CHARACTERIZATION OF POROUS SILICON FOR
MICROPYROTECHNIC APPLICATIONS

A Dissertation in
Mechanical Engineering
by
Venkata Sharat Parimi

© 2015 Venkata Sharat Parimi

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

May 2015
The dissertation of Venkata Sharat Parimi was reviewed and approved* by the following:

Richard A. Yetter
Professor of Mechanical Engineering
Dissertation Co-Advisor, Co-Chair of Committee

Srinivas A. Tadigadapa
Professor of Electrical Engineering
Dissertation Co-Advisor, Co-Chair of Committee

Gary S. Settles
Distinguished Professor of Mechanical Engineering

Donghai Wang
Associate Professor of Mechanical Engineering

David L. Allara
Professor of Chemistry and Material Science

Karen A. Thole
Professor of Mechanical Engineering
Head of the Department of Mechanical and Nuclear Engineering

*Signatures are on file in the Graduate School.
Abstract

The current interest towards developing and deploying functional microscale devices is aimed at increasing the efficiency while reducing the cost, mass, and energy consumption. While functional microelectromechanical systems provide several advantages, their reduced length scales also pose several formidable problems in terms of powering and actuating such devices. One promising means to address this problem is to incorporate small amounts of high-energy-density energetic materials on-board microscale systems, and use the stored chemical energy for power and actuation, which is known as micropyrotechnics. The reactive properties of materials change significantly as their dimensions shrink to the nanoscale domain, and the high reactivity of nanoscaled/nanostructured materials can be exploited to form a new class of energetic materials known as nanoenergetic materials (nEMs), which are capable of sustaining a reactive wave propagation at sub-millimeter length scales. A nEM of significant interest in this regard is nanoporous silicon (PS), which is capable of high energy densities, efficient chemical energy conversion even at small length scales, and monolithic integration onto microscale devices. This work deals with understanding the behavior of porous silicon-solid oxidizer composites, which is required for successful micropyrotechnic applications.

As a part of this research effort, PS was prepared from silicon substrates with different dopant atom types and concentrations, and was characterized using SEM, BET, and sound speed measurements. Energetic composites were prepared by depositing oxidizers (sodium,
magnesium, or calcium perchlorate salts) within the nanoscale pores. The reactive wave propagation within the energetic composites was characterized by high speed imaging and spectroscopic temperature measurements using multiwavelength pyrometry. The interaction between the condensed phase and the gaseous medium was studied in a high speed shadowgraphy system used to visualize the density gradients in the gas. Thermal analysis by simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) was used to characterize the interfacial reactions between PS and the oxidizer. The experimental results were combined with thermochemical equilibrium calculations and reaction models to understand the reactive wave propagation in PS composites.

A detailed combustion analysis of energetic PS composites indicated that heavily doped P or N-type silicon substrates (resistivity between 0.001 to 0.005 Ω-cm) yield PS substrates which always exhibit low reactive wave propagation speeds on the order of 1 m/s. PS composites prepared from heavily doped N-type substrates were found to yield higher reactive wave propagation speeds than PS prepared from heavily doped P-type substrates, which is a consequence of the difference in the microstructure of the PS formed. Changing the amount of oxidizer within the pores of PS etched from heavily doped silicon substrates was found to not affect the reactive wave propagation speeds or temperatures obtained. A reaction model incorporating thermochemical equilibrium calculations and diffusion considerations showed that the inhomogeneity of PS-oxidizer composites is important, despite pore diameters being on the order of a few nanometers. Further, one of the significant problems associated with PS composites, the deposition of oxidizer within the pores, was shown to be less important than the specific surface area and microstructure of PS in terms of the reactive wave propagation.

PS prepared from low doped P or N-type substrates (with resistivity between 1 to 20 Ω-cm) was found to exhibit reactive wave propagation speeds on the order of 100 to 1000 m/s. The high speeds in the case of PS prepared from low doped N-type substrates were found
to be a consequence of randomly forming micro-crack patterns. PS etched from low doped P-type substrates exhibited the highest reactive wave propagation speeds (~1000 m/s) and were capable of driving strong shock waves in the gaseous medium above the PS. Activation energy estimations from thermal analysis, and sound speed measurements were used to narrow down the mechanisms responsible for the high speed reactive wave propagations as a combination of heat transfer through the condensed phase and permeation of hot gaseous products within the porous layers, or reactive wave propagation assisted by high speed crack propagations in crystalline PS.

A novel technique to control the reactive wave propagation speeds in nEMs was developed, and successfully demonstrated using PS. Standard microfabrication techniques such as photolithography and plasma etching were used to create organized microscale structures in PS, which resulted in a two-order-of-magnitude enhancement in the reactive wave propagation speeds (from 2 m/s to 500 m/s). The creation of controlled microscale structures in PS results in the formation of hierarchical structures which organize the reactive material (the nanoscale features) in specific geometric configurations (imposed by the microscale features) conducive to effective permeation of the gaseous reaction products, which results in enhanced reactive wave propagation rates.
# Table of Contents

List of Figures x  
List of Tables xvi  
Acknowledgments xviii  

## Chapter 1  
### Introduction  
1.1 Background ................................................. 1  
1.1.1 Energetic materials ........................................ 1  
1.1.2 Micropyrotechnics ......................................... 2  
1.1.2.1 Nanoenergetic materials (nEMs) .......................... 7  
1.2 Review of porous silicon literature ............................. 10  
1.2.1 Formation and structure of porous silicon ..................... 10  
1.2.1.1 Factors affecting the structure of porous silicon ............ 13  
1.3 Combustion of porous silicon composites ......................... 16  
1.3.1 Ignition mechanisms for porous silicon ...................... 21  
1.4 Research objectives ......................................... 22  

## Chapter 2  
### Experimental methods  
2.1 Safety ..................................................... 26  
2.2 Preparation and characterization of porous silicon .............. 26  
2.2.1 Electrochemical etch process ................................ 26  
2.2.2 Characterization of porous silicon ........................... 28  
2.2.2.1 Gravimetric determination of porosity ...................... 29  
2.3 Thermal and combustion analysis of porous silicon ............. 30  
2.3.1 Reactive wave propagation speed and spectroscopic temperature measurements .......................... 30  
2.3.1.1 Multiwavelength pyrometry ................................. 31  
2.3.2 Thermal analysis methods .................................. 33  
2.3.2.1 Estimation of reaction kinetics from thermal analysis ..... 35
5.1.3 Convective burning ........................................ 87
5.2 Control of reactive wave propagation speeds by microscale structures .... 89
  5.2.1 Shadowgraph analysis of the reactive wave propagation in patterned
          PS composites ............................................ 94
  5.2.2 Reactive wave propagation in PS composites with microchannels .... 98
5.3 Conclusions .................................................. 101

Chapter 6
Mechanistic investigation of reactive wave propagation in low doped
P-type PS composites ........................................ 104
6.1 Background .................................................. 105
6.2 Results and discussion ...................................... 106
  6.2.1 Speed of sound measurements ............................. 106
  6.2.2 Interaction with the shock above the PS surface .......... 107
    6.2.2.1 Influence of the pressurizing gas on the high speed reactive
            wave propagation ....................................... 111
  6.3 Possible reactive wave propagation mechanisms .................. 112
  6.3.1 Conductive and convective burning ....................... 112
    6.3.1.1 Conductive burning .................................. 112
    6.3.1.2 Estimation of reaction kinetics for PS composites using ther-
            mal analysis ........................................... 114
    6.3.1.3 Convective burning by gas permeation within the nanoscale
            pores ..................................................... 116
  6.3.2 Other mechanisms leading to high speed reactive wave propagations 118
6.4 Conclusions .................................................. 118

Chapter 7
Conclusions and future work .................................... 120
7.1 Summary of research and conclusions .......................... 120
  7.1.1 Effect of composite equivalence ratio and inhomogeneity of the system 121
  7.1.2 Effect of substrate properties on PS composites ................ 122
  7.1.3 Control of the reactive wave propagation through microfabrication
        techniques .............................................. 123
  7.1.4 High speed reactive wave propagation in low doped P-type PS com-
        posites .................................................. 124
  7.2 Recommendations for future work ........................... 125
    7.2.1 Further analysis of low doped P-type PS composites .......... 125

Appendix A
Electrochemical etch and photolithography recipes ..................... 129
A.1 Details of the electrochemical etch process .................... 129
A.2 Recipes for Photolithographic patterning ........................ 131
Appendix B

Supplementary data
B.1 Gravimetric porosity measurements for heavily doped P-type PS samples . 134
B.1.1 A note on the oxidizer deposition within the pores . . . . . . . . . . . . 134
B.2 Gravimetric estimation of the oxidizer deposition within the pores . . . . 136
B.3 Heat of formation values used for thermochemical equilibrium calculations . 136
B.4 Heat flow from the reaction zone calculated from thermochemical equilibrium calculations . . . . . . . . . . . . . . . . . . . . 137

References 147
List of Figures

1.1 Surface to bulk atom ratio for spherical iron crystals (adapted from [56], Copyright 1996, American Chemical Society) .................................................. 8

1.2 Typical J-V curve for the electrochemical dissolution of silicon in diluted aqueous HF solution (from [64]). Porous silicon is formed when (0 < J < J_{ep}) .................................. 14

1.3 Left side: Picture of a single PS-based explosive element (bottom), a prototype of the airbag igniter (upper left) in comparison with a Eurocent coin. Right side: Image of the ignited single explosive element. From [76] .................................................. 18

1.4 Two-dimensional sketch of the three principal steps (A, B, and C) of the explosive reaction of oxygen with hydrogenated porous silicon. Black circles: oxygen atoms, gray circles: silicon atoms, open circles: hydrogen atoms. The Si dangling bonds are indicated by black lobes. The dashed circumference indicates the ignition site of the reaction. From [71] .................................................. 25

2.1 Cross sectional view of the electrochemical etch cell. The silicon wafer is sandwiched between the two Teflon blocks, and the well is filed with up to 150 ml of the electrolyte. The O-ring exposes only the top side of the wafer to the electrolyte, and the groove in the electrolyte well is used to support the cathode (silver mesh) at a fixed distance from the silicon wafer. ............... 27

2.2 Schematic of the focused shadowgraphy system used in this work ......................... 37

2.3 Schematic showing the process for preparing PS samples with microscale features etched using Photolithographic patterning followed by DRIE .................................................. 41

3.1 Schematic showing the maximum permissible oxidizer deposition within the pores. If the pore is completely filled with the oxidizer solution as shown in the middle figure, upon the evaporation of the solvent, only a thin layer of the oxidizer can be expected to remain in the pore, as depicted in the rightmost figure .................................................. 44

3.2 (a) Top view of the porous layer showing pores with diameters ~30 nm. (b) Low magnification cross sectional view showing bulk silicon with porous layer on the top. The thickness of the porous layer is 140 μm. ............... 47
3.3 (a) Collected raw spectrum, and the corrected spectrum accounting for the collection efficiency of the optics. (b) \( Z \) vs \( 1/\lambda \) plot for estimating the temperature of the reaction zone, for the case \( \varepsilon = \text{constant} \), for PS-magnesium perchlorate composite with an equivalence ratio \( (\varphi_{\text{min}}) \) of 6.7, described in Table 3.1. The flame temperature is \( C/\text{slope} \), where \( C = 1.44 \times 10^2 \), which yields a temperature of 1901 K.  

