two
compositions. After a 10 min heat treatment at 490 °C, roughness increases further, and all films
of the three compositions have higher roughness than under the 465 °C heat treatment. The
roughness in 49.7 and 50.8 at% Ni films are on the same level (4.72 nm) which is higher than that
(2.75 nm) in 50.3 at% Ni film. Above 490 °C, heat treatment does not produce significant
change in roughness such as 0.4 nm for 49.7 and 50.3 at%, and 0.7 nm for 50.8 at% at both 515
and 540 °C. Thus, as the heat treatment temperature increases, the resulting roughness first
increases significantly, and above a certain temperature point remains at the same level as the as-
deposited films; the trend is shown by superposing an imaginary dash line to Figure 4-18. The
similar trend has recently been reported to the micrometer-thick sputtered NiTi films.
[138,139,146]
Evolution of surface morphology can be associated with the changes in crystallite size via the well-known structure zone model.\[53,128\] The preceding sections demonstrated that the as-deposited BTIBD films exhibit the characteristics of fibrous columns and smooth surface, being consistent with “transitional” zone (ZT) in the structure zone model.\[111\] The fibrous columns are typically tens of nanometers in diameter; the end cap of columns are dome-like, but at the surface, the domes are absent due to high mobility of adatom, leading to smoothness. At increased temperature, a Z2 zone occurs in which columns have tight grain boundaries and increased diameter. The columns are facetted on the surface of thin films, resulting in rough surfaces. The facets on the surface are due to re-constructing of minimum surface energy. At even higher temperature, a Z3 zone takes place in which the bulk of films is annealed so that large, isotropic equiaxed crystallites develop. The assembly of the large crystallites render the film surface becoming smooth. The Ti-49.7 at% Ni, Ti-50.3 at% Ni and Ti-50.8 at% Ni thin films have isotropic orientation of crystallites instead of preferred orientation, evidenced in
Figure 4-16(A)–(C) that no main peaks are missing for each phase, and the spectra of peak profiles are in correct shape compared to the standard diffraction pattern.

In summary, RTA is able to crystallize NiTi ultrathin films prepared by BTIBD. Controlling the heat treatment temperature allows for tailoring of the crystallite size and the presence of crystalline phase. In near-equiaximatic and Ni-rich films, the crystallization temperature is between 465 and 490 °C. Higher heat treatment temperatures give rise to larger crystallite sizes and a larger fraction of the B2 phase. Ni₄Ti₃ phase appears in the film with Ni concentration above 50 at%. With the increasing temperature, the surface of thin films consistently become rough and then return to smooth. The evolving surface morphology is explained by the structure zone model.

§ 4.4 Thermally-induced shape memory behaviors of nanoscale NiTi thin films fabricated by BTIBD

The preceding sections deal with the fabrication of ultra-smooth, ultra-thin NiTi films by using BTIBD. The crystallization behavior and microstructural development have been studied on the as-deposited amorphous films. In order to achieve the shape memory functionality at the nanoscale, a demonstration of the occurrence of phase transformations — the underlying mechanism of shape memory behaviors — is an essential step. The current section examines the characterization of the phase transformations in the crystallized NiTi ultrathin films prepared by BTIBD. The characterization method is standard for thin films by measuring the film stress as a function of temperature. The film condition and the heat treatment parameters are shown in Table 4-3.
Table 4-3. Summary of BTIBD film condition, heat treatment and substrate.

<table>
<thead>
<tr>
<th>Composition (at% Ni)</th>
<th>Thickness (nm)</th>
<th>Heat Treatment Parameters</th>
<th>Substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>49.7</td>
<td>65</td>
<td>600 °C, 10 min + 450 °C, 10 min</td>
<td>Substrate 1</td>
</tr>
<tr>
<td>50.3</td>
<td>65</td>
<td>500 °C, 10 min</td>
<td>Substrate 2</td>
</tr>
<tr>
<td>51.7</td>
<td>65</td>
<td>Ultra-thin Si (100 micron thick, 1 inch by 1 inch area)</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4-19 shows the stress-temperature behavior of thin films without the occurrence of phase transformations. As temperature increases in Figure 4-19(A), the stress is decreasing. Upon cooling, the stress recovers from low to high level. Both curves in heating and cooling are straight lines, and the slope of both curves is constant and negative. The straightness of the lines shows the dependence of thermal stress on temperature. Figure 4-19(B) shows the temperature-dependent thermal stress in the Ti-49.7 at% Ni thin film prepared by BTIBD. The film has 65 nm thickness and undergoes heat treatment of at 600 °C for 10 min and subsequently at 450 °C for 10 min. The slopes of heating and cooling curves are negative and no change in slope value is observed. The negative slope in temperature-dependent thermal stress is explained in the following: Since the thickness of a thin film is much thinner than that of a substrate, and the stiffness of the film/substrate system is dependent on the substrate,[62] the final length of the film should always be the length of the substrate. Extensional strain is defined with respect to the original length, and the mismatch strain is similarly defined. Thus, the mismatch strain between the substrate and the film is expressed as follows:

$$\varepsilon_m = (\alpha_s - \alpha_f)(T - T_0) = (\alpha_s - \alpha_f)\Delta T,$$

(4-3)

where $\alpha_s$ and $\alpha_f$ are the coefficient of thermal expansion of the substrate and the film, respectively. $T_0$ is the temperature where there is no mismatch stress. Combining the Hooke’s law and the above equation yields the mean stress in the film:
\[ \sigma_m = M_f \varepsilon_m = M_f (\alpha_s - \alpha_f) \Delta T, \]  

(4-4)

where \(M_f\) is biaxial modulus of elasticity in the film. Since there is intrinsic stress in the film after deposition, it is difficult to separate the intrinsic stress from the absolute value of measured stress to obtain thermal stress. Derivative of measured stress with respect to temperature gives a reasonably good expression of temperature-dependent thermal stress, as follows:

\[ \frac{d\sigma}{dT} = M_f (\alpha_s - \alpha_f). \]  

(4-5)

For Si substrate, \(\alpha_s = 3 \times 10^{-6}/\degree C\), and NiTi has \(\alpha_f \approx 9 \times 10^{-6}/\degree C\). \(M_f\) is positive. Since \(\alpha_s - \alpha_f\) is negative by using the value of Si and NiTi, the slope of stress versus temperature, or stress rate, is negative as the temperature increases.

Figure 4-19. (A) Schematic of temperature-dependent thermal stress during heating and cooling. (B) Stress-temperature curve of a Ti-49.7 at% Ni thin film with 65 nm thickness prepared by BTIBD.
Figure 4-20. (A) Sketch of stress-temperature curve when there is phase transformations taking place during heating and cooling. Four transformation temperatures under stress, $T_{MS}$, $T_{MF}$, $T_{AS}$, $T_{AF}$, and the thermal hysteresis, $H$, can be identified. (B) Sketch of stress-temperature curve when the temperature-dependent thermal stress is combined with phase transformations. Phase transformations occur in the middle range of the temperature. (C) Experimental stress-temperature curve of a Ti-50.3 at% Ni thin film, 800 nm after the heat treatment 600 °C, 10 min + 450 °C, 10 min.

When phase transformations occur, stress-temperature behaviors are different from that of thermal stress, as shown in Figure 4-20. The dependence of transformation-related stress on temperature is a curved line instead of a straight line. During the reverse transformation from martensite to austenite by heating, the curve starts with a low stress level, and up to one critical temperature, the stress increases considerably to a critical stress level. The critical stress level will remain flat as temperature increases. Upon cooling, the forward transformation from
austenite to martensite starts with the same critical stress level but at a displaced temperature. As the transformation proceeds, the stress decreases until the transformation ends at a low stress level and keep flat. The temperature at which there is a slope change in the stress-temperature curve indicates one transformation temperature, and thus the four transformation temperatures, \( T_{MS}, T_{MF}, T_{AS}, T_{AF} \) under the presence of stress can be identified. The displaced temperature region is temperature hysteresis, \( H \).

During a complete thermal cycling from heating to cooling, temperature-dependent thermal stress and transformation-related stress can co-exist, as shown in Figure 4-20(B). As temperature increases, the first and third segment is temperature-dependent thermal stress manifested as a decreasing straight line. Phase transformations occur when the slope changes, as shown in the second segment. Figure 4-20(C) shows the coexistence of thermal stress and transformation-related stress in the 800-nm-thick Ti-50.3 at% Ni thin film prepared by BTIBD. Two segments of thermal stress take place together with the middle segment of phase transformations. From the middle segment, four transformation temperatures \( T_{MS}, T_{MF}, T_{AS}, T_{AF} \) can be identified as 61 °C, 49 °C, 53 °C, and 66°C, respectively. The hysteresis \( H = |T_{AF} - T_{MS}| \) is 4 °C. According to the relation between transformation temperature and Ni concentration at bulk in Figure 2-2(B), the four transformation temperatures of Ti-50.3 at% Ni bulk alloys under stress-free are 36.42 °C, 10.22 °C, 53.72 °C, 73.62 °C, respectively, and the thermal hysteresis is 37.2 °C.[18] Thus, the current film has a higher transformation temperature than the bulk counterpart; the raised temperature is attributed to the stress from the substrate via the Clausius-Clapeyron equation. The hysteresis of the film, however, is smaller than that of bulk.
Two-stage phase transformations can occur instead of the direct transformation between martensite and austenite. The two-stage transformation from austenite to R-phase, R-phase to martensite is caused by the stored mechanical energy which can result from precipitates, dislocations due to processing, and/or detwinning.[4] The formation of R-phase can be
associated with the local stress due to precipitates after heat treatment. The sketch of two-stage transformation is shown in Figure 4-21(A). During heating, the transformation temperatures $T_{As}$, $T_{Af}$ can be identified. Upon cooling, the transformation from austenite to R-phase occurs with $T_{Rs}$, $T_{Rf}$ identified. The second stage is R-phase to martensite with the transformation temperatures $T_{Ms}$, $T_{Mf}$. Figure 4-21(B) shows the experimental two-stage transformation in the Ti-49.7 at% Ni thin film with 800 nm thickness after heat treatment at 600 °C, 10 min + 450 °C, 10 min. The values of transformation temperature read as in Table 4-4.

Table 4-4. Values of transformation temperature and hysteresis in the Ti-49.7 at% Ni BTIBD thin film.

<table>
<thead>
<tr>
<th>Value</th>
<th>$T_{As}$</th>
<th>$T_{Af}$</th>
<th>$T_{Rs}$</th>
<th>$T_{Rf}$</th>
<th>$T_{Ms}$</th>
<th>$T_{Mf}$</th>
<th>$T_{Af} - T_{Rs}$</th>
<th>$T_{Af} - T_{Ms}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>59</td>
<td>70</td>
<td>66</td>
<td>54</td>
<td>50</td>
<td>31</td>
<td></td>
<td>4</td>
<td>20</td>
</tr>
</tbody>
</table>

Since the starting temperature of the transformed phase and the finishing temperature of the original phase are experimentally easy to measure, the hysteresis is defined as the difference between these two temperatures.[5] Of note is that in Figure 4-21(B), full recovery to the same stress level is achieved after a complete cycle of heating and cooling.
Figure 4-22. Stress-temperature curve showing the change of stress level after one thermal cycle is completed. (A) Ti-51.7 at% Ni, 800 nm and (B) A Ti-49.7 at% Ni thin film, 800 nm under the heat treatment 600 °C, 10 min + 450 °C, 10 min; (C) A Ti-49.7 at% Ni thin film, 800 nm under the heat treatment 500 °C, 10 min.

After the heat treatment, NiTi thin films have the initial stress state which could be sensitive to thermal cycling. The effect of one cycle of heating and cooling on the stress is shown in Figure 4-22. The Ti-51.7 at% Ni thin film in Figure 4-22(A) has no slope change, i.e. no occurrence of phase transformations, but the stress upon cooling is lower than the initial level. The slope during heating and cooling is nearly constant and remains negative. Figure 4-22(B) and Figure 4-22(C) show phase transformations manifested by slope changes, but after the reverse transformation, the stress level increases in both two cases. In order to testify if the stress
after a second thermal cycling returns to the increased level or recovers to the initial, the second thermal cycling with the same parameters was conducted, and the result is shown in Figure 4-23.

Full recovery is achieved after the second thermal cycling in Figure 4-23. The stress after recovery is at an increased level. The observation that the starting and recovering stress at the same, increased stress level during the second thermal cycle indicates that the first cycle could have introduced certain microstructural changes so that the stress is increased. The microstructural change, although affecting the stress level, does not influence the full recovery in phase transformations. One example of the microstructural changes is the introduction of precipitates into the NiTi matrix, which will cause a local stress change.[4]
Figure 4-24. Stress-temperature behavior of a Ti-50.3 at% Ni thin film, 800 nm under the heat treatment 600 °C, 10 min + 450 °C, 10 min. The behavior of the first cycle is identical to the fourth one, indicating the stability of the phase transformations in the NiTi thin film prepared by BTIBD.

In order to verify the stabilization of phase transformations in BTIBD thin films, multiple thermal cycles of heating and cooling are necessary. Figure 4-24 shows the stress-temperature behavior of the Ti-50.3 at% Ni thin film after four cycles. The temperature-dependent thermal stress behavior and the phase transformations in the first cycle is identical to that in the fourth one. The range of transformation temperature is between 50 °C and 65 °C, and the thermal hysteresis remains at 4 °C. The stable stress-temperature behavior without shifting shows the potential of long fatigue life in NiTi films prepared by BTIBD.

Note that as for the same composition, the Ti-49.7 at% Ni thin film in Figure 4-19(B) and Figure 4-23, the phase transformations occur in the thin film with 800 nm thickness but not for the 65 nm film. It is thus assumed that when the film thickness is reduced to tens of nanometers, the mismatch strain between film and substrate should be taken into consideration in order to exhibit phase transformations. Crystal Si substrate (100) has the lattice dimension 0.54306 nm,
NaCl substrate 0.56402 nm, and MgO substrate 0.4212 nm. NiTi thin films in austenite have B2 cubic structure with lattice dimension 0.3015 nm. The difference in lattice dimension between film and substrate could lead to a significantly high mismatch strain which may oppose the lattice distortion and even suppress the phase transformations.

In summary, phase transformations occur in the NiTi thin films with sub-micrometer thickness prepared by BTIBD. One-stage and two-stage phase transformations have been observed, and the thermal hysteresis is narrow in both cases. After one thermal cycle, the initial stress level of NiTi thin films is low due to thermal expansion or high due to phase transformations. The changed stress level is fully recoverable after a second thermal cycle is applied. The phase transformations in BTIBD films are stable and repeatable, even after four thermal cycles.
Chapter 5

Preliminary results for future work on top-down nanomachining/ nanofabrication

PREVIEW

Nanofabrication by nanoskiving is explored on NiTi alloy in order to fabricate NiTi nanowires. The strategy is to test the applicability of nanoskiving on NiTi alloy under extreme condition: The NiTi composition is selected to be most resistant to thin sectioning, and the nanoskiving configuration is set most prone to fragmentation. Ultimately, intact NiTi nanowires are generated and the yield is substantial. Top-down nanomachining by focused ion beam is used to fabricate objects with different geometry, including pillar, thin sheet and double shear specimen.

§ 5.1 1D nanowires with nanometer cross section machined using nanoskiving

Nanowire is a new object in the experimental field of shape memory alloys, compared to the extensively-studied thin films. The first demonstration of preparing shape memory alloys nanowires was on InTi alloys by using mechanical pressure injection in 2011. In 2014, electrochemical deposition method was used to fabricate Cu-based alloys nanowires,[147,148] and Co-Ni alloys nanowires. [149] There are issues in the above two methods; for example, mechanical pressure injection has an essential template including aluminum element that has low melting point, and thus is limited to alloys with low melting point; the composition and dimensions of generated nanowires are not ideal in electrochemical deposition. Nanoskiving,
however, potentially advances the controllable fabrication of shape memory alloys nanowires. Nanoskiving as a nanofabrication method, was proposed in 2006, and its applicability was demonstrated on pure gold nanowires.[150] Since then, a large range of materials, from metals to ceramics, semiconductors to polymers, have been tested for their applicability with nanoskiving.[151-154] The results have been tabulated into one periodic table of elements.[155,156] Nanoskiving has produced pure metal (or single material) nanowires from thin films with controllable dimensions [150,154-164] and its applicability for fabricating pure titanium (Ti) and nickel (Ni) metallic films has been assessed.[155] The applicability of nanoskiving to alloys has yet to be ascertained, and specifically, there is no fabrication of NiTi alloy nanowires by using nanoskiving, although NiTi alloy are most commercially successful and intensively-investigated.

§ 5.1.1 Methodology

The nanoskiving approach for NiTi alloy nanowires is illustrated in Figure 5-1. Film deposition by magnetron sputtering and ultramicrotomy for thin sectioning can define the cross-section dimensions of nanowires. The NiTi alloy thin film was deposited by magnetron co-sputtering from separate Ti and Ni elemental targets onto an NaCl (100) substrate such that the film was ~120 nm thick. In step A, after film deposition, epoxy (Araldite 502) was cured on the film surface. The NaCl was dissolved into water enabling exposure of the other side of the magnetron sputtered film. In step B, epoxy was cured on the freshly exposed side, which embedded the film. Subsequently, the embedded film was cut with a razor blade into a strip with longitudinal size 14 mm, and a cross section $0.3 \pm 0.1 \text{ mm} \times 0.25 \text{ mm}$. In Step C, the strip was sectioned using an ultramicrotome.
Figure 5-1. Schematic illustration of nanoskiving. Three steps can independently control the nanowire dimensions. In Step A, the NiTi thin film is deposited with precisely-controlled composition and thickness, followed by embedding and cutting into a strip in Step B. In Step C, the nanowire is generated by sectioning the strip.