3.4 Adiabatic flame temperatures calculated using CHEETAH 4.0 equilibrium code and spectroscopically measured flame temperatures as a function of equivalence ratio for PS-magnesium perchlorate composites. The predicted minimum equivalence ratio \( (\varphi_{\text{min}}) \) described by equation 3.4 is used to represent the composite equivalence ratio in this plot. 

3.5 Thermochemical equilibrium calculations showing the Concentrations of product species and the adiabatic temperature as a function of equivalence ratio for PS – magnesium perchlorate composites. The first plateau in temperature between 2000-2100 K is due to the equilibrium between SiO (gas), Si (liquid), and SiO \(_2\) (liquid). The second plateau at 1683 K in temperature is due to phase change of silicon. 

3.6 Thermochemical equilibrium calculations for the reaction between PS and the oxidizers used in this study. The three perchlorate salts used to test the effect of mixture composition on the reactive wave propagation exhibit similar adiabatic flame temperature dependence on the equivalence ratio. 

3.7 Schematic of the model used to describe the reaction between porous silicon and the oxidizer on the basis of a single pore. Figure 3.7(a) represents how the porous layers were approximated to consist of repeating cells with a cylindrical void surrounded by silicon. Figure 3.7(b) depicts a uniform layer of oxidizer coating the pore wall, and the thin reaction zone where the silicon and oxidizer react stoichiometrically. The silicon and the oxidizer beyond this region is assumed to be unable to react on the time scales associated with the reactive wave propagation, and only absorb the heat generated by the reaction zone. 

3.8 Temperatures predicted by the phenomenological model and thermochemical equilibrium calculations as a function of equivalence ratio. 

3.9 Spectroscopically measured and predicted temperatures as a function of equivalence ratio. The predicted minimum equivalence ratio \( (\varphi_{\text{min}}) \) described by equation 3.4 is used to represent the composite equivalence ratio for the spectroscopically measured temperatures.
3.10 Comparison of the temperatures predicted by thermochemical equilibrium calculations and the model for Si - Ca(ClO$_4$)$_2$ system with a porosity ($P$) of 0.60. The maximum allowable thickness of the silicon layer ($\Delta r_r$) that can react with the oxidizer was fixed to be 0.1, 0.2, and 0.3 nm. It can be seen that the temperature predicted by the model can reduce as the equivalence ratio approaches unity, based on the maximum allowable $\Delta r_r$, while the temperature predicted by the thermochemical equilibrium calculations increases. This is due to the excess oxidizer within the pores at lower equivalence ratios acting as a diluent over the time scale associated with the reactive wave propagation.

4.1 Potential energy diagram for the Ge-MoO$_3$ system, adapted from [109]. The addition of the N-type dopant atoms results in an increase of the potential of the Ge-MoO$_3$ system, resulting in the activation energy reducing from $E_a$ to $E_a^*$. 70

4.2 Thermogravimetric analysis (TGA) traces for PS samples prepared from the four different kinds of substrates described in Table 4.1. The PS was heated to 1200 °C at a rate of 20 °C/min, which was followed by a 1 hour isotherm at the same temperature, in an oxygen environment. 76

4.3 The DSC traces of PS samples etched from four different substrates treated with a 0.4 M sodium perchlorate solution and heated in an inert helium environment. 78

4.4 DSC traces of annealed and fresh heavily doped P-type PS samples, and silicon nanoparticles treated with 0.4 M NaClO$_4$ solution. Only the fresh PS exhibits a low temperature exothermic reaction, but all three samples start reacting with the oxidizer below the decomposition temperature of the oxidizer. The exothermic reaction initiates shortly after the oxidizer melts, which can be seen as an endothermic kink in the DSC trace. 79

4.5 DSC traces of heavily doped N and P substrates heated in an inert environment after being impregnated with sulfur. The N-doped PS exhibits a low temperature exothermic reaction with sulfur immediately after the melting point of sulfur, while the P-doped PS does not. 81

5.1 SEM image of the porous silicon etched on low doped N-type substrates with resistivity between 2 and 5 Ω-cm showing the random micro-crack pattern formed during the electrochemical etch process (top view). 88

5.2 Schematic depicting the convective burning mechanism in a granular bed, obtained from [125, 131]. The reactive wave propagates from left to right, and the hot gaseous products generated are driven upstream into the unreacted material by localized pressure build up. The upstream heat transfer is enhanced by the convective heat transfer from the permeation of the gaseous products, and when the convective preheat exceeds the conductive preheat zone, the reactive wave propagation speeds are enhanced. This phenomenon is known as convective burning. 89
5.3 Top view of the etched pillar structures, showing square bases with a side of 8 \( \mu \)m separated by 8 \( \mu \)m. (b) Side view of the pillared structures showing the sidewall profile. These pillars are about 35 \( \mu \)m tall.

5.4 (a) SEM image of a single pillar showing the nanoscale features. (b) High magnification image of a single pillar showing pores with diameters \(~30\) nm, similar to the PS samples shown in Figure 3.2.

5.5 The four different configurations of patterned PS substrates prepared. The shaded region in the images represents the nanoporous region. The thickness of the substrates used in all these cases was 525 \( \mu \)m. Note that the image is not to scale.

5.6 Reactive wave propagation on patterned substrate with only nanopores on the bottom half and nanoporous pillars \(~35\) \( \mu \)m tall on the top half. Note the non linear time change between photographs. The reactive wave propagation speed exhibited a sudden transition from \(~2.5\) m/s to \(~360\) m/s as shown in the following x-t plot.

5.7 x-t plot for sample shown in Figure 5.6. The slope of the straight line fit indicates the reactive wave propagation speed.

5.8 SEM images of the square cylindrical pillars etched on heavily doped P-type substrates. (a) Top view showing 12 \( \mu \)m \( \times \) 12 \( \mu \)m square bases separated by 7 \( \mu \)m. (b) The silicon-PS interface (c) Side view of the square cylindrical pillars and the PS layer etched on the silicon substrate. The PS layer below the pillars is 133 \( \mu \)m thick, and the initial thickness of the silicon wafer was 525 \( \mu \)m. (d) Side view of a pillar showing the sidewall profile arising due to the plasma etch process (DRIE). The pillars are 57 \( \mu \)m tall. The curvature in the side wall profile is due to the isotropic component of the DRIE.

5.9 Series of images from the high speed side view shadowgram captured for samples in which the non patterned PS was ignited and the reactive wave was allowed to propagate into the patterned region. The high speed video was recorded at a frame rate of 80590 fps, with an exposure of 1.02 \( \mu \)s. Note the non linear time scales used. The dark strip seen on the left side in each of the images in the panel is the side view of the silicon wafer and the mounting block placed in the shadowgraph system depicted in Figure 2.2. (a) and (b): Consecutive images acquired following the ignition of the PS sample by a spark. The arrows point to the location of the weak shock that was generated upon ignition. (c) and (d) depict the formation and growth of a localized ignition front resulting in a “flame jump”. (e) and (f) show the steady state propagation, and (f) is the frame right before the reactive wave encounters the patterned region. In (a)-(f), the plume containing the hot gaseous products is directed away from the direction the reactive wave propagates. (g) shows the shock formation when the reactive wave enters the patterned region. In (g)-(l), gas permeation ahead of the luminous flame front can be seen.
5.10 Schematic explaining the directionality of the gaseous product plume seen in Figure 5.9. In the non patterned region, the gaseous products formed at the reaction zone are confined in the upstream direction by the silicon substrate and the PS layer, forcing the gases to be ejected in a direction away from the reactive wave propagation. However, the small micrometer sized pillars are expected to disintegrate and burn, or explode, resulting in the gaseous products being ejected ahead of the reaction zone, resulting in convective burning.

5.11 Representative SEM image of the microchannels etched on PS samples. For the PS sample shown in this figure, the spacing between the sidewalls is 8 μm, and the thickness of the sidewalls is 12 μm. The height of the sidewalls is 82 μm, and the thickness of the PS layer below is 118 μm.

5.12 Representative SEM image of the microchannels with wider channels. The aspect ratio of the void is used to plot the enhancement in the reactive wave propagation speeds due to the microchannels etched on the silicon substrates, and is defined as W/H. Since this is an unconfined system, W and H phenomenologically represent the inverse of the ratio of the resistance to the gas flow away from the PS sample (through the opening at the top) versus along the microchannel, respectively. The permeation of hot gaseous combustion products along the microchannels can convectively transfer heat to the sidewalls, resulting in an enhancement in the reactive wave propagation speeds.

5.13 Reactive wave propagation speeds parallel and perpendicular to the microchannels etched on heavily doped P-type PS as a function of the void aspect ratio. No specific dependence of the reactive wave propagation speed on the channel width or height was observed. The highest speeds were obtained when the reactive wave propagation was along the microchannels, and at low void aspect ratios.

6.1 Longitudinal speed of sound in low doped P-type PS from literature and the values measured by acoustic microscopy. For the low doped P-type PS samples used in this work, the measured speed of sound was between 2169 m/s and 2479 m/s, while the reactive wave propagation speeds measured were below 1500 m/s, indicating that the reactive wave propagation was subsonic.

6.2 Side view shadowgram image of the reactive wave propagation in low doped P-type PS samples impregnated with sodium perchlorate. The reactive wave front moves supersonic with respect to the air, and drives the shock. A small stand-off distance was observed between the shock-PS surface and the luminous reactive wave front on the PS surface.
6.3  (a) Schematic (not to scale) of the test samples prepared to study the interaction of the gas phase shock with PS. The PS in the top and bottom regions of the test sample is impregnated with sodium perchlorate while the PS in the middle is not. (b), (c), (d) and (e) are a series of images from a high speed shadowgraph recording, and the time delay between each image is 12.5 µs. (b) shows the reactive wave front in the first PS region impregnated with the oxidizer. In this image, the shock is driven by the reactive wave front. (c) shows the propagation of the decaying shock upon the complete combustion of the reactive PS in the first filled region. (d) and (e) show the ignition and combustion of the second reactive PS region as the shock from the first region passes over it.

6.4  DSC traces of PS samples with different SSA treated with a dilute (0.4 M) NaClO₄ solution and heated 20 °C/min in an inert helium environment. The temperature of the first exothermic peak was found to shift to lower temperatures as the SSA increases, with most of the heat release from the PS samples with the highest SSA used in this work (730 m²/g) being associated with the lowest temperature exothermic peak.

7.1  PS microchannels etched on silicon wafers masked with silicon nitride. The dark regions are PS while the reflective regions are silicon nitride. The width of the PS microchannels was approximately 200 µm, and the smallest separation between the microchannels was approximately 300 µm, as seen in the inset (post combustion image). No cross-talk between the PS microchannels was observed at this separation, and the reactive wave front propagated for 120 ms.
List of Tables

1.1  Scaling laws for various physical phenomena, adapted from [7]. As the length scales reduce, the importance of the phenomena with a stronger dependence on the length scale diminishes rapidly, resulting in the different behavior of microscale systems compared to macroscale systems. ............................................. 3

1.2  The actuation pressure provided by different actuation mechanisms (from [8]) ................................................................................................................. 5

1.3  An investigation of the occurrence of explosive reactions in PS composites prepared by depositing various oxidizers in the pores using organic solvents (adapted from [76]) ................................................................. 19

3.1  Equivalence ratio, reactive wave propagation speeds, and spectroscopically determined temperatures for porous layers etched on heavily doped P-type substrates impregnated with magnesium perchlorate. The reported ranges of the temperature and the reactive wave propagation speed ($\theta$) are measurements over several samples. $\varphi_{\text{min}}$ is the theoretical equivalence ratio as described in equation 3.4. The spectroscopic temperatures were estimated using a gray body assumption, as described in section 2.3.1.1 on page 31. ........................................................................................................ 49

3.2  Solubilities of selected perchlorate salts in methanol, grams per 100 grams of solvent at 25 °C (From [99]). $\varphi_{\text{min}}$ was calculated for saturated solutions and porous layers with $P = 0.60$, ignoring the surface hydrides as described in equation 3.4. ........................................................................................................... 52

3.3  Reactive wave propagation speeds and temperatures for PS composites prepared using porous layers etched on a heavily doped P-type substrate with a porosity of 0.6. The dilute calcium perchlorate solution was prepared to yield composites with the same theoretical equivalence ratios as a saturated sodium perchlorate solution. The measured flame speeds and temperatures over several samples (at least three samples for each case) are shown as the range of values (minimum – maximum) from all experiments. .......................... 54

4.1  Substrate dopant type and resistivity of the silicon wafers used to prepare porous silicon for thermal analysis, the current density for the electrochemical etch, and the specific surface area (SSA), porosity, and average pore width of the etched samples determined using a multi-point BET measurement. .......................... 73
4.2 Porosity, SSA, and Reactive wave propagation speeds measured on PS etched from four different silicon substrates. ................................................. 82

6.1 Reactive wave propagation speeds in air and helium ......................... 112
6.2 Estimated activation energies for the first exothermic reaction between PS and sodium perchlorate for PS etched from heavily doped and low doped P-type substrates. ................................................. 115

B.1 Gravimetric porosity calculations for PS etched on heavily doped P-type substrates with resistivity between 0.001 – 0.005 Ω-cm. ................................. 134

B.2 Sample data for magnesium perchlorate deposition and equivalence ratio estimations described in section 3.2.1. The data presented in the following table are for sample #3 from the above table, with a calculated porosity of 75.06 %. Oxidizer solutions in methanol of varying concentrations are used to deposit the oxidizer within the pores. ................................. 136

B.3 Heat of formation data used for thermochemical equilibrium calculations (from [99]) ................................................................. 137

B.4 Heat flow from the reaction zone from thermochemical equilibrium calculations ................................................................. 137
Acknowledgments

This dissertation marks the end of my long, but rewarding stay at Penn State, and I owe thanks to several people who have helped me immensely before and during my graduate education. First and foremost, I want to thank both my advisors, Dr. Richard Yetter and Dr. Srinivas Tadigadapa. I have known Dr. Yetter since my first semester of classes at Penn State, and Dr. Srinivas since I started my work on porous silicon. I am grateful for the time, energy, and resources they have invested in me, which will undoubtedly play a vital role in my future success as a researcher. Beyond the obvious technical and financial support, I have greatly benefited from the freedom they have provided me to formulate and explore research ideas while ensuring that I remain focused enough to advance my dissertation. Their timely pep talks have helped me keep my spirits up during difficult times and work towards my goals. Over the last several years, I have very much enjoyed interacting with them, and I would like to thank them for providing the opportunity to be a part of their research groups, and I hope I have learned as much as I can from them during my stay here.

I would like to acknowledge the support provided by my doctoral committee, Dr. Gary Settles, Dr. David Allara, and Dr. Donghai Wang. I would like to thank Dr. Settles for the interesting compressible flow classes, for taking the time to speak with me about my research, for helping me interpret the compressible flow phenomena I encountered in my work, and for helping me improve my dissertation. I would also like to thank Dr. Allara for the help with surface chemistry, through course work and research discussions. Thanks
are also due to the several teachers over the years, and particularly to Dr. T. Sundararajan at IIT Madras whose classes and guidance during my undergraduate days encouraged me to pursue research in the field of thermal-fluid sciences.

As a member of two research groups, I have immensely benefited from several wonderful lab mates, who helped me both in and out of the lab. I have enjoyed the conversations, technical and otherwise, outings, group meetings, and the diverse perspectives they offered, which helped me broaden my knowledge beyond the confines of my specific research projects. I am grateful to the past and present members of both research groups, and thank them for several fond memories. In particular, I would like to thank Jonathan Malchi for taking the time to give me a thorough tour of Dr. Yetter’s labs and explaining the various projects when I expressed an interest in joining the group; Justin Sabourin for helping me with the design and initial steps of the thermal conductivity measurement work; Michael Weismiller for always making time to speak about reactive materials, and for always offering to help, many times without even having to ask; Steven Dean for the many interesting weekly meetings, getting me started with thermal analysis, the various experimental setups that he built and let me use, and help with SEM images; Marcelo Pisani for getting me started in the clean room, and developing and/or maintaining meticulous records of the various processes several of us used; Prasoon Joshi for inspiring all of us to be a little more organized than we were.

This work would not have been possible without the help of Dr. Jong Guen Lee and Terrence Connell. Dr. Jong Guen Lee helped me get started with experimental research at Penn State, spent time with me during my first several weeks in the lab, and patiently answered my oftentimes silly questions. I learnt a lot from him about how to conduct experiments. Terry Connell, who is incapable of saying no, has always been available and more than willing to help with machining, setting up experiments, and anything else, regardless of the time of the day (or night).
Special thanks to Pulkit Saksena and Kuni Togai, whose company I have greatly enjoyed both in and out of the lab. Thanks to Pulkit, who has been a member of both Dr. Yetter’s and Dr. Srinivas’ research groups, for giving me company in the several courses we took together as well as in the clean room, for the several long trips, opening his house for the fun evenings, and being the sure-shot designated driver. Thanks for always being there, and helping me out whenever I needed, even when it was not the most convenient thing for you to do. Thanks to Kuni, for the several stimulating conversations we had in our office about thermal-fluid sciences, the several scripts and tips, and spending the time to introduce me to Japanese. Thanks to both of you for making my stay at Penn State more enjoyable. Also, thanks to my several other friends and roommates over the years, with special thanks to Syamal Tallury, Raghavan Balaji, Deepak Trivedi, Dilip Sundaram, Varadhan Srinivasan KariyaMaanikam, Shankar Prasad Sastry, Josh Heyne, and Mike Szedelmayer.

I would also like to thank the people who went out of their way to help me during the rather taxing first few weeks at Penn State, and deal with the arduous task of replacing documents in a foreign country and adapting to graduate school: Raghavan Balaji, Anoop Srikar, Jenny Houser, Masume Assaf, and Dr. Stefan Thynell. Thanks are also due to Mary Newby for taking care of all the paperwork and making my life easy over the years.

Thanks to my parents who have supported me in every possible way. Thanks especially to my mother, who put my happiness and interests over her own, and for the numerous compromises and sacrifices, small and large, that she has made over the years to ensure that I always had the best possible opportunities. No words can express my gratitude for her, and I hope to live my life in such a way that it is worth what she has done for me. Finally, thanks to my fiancée, Rashmy, whose unwavering faith in me and unquestioning support over the last dozen years has kept me going. Thank you for believing in me even when I did not, for always being there for me, and for making several compromises to let me have the best possible shot at everything I desired. I am looking forward to our life together.
“The purpose of a PhD degree is to learn how to learn.”
Chapter 1

Introduction

1.1 Background

1.1.1 Energetic materials

Energetic materials (EMs) are substances that store large amounts of energy chemically, and are classified into explosives, propellants, or pyrotechnic materials based on the rate of energy release. Propellants and pyrotechnics release energy slowly by means of deflagration processes lasting several seconds, whereas explosives release large amounts of energy over a very short time, typically on the order of microseconds or lesser, by means of detonation processes. Energetic materials have played an important role in civilian and military applications, ranging from the incendiary compounds used in the Trojan Wars (circa 360 B.C.) to black powder and pyrotechnic materials used by the ancient Chinese (circa 12th century) to the modern day explosives, propellants, and pyrotechnic materials. Based on their formulation, traditional EMs can be broadly divided into two groups:

1. Monomolecular compounds comprising both the fuel and the oxidizer such as trinitrotoluene (TNT), cyclotrimethylenetrinitramine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) etc.
2. Composites made by mixing fuel and oxidizer together, such as black powder, thermites, etc.

Extensive use of EMs in the modern world as propellants and explosives has driven the research towards understanding, predicting, and controlling the properties of EMs, and a detailed review of the advances made in the design and synthesis of EMs can be found elsewhere [1,2].

1.1.2 Micropyrotechnics

MEMS (micro-electromechanical systems) refers to microscale devices consisting of one or more micromachined components that enable higher level functionality. These devices have length scales between 1 mm and 1 μm, and consist of sensors, actuators, and passive structures. Microscale devices whose base material is silicon utilize many of the well developed and well understood microfabrication techniques used to manufacture semiconductor devices. Thus, these microscale devices can be machined precisely and can be batch manufactured, greatly reducing the unit cost as demonstrated by the semiconductor industry. In fact, the recent transformation of smartphones to powerful computers which can interact with a variety of sensors has resulted in a significant spike in the consumer MEMS industry, with the MEMS component market expected to grow to $16 billion by the end of 2016 [3].

Further, the biological and biomedical applications of micro- and nanotechnology (known as BioMEMS), which can be used for diagnostics, therapeutics, and tissue engineering have attracted significant research attention and are expected to result in miniature consumer lab-on-chip devices capable of detection and diagnostics. The BioMEMS market is also expected to grow into a multibillion dollar industry, with affordable and simple microscale devices providing a means to quickly and remotely perform simple biological/chemical assays to provide diagnostic information [4,5].

Currently, there is a significant amount of research effort directed at miniaturization of functional devices, as the reduced length scales can present several additional advantages such as increased performance, reduced mass, and significantly reduced energy consumption
However, these reduced length scales also result in a drastic difference in the physical forces controlling the behavior of these devices due to the greatly increased surface area to volume ratios. Thus, the volumetric forces such as inertia, gravity, electromagnetic forces, which are prominent in the macroscopic world become less important than surface area controlled phenomenon such as surface tension, adhesion, friction, stiction, etc. [7]. The relative importance of various physical phenomenon at different length scales, and their scaling laws are shown in Table 1.1.

Table 1.1. Scaling laws for various physical phenomena, adapted from [7]. As the length scales reduce, the importance of the phenomena with a stronger dependance on the length scale diminishes rapidly, resulting in the different behavior of microscale systems compared to macroscale systems.