The ultramicrotome (EM UC6, Leica Microsystems Inc.) was equipped with a custom-made glass knife and a sample-collecting reservoir. During sectioning, nanowires were generated in 5 sessions with an uninterrupted series of 20 slabs sectioned per session. The glass knife was freshly cleaved and solely used in one single session of sectioning in order to prevent the degradation in the quality of slabs. The strip was oriented with the edge of the film parallel to the sectioning direction in Step C.(1). The knife was stationary while the strip moved downwards through the knife. An epoxy slab with one nanowire in the middle was generated and floated on the water surface in the reservoir. The slab dimensions were defined by programming the sectioning increment so that the strip advanced to generate a series of slabs in a repeated, sequential manner. The twenty slabs were generated in one session at the rate of 1 Hz. In principle, this sectioning rate allows that over 500 slabs can be generated in 15 min. The upper
The limit number of slabs is determined based on the long dimension of the strip (14 mm) for the orientation shown in Step C.1 and the programmed sectioning increment (about 75 nm), and up to $10^5$ slabs can be generated. Ultramicrotomy enables the generation of nanometer-sized slabs from 10 nm to 100 nm. [165] The 75 nm dimension was near the middle of that thickness range. A honeycomb TEM grid was submerged into the water reservoir attached to the glass knife in order to collect the sectioned slabs. With the nanowires embedded in epoxy, they were easily mechanically manipulated and positioned. Etching removed the epoxy using a dry etcher (M4L, PVA TePla America) to obtain free-standing nanowires.

The detailed procedure in Step A–C of Figure 5-1 is the following. Epoxy was made by using the Araldite 502 kit (purchased from Ted Pella, CA) at the specified ratio of each component in the kit. The specified ratio is 19 mL of Bisphenol A Diglycidyl Ether (BADGE), 21 mL of Dodecenyl Succinic Anhydride (DDSA), and 1.2 mL of Benzylidimethylamine (BDMA). The freshly mixed epoxy was viscous. After the epoxy was poured and spread on the top surface of NiTi film, a sandwich structure consisting of salt (bottom), NiTi film (middle), and epoxy (upper) was formed. The sandwich structure then was placed into the oven at 60 °C overnight for curing. After being removed from the oven, the sandwich structure was immersed in deionized (DI) water to dissolve the NaCl until the dissolution was complete and the film was visibly exposed. The epoxy with NiTi film on top was then taken from the DI water and dried in an ambient atmosphere. After drying, a second viscous epoxy was poured on the exposed side of NiTi film, and cured. Then, the NiTi film was embedded into epoxy. A razor blade was used to cut out one strip of NiTi film from the embedded epoxy. The dimension of the strip was about 3 mm in height, 3 mm in width, and 14 mm in length.

Trimming was conducted on one end of the strip by the razor blade to obtain an area of 0.2 mm (top) by 0.4 mm (bottom) by 0.25 mm (height). The trimmed strip was then secured in a chuck holder and mounted to the ultramicrotome. The layout of the ultramicrotome is shown in
Figure 5-2(A), and the setup for sample and the glass knife in the ultramicrotome is in Figure 5-2(B). The glass knife was freshly created by bisecting one glass square, which is comparable in sharpness to a diamond knife, and also is less risky for knife damage in terms of cost (~$0.50 per glass knife versus ~$3000 per diamond knife).

Directional alignment between knife and sample surface was carefully conducted to achieve uniform thickness over the entire area of the sample surface. The trimmed sample and the mounting of the sample are shown in Figure 5-3(A) and Figure 5-3(B), respectively while the layout of knife versus the trimmed sample is in Figure 5-3(C). Detailed description of alignment can be referred to [163,165]. With the preset cutting speed, sectioning was then performed from the bottom to the top of the surface area, and a series of slabs were generated in an automatic manner by using a motor controller. The nanowires were in the middle of slabs. The parameters used in sectioning are listed in Table 5-1. The slabs sequentially floated to the water surface of
the reservoir from the knife edge, as shown in Figure 5-3(D). The thickness of the slabs can be estimated by comparing the color of slabs to the Interference Card. A fine brush with eyebrow was used to separate the agglomeration of the slabs. The separated slabs are shown in Figure 5-3(E). A copper TEM grid clipped by tweezers was collecting the slabs by firstly immersing into the water and then pulling back in a manner that the slabs of interest were captured through capillary. The process of collecting is demonstrated in Figure 5-3(F). The TEM grid contains honeycomb holes which are ready to examine in SEM and TEM. After collecting, all the TEM grids were placed into the storage box to wait the slabs to dry. The slabs then underwent the etching in a dry etcher to remove the epoxy so that free-standing nanowires can be obtained. The etching was conducted in M4L plasma etcher under the conditions of 265 mTorr pressure, 200 Watts power, and 180 s time with the flowing gas of oxygen and helium. The reliability of generating NiTi nanowires can be examined by collecting the entire set of the generated nanowires within the TEM grid, and counting the number of the intact nanowires. The ratio of the number of intact nanowires to the entire number of the generated nanowires is the yield, which is one index of reliability.
Table 5-1. Parameters of sectioning the strips by using ultramicrotome.

<table>
<thead>
<tr>
<th>Description</th>
<th>Parameter</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin film material</td>
<td>NiTi</td>
</tr>
<tr>
<td>Embedding resin</td>
<td>Epoxy (Araldite 502)</td>
</tr>
<tr>
<td>Ultramicrotome</td>
<td>Leica EM UC6</td>
</tr>
<tr>
<td>Knife</td>
<td>Glass, 45 °</td>
</tr>
<tr>
<td>Cutting direction</td>
<td>Edge of thin film parallel to sectioning direction</td>
</tr>
<tr>
<td>Radius of knife edge (nm)</td>
<td>3-5 *</td>
</tr>
<tr>
<td>Clearance angle (Degree)</td>
<td>4</td>
</tr>
<tr>
<td>Sectioning frequency (Hz)</td>
<td>1</td>
</tr>
<tr>
<td>Cutting speed (mm/sec)</td>
<td>0.3</td>
</tr>
<tr>
<td>Feed speed, i.e. nominal width (nm)</td>
<td>90</td>
</tr>
</tbody>
</table>

* The range of value is from reference [166].

The orientation of the thin film with respect to the sectioning direction is critical to generate unfragmented nanowires, and thus specific orientation of the knife with respect to the thin film are described. When the longitudinal dimension of the thin film is parallel to the direction of sectioning as shown in Figure 5-4(A), the sectioning is referred to as parallel sectioning. In parallel sectioning, the knife starts with one end of the film length. In the progression of sectioning, the thin film is cut along the longitudinal dimension step by step in a sequential manner. Perpendicular sectioning takes place when the direction of sectioning is perpendicular to the longitudinal dimension of the thin film but parallel to the lateral dimension as in Figure 5-4(B). The findings of the survey on different materials, from metallic to ceramic, semiconducting to polymeric, consistently confirm that the sectioned nanowires are more subjected to fragment in parallel sectioning than in perpendicular sectioning.[155,156] It should be noted that the speed of sectioning (0.1 to 10 mm/s) was reported no effect on the fragmentation.[155]
Figure 5-3. Images of mounting, slicing and collecting in the process of generating slabs. (A) shape of trimmed block, (B) mounting the trimmed block to the ultramicrotome, (C) alignment of knife with respect to the block, (D) serial slicing of the block into slabs, (E) separating and grouping the generated slabs, and (F) collecting the slabs of interest by using a TEM grid.
Figure 5-4. Illustration of film-based description on sectioning direction. (A) Parallel sectioning: longitudinal dimension of the thin film parallel to direction of sectioning; compressive cutting forces parallel to the film/epoxy interface. (B) Perpendicular sectioning: direction of sectioning perpendicular to longitudinal dimension of the thin film but parallel to lateral dimension; compressive cutting forces perpendicular to the interface.

Here, the composition of NiTi film and the sectioning orientation were chosen most susceptible to fracture in order to unequivocally demonstrate the feasibility of producing intact alloy nanowires by nanoskiving. Parallel sectioning as illustrated in Figure 5-4(A), has been shown to promote fracture compared to perpendicular sectioning.[155,156] Note that for parallel versus perpendicular sectioning, observations from SEM images of the renascent surface within nanowires, the just-cut surface that contacted the blade, was contrasted. Features on the renascent surface from parallel sectioning illustrated a rough surface morphology and similar features were not evident for the surface by perpendicular sectioning.[155,160] It was noted that the rough surface resembled the shear lamella in microtomed chips of bulk metals.[155] A reasonable conclusion can be drawn that parallel sectioning can produce more defects because compressive
cutting forces on the embedded film and the epoxy matrix are along the axis of sectioning. Deformation along the sectioning axis can cause the nanowire to experience buckling loads, similar to a slender column under compression.[33] Furthermore, the forces will tend to shear the interfaces between the nanowires and the epoxy matrix and may facilitate debonding loads. The compressive cutting forces during perpendicular sectioning are transverse and perpendicular to the sectioning axis; thus buckling loads likely will not arise. Compressive forces at the interfaces can inhibit debonding. Thus, relative to the state of loading in the perpendicular sectioning case, the loading is far more complex and detrimental for parallel sectioning. The rationale supports the reported rough surface and fracture becoming prominent during parallel sectioning. The thin film composition was determined with inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Optima 5300, Perkin-Elmer Inc.) as Ni$_{77.4}$Ti$_{22.6}$ at. %. The Ni-rich NiTi thin films have non-ideal mechanical properties for nanoskiving since they are stiff materials with high elastic modulus and low fracture strain, [123,167,168] which tend to fragment.[155,165] The as-deposited thin films were examined by a TEM (JEM-2010 LaB6, JEOL Inc.) at the accelerating voltage of 200 kV and an image is displayed in Figure 5-5. As-deposited NiTi alloy films are typically amorphous and require heat treatment in order to crystallize the B2 crystal structure, which is required for shape memory behaviour.[114,123] Nanograins with a size of ~6 nm coexist with amorphous regions. The B2 crystal structure, with a lattice constant of 0.3015 nm,[17] is present by viewing from the crystallographic direction [-111] and recognizing that the (110) lattice spacing is 0.213 nm.
Figure 5-5. High resolution TEM micrograph of the as-deposited NiTi thin film. The yellow lines delineate two representative nanograins in amorphous matrix of the thin film.

§ 5.1.2 Feasibility of nanoskiving on NiTi nanowires

The NiTi compositional ranges that exhibit shape memory behaviors have a CsCl atomic crystal structure, referred to as body centered cubic (BCC) B2.[18] It is well known that the failure of metallic material is dependent on the atomic crystal structure and the availability of slip systems; preferred crystallographic planes and directions are for dislocation motion that produces plastic deformation in metals.[169] When nanoskiving was undertaken for pure Ni and pure Ti, the Ti nanowires typically fragmented whereas the Ni nanowires did not readily fragment so that intact Ni nanowires were produced that were markedly longer than Ti nanowires. [155,156] The structure of Ti is hexagonal close-packed (HCP) and Ni is face-centered cubic (FCC). The
inherent number of available slip systems in Ti is three and twelve for Ni. Due to the stark
differential in available slip systems, the mechanical response of pure Ti is expected to be brittle
whereas Ni should be ductile and thus the reported fragmentation of Ti is expected. Since BCC
structures can have 12 slip systems, we hypothesize that the NiTi alloy films will be amenable to
nanoskiving.

Free-standing nanowires were produced with the width (~120 nm) controlled by the
duration of film deposition, the length (~250 μm) specified by the rough cut by a razor blade to
produce the strip, and the thickness (~75 nm) determined by sectioning. A representative NiTi
alloy nanowire is shown in Figure 5-6. The free-standing nanowire is being transferred with a
nano-manipulator (AutoProbe 200, Omniprobe Inc.) to a V-shape TEM grid (see Figure 5-6(B))
for characterization of the continuity in a SEM (Quanta 3D 200, FEI Inc.). Figure 5-6(A) shows
the as-sectioned nanowire picked by the nano-manipulator. Figure 5-6(B) and Figure 5-6(C)
demonstrate the nanowire does not fracture during manipulation and handling. The residual
epoxy is due to mild etching and should be completely removed when the nanowires are
integrated into the potential applications. The high magnification image in Figure 5-6(D)
confirms the absence of local fracture, with no apparent breaks, holes or discontinuities present
over 250 μm length.
Figure 5-6. SEM images (A), (B), (C), and TEM image (D) of a representative NiTi nanowire acquired from parallel sectioning in nanoskiving. (A), (B) and (C) are images captured in the process of transferring from a honeycomb TEM grid to a V-shape TEM grid. Residual epoxy are discernible along the nanowire probably due to incomplete etching. (D) is TEM micrograph of the zoom-up regions within the box in (C); the wire is smooth on one side (contacted with NaCl substrate) and rough (top of sputter-deposited film) on the other side.

The SEM images in Figure 5-7 show the nanowires for determination of the yield after etching. Figure 5-7(A) is the overview of the entire TEM grid. The SEM images in Figure 5-7(B.1) and Figure 5-7(B.2) show the second successfully transferred nanowire for characterization of continuity. Reproducibly, we can pick up other nanowires to conduct the
same characterization as in Figure 5-6. Additional intact nanowires are highlighted with yellow lines in Figure 5-7(B.3–B.5). The nanowires with the length ~50 μm can be found in Figure 4-13(C.1–C.3). By searching the entire range of the TEM grid, twelve nanowires are found having length over 100 μm, four nanowires are found about 50 μm length, and four are missing probably due to the multiple mechanical handling of TEM grid by a tweezer or due to the slipping through the holes of TEM grid after etching.

Figure 5-7. SEM images of multiple nanowires produced from parallel sectioning, as supplementary to the nanowire in Figure 5-6. (A) is the image of TEM grid hosting the nanowires. (B.1–B.2) are the images captured during the FIB transferring of a second nanowire. (B.3–B.5) are the images of three intact nanowires in the grid. Each yellow line delineates the length of one nanowire. (C.1–C.3) are images of the fragmented nanowires. The green lines delineate the length.
In order to determine the yield of the nanoskiving from one session, all the nanowires on the TEM grid are counted. A characteristic length for “intact” or unfragmented nanowires has been defined.[156] Unfragmented wires exhibited lengths greater than 100 μm and fragmented wires exhibited lengths less than 10 μm. Among the twenty slabs generated in one session, twelve nanowires with length > 100 μm could be located after etching. Four nanowires were identified with lengths equal to about 50 μm. Note that the lengths of shape memory alloys nanowires fabricated by other techniques were on the order of 1 μm.[147,148,170] and thus the 50 μm nanowires are much longer and thus considered intact. The remaining nanowires were likely lost through the holes in the TEM grid during transfer after etching. Note that an alternative method, which can overcome losing nanowires, is to float a ribbon of slabs onto a Si wafer, etch the epoxy, and count the structures by SEM.[154,164,165,171] Including nanowires with lengths nearly 50 μm as intact and presuming that the lost wires were fragmented, the yield for the current nanoskiving of NiTi alloy is 16/20 (80 %). Hence, the yield of nanoskiving on NiTi alloy is substantial and the technique exhibits promise.

Figure 5-8 shows the elemental mappings of Ni and Ti and thickness mapping as well as the thickness profile. Energy-filtering TEM (EFTEM) mapping was performed by using a post-column energy-filters (Gatan Imaging Filter, Gatan Inc.) in the TEM operated at 200 kV. Note that the brightness in Ti map, Figure 5-8(A), is reduced compared to the Ni map, Figure 5-8(B). The higher brightness in the Ni map than that in Ti map suggests more Ni atoms, which is consistent with the Ni-rich composition. Figure 5-8(C) shows the EFTEM relative thickness map. The log-ratio method [116] was used to obtain the relative thickness, t/λ, where t is absolute thickness, and λ is the total electron inelastic mean free path. Figure 5-8(D) quantifies the absolute thickness variation, using the reported value λ = 100 nm for NiTi[172,173] to
convert the relative thickness. Arrows in Figure 5-8(C) correspond to peaks in Figure 5-8(D), also marked with arrows. These peaks are distinct with respect to the minor serrations, examples of which are circled within Figure 5-8(D). Ultimately, the variations in section thickness analysis illustrates the thickness is uneven after thin sectioning.

Figure 5-8. Energy-filtering TEM images of NiTi nanowires. Elemental map of Ni (A) and Ti (B), thickness map (C), and profile (D) of thickness map within the dashed boundary in (C). The halo-like layer at bottom-side of nanowire in (C) is probably due to the residual NaCl after dissolution. The inserted direction coordinates, thickness (T), length (L), and width (W), correspond to Step C in Figure 5-1: lower left applies to (A–C) and the other only applies to (D).

The variation in section thickness provides insight into the sectioning mechanism for the NiTi alloys. The two commonly proposed sectioning mechanisms are shearing in Figure 5-9(A),[155,165,174] and cleavage-fracture/cracking in Figure 5-9(B).[155,165,175,176]

Shearing is the predominant mechanism expected for ductile materials and cracking is expected
for brittle materials. In literature, shear lamella in TEM images and a wavy surface in SEM images were characterized after ultramicrotomy. Those features gave rise to thickness variations that are evidence for the shearing mechanism. The thickness variation in Figure 5-8(D) supports the shearing mechanism. The findings support our hypothesis that the B2 NiTi alloy is amenable to nanoskiving due to its ductile nature.