<table>
<thead>
<tr>
<th>Phenomena</th>
<th>Power of linear dimension</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow</td>
<td>$l^4$</td>
</tr>
<tr>
<td>Gravity</td>
<td>$l^3$</td>
</tr>
<tr>
<td>Inertial force</td>
<td>$l^3$</td>
</tr>
<tr>
<td>Magnetic force</td>
<td>$l^2, l^3, l^4$</td>
</tr>
<tr>
<td>Thermal emission</td>
<td>$l^2$ or $l^4$</td>
</tr>
<tr>
<td>Electrostatic force</td>
<td>$l^2$</td>
</tr>
<tr>
<td>Friction</td>
<td>$l^2$</td>
</tr>
<tr>
<td>Pressure</td>
<td>$l^2$</td>
</tr>
<tr>
<td>Piezoelectricity</td>
<td>$l^2$</td>
</tr>
<tr>
<td>Shape-memory effect</td>
<td>$l^2$</td>
</tr>
<tr>
<td>Velocity</td>
<td>$l$</td>
</tr>
<tr>
<td>Surface tension</td>
<td>$l$</td>
</tr>
<tr>
<td>Diffusion</td>
<td>$l^{1/2}$</td>
</tr>
<tr>
<td>Van der Waal force</td>
<td>$l^{1/4}$</td>
</tr>
</tbody>
</table>

The difference in the physical phenomena controlling the behavior of microscale systems results in several issues associated with scale effects, as several conventional actuation methods commonplace in macroscopic systems are impractical, inefficient, or difficult to integrate onto MEMS platforms. In addition to difficulties associated with actuation, finding suitable low cost energy sources capable of providing sufficient quantity of easily accessible energy which can be integrated on microscale devices has been an ongoing effort for decades [8]. Conventional approaches to mechanical actuation based on electromagnetic effects are very efficient, but difficult to integrate into microscale devices [9]. While ele-
trostatic forces provide a powerful actuation mechanism that can also be integrated easily with MEMS platforms, these forces are limited to only small displacements \cite{10–12}. One example of the several problems associated with powering and actuating microscale devices is the slow growth of the BioMEMS industry, especially in regards to microfluidic devices. Despite their potential to provide simple, inexpensive, effective, and miniature diagnostic devices, which have been predicted to be ubiquitous by this time, BioMEMS are still largely restricted to the developed world and laboratories. Complex microfluidic devices capable of performing biological/chemical assays have been successfully demonstrated by several researchers, and even integrated onto microfluidic platforms to perform complex analyses. However, currently these microfluidic devices require expensive bench-top equipment such as pumps and switches for fluid actuation, which negates many of the advantages provided by microscale devices \cite{5}.

One way to address the issue of powering and actuating microscale devices is to integrate a small amount of an EM on-board the device, and harvest the chemical energy stored within the EM. While the energy density of modern lithium-ion batteries is \( \approx 0.5 \text{ MJ/kg} \) \cite{13}, the combustion of typical propellants and explosives yields \( \approx 5 \text{ MJ/kg} \) \cite{8}. Thus, even at modest conversion efficiencies, propellants and explosives are capable of providing more energy than batteries. Further, when dealing with mechanical actuation at the micrometer scale, Rossi et al. \cite{8} suggest that an “actuation pressure parameter”, which is the volumetric energy density of an actuation mechanism, is a more appropriate metric to describe the efficacy of an actuation mechanism. The actuation pressures that can be achieved from various mechanisms are shown in Table 1.2, which indicates that EMs are the most promising sources of energy for mechanical actuation.

Thus, the integration of EMs into a multi-functional microsystem, and the exploitation of the thermal, mechanical, and chemical energy released by their decomposition has received significant attention recently, and is known as micropyrotechnics \cite{8}. Beyond satisfying power and actuation needs that battery systems cannot, this approach provides several other advantages:
Table 1.2. The actuation pressure provided by different actuation mechanisms (from [8])

<table>
<thead>
<tr>
<th>Type of actuation</th>
<th>Actuation pressure (J/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Piezoelectric (PZT)</td>
<td>$10^5$</td>
</tr>
<tr>
<td>Electrostatic</td>
<td>$10^3$</td>
</tr>
<tr>
<td>Electromagnetic</td>
<td>$10^5$</td>
</tr>
<tr>
<td>Thermomechanic</td>
<td>$10^5$</td>
</tr>
<tr>
<td>Thermopneumatic</td>
<td>$10^6$</td>
</tr>
<tr>
<td>Shape memory alloy (SMA)</td>
<td>$10^7$</td>
</tr>
<tr>
<td>Phase change (solid↔liquid)</td>
<td>$10^6$ to $10^7$(acetimine) to $10^5$ (paraffin)</td>
</tr>
<tr>
<td>EM combustion</td>
<td>$10^7$ to $10^8$</td>
</tr>
</tbody>
</table>

- Since the initiation of EM decomposition typically requires only a small amount of energy for initiation, EMs as an on-board energy source can provide a much longer shelf life.

- Based on the choice of EM, the energy release can occur over a wide range of time scales. Choosing highly reactive EMs which release their chemical energy over a very short time scale can provide high impulses, which can exceed the impulses obtainable upon discharging a battery.

- While battery systems only provide electrical energy, EMs can also be chosen to provide chemical species to achieve a specific task (for example, generate specific spectral lines for spectroscopy, produce gaseous products with antibacterial properties, etc.), or gaseous products to generate thrust, or high local heating rates, in addition to simply providing heat that can be harvested and converted to electrical energy.

The versatility of micropyrotechnics is evident from the wide range of devices already developed using EMs as on-board energy sources, such as microthrusters [14–23], microinitiators [24–28], actuators utilizing gaseous products from EMs [29–33], chemical reactions initiated or driven by the hot gaseous products [34–36], explosive welding [37], switching [38], and drug delivery and cell transfection [39]. Successful integration and energy harvesting from EMs in a manner compatible with standard microfabrication techniques...
can help move several microscale systems from laboratory scale experiments to inexpensive and commercially viable devices.

While micropyrotechnics can solve many of the power and actuation challenges faced by microscale devices, integrating EMs as on-board energy sources presents several new technological and scientific challenges. A detailed discussion of the various challenges can be found in the review article by Rossi and Esteve [8], and the important issues outlined by them are presented below:

1. Optimization of the initiation mechanisms to minimize the energy required to initiate the EM reactions.

2. Choosing an appropriate EM based on the power/actuation needs of a specific device. This is crucial, since the energy released from the EM needs to be harvested to perform a specific function.

3. Reducing the dimensions of micropyrotechnic devices to fully exploit the several advantages of MEMS.

4. The ability to develop and execute manufacturing processes to obtain simple, reliable, and robust micropyrotechnic devices. This applies to both the substrates on which the devices are built, and the EMs which are to be integrated.

While there are several advantages to building smaller devices, the increased surface area to volume ratios also greatly increase the heat losses which affects the performance of EMs. Due to their slow reaction rates, heat losses in traditional EMs start to exceed the heat generation rates resulting in the reaction being quenched at length scales on the order of several mm. For example, HMX deflagrations quench in tubes several millimeters in diameter, and glycidyl azide polymer and ammonium perchlorate (GAP/AP) formulations fail to propagate in tubes with diameters less than 1.4 mm [40]. To sustain a reactive wave propagation at such small length scales, more reactive materials are required, and some efforts to enhance the reactivity of traditional EMs have focused on incorporating micro
and nanoscaled metallic particles into EMs. While faster reactive wave propagation speeds have been demonstrated by these composite materials [41–43], their increased reactivity also makes their handling difficult [40].

1.1.2.1 Nanoenergetic materials (nEMs)

It has been found that the highest increase in the reactivity of traditional EMs was achieved by mixing nanoscale metallic particles into the EM formulations. Further, the energy density of traditional EMs are limited by the enthalpies of the product species formed, which are typically CO$_2$ and H$_2$O [44]. This limitation becomes more important when the volumetric energy density, i.e. the actuation pressure parameter is considered, which is important for microsystems. Significantly higher energy densities can be obtained upon combustion of metals due to the difference in the enthalpies of the product species formed. Inorganic EMs consisting metal-metal oxide systems which participate in redox reactions have been found to have energy densities higher than traditional EMs. Unlike monomolecular organic EMs whose combustion processes are kinetically controlled, the ignition and combustion of metal particles are usually in the diffusion controlled regime. Micrometer scale metal particles have large ignition delays and burn times when incorporated into EM formulations, as the oxidizing species or the metal vapor typically need to diffuse through the native oxide layer to initiate and sustain the reaction, resulting in poor combustion efficiencies [45–48]. With recent advances in material sciences, nanoscale and/or nanostructured metal particles can be produced in a controlled manner and can be accurately characterized. One of the obvious advantages of using nanoscale metal particles in EM formulations is the greatly reduced transport length scales, which translates into smaller reaction time scales resulting in increased combustion efficiencies. For example, among thermite systems (metal - metal oxide particle formulations, also known as metastable intermolecular composites or MICs), the highest burning rates have been observed with nanoscale constituents [40].

Another advantage of using nanoscale/nanostructured materials (in the case of particles, the length scales of interest are less than 10 nm) is that they can exhibit properties
significantly different than the same material in its bulk form. For example, the melting points, freezing points, and the heat of fusion change significantly with size [49–52], the reactivity of the particles increases with reducing diameters [53,54], and nanoscale particles demonstrate excellent catalytic properties [55] to name a few effects of the reduced dimensions. These interesting properties of nanoscale particles are a consequence of the enhanced surface to volume ratios at small length scales. While bulk materials only contain a small fraction of their atoms at their surfaces, the proportion of atoms at the surface increases with reduced diameters, as shown in Figure 1.1.

![Figure 1.1. Surface to bulk atom ratio for spherical iron crystals (adapted from [56], Copyright 1996, American Chemical Society).](image)

The coordination number for the surface atoms (the surface coordination number) is always lesser than the bulk coordination number, as a result of which, the surface atoms are at a higher energy state than their bulk counterparts. The excess energy of the surface atoms is responsible for the different properties of nanoscale materials, and this enhanced
reactivity coupled with the reduced transport length scales can be exploited to form highly reactive formulations such as MICs, nanolaminates (which may contain alternating layers of metals which participate in exothermic intermetallic reactions), and nanoporous materials. A detailed review of several nanoenergetic material formulations can be found elsewhere (nanostructured energetic composites [57], nanoenergetic materials with emphasis on micropyrotechnics [40], and a detailed review of metal combustion with emphasis on aluminum nanoparticle combustion mechanisms [58]). The enhanced reactivity of nanoenergetic materials (nEMs) allows them to sustain reactive wave propagations without being quenched even in micrometer scale channels [59]. However, this enhanced reactivity also makes integration of EMs onto MEMS platforms difficult.

One unique nEM of significant interest is porous silicon (PS), which is essentially bulk silicon with missing crystal atoms. The nanometer scale pores formed due to the missing silicon atoms result in the formation of highly developed internal surfaces with specific surface areas (SSA) of several hundreds of m$^2$/g [60]. By exploiting the large surface areas, highly reactive composites capable of storing and releasing large amounts of energy can be created. Further, these PS composites have an important advantage over other nEMs, as their base material is silicon, which is also the base material for microelectromechanical systems (MEMS). Thus, PS can be expected to be compatible with standard microfabrication techniques, presenting the possibility of low cost batch processing and simplified integration into microscale devices. Another significant advantage of PS over the most commonly used metal for nEMs (aluminum) is that PS surfaces are hydrogen terminated with minimal loss of reactive metal as a native oxide. This is of significance, as mass fraction of the inert oxide layer on conventional nanoparticles starts increasing rapidly as the particle sizes shrink, offsetting the advantages of increased reactivity. Also, chemical treatments can be used to replace the passivating oxide layer on silicon or create monolayers on PS surfaces without an oxide layer separating the silicon atoms and the coating material to create highly organized reactive formulations. Such functionalizations have not been demonstrated till date with other metals of interest such as aluminum or boron. Silicon based EMs also have better ag-
ing properties than aluminum based materials as the thickness of the native oxide on silicon particles is only about half as thick as the native oxide on aluminum particles. A preliminary demonstration of the compatibility of PS with standard microfabrication techniques was shown by Currano and Churaman, who fabricated a monolithic device containing an accelerometer and an igniter for PS [61]. However, a thorough understanding of the combustion and reactivity of PS composites is lacking, which is essential to fully exploit the advantages of PS as an easily integrable nEM.