Figure 5-9. Schematic of two sectioning mechanisms: shearing (A) and cracking (B); adapted from [155,174,176]. In (A), the abruptness in the neutral axis locates the region of intense shearing in the slab. In (B), the knife cleaves the slabs by initiating and propagating the crack; cleaved slab has the neutral axis curved gradually.

Stress is involved in the sectioning of slabs during nanoskiving. The mechanics analysis during sectioning is shown in Figure 5-10. The section 1 of the slab is with the strip and section 2 is already delaminated from the strip. The section 1 and section 2 impose different forces on the sectioning knife. The force from section 1 of width, \( H_1 \) can be decomposed into horizontal force \( F_h \), and vertical force \( F_v \), as shown in Figure 5-10(B). Due to mutual reaction, the section 1 undergoes the forces, \( F_h \) and \( F_v \) (with the opposite directions to those in Figure 5-10(B)), from the sectioning knife. The section 2 of width, \( H_2 \) is primarily under the vertical force \( F'_v \), as illustrated in Figure 5-10(C). From stress analysis, section 2 is in the state of shear stress and bending stress.
Figure 5-10. (A) Schematic of sectioning procedure, adapted from [179]. Free body diagram of (B) the sectioning knife and (C) the slab in sectioning.

The delamination of a slab from the strip can draw an analogy to generate a macroscopic crack in fracture mechanics. Out of the three modes in a cracked body, mode I — opening mode — as shown in Figure 5-11(A) and mode II — sliding mode — as in Figure 5-11(B) are closely related to the slab delamination and thus are introduced herein. The renascent surface of the upper side and lower side in mode I are simply moving apart under the tension, $F_t$. The propagation direction of the crack is perpendicular to the line of action of $F_t$. Mode II is involved with the sliding of the upper side with respect to the lower side, and the propagation direction of the crack is along the line of act of the force, $F_c$. Free body diagram in Figure 5-10(C) shows the tension, $F_v$, and horizontal force, $F_h$, are acting on the section 1. The
tension, $F_t$, will lead to the mode I opening so that the delamination occurs. The horizontal force, $F_h$, brings the mode II sliding to promote the delamination. Thus, the delamination of the slab during sectioning can be considered as the combination of mode I and mode II, although the mode I is likely the primary one.

![Figure 5-11. Schematic of two displacement modes in fracture mechanics. A) Mode I, tensile opening. B) Mode II, in-plane sliding. Adapted from [180].](image)

In summary, nanoskiving is capable of fabricating free-standing NiTi alloy nanowires. The hypothesis that NiTi alloy will exhibit ductile behavior, and thus is favorable for nanoskiving is confirmed. The current approach investigates a NiTi alloy composition expected to be most resistant to thin sectioning and the nanoskiving configuration most prone to cause fragmentation during sectioning. Regardless, nanoskiving produces intact NiTi nanowires. The atomic crystal structure is confirmed as B2. The yield of intact nanowires is substantial. Thin film deposition allows homogeneous composition and control of one dimension of the nanowires. Ultramicrotomy for nanoskiving controls the remaining two dimensions in the nanowires. The
stress during sectioning is analyzed via free body diagram, and the generation of slabs is deemed as the combination of opening mode and sliding mode.

§ 5.2 1D micropillars fabricated using focused ion beam

1D pillars (or post) for uniaxial compression experiment was firstly introduced by Uchic in 2004 to test the Ni micro-pillar fabricated by ion lathing[181], and then extended by Greer to nanoscale pillar by concentric milling.[41,182] The fabrication is categorized as top-down since the pillars are made directly from the bulk materials by using focused ion beam. Herein, both concentric milling and ion lathing are utilized to produce NiTi pillars. The shape and dimensions of the fabricated pillars are demonstrated, and the influence of the geometrical factors on the load vs displacement curve are discussed.

§ 5.2.1 Methodology

Concentric milling consisted of two main steps to fabricate a pillar. The first step was to make a crater from bulk materials to host the pillar. A circle was milled on the surface for identifying the pillar. Perpendicular to the circle, ion-milling was set with large diameter so that the materials surrounding the pillar were milled away, until a predefined depth of the crater was achieved. The second step refined the wall of the pillar as vertical as possible by consecutive concentric millings with decreasingly small diameters. The consecutive milling was performed until the pillar wall was close to vertical and the diameter of pillar was near the predefined value. The illustration of concentric milling is in Figure 5-12, and the serial process is shown in Figure 5-13. From the final pillar in Figure 5-13(E), the pillar is round-shaped at the top and the bottom. The diameter at the top is 1.38 μm and 2.03 μm at the bottom. Slight tapering appears at the wall,
with a tapering angle of $2^\circ$. The observable height of the pillar is roughly $10 \, \mu m$ but the total height contacting the base materials is unknown due to the contacting part hidden by a hole surrounding the pillar as shown in Figure 5-13(E).

Figure 5-12. Schematic illustration of concentric milling to fabricate a pillar. Milling circles with decreasing diameters are made step by step on the bulk sample until the desired pillar diameter is achieved.

Geometrical factors affect the loading-displacement measurement of the pillar fabricated by concentric milling. One factor is the tapering at the wall of the pillar. The presence of tapering influences the distribution of stress along the pillar, causing a stress gradient so that the deformation will start from the top and proceed toward the bottom. The second factor is the actual height of the pillar. Because penetration of the pillar into the crater is inherent in fabrication as observed in Figure 5-13(E), it is thus difficult to obtain the actual pillar height to
calculate height change for strain, which will lead to relatively high strain. The third factor is substrate compliance. The crosshead in a bulk test machine is stiffer than the specimen in terms of materials volume and properties, whereas the pillar has the same materials as the supporting substrate. It requires the separation of the substrate displacement from the measured value in order to obtain the accurate displacement in specimen.

Figure 5-13. SEM images (A)–(E) during concentric milling. In (E), a hole with the diameter larger than that of the pillar is surrounding the pillar.

Ion lathing, similar to the lathe in machining metal parts, proceeded in an incremental manner. The lathing procedure was conducted by using an automatic script (written by Paul Shade and Mike Uchic at the United States Air Force Research Laboratory). The illustration of ion lathing is shown in Figure 5-14. In order to reset the position of lathing during incremental steps, a Fiducial Mark with 2.5 μm in diameter was made on the area of interest under the condition of the ion milling being perpendicular to the surface of the area. The diameter of the
circle was smaller than that of the desired pillar. During lathing, the surface area was firstly tilted at $-9^\circ$; a milling box was drawn, and milling was performed to remove the unwanted materials; rotated $5^\circ$, and repeated the removal of materials. The rotation and materials removal continued until the rotation had completed $360^\circ$ for the incremental ion lathing. The images during the process of ion lathing are shown in Figure 5-15(A)–(H). The fabricated pillar in Figure 5-15(I) has vertical wall without tapering. The diameter is about $5 \mu m$ and the height is $10 \mu m$.

Compared to the pillar fabricated by concentric milling, ion lathed pillar has no tapering and the actual height can be directly measured. The absence of tapering allows the stress distribution to be uniform in any cross section along the axis of the pillar. The measured actual height ensures an accurate strain calculated by the change in length divided by the original length. The issue of substrate compliance, however, still exists due to the pillar being directly fabricated out of the bulk materials. Note that it is likely to produce pillars with nanometer diameter by using focused ion beam, and care should be given to the setting in incremental steps and milling rates.
Both concentric milling and ion lathing could inevitably leave a damage layer at the outer surface of the pillar due to Ga\(^+\) implantation during milling process. The damage layer may alter the mechanical properties of the pillar. Fortunately, it has been recognized that the damaged layer is about 3 nm thick, and the concentration of Ga\(^+\) is less than 1 at\%, which would have minor influence on the mechanical behaviors of pillars [1].
Figure 5-15. SEM images (A)–(H) during ion lathing. A Fiducial Mark with diameter smaller than that of the desired pillar is made to collimate the lathing after each rotation. (I) shows the shape of final pillar made by ion lathing.

§ 5.2.2 Nanoindentation

The load-depth behaviors were acquired by using a nanoindentor (TI-900 TriboIndenter, Hysitron Inc.) equipped with a conospherical tip. Figure 5-16(A.1) shows the pillar fabricated by concentric milling and Figure 5-16(A.2) is the load-depth response during loading and unloading. The load is up to 100 μN during loading, and after unloading, the depth of 20 nm is completely recovered. A small hysteresis exists and the dissipated energy can be quantified by the area
within the loop. Six cycles of loading-unloading for the pillar fabricated by ion lathing as in Figure 5-16(B.1) were conducted and the results are shown in Figure 5-16(B.2). After the first cycle, the depth is not recovered completely, and there are residual depth. However, the following five cycles of loading-unloading are nearly repeatable. Over 100 nm depth is completely recoverable and a slim hysteresis is constantly generated. The observation on the recoverable depth confirms the stress-induced shape memory behaviors in the pillars fabricated by both concentric milling and ion lathing.

Figure 5-16. SEM image of micropillars fabricated by (A.1) concentric milling and (B.1) ion lathing, and the corresponding compression load vs depth curve in (A.2) and (B.2). Note (A.1) from Figure 5-13 and (A.2) from Figure 5-15 are placed here for the sake of comparison.
§ 5.3 2D thin sheet with nanometer thickness fabricated using focused ion beam

2D thin sheet was fabricated by focused ion beam from bulk materials. Three regions within the sheet were identified to have three distinct thickness and three types of grain size. The transformation temperatures of the bulk materials were acquired in differential scanning calorimetry (DSC), while those in the thin sheet were obtained by in-situ TEM cooling test. The crystallographic response of the three regions in the cooling test were observed. A postulation for the difference in response was proposed.

§ 5.3.1 Methodology

NiTi bulk materials were purchased from SAES Smart materials, Inc. From the specification, the as-received NiTi was a bar with 1.27 inch in diameter and 50.8 at% composition; the materials underwent hot rolling and full annealing, and possessed centerless ground surface. Cubes of 4 mm³, as shown in Figure 5-17(A) were machined from the surface region of the bar by using wire electrical discharge machining (WEDM). One surface in a selected cube was mechanically ground and polished firstly with a 1 µm diamond glycol suspension, and then with a 0.05 µm colloidal silica. A thin sheet was vertically lifted out from the polished surface of the NiTi cube by using a focused ion beam equipment (FIB, FEI Quanta 3D 200). Sequential titled thinning was performed to produce the wedge-like cross section in the thin sheet with 5 kV, 29 pA as the final thinning condition. The fabricated thin sheet is shown in Figure 5-17(B).
Figure 5-17. Photograph of (A) NiTi bulk materials and (B) fabricated thin sheet by using focused ion beam.

The NiTi bulk materials were characterized in DSC (DSC 8500, Perkin-Elmer, Inc.) with the scan rate at 40 °C/min. The microstructure and crystal structure of the thin sheet was characterized using a TEM (JEM-2010 LaB6, JEOL Inc.) under accelerating voltage 200 kV. In-situ TEM cooling on the thin sheet was achieved by using a single tilt liquid nitrogen cooling holder (Gatan 613 Cryo, Gatan Inc.). The holder was capable of operation from −170 °C to +100 °C, and up to five hours of operation at −170 °C. The temperature was controlled in the manual mode by tuning the current in the controller, and the temperature stability was within 1 °C. Bright-field images and diffraction patterns were captured at the target temperature after no drifting occurred to the specimen.

§ 5.3.2 Microstructure characterization

Figure 5-18 shows the DSC plot of bulk materials to identify the transformation temperatures. Upon cooling, austenite B2 phase first transforms to R-phase, and then R-phase transforms to martensite. During heating, martensite directly transforms back to austenite. The transformation temperature of B2 to R phase is \( R_s = -10 \) °C and \( R_f = -30 \) °C. The martensitic
start temperature $M_s$ is $-38^\circ C$ and finish temperature $M_f$ is $-55^\circ C$. The reversible transformation temperature $A_s$ is $-18^\circ C$, and $A_f$ is $0^\circ C$.

Figure 5-19 shows the grain size and morphology of NiTi thin sheet lifted out from the bulk. The region boxed in blue in Figure 5-19(A) is examined in dark-field mode for morphology of large grains as in Figure 5-19(B); three regions circled in red in Figure 5-19(A) are zoomed in Figure 5-19(C). The grains in region 1 and region 3 are 20 nm and 50 nm respectively after comparing to the scale bar in Figure 5-19(C), and thus nanograins exist. The presence of nanograins can be attributed to that recrystallization in hot rolling process reduces the average grain size, and the subsequent heavy deformation produces the nanograins.[43,46] Region 2 in Figure 5-19(C) shows lath-like morphology, and from Figure 5-19(B), the lath-like morphology resemble the twinned martensite which is typically accommodated in one grain.[183] Since the martensite is included in one grain and the length of the twinned martensite read $\sim 1 \mu m$ from Figure 5-19(B), the grain size in region 2 is estimated $1 \mu m$. A straight, bright line near region 3 is likely the boundary between region 2 and 3, and the grain morphology in region 2 and 3 are quite different.
Figure 5-18. DSC thermo-grams of Ti-50.8 at% Ni bulk materials. For clarity, the tangential to the side of each peak is to intersect with the horizontal line to identify the transformation temperatures.

The thickness of the three regions can be estimated in terms of electro-transparent contrast. Region 1 has the smallest thickness because of the brightest contrast, and with the darkest contrast region 3 has the largest thickness. By using the mean free path of NiTi (~100 nm),[172] the value of thickness for region 1, 2, 3 are estimated 70, 90, 120 nm respectively. The chart in Figure 5-20 shows the grain size, thickness and ratio of grain size to thickness at the three regions. The thickness of the three regions are on the same order, while the grain sizes are starkly different. Region 2 has the largest grain, and the ratio is up to 1111 %. The ratio in region 3 is 42 %, and region 1 has the lowest ratio, ~29 %.
Figure 5-19. (A) Bright-field TEM image of grain morphology in thin sheet prepared by focused ion beam. (B) Dark-field TEM image of the boxed part in (A). (C) Zoomed-in view on the three regions circled in (A).

Figure 5-21 shows the TEM diffraction patterns of the three regions during in-situ TEM cooling. At room temperature in Figure 5-21(A), the diffraction pattern of region 1 is rings which are indexed as a FCC crystal structure. Upon cooling to 103.5 °C, the diffraction pattern becomes discrete spots as in Figure 5-21(B), and the crystal structure is indexed as B19’. The change in crystal structure indicates the occurrence of phase transformations from FCC to B19’. After the temperature is returned to room temperature in Figure 5-21(C), the diffraction pattern in region 1 still has the discrete spots, meaning B19’ does not transform back to the FCC structure. As for the region 2, discrete spots appears in the room temperature diffraction pattern in Figure 5-21(D), in contrast to the diffraction rings in region 1. Upon cooling in Figure 5-21(E) and after returning to room temperature in Figure 5-21(F), the discrete spots remain unchanged, meaning the B19’ phase keeps stable and there is no transformation occurring. As for the region 3, the diffraction pattern at room temperature in Figure 5-21(G) are the FCC diffraction rings which remain
unchanged upon cooling in Figure 5-21(H) and after returning to room temperature in Figure 5-21(I); there is no any transformation happening to region 3. Note body centered cubic (BCC) B2 crystal structure is expected present as the high temperature phase in NiTi; the presence of FCC instead of BCC in NiTi could be attributed to the incomplete crystal formation process.[169]

Figure 5-20. Chart on grain size and thickness in the three regions. The ratio of grain size to the thickness are inserted for each region.

Figure 5-18 shows the finishing transformation temperature for the low temperature phase B19’ is −55 °C and 0 °C for the high temperature phase. Thus, B19’ is not expected above 0 °C, and the high temperature phase is expected to transform into B19’ below −55 °C. However, from Figure 5-21 there are three observations which are contradicting to expectations: 1) Upon returning to room temperature from −103.5 °C, B19’ in region 1 does not transform back to the high temperature phase, 2) B19’ exist in region 2 at room temperature, and 3) during cooling to −103.5 °C, the transformation to B19’ does not occur for region 3.
Figure 5-21. Diffraction patterns of the three regions during in-situ TEM cooling. Scale bar, 5 1/nm. The indexing superposed to (A) and (B) also apply for (C)–(I).

The contradiction can be associated with grain size, thickness, and the ratio between these two as summarized in Figure 5-20, and the configuration of grain size and thickness are sketched in Figure 5-22(A). Region 2 has the largest ratio of grain size to thickness and has the free surface as the boundary; region 3 has the medium ratio and significant amount of grain boundaries in the relatively high thickness; region 1 has the smallest ratio and thus a few grain boundaries in the limited thickness. Specifically, the contradiction can be explained as follows:
1) The starting temperature of high temperature phase in thin sheet is larger than at bulk. The higher free-surface-area-to-volume ratio facilitates the stabilization of B19’ in thin sheet, even in the temperature regime unstable for B19’ at bulk. 2) B19’ becomes stabilized in region 2 after the twinned microstructure is exposed to free surface. The stored elastic energy is released when microstructural twins reach the free surface boundary, and thus the driving force for transformation from B19’ to high temperature phase is reduced. B19’ thus becomes stable and not transformed across a large range of temperature, including the range of −103.5 °C to room temperature. The rationale is consistent with the stabilization of martensite on micropillars.[33] 3) The energy barrier for transformation is high in region 3, and may result from two contributions: The grains are small so that there is limited available space to accommodate the transformation, and grain boundaries are the source of incompatibility between two crystallographic grains and more grain boundaries leads to larger degree of incompatibility and thus higher energy barriers. [49] The promoting effect of free surface and the adverse effect of grain boundary on the stabilization of martensite are incorporated in Figure 5-22(B).
Figure 5-22. (A) Schematic diagram of grain size and thickness in the thin sheet, and (B) illustration showing the effect of thickness and grain size on transformation temperature.