1.2 Review of porous silicon literature

Porous silicon was discovered accidentally by Uhlir [62] while attempting to develop a polishing technique for silicon and germanium. The formation of PS was considered more of an annoyance by the semiconductor fabrication industry, and received little attention for the next several decades until the demonstration of room temperature photoluminescence and its potential optoelectronic applications by Canham [63] in 1990. Most of the research efforts on PS focused on exploiting its optical and electric properties. This led to an extensive investigation of the structure of thin porous layers suitable for such applications. A detailed review of fabrication and the structural and electronic properties of porous silicon can be found elsewhere [64]; formation of PS, and properties of PS pertinent to the work presented in this dissertation are described in this chapter.

1.2.1 Formation and structure of porous silicon

PS is formed by a simple electrochemical process with aqueous hydrofluoric acid (HF) based electrolytes which results in the selective dissolution of silicon atoms leading to the formation of a porous structure. The selective dissolution of silicon atoms can be accomplished in three ways

1. Electrochemical dissolution

In this process, the dissolution of silicon is accomplished in an electrochemical cell,
with an external power source. While the pore initiation and propagation mechanisms are still unclear, the generally agreed mechanism is described in the following three equations requiring positive charge carriers (holes, h$^+$) [65,66]

\[
\text{Si} + 2\text{HF} + \lambda \text{h}^+ \rightarrow \text{SiF}_2 + 2\text{H}^+ + (2-\lambda)\text{e}^-(1.1)
\]

\[
\text{SiF}_2 + 2\text{HF} \rightarrow \text{SiF}_4 + \text{H}_2 (1.2)
\]

\[
\text{SiF}_4 + 2\text{HF} \rightarrow \text{H}_2\text{SiF}_6 (1.3)
\]

while P-type silicon, in which holes are the majority charge carriers can be etched even in darkness, N-type silicon, in which the majority charge carriers are electrons requires illumination to generate holes. During the electrochemical dissolution process to form porous silicon, the silicon substrate acts as the anode, and a HF resistant metal (gold, platinum, or silver) acts as the cathode. Due to the highly corrosive nature of HF, the electrochemical etch is typically carried out in a cell made of HF resistant polymer such as Teflon. The uniformity of the porous layers can be improved by reducing the current gradients across the wafer surface by using a Teflon cell equipped with an O-ring to expose only one side of the wafer to the electrolyte. This set up allows a uniform electrical contact on the backside of the silicon wafer. For heavily doped silicon substrates with low resistivities (on the order of a few m$\Omega$-cm), uniform backside electrical contact can be obtained without any special preparation. For silicon substrates with lower dopant atom concentrations (and subsequently higher resistivities), backside electrical contact can be achieved by:

(a) High dose ion implantation on the backside of the wafer followed by an anneal.

The anneal helps to correct the damage to the silicon crystal structure due to the ion bombardment and helps the dopant atoms diffuse into the silicon substrate and incorporate themselves into the silicon crystals. This results in the formation of a thin heavily doped region on the backside of the silicon wafer, which can be
used to create uniform backside electrical contact.

(b) Deposition of a thin layer of platinum or titanium on the backside of the wafer (using sputtering, evaporation etc.) followed by an anneal at elevated temperatures. The high temperature anneal in this case results in the formation of conductive platinum or titanium silicide at the metal-silicon interface, which allows an electrical contact to be established.

2. Stain etching

The stain etching process involves the selective dissolution of silicon in solutions containing HF and nitric acid. In this method, the pore propagation occurs by the sporadic oxidation of silicon by nitric acid, followed by oxide layers being etched away by HF. The overall chemical reaction can be described by equation 4 [64]

\[
3\text{Si} + 4\text{HNO}_3 + 18\text{HF} \rightarrow 3\text{H}_2\text{SiF}_6 + 4\text{NO} + 8\text{H}_2\text{O} + 3(4-\lambda)\text{h}^+ + 3(4-\lambda)e^- \quad (1.4)
\]

While stain etching process can be carried out easier than the electrochemical process, the porous layers formed by stain etching are limited to very small thicknesses, and suffer from lack of repeatability when thicker films need to be etched. Recently, a modified version of stain etching, utilizing nitrate salts, has been successfully used to etch small silicon particles (nm - few \(\mu\)m scale particles) with repeatably for use in batteries [67].

3. Galvanic etching

This process is similar to the electrochemical dissolution process in terms of the formation mechanism. However, in this method, no external power source is needed; the fact that platinum and gold have lower standard potentials compared to silicon is exploited by coating the backside of the silicon wafers with these metals. When this silicon wafer is immersed in an oxygen containing HF electrolyte (typically consisting a small amount of hydrogen peroxide), the galvanic cell formed between silicon and
the platinum or gold layer causes current to flow within the layer in the right direction to result in the formation of porous silicon [68, 69]. The current density within the silicon substrate is controlled by the surface area ratio of the metal to the silicon surface, and the concentration of hydrogen peroxide.

The work presented in this dissertation predominantly deals with PS formation in an electrochemical cell, and the formation and structure of PS will be discussed from this perspective in this chapter.

The typical current density ($J$) – voltage ($V$) curve for the electrochemical dissolution of silicon in HF electrolytes is shown in Figure 1.2. Pore formation occurs when $0 < J < J_{ep}$, which corresponds to the sharp peak in the J-V curve known as the electropolishing peak. The peak current, $J_{ep}$, depends primarily on the solution composition. For $J > J_{ep}$ the silicon surface is etched away uniformly without pore formation, and this phenomenon is known as electropolishing. At current densities below the electropolishing peak, the rate limiting parameter for the dissolution of silicon is the diffusion of the holes required for the electrochemical dissolution to the silicon - electrolyte interface. At current densities above the electropolishing peak, the limiting parameter is the diffusion of the fluoride ion in the electrolyte. This results in the formation of a silicon dioxide layer at the surface, which is then attacked and dissolved by the fluoride ions, resulting in electropolishing.

1.2.1.1 Factors affecting the structure of porous silicon

The structure of the PS formed strongly depends on several factors, such as illumination, electrolyte composition, duration of the etch process, current density, and the dopant type and concentration in the silicon substrate. A parametric discussion illustrating the effect of various experimental conditions follows:

1. Effect of illumination

The electrochemical dissolution reactions proposed to describe the formation of PS require holes. For n-type substrates, the structure strongly depends on illumination
due to the electron/hole pairs created by the light. Anodization of n-type silicon in the dark only occurs at high voltages, and results in a macroporous substrate (pore width > 50 nm) with low porosities, between 1-10%. Under illumination, much larger porosities can be obtained, with a wide distribution in the pore radii and the porous structure depends strongly on the light intensity [64].

2. **Effect of the electrolyte composition**

The formation of porous silicon is accompanied by the evolution of hydrogen at the anode. The efficient removal of the hydrogen bubbles formed is important to ensure stability and uniformity of the porous structure. When purely aqueous HF is used as the electrolyte, the bubbles stick to the surface and create non uniformity and may lead to cracking of the porous layer. This can be avoided by using surfactants to reduce the surface tension of the solution which allows the bubbles to leave the surface sooner. Several solvents can be used to accomplish this, such as ethanol, acetic acid, and commercial surfactants. While a minimum concentration of 15% by volume ethanol is required for efficient bubble removal, lower concentrations of acetic acid (5% by volume) are sufficient and commercial surfactants allow for an
even higher HF concentration in the electrolyte. The preferred electrolytes according to the extensive literature on PS are typically aqueous HF and ethanol mixtures. For a given current density, the pore diameters and porosity reduce with increasing HF concentrations in the electrolyte. However, for heavily doped p-type substrates with low resistivity, the pore diameters remain unchanged regardless of the experimental conditions [64].

3. **Current density and etch duration**

The porosity of the PS layers formed increase with an increase in the anodization time or current density. The thickness of the porous layers increases linearly with anodization time. The pore diameters typically increase as the current density increases, till the electropolishing regime is reached.

4. **Substrate dopant type and concentration**

For fixed electrolyte composition, current density and illumination conditions, the pore diameters of P-type substrates become smaller as the dopant concentration reduces (increasing the resistivity). Lower dopant concentrations result in smaller pores for a given electrolyte composition and current density for P-type samples. The porous layers formed on moderately doped and heavily doped substrates have been observed to have qualitatively different structures. In degenerately doped (heavily doped) N-type or P-type silicon, the pore structure consists of many long voids running perpendicular to the surface with possible branching, while non-degenerate substrates have non-directional and random but interconnected distribution of voids. The effect of various etch parameters differs based on the dopant atoms, as described below.

- **P-type**

  Heavily doped P-type substrates were found to yield the same pore size range for the same porosity regardless of the etch parameters. The specific surface areas were found to be around 200 m²/g. In low doped P-type substrates, the pore walls are always very thin, and the pore sizes are typically between 1 to 5 nm. The PS etched on
low doped P-type silicon substrates has much larger SSA (up to 800 m\(^2\)/g) than the heavily doped substrates.

- **N-type**
  For heavily doped N-type substrates, the pore radii and the distribution broaden with increasing thickness of N-type and P-type porous layers, resulting in a porosity gradient. Heavily doped N-type substrates yield pores with large diameters (50 to 70 nm) for current densities around 30 mA/cm\(^2\). Specific surface areas of heavily doped N-type substrates are reported to be around 200 m\(^2\)/g. The electrochemical etching of lightly doped N-type substrates in darkness results in the formation of only macropores with pore radii in the micrometer range with very low porosities (~10%). Etching under illumination creates meso- and nanopores along with macropores, and the porous structure strongly depends on the light intensity. Etching low doped N-type PS under illumination also results in the formation of random micro-crack patterns, as shown in Chapter 5.

A more detailed parametric description of the various factors affecting the pore morphology can be found in the review by Canham [64].