§ 5.4 2D double shear specimen fabricated using focused ion beam

2D micro-double shear specimen are illustrated in Figure 5-23(A). The specimen in red will be mostly under shear stress after the load is applied by the flat punch. [184] After deformation, the shear strain can be determined by measuring the shear displacement. Compared to other micro-scale experimentations, the advantages of micro-double shear test includes the following: 1) direct application of shear force to a specific crystallographic directions on a particular crystallographic plane, 2) elimination of the complication of fastening the loading grips on specimen, and 3) convenient preparation of TEM sample out of the tested specimen for microstructure analysis. As for shape memory alloys, micro-double shear test enables the shear loading to a specific habit plane for observation of twinning direction on a twinning plane.
Figure 5-23. (A) Schematic of micro-double shear test setup. The dimensions of sheared specimen are optimized for measurable shear strain and for minimizing unwanted bending stress. (B) Side view and (C) top view of SEM images on the micro-double shear specimen fabricated by focused ion beam.

Micro-double shear specimen was fabricated from the same bulk materials as for NiTi thin sheet. The polished surface of the bulk NiTi was chosen and the fabrication was conducted in the focused ion beam equipment (FIB, FEI Quanta 3D 200). A marker for positioning was firstly made by using a milling strip of 15 μm by 8 μm area. A series of vertical milling boxes
were set to outline the profile of the specimen. Oblique milling boxes were through the bottom of the specimen in order to free it from the underlying parts. All millings were performed under conditions of 30 kV, 7 nA. The final cleaning for every exposed edge of the specimen was performed under conditions of 5 kV, 29 pA. The fabricated micro-double shear specimen is shown in Figure 5-23(B) and Figure 5-23(C). Nanoscale double shear specimen can also be fabricated by focused ion beam with small milling boxes.
Chapter 6
Summary and conclusions

§ 6.1 Conclusions

In this dissertation, biased target ion beam deposition (BTIBD) equipped with a low-energy ion beam source was used to fabricate high-quality NiTi shape memory alloys thin films with one dimension on the nanometer scale. The following conclusions have been drawn from the research:

- Controlling the adatom energy is able to tailor the quality and properties of ultrathin NiTi films. BTIBD employs a low-energy ion source and low processing pressure, enabling better control of the energy of depositing atoms. Continuous films without holes are deposited on the thickness order of tens to hundreds of nanometers. A large range of composition is precisely, repeatedly controlled from Ni-rich, near-equiatomic NiTi, to Ti-rich. BTIBD produces high-quality ultrathin films, compared to conventional technique — magnetron sputtering. Manifestation of the high qualities are improved surface topography (roughness) on large area over large composition, and a minimized substrate/film interfacial diffusion.

- Microstructure of BTIBD NiTi films with nanometer thickness are tunable via heat treatment. BTIBD films in the as-deposited condition are amorphous, the same as magnetron sputtered films. Pure B2 phase is induced via low-energy ion beam preheating the film during deposition. Coexistence of B2 phase and B19' phase are achieved by post-deposition annealing on the as-deposited films; higher annealing temperatures lead to larger grain size.
• Columnar-void surface morphology is an imposing constraint on crystallization, and the absence promotes the formation of large grains. Absence of columnar-void morphology brings about large grains in BTIBD films.

• One-stage and two-stage thermally-induced phase transformations occur in 800-nm-thick BTIBD films. The thermal hysteresis in BTIBD films is considerably smaller (up to 50 %) than that in magnetron sputtered films. These phase transformations were not observed for 65-nm-thick films.

• As complementary objects to thin films, NiTi alloy wires with two dimensions on the nanometer scale are generated for the first time by using nanoskiving. NiTi alloy with B2 cubic structure and twelve slip systems is compatible with nanoskiving. The yield of NiTi nanowires is substantial (80 %), and the length of nanowires is significantly larger than that reported in state-of-the-art shape memory alloy nanowires.

§ 6.2 Contributions

This research has provided key contributions to scaling down of NiTi shape memory alloys in two-dimensional and one-dimensional categorizations. Specifically, the contributions are listed one by one as below:

• Ultra-smooth and ultra-thin NiTi alloys thin films have been fabricated by using BTIBD. Such films are difficult, if not impossible, to be prepared using the conventional deposition technique.

• A critical minimum ratio of interfacial diffusion layer thickness to film thickness has been identified in order to exhibit martensitic transformation. Minimizing substrate/film interfacial diffusion provides a possible solution for the martensitic transformation constrained by the substrate/film interface, particularly at sub-micrometer thickness range.
• Insights on reducing the nucleation barrier for large grains have been acquired. The insights provide a connection between columnar-void surface topography and microstructural morphology, enabling a better understanding on microstructure control.

• Ultra-small thermal hysteresis has been generated in NiTi thin films with nanometer thickness. The small hysteresis is critical to shape memory alloys components requiring fast response, and could find useful applications in potential nanoscale devices that utilize rapid-response shape memory alloys.

• BTIBD that allows for controlling adatom energy is demonstrated advantageous for improving surface smoothness, minimizing interfacial diffusion, reducing nucleation barrier for large grains, and producing small thermal hysteresis shape memory alloys.

• For the first time, nanoskiving is demonstrated capable of fabricating alloy nanowires. The applicability of nanoskiving on material type is expanded. Nanoskiving could enable the preparation of shape memory alloy nanowires so as to ascertain the effect of geometric size and the effect of microstructural constraint.

• A groundwork for thermo-mechanical characterization to investigate the effect of geometric and microstructural size on nanoscale martensitic transformation morphology and shape memory behaviors is provided.

§ 6.3 Future directions

The current work has made the first and the essential step — fabrication of NiTi alloys with nanometer dimensions — toward fundamental thermo-mechanical experimentation on shape memory properties at nanoscale, which is critical to the design and reliability of shape memory alloys as components of potential nanoscale devices. The future directions that could bring high impact to the research community include the following:
• **Mechanical experimentation for recoverable strain in nanoscale shape memory alloys.**

As for the high-quality NiTi shape memory alloys thin films fabricated by BTIBD, to date, there is no experimental work on the measurement of recoverable strain. Compared to purely thermally-induced shape memory behaviors demonstrated in the current research, shape memory effect (during cycles when a loading is applied and then heating) and superelasticity (during cycles of loading-unloading) are of practical importance, and since both involve recoverable strain, assessment on recoverable strain of high-quality NiTi alloys (as well as Cu-based and Fe-based alloys) ultrathin films prepared by BTIBD should be conducted soon. 

Nano-mechanical experimental protocols of MEMS-based uniaxial tensile testing, beam deflection method, substrate curvature method and instrumental nanoindentation can be utilized.

• **In-situ experimentation to elucidate geometric size effect, microstructural constraint and the mutual interplay on nanoscale martensitic transformation and shape memory behaviors.** This research demonstrates control of geometric size including the thickness of NiTi ultrathin films and the cross section of nanowires, and on microstructural grain size. To this date, no thorough understanding on martensitic transformation and shape memory behaviors scaling with geometric size, with microstructural dimensions, and their coupling in nanoscale shape memory alloys. With the geometric and microstructural size controlled, in-situ experimentations that enable simultaneous determination of overall mechanical behaviors and characterization of microstructure morphology will provide experimental evidences for the size-dependence of transformation behaviors. The transformation morphology including the crystallographic transformation path, width and periodicity of martensite variants, and the metric parameters from mechanical behaviors for interfacial energy, twin strain energy, friction work and bulk volumetric energy should be determined in order to fundamentally expand the understandings on nanoscale shape memory alloys.
• **Formulation of constitutive relations unifying the geometric size, and the microstructural dimensions as boundary conditions for theoretically explaining size-dependent shape memory behaviors.** Constitutive relations are the core of mechanics, and to date, there is no work incorporating both geometric size effect and microstructural constraint into constitutive relations. The free surface related to the geometric size can be treated as a unique boundary condition on the confined, periodic lattice volume; the same principles applies to the grain boundaries associated with microstructural constraints. The constitutive relations incorporating the observation on lattice structure, the mechanical behaviors of the lattice volume and the unique boundary conditions are extremely useful to quantify the size-dependent shape memory behaviors, and are valuable in deep understanding of the physical size as unified boundary conditions on nanoscale deformation behaviors.