### 1.3 Combustion of porous silicon composites

While the oxidation of silicon is highly exothermic (the standard heat of reaction \(\Delta H^R = -911\) kJ/mol), bulk silicon requires high temperatures to rupture the Si-Si bonds for oxidation. Further, the product of the reaction, silicon dioxide, is a solid which results in the growth of a diffusion layer which results in a slow, diffusion controlled reaction. However, the large SSA of PS results in a significant proportion of silicon atoms existing as highly reactive surface atoms with low coordination numbers. The enhanced chemical reactivity of PS was first discovered by McCord et al. [70] who found that freshly prepared PS exhibited chemiluminescence when immersed in nitric acid solutions and rapidly dissolved in a 1 M aqueous sodium hydroxide solution. Further, it was observed that contact with concen-
trated nitric acid produced a flash of light accompanied by an audible pop, which is the first account of the ability of PS to rapidly oxidize and release energy. Another early instance of the highly energetic nature of PS reactions was demonstrated by Kovalev et al. [71], who inadvertently created an explosive reaction when they treated freshly prepared PS with liquid oxygen at temperatures between 4.2 and 90 K. The first instance of room temperature explosive oxidation of PS using a solid oxidizer was reported by Mikulec et al. [72] who deposited gadolinium nitrate within the pores and created explosive composites which were used as an *in-situ* excitation source for atomic emission spectroscopy. Lazarouk et al. [73] studied the effect of the thickness of porous layers on the fast oxidation reactions on PS formed from low doped p-type substrates and treated with aqueous potassium nitrate solutions. It was found that porous layers less than 15 µm did not ignite. As the porous layer thickness exceeded 50 to 60 µm explosions were observed with a shriller acoustic report and a shift in the color of the accompanying flash towards the blue end of the spectrum indicating higher temperatures. This change in behavior with respect to the film thickness was attributed to transition to a thermal explosion, wherein the heat generation exceeds the heat losses resulting in an exponential increase in the heat release rate due to the Arrhenius nature of the kinetics. It must be noted that this work [73] utilized aqueous solutions to impregnate potassium nitrate within the pores, which is not optimal as:

1. The surfaces of PS are hydrogen terminated and extremely hydrophobic, which makes water an unsuitable solvent to fill the pores, and

2. Water accelerates oxidation of PS rapidly, resulting in a loss of active material [74].

Lazarouk *et al.* [75] used combustion of porous silicon microchannels etched on silicon wafers to dice the wafers. Photolithographic techniques were used to pattern 40 µm thick channels on silicon wafers. The silicon in these exposed tracks was etched to form porous silicon, which was impregnated with potassium nitrate and ignited. This method successfully divided the substrate with dividing tracks smaller than that possible by conventional cutting methods such as laser or diamond cutting.
Clement et al. [76] developed an etch gradient method, in which they electrochemically etched silicon wafers incorporating strategic etch breaks (“etch-stop-etch” method) to prepare thick porous layers. These porous layers were impregnated with a several solid oxidizers, and ignited by placing them on a hot plate, by flowing current through the wafer, or by ignition bridges. Clement et al. also studied the behavior of PS composites filled with several different oxidizers, and summarized their findings, which can be seen in Table 1.3. The choice of oxidizers is limited due to the hydrophobic nature PS and the small size of the pores. Also, the surface tension of the liquids used to deposit oxidizers needs to be low, as the porous structure can collapse due to capillary forces [64]. Since most oxidizers are poorly soluble in organic solvents, perchlorate salts are considered the best candidates due to their moderate solubility in alcohols. Clement et al. [76] cut their etched PS into 500 μm squares, and created small explosive elements, shown in Figure 1.3. These miniature explosive devices were tested for their performance as airbag igniters, wherein long term storage is an important factor. While sodium perchlorate impregnated devices were found to provide the best performance, sulfur was considered to be the better choice for airbag initiators due to the highly hygroscopic nature of sodium perchlorate. The energy yield for PS-calcium perchlorate samples was estimated to be 7.3 MJ/kg by bomb calorimetry, and the spectroscopically estimated temperature using a “quasi-black body” assumption was 6750 K (Note: this is higher than the adiabatic temperature calculated for silicon-perchlorate systems presented in Chapter 3).

![Figure 1.3.](image.png)

**Figure 1.3.** Left side: Picture of a single PS-based explosive element (bottom), a prototype of the airbag igniter (upper left) in comparison with a Eurocent coin. Right side: Image of the ignited single explosive element. From [76].
Table 1.3. An investigation of the occurrence of explosive reactions in PS composites prepared by depositing various oxidizers in the pores using organic solvents (adapted from [76])

<table>
<thead>
<tr>
<th>Oxidizer</th>
<th>Solvent(s)</th>
<th>Explosion (Y/N)/Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca(ClO$_4$)$_2$.4H$_2$O</td>
<td>Methanol, Ethanol</td>
<td>Y/-</td>
</tr>
<tr>
<td>NH$_4$ClO$_4$</td>
<td>Methanol, Ethanol</td>
<td>Y/Weak reaction</td>
</tr>
<tr>
<td>LiClO$_4$.3H$_2$O</td>
<td>Methanol, Ethanol, Acetone</td>
<td>Y/-</td>
</tr>
<tr>
<td>NaClO$_4$.H$_2$O</td>
<td>Methanol, Ethanol</td>
<td>Y/Standard oxidizer</td>
</tr>
<tr>
<td>AgClO$_4$.H$_2$O</td>
<td>Methanol, Ethanol</td>
<td></td>
</tr>
<tr>
<td>FeClO$_4$.xH$_2$O</td>
<td>Methanol, Ethanol</td>
<td>Y/Very hygroscopic</td>
</tr>
<tr>
<td>KClO$_4$</td>
<td>Methanol, Ethanol, Acetone</td>
<td>N/Sparingly soluble</td>
</tr>
<tr>
<td>Ca(NO$_3$)$_2$.4H$_2$O</td>
<td>Methanol, Ethanol</td>
<td>Y/Strongly hygroscopic</td>
</tr>
<tr>
<td>NH$_4$NO$_3$</td>
<td>Methanol, Ethanol</td>
<td>Y/Poor solubility</td>
</tr>
<tr>
<td>LiNO$_3$</td>
<td>Methanol, Ethanol</td>
<td>Y/Weak reaction</td>
</tr>
<tr>
<td>AgNO$_3$.H$_2$O</td>
<td>Methanol, Ethanol</td>
<td>N/-</td>
</tr>
<tr>
<td>KNO$_3$</td>
<td>Methanol, Ethanol</td>
<td>N/Sparingly soluble</td>
</tr>
<tr>
<td>K$_2$Cr$_2$O$_7$</td>
<td>Methanol, Ethanol, Acetone</td>
<td>Y/Only with Acetone</td>
</tr>
<tr>
<td>Sulfur</td>
<td>Molten sulfur/carbon disulfide</td>
<td>Y/-</td>
</tr>
</tbody>
</table>

Du Plessis [77,78] qualitatively studied explosive composites of PS with sulfur, gadolinium nitrate, and sodium perchlorate, for which the reaction initiation was reported to be 261 °C, 243 °C and 313 °C, respectively. A fill factor was gravimetrically estimated, but the experimental conditions and how the oxidizer residues on the surface of the samples were accounted for is unclear. The fill factor measurements indicated a reduction of the filling efficiency with reducing pore diameters. The interaction between the filling efficiency, the increased surface areas, and reactivity from reduction of pore diameters was explored to find an optimum pore diameter. This was carried out using a very qualitatively defined figure of merit, which was based on reaction characteristics such as the acoustic report, substrate damage, plume height, and integrated optical output. Based on these parameters, the optimal pore diameter was found to be ~ 3 nm.

Reactive wave propagation, gas generation, and energy output from PS-NaClO$_4$ composites were studied by Currano et al. [79], Churaman et al. [80], Becker et al. [81], and Plummer et al. [82]. It must be noted that all these studies used low doped P-type substrates (Boron doped), with resistivity between 1 and 20 Ω-cm. The volume of gaseous
products generated upon combustion of PS impregnated with NaClO₄ was calculated to be 0.0189 mol/g(Si) from experiments conducted by burning PS samples in a pressure vessel. For comparison, black powder produces 0.0125 mol/g and modern propellants generate around 0.045 mol/g of gaseous products [79]. About 70% of the gas generated is attributed to the surface hydrogen termination. Churaman et al. also measured the gas generation of PS impregnated with NaClO₄ and found that annealing PS in a low temperature oxygen environment to remove the surface hydrides resulted in a reduction of gaseous products from 0.0129 mol/g(Si) to a negligible 0.004 mol/g(Si) [80]. Plummer et al. measured the reactive wave propagation as a function of porosity and thickness of the porous layer. Their experiments indicated no specific trend with respect to porosity, and an increase in the burning rate with an increase in the thickness of the porous layer. Plummer et al. also studied the effect confinement had on the burning rate by placing a block close to the surface of the PS sample. Adding confinement was found to result in a significant increase in the burning rates (for example, from 199 ± 53 m/s to 399 ± 124 m/s for porous layers 72.0 ± 0.6 μm thick). Piekel et al. [83] also studied the effect of porosity on the reactive wave propagation in fast galvanically etched PS which yielded significantly higher reactive wave propagation speeds (> 1,000 m/s). Their results indicate that there is an optimum porosity (around 70 %), and an optimum pore diameter (around 3.3 nm), but showed no specific trend with respect to SSA. The highest reactive wave propagation speeds were demonstrated by Becker et al. and Piekel et al. in galvanically etched PS. These samples were etched in an electrolyte consisting of 20:1 HF:ethanol, and 2.4 % by volume 30 % aqueous hydrogen peroxide, and a platinum to silicon surface area ratio of 5. Becker et al.’s samples exhibited reactive wave propagation speeds up to 3,100 ± 230 m/s. Piekel et al. recorded the highest reactive wave propagation speed (3,660 m/s) among all nanoenergetic material formulations on galvanically etched PS utilizing organized microstructures on the silicon substrates. This enhancement in reactive wave propagation using organized microstructures was developed as a part of this dissertation [84], which is described in detail in Chapter 5. The energy released upon the combustion of PS-NaClO₄ composites was studied measured by Chura-
man et al. [80] and Becker et al. [85]. The energy yield from their composites was 9.9 ± 1.8 kJ/g(Si), which places PS composites among the most energy dense materials. The effect of hydrogen termination on the energy yield was studied by Churaman et al., who found that annealing the PS samples to remove the surface hydrogen atoms resulted in only a small reduction in the energy yield (from 5.74 kJ/g(Si) to 5.43 kJ/g(Si)).

1.3.1 Ignition mechanisms for porous silicon

A mechanism for the initiation and explosive propagation of PS reactions was proposed by Kovalev et al. [71] based on their study on PS-condensed oxygen at cryogenic temperatures. The proposed mechanism involved an initiation step, which involves unsaturated Si bonds. Typically, the concentration of unsaturated bonds in hydrogen terminated porous silicon is about 10^{-16} cm^{-3} [71]. These unsaturated bonds, which are essentially free radicals, are highly reactive and initiate the reaction upon contact with oxygen molecules. This was further verified by the fact that naturally aged samples, which have the same number of surface Si-H bonds, but fewer unsaturated bonds, have a lower probability of spontaneous ignition upon immersion in liquid oxygen. Further, these naturally oxidized samples could be ignited by using an intense ultraviolet illumination source, which ruptures Si-H bonds and creates free radicals. Further validation of this initiation mechanism is provided by the fact that weak impact can initiate the reaction between aged PS and liquid oxygen. This is attributed to the fact that PS is a mechanically non-contiguous medium, which is very efficient in transforming the mechanical energy into energy required to rupture Si-Si bonds and create free radicals [71]. The Si-H bonds are stronger than Si-Si bonds, and they act as a buffer between the silicon and oxygen atoms, preventing the slow oxidation of the silicon nanocrystal network. To explain the explosive nature of the reaction, the second stage of the proposed mechanism involves the removal of these hydrogen atoms by energy transfer to neighboring Si-H bonds. Since the Si-O bond enthalpy is lower than the O-O bond, multiple dangling bonds are required to provide the required energy. It was proposed that the efficient energy transfer between neighboring surface atoms due to their
weak vibrionic coupling with the nanocrystal core facilitates this energy transfer, which is necessary for the explosive reaction [71]. The removal of the hydrogen atoms creates water or OH radicals, and the disruption of Si-Si bonds creates new radicals, thereby continuing the reaction. Interaction between molecular oxygen and dangling bonds also creates free radicals, fulfilling the required conditions for a branched chain reaction, i.e., every step in the reaction forms new free radicals, resulting in an explosive reaction. The mechanism described here is schematically explained in Figure 1.4 by Kovalev et al.

1.4 Research objectives

As seen from the preceding literature review, there are several reports about energetic composites made by filling PS with different solid oxidizers. However, the published literature is qualitative in nature, which essentially reports several observations. The factors affecting the flame propagation rates are not clearly understood, which is necessary for the successful integration of PS into devices. The objective of this research is to provide a fundamental understanding of the behavior of PS-solid oxidizer composites, and identify the important physical/chemical phenomenon, which can be exploited to control these highly energetic reactions. More specific objectives are listed below:

1. Conduct a fundamental combustion analysis of PS composites to provide both qualitative and quantitative understanding of the reactive wave propagation in PS composites. The quantitative analysis of the combustion performance of PS composites (reactive wave propagation speeds and spectroscopic flame temperatures) can be coupled with thermochemical equilibrium calculations to identify the reactive wave propagation mechanisms and the important parameters controlling the energy release. Parameters of specific interest are:

   (a) The composite equivalence ratio: Deposition of oxidizer within the nanometer scale pores is a significant challenge as seen in the previous section, and it is
important to examine how important the effect the composition has on the energy release

(b) The substrate properties: The dopant atom type and concentration in silicon have a strong effect on the electrical properties of silicon. Given the documented effect of the substrate properties on the morphology of PS, how does the combustion performance of PS depend on the dopant atoms?

2. Investigate how the reactive wave propagation in PS composites can be controlled beyond varying the electrochemical etch parameters and the substrate properties. The ability to tune the combustion performance independent of the electrical properties can be advantageous in terms of micropyrotechnic applications.

(a) What is the role of the microscale structure of PS on the reactive wave propagation rates? The substrate, silicon, is unique, as there is a vast knowledge of micromachining, which can be exploited to create microscale structures with great control. Understanding and exploiting this effect would enable engineering a wide variety of monolithic devices, which can offer improved functionality while simplifying the on-board integration of EMs.

3. What is the effect of the dopant atoms on the fast oxidation reactions and on the behavior of the PS-oxidizer interface, through structure or otherwise? More specifically, what is the difference between the PS samples which exhibit slow reactive wave propagation ~ 1 m/s and PS samples which exhibit reactive wave propagation ~ 1,000 m/s?

The dissertation is organized as follows: Chapter 2 describes the various experimental methods used in this work (preparation and characterization of PS, spectroscopic temperature measurement using multiwavelength pyrometry, flow visualization using high speed focused shadowgraphy, and semiconductor microfabrication methods). Combustion analysis of PS-perchlorate composites using smooth, uniform PS etched from heavily doped P-type sub-
strates is presented in Chapter 3. Experimental measurements of the reactive wave propaga-
tion speed and spectroscopic temperatures are presented, and compared with thermochem-
ical equilibrium calculations, and a phenomenological model is developed to elucidate the
heterogeneity of the system despite the small nanometer length scales involved. The effect
of the substrate doping properties on the reactive properties of PS composites is examined
in Chapter 4, using TGA/DSC and reactive wave propagation speeds. While the work
presented in Chapter 3 examines slow conductively driven reactive waves in PS, Chapter
5 describes faster reactive wave propagations which are a result of convective heat transfer
driven reactive wave propagations. The randomly forming micro-crack patterns leading to
convective burning are presented, and a method to achieve over two-order-of-magnitude
enhancement in the reactive wave propagation speeds, demonstrated using heavily doped
P-type PS, is also described. This is the first demonstration of how semiconductor micro-
fabrication techniques can be exploited to achieve enhanced reactive wave propagations,
and this method can be extended to other gas generating nanoenergetic materials. Chapter
6 provides a mechanistic investigation of the high speed reactive wave propagations ob-
tained on low doped P-type PS, by examining the interaction between the reactive waves
in the condensed phase and compressible flow effects in the surrounding gaseous medium.
Chapter 7 concludes the dissertation by summarizing the important findings and discussing
interesting future research avenues.
Figure 1.4. Two-dimensional sketch of the three principal steps (A, B, and C) of the explosive reaction of oxygen with hydrogenated porous silicon. Black circles: oxygen atoms, gray circles: silicon atoms, open circles: hydrogen atoms. The Si dangling bonds are indicated by black lobes. The dashed circumference indicates the ignition site of the reaction. From [71].
Chapter 2

Experimental methods

2.1 Safety

This chapter describes the experimental methods used in this work, which includes preparation of PS and testing PS based energetic composites. Several of the experimental methods described herein involve handling of toxic and corrosive chemicals and highly sensitive reactive composites. Proper training and following safety protocols are necessary to perform this work. Further, researchers wishing to work with PS composites are urged to work with small samples until they are familiar with PS impregnated with an oxidizer.

2.2 Preparation and characterization of porous silicon

2.2.1 Electrochemical etch process

The PS used in this study was prepared using an electrochemical etch process as described in Chapter 1. Due to the highly corrosive nature of electrolytic solutions consisting hydrofluoric acid, a custom etch cell made of Teflon (Polytetrafluoroethylene) was used for the electrochemical etch process. A schematic of the etch cell which is designed to etch 4” diameter silicon wafers is shown in Figure 2.1. During the electrochemical dissolution process, the silicon wafer acts as the anode, and a hydrofluoric acid resistant silver mesh held
at a fixed distance from the silicon wafer was used as the cathode. The electric current for the etch process is provided by an Agilent E3614A DC power supply, capable of providing a current up to 6 amperes in a constant current mode.

Figure 2.1. Cross sectional view of the electrochemical etch cell. The silicon wafer is sandwiched between the two Teflon blocks, and the well is filled with up to 150 ml of the electrolyte. The O-ring exposes only the top side of the wafer to the electrolyte, and the groove in the electrolyte well is used to support the cathode (silver mesh) at a fixed distance from the silicon wafer.

The electrolyte used for the etch processes described in this work consisted of a 1:1 (by volume) mixture of 49% aqueous hydrofluoric acid (CMOS grade, obtained from J.T. Baker, USA) and ethyl alcohol (anhydrous 200 proof ethanol Obtained from KOPTEC, USA). The ethyl alcohol in the electrolyte acts as a surfactant and helps remove the hydrogen bubbles formed at the silicon surface during the electrochemical etch process. The efficient removal of the hydrogen bubbles is necessary for a repeatable and uniform etch process, as accumulation of bubbles on the silicon surface creates an insulating layer and sporadically changes the current density. Other surfactants that have been used for this purpose are acetic acid and commercially available Triton X-100. The lower surface tension of the ethanoic electrolytes also permits better wetting of the hydrophobic hydrogen terminated nanoscale pore walls. While acetic acid and Triton X-100 are effective at much
smaller volume fractions than ethanol [64], ethanol was used in this study to reduce the HF concentration in the electrolyte. Several different electrolyte compositions were tested, and the 1:1 (by volume) mixture was found to yield the best results in terms of etching a stable thick porous layer. The stability in this context refers to the absence of unintentional delamination of the porous layer from the silicon substrate during or after the etch process. Several different etch processes have been tested to prepare thick, stable porous layers, and the final etch processes developed as a part of this work can be found in Appendix A. Silicon substrates with high dopant atom concentrations that exhibit metal-like electronic behavior are commonly referred to as degenerately doped semiconductors, and are often used to replace metal contacts in modern integrated circuits. Typically, silicon substrates having a dopant atom concentration greater than $10^{18}$ atoms/cm$^3$ (resistivity ~ $10^{-3}$ Ω-cm) are considered to be degenerately doped at room temperature. A uniform backside electrical contact can be achieved just by using an aluminum foil for these wafers. However, for low doped P-type substrates with resistivity ~ 1 Ω-cm or greater, a simple ohmic contact on the backside cannot be directly achieved across the native oxide and the metal-semiconductor interface. To obtain an ohmic contact with the low doped P-type silicon wafers, a thin layer of platinum (between 50 and 170 nm) was deposited on the backside of the silicon wafer by a physical vapor deposition process (evaporation). This was followed by a rapid thermal anneal (RTA) in an inert (argon or nitrogen) environment at 350 °C for 2 minutes. This results in the formation of a Pt-PtSi-Si layer through which uniform backside electrical contact can be established.

2.2.2 Characterization of porous silicon

The thickness of the etched porous layers was measured using optical or scanning electron microscope (SEM) images, and the properties of the porous structure such as the SSA and the pore size distribution were measured using gas adsorption measurements such as the Brunauer-Emmet-Teller (BET) [86] or the Barrett-Joyner-Halenda (BJH) [87] methods. The BET method allows for determination of the SSA, whereas the pore size distribution
can be estimated from the BJH method. In addition to the optical measurements and the gas adsorption measurements, the porosity of the PS films was also determined using a gravimetric technique exploiting the high reactivity of PS compared to bulk silicon to selectively dissolve the porous layer [64].

### 2.2.2.1 Gravimetric determination of porosity

The silicon wafers were weighed before the electrical etch \( (M_1) \) and after the electrochemical etch \( (M_2) \). The wafers were then scribed on the backside using a diamond tip scribe and cleaved into smaller test samples. Several small test samples were cut from different locations on the etched silicon wafer such that their top side is completely covered with PS and weighed \( (m_2) \). The mass of these test samples before the electrochemical etch process \( (m_1) \) was estimated based on \( m_2, M_1, \) and \( M_2 \), and the area of the wafer surface exposed to the electrolyte compared to the total area of the 4” wafer. The porous layers on these pieces were completely dissolved using a 1 M aqueous NaOH solution (equation 2.1), and the mass after the complete dissolution of PS \( (m_3) \) was recorded.

\[
\text{Si} + 2\text{NaOH} + 4\text{H}_2\text{O} \rightarrow \text{Na}_2\text{Si(OH)}_6 + 2\text{H}_2 \quad (2.1)
\]

Wetting the porous surface with a small amount of methanol or ethanol before the NaOH etch significantly accelerates the dissolution process, as the reduced surface tension permits better wetting of the pores. While dry porous layers take several minutes to dissolve completely, porous layers wetted with methanol completely dissolve in a few seconds. Since the base attacks bulk silicon at a slow etch rate, wetting the surfaces with methanol improves the accuracy of this method. The end point of the dissolution is marked by the cessation of hydrogen bubbles evolving from the surface. The porosity \( (P) \) is given by equation 2.2.

\[
P = \left( \frac{m_1 - m_2}{m_1 - m_3} \right) \quad (2.2)
\]
2.3 Thermal and combustion analysis of porous silicon

2.3.1 Reactive wave propagation speed and spectroscopic temperature measurements

The silicon wafers etched in the previous step were scribed and cleaved to yield test samples 5 mm wide and with lengths between 30 to 60 mm. Reactive PS composites were prepared by impregnating an oxidizer within the pores in these test samples. The oxidizers used in this study are sodium perchlorate, magnesium perchlorate, and calcium perchlorate. The oxidizer was deposited into the pores by soaking the test samples in solutions of the oxidizer salt dissolved in methanol for several hours (between 12 to 16 hours). While samples soaked in the oxidizer solution for a short duration on the order of a few minutes did not behave differently compared to the samples soaked for a longer duration, a long soaking time was chosen to eliminate any unrepeatability due to changes in the oxidizer deposition. This was carried out in a humidity controlled chamber purged with dry nitrogen due to the highly hygroscopic nature of the oxidizers, as water absorption by the oxidizer degrades the PS combustion performance. In the case of samples exhibiting a micro-crack pattern (described in Chapter 5) and PS samples etched on low doped P-type substrates, the oxidizer was deposited in the pores by applying several drops of oxidizer-methanol solution to the porous surface. The presence of the micro-crack pattern precludes the porous layers from being soaked in the oxidizer solution and then being dried, due to the risk of unintentional ignition, and the highly reactive nature and high sensitivity of low doped P-type PS poses a safety risk in terms of handling loaded samples. The samples treated with the oxidizer-methanol solutions were then mounted on glass slides using a double sided adhesive tape, and dried by heating them to 80 °C under vacuum (-90 kPa gage) in a test chamber (a metal chamber with optical windows) and holding them at that temperature for 10 minutes. The test chamber was then back-filled with argon and the samples were allowed to cool down to room temperature before being ignited. The samples were ignited by a 10 ms pulse from a 200 W continuous wave CO₂ laser (wavelength: 10,400 nm) or by an electric spark. Ignoring
the surface hydrogen atom termination, the global combustion reaction responsible for the reactive wave propagation can be described as

\[ 2x\text{Si} + \text{M(ClO}_4\text{)}_2 \rightarrow 2x\text{SiO}_2 \text{ + MCl}_x \]  

(2.3)

where M represents the anion (Na, Mg or Ca), and x is 1 for sodium perchlorate, and 2 for both magnesium and calcium perchlorates. The reactive wave propagation was studied by high speed imaging using either a Phantom V 7.3 or a Phantom V 310 high speed camera. The high speed camera was arranged to look at the edge or the face of the burning sample. A static image of the sample with a ruler beside it was used to calibrate the distances in the high speed video. The flame propagation speeds were measured by tracing the movement of the reactive front as a function of time.