• **Novel design paradigm utilizing microstructural and architectural properties of nanoscale shape memory alloys to achieve performance-oriented functionalities.** The conventional material design depends on microstructure tailoring to achieve desired properties. For example, introducing microstructures impeding the dislocation motions increases the yield stress in crystalline materials because the plasticity reply on the motions of dislocations. Since at nanoscale, the size of microstructure is comparable to the scale of the material size, direct tailoring the material becomes possible. Thus, the microstructural design on each material component and the architectural design on overall material structure will allow the design from the fundamental level by tailoring the microstructure of components and controlling the architectural layout in order to ultimately achieve the targeted properties and performance. The design paradigm utilizing microstructural and architectural properties of nanoscale shape memory alloys will fundamentally transform the conventional design of shape memory functionalities by adding flexibility and controllability.
Engineering multiferroic properties — ferromagnetism, ferroelectricity and ferroelasticity — on nanoscale alloys by utilizing the coupling of magnetism, electricity, elasticity and temperature. Beyond NiTi alloys system, what is more promising are the alloys with phase transformations and multiferroic properties. Phase transformations in nanoscale alloys could lead to large change in lattice parameters, to produce latent heat and to generate microstructures with the dimensions comparable to the material size. Ferromagnetism and ferroelectricity are extremely sensitive to the change of lattice parameters so that phase transformations induced by changing a few degree in temperature can transform a strong magnetic material into a nonmagnetic. Ferroelectricity with rapid heat transfer associated with large surface-area-to-volume ratio may efficiently convert heat into electricity. In addition, since the microstructures of martensite variants reaching free surface can release stored elastic energy, large energy dissipation may be expected and the ferroelasticity may allow for the design of nanoscale alloys with large damping capability. The coupling of magnetism, electricity, elasticity and temperature renders the nanoscale alloys with phase transformations and multiferroic properties versatile, and creates a host of opportunities in nanoscale functional applications.
References

1. Van Humbeeck, J.; Shape memory alloys: A material and a technology. *Advanced Engineering Materials; 2001; 3; 837.*
15. Ueland, S. M.; Schuh, C. A.; Surface roughness-controlled superelastic hysteresis in shape memory microwires. *Scripta Materialia; 2014; 82; 1.*

22. Dunand, D. C.; Mullner, P.; Size effects on magnetic actuation in Ni-Mn-Ga shape-memory alloys. *Advanced Materials*; 2011; 23; 216.

23. Stupkiewicz, S.; Petryk, H.; *European Symposium on Martensitic Transformations*; Prague, Czech Republic; 2009.


44. Waitz, T.; Kazykhanov, V.; Karnthaler, H. P.; Martensitic phase transformations in nanocrystalline NiTi studied by TEM. *Acta Materialia*; 2004; 52; 137.
57. Liu, Y.; Huang, X.; Substrate-induced stress and transformation characteristics of a deposited Ti-Ni-Cu thin film. *Philosophical Magazine*; 2004; 84; 1919.


Niakan, H.; Yang, Q.; Szpunar, J. A.; Structure and properties of diamond-like carbon thin films synthesized by biased target ion beam deposition. *Surface and Coatings Technology*; 2013; 223; 11.


Chen, W.; Nam, D. N. H.; Lu, J. W.; West, K. G.; Wolf, S. A.; Effects of target bias voltage in magnetic tunnel junctions grown by ion beam deposition. *Journal of Applied Physics*; 2009; 106; 013905.

Quan, J. J.; Wolf, S. A.; Wadley, H. N. G.; Low energy ion beam assisted deposition of a spin valve. *Journal of Applied Physics*; 2007; 101; 074302.

Rossnagel, S. M.; Directional and ionized physical vapor deposition for microelectronics applications. *Journal of Vacuum Science & Technology B*; 1998; 16; 2585.


120. Greer, J. R.; De Hosson, J. T. M.; Plasticity in small-sized metallic systems: Intrinsic versus extrinsic size effect. *Progress in Materials Science; 2011; 56; 654.*


144. Nakane, R.; Sugahara, S.; Tanaka, M.; Structural and magnetic properties of ferromagnetic Fe1-xSix (0.18 <= x <= 0.33) films formed by rapid thermal annealing on silicon-on-insulator substrates. *Journal of Applied Physics; 2015; 117; 133906.*

145. Scherrer, P.; Göttinger Nachrichten Math. Phys; 1918; 2; 98.


149. Kwag, Y. G.; Ha, J. K.; Kim, H. S.; Cho, H. J.; Cho, K. K.; Co-Ni alloy nanowires prepared by anodic aluminum oxide template via electrochemical deposition. *Journal of Nanoscience and Nanotechnology; 2014; 14; 8930.*


151. Lipomi, D. J.; Chiechi, R. C.; Dickey, M. D.; Whitesides, G. M.; Fabrication of conjugated polymer nanowires by edge lithography. *Nano Letters; 2008; 8; 2100.*


Lipomi, D. J.; Kats, M. A.; Kim, P.; Kang, S. H.; Aizenberg, J.; Capasso, F.; Whitesides, G. M.; Fabrication and replication of arrays of single- or multicomponent nanostructures by replica molding and mechanical sectioning. *ACS Nano*; 2010; 4; 4017.

Lipomi, D. J.; Martinez, R. V.; Rioux, R. M.; Cademartiri, L.; Reus, W. F.; Whitesides, G. M.; Survey of materials for nanoskiving and influence of the cutting process on the nanostructures produced. *ACS Applied Materials & Interfaces*; 2010; 2; 2503.

Lipomi, D. J.; Martinez, R. V.; Whitesides, G. M.; Use of thin sectioning (nanoskiving) to fabricate nanostructures for electronic and optical applications. *Angewandte Chemie International Edition*; 2011; 50; 8566.

Dickey, M. D.; Lipomi, D. J.; Bracher, P. J.; Whitesides, G. M.; Electrically addressable parallel nanowires with 30 nm spacing from micromolding and nanoskiving. *Nano Letters*; 2008; 8; 4568.


Xue, M. Q.; Li, F. W.; Cao, T. B.; Fabrication of ultra-fine nanostructures using edge transfer printing. *Nanoscale*; 2012; 4; 1939.


Xu, Q. B.; Bao, J. M.; Rioux, R. M.; Perez-Castillejos, R.; Capasso, F.; Whitesides, G. M.; Fabrication of large-area patterned nanostructures for optical applications by nanoskiving. *Nano Letters*; 2007; 7; 2800.


Appendix

Nontechnical abstract

Shape memory alloys offer the highest work output per unit volume among smart materials and have both high actuation stress and large recoverable strain. Miniaturization of materials and devices requires shape memory actuation which is uncompromised at a small scale. However, size effects need to be understood in order to scale shape memory actuation with the minimum size critical to device design. Controlling material quality and properties is essential in fabrication of shape memory alloys into nanometer regime. This work demonstrates a novel fabrication technique — biased target ion beam deposition — which uses additional adatom energy in order to fabricate high-quality NiTi alloys thin films with nanometer thickness. These fabricated ultrathin NiTi films provide insight into the size scale dependence of shape memory functionality at nanoscale regime.

Biased target ion beam deposition which allows for controlling adatom energy is demonstrated advantageous for improving surface smoothness, minimizing interfacial diffusion, reducing nucleation barrier for large grains, and producing small thermal hysteresis in the NiTi ultrathin films. As complementary objects to thin films, NiTi alloy wires with two dimensions on the nanometer scale are generated for the first time by using a novel nanofabrication technique — nanoskiving. The advancements on fabrication and characterization of NiTi alloys with dimensions on the nanometer scale lay the groundwork for fundamental thermo-mechanical experimentation of characterizing shape memory properties at ultra-small scale.
VITA

Huilong Hou

**Date and place of birth:** April 17th, 1986; Xinxiang, Henan province, China.

**Education**

- Ph.D. (Longenecker and Associates Scholarship), Engineering Science and Mechanics, The Pennsylvania State University, USA  12/2015
- M.S. (Outstanding Thesis), Solid Mechanics, Beihang University (Previously known as Beijing University of Aeronautics and Astronautics), China  01/2012
- B.S. (Best Graduate), Engineering Mechanics, Southwest University of Science and Technology, China  07/2009

**Publications**


**Honors and awards**

5. Outstanding Mechanics Student Award of China, Chinese Society of Theoretical and Applied Mechanics, 2009/05.
6. First Place, Annual “Sun Xunfang” Mechanics Competition, Sichuan Province, China, 2008/04.

**Career plans**

- Short-term: Conducting post-doctoral research in universities/national laboratories.
- Long-term: Being a faculty in academia.