### 2.3.1.1 Multiwavelength pyrometry

Unlike gas phase combustion systems where the flame can be stabilized at a fixed location, the transient high speed reactive wave propagation in PS precludes temperature measurement by conventional instruments such as thermocouples. The flame temperatures in such systems can be estimated using spectroscopic techniques, and a technique known as multiwavelength pyrometry [88–90] was used in this work. A single, time integrated spectrum was collected from the combustion zone using a 400 µm fused silica core optical fiber and delivered to a spectrometer (Ocean Optics HR-2000). The spectrometer has a full width half maximum (FWHM) spectral resolution of 0.75 nm and a spectral range of 188-1107 nm and is capable of recording a 50 ms time integrated spectrum upon receiving an external trigger signal.

The camera and the shutter for the laser were triggered by a delay generator (Stanford Research DG535) at t=0. The spectrometer was triggered with a delay to ensure that the reactive wave passes through the collection zone at some point during the 50 ms acquisition process. The mechanically operated shutter takes approximately 50 ms to open completely.
and it was kept open for a total duration of 10 ms to ensure repeatability of the laser energy delivered between experiments. The spectrum was collected far away from the ignition region to avoid any effect of laser induced hot spots on the results. The spectral sensitivity of the collection optics and detection elements was determined using a calibrated NIST traceable tungsten lamp. The spectrum from this lamp is that of a blackbody at a given temperature, whose spectral intensity can be calculated. The acquired data was compared to that of an ideal black body, and the collection efficiency for each wavelength was determined. The spectral output of a portable reference light source (Ocean Optics LS-1) was compared to the NIST traceable source, and the apparent blackbody temperature of the portable source was determined. This reference source was used at the end of each set of measurement to accurately correct for the collection efficiency of the optics.

The intensity of thermal radiation emitted from a condensed medium is described by Planck’s law of blackbody radiation (equation 2.4)

\[
E(\lambda, T) = \varepsilon(\lambda, T) \frac{C_1}{\lambda^5 \left( e^{C_2 \lambda T} - 1 \right)}
\]  

(2.4)

where \(C_1 = 2\pi hc^2\) and \(C_2 = hc/k\). The variables \(h\), \(c\), and \(k\) are Planck’s constant, the speed of light, and Boltzmann’s constant, respectively. The dependence of the emissivity on wavelength and temperature poses a problem as this dependence is not always known, and multiple condensed phase species may exist within the hot reaction zone, whose properties may not be known. Using the approximation that the quantity \(e^{-\left(\frac{C_2}{2}\lambda T\right)}\) approaches zero at short wavelengths, Planck’s law for blackbody radiation can be rewritten as follows:

\[
\ln \left( \frac{\varepsilon(\lambda, T)}{E(\lambda, T) \cdot \lambda^5} \right) = \frac{C_2}{\lambda T}
\]  

(2.5)

Assuming a temperature independent behavior for emissivity, the emissivity can be expressed only as a function of wavelength as \(\varepsilon = C_3/\lambda^n\). Using this, equation 2.5 can be
rewritten as follows. introducing a non dimensional parameter $Z$:

\[
Z = \ln \left( \frac{C_1}{E(\lambda, T)^{\lambda(n+5)}} \right) = \frac{C_2}{\lambda T} - \ln(C_3)
\]  

(2.6)

Equation 2.6 allows for an estimation of the temperature from the intensity $E(\lambda, T)$ measured by the spectrometer using an appropriate wavelength dependence for $\varepsilon$. The temperature is estimated from the slope of $Z$ when plotted against $1/\lambda$ between a range of wavelengths which yield a linear fit. As seen from section 3.3, thermochemical equilibrium calculations using the CHEETAH 4.0 equilibrium code [91] utilizing the JCZS library [92] indicate flame temperatures above the melting point of silicon (1687 K), where the spectral emissivity of liquid silicon was found to be almost constant and a weak function of temperature [93], indicating that a gray body approximation is the most appropriate emissivity model for the multiwavelength pyrometry algorithm. Thus, the spectroscopic temperatures presented in this work were calculated assuming a constant temperature wavelength independent behavior for the emissivity. However, it must be noted that the actual composition of the reaction zone is not exclusively liquid silicon, and the thermal radiation from the other condensed phase species (SiO$_2$, NaCl, and other intermediate products) too is collected by the spectrometer. Treating this integrated spectrum as originating from various species from the preheat, combustion, and the post combustion products as they cool down results in an error in the estimated temperature, which is inherent to the present spectroscopic measurements.

2.3.2 Thermal analysis methods

The properties of the prepared PS such as the active silicon content and the chemical reactions between the PS and the oxidizer deposited within the pores were analyzed using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Combined TGA and DSC characterization is known as simultaneous thermal analysis (STA), which is routinely used to characterize energetic materials. TGA is essentially an accurate mea-
surement of weight changes of a test sample as a function of time or temperature in a controlled gaseous environment (inert, oxidizing, or reducing). TGA analysis illustrates the physical or chemical processes such as sublimation, evaporation, decomposition, oxidation, or reduction which affect the weight of the sample. DSC is a method to detect heat flow from/to the sample by comparing the temperature behavior of the sample crucible to an empty test crucible. This allows an analysis of the exothermic or endothermic processes occurring within the sample. Thus, combining TGA and DSC analyses allows to correlate the weight changes to the exothermic/endothermic phenomenon, to develop an accurate understanding of the sample behavior.

In this work, thermal analysis was conducted using a simultaneous TGA/DSC apparatus (Netzsch STA 449 F1 Jupiter). The typical sample mass used in the experiments was up to 5 mg of PS for purely oxidation experiments, and between 1 to 1.5 mg of PS when treated with the oxidizer solution. For thermal analysis, the PS samples were treated with a very dilute oxidizer solution (0.4 M NaClO$_4$ and 0.2 M Mg(ClO$_4$)$_2$) to prevent ignition and explosive reactions within the instrument. The samples were placed in alumina crucibles or platinum crucibles with an alumina liner. While the alumina crucibles are inexpensive and can be heated to a higher temperature than the platinum crucibles, the platinum crucibles provide better DSC signal due to the difference in thermal properties of the crucible material. The TGA/DSC is equipped with a silicon carbide furnace with a maximum operating temperature of 1550 °C and a maximum heating rate of 50 °C/min. The thermocouples which measure the furnace temperature and sample temperature, which form the DSC system, were calibrated by measuring the onset of melting temperatures of five high purity metals (indium, tin, zinc, aluminum, and gold). The test chamber was evacuated and backfilled prior to the start of each experiment to control the gaseous environment in the chamber. For experiments conducted in an inert environment, the chamber was evacuated and backfilled thrice with the purge gas (helium or argon), and in case of oxidation experiments, the chamber was backfilled once and purged with a mixture of helium or argon and oxygen. Also, before each set of experiments to be conducted under the same conditions, a baseline
measurement was performed (without a sample) to correct for the buoyancy effects which affect the TGA and specific heat changes of the crucible material which affects the DSC.

### 2.3.2.1 Estimation of reaction kinetics from thermal analysis

Beyond the qualitative description of the reactive phenomena obtained from thermal analysis, a series of thermal analyses can be conducted to provide a basis for extracting important quantitative data such as the preexponential factor \( A \) and activation energy \( E_a \). Based on the latest recommendations by the International Confederation for Thermal Analysis and Calorimetry (ICTAC), a combination of isothermal, isoconversional, and constant heating rate experiments provides the most comprehensive and accurate estimation of the kinetic parameters [94]. However, an adequate estimation of activation energy for reactions of any order can be obtained from a series of constant heating rate experiments using the analysis developed by Kissinger [95]. This method was developed for reactions of the type solid \( \rightarrow \) solid + gas, but the theory can be extended to any solid phase reaction as long as there it can be ascertained that the transport phenomena do not affect the analysis. For example, in the case of PS impregnated with an oxidizer, this method can be used to study the interfacial solid-solid reactions under certain conditions, but cannot be used to analyze the reaction between PS and oxygen or reactions that require diffusion of the oxidizing species away from the interface. Further justification for the applicability of this analysis to PS-oxidizer systems is provided in Chapter 4. In Kissinger’s method, an array of constant heating rate experiments are conducted at different heating rates. The change in the temperature of the exothermic peak observed on the DSC \( T_P \) as a function of the heating rate \( \dot{\phi} \) is noted. The activation energy can be correlated to the measured values as:

\[
\frac{d \left( \frac{\ln \left( \frac{\phi}{T_P} \right)}{T_P} \right)}{d \left( \frac{1}{T_P} \right)} = -\frac{E_a}{R}
\]  

(2.7)
where \( R \) is the universal gas constant. The activation energy can be calculated from a plot of \( \ln \left( \frac{\phi}{T^2 P} \right) \) vs \( \frac{1}{T} \). Due to the limitations on the heating rate imposed by the apparatus, the heating rates used for Kissinger’s analysis were 10 K/min, 20 K/min, and 40 K/min. These experiments were conducted in an inert argon environment.

### 2.3.3 Focused shadowgraph system

As previously described in Chapter 1, the combustion of PS composites produces a large volume of gaseous products, primarily due to the surface hydrogen atoms on the pore walls. To examine the behavior of the gaseous combustion products and the interaction of the condensed phase sample with the gaseous medium around it (specifically in case of high speed reactive wave propagations exceeding the speed of sound in the gaseous medium in the test chamber), PS samples were analyzed by high speed shadowgraph recordings. Since the aim of these experiments was to study the interaction between the gaseous medium above the sample and the condensed phase PS by shock waves, shadowgraphy was chosen for the flow visualization instead of schlieren imaging. In the context of the current study, shadowgraphy is more suitable as it is simpler, requires inexpensive optics, and is better suited to study sharp gradients such as those presented by a shock.

A schematic of the experimental setup used for focused high-speed shadowgraphy [96] is shown in Figure 2.2. The illumination was provided using a 300 W Xe arc lamp, and the collimated beam for the test section was created using two 100 mm diameter plano-convex lenses with a focal length of 300 mm each. The shadowgram was focused onto the image sensor of a high speed camera (Vision Research Phantom V310) using a focusing lens (Nikon 28mm f/2.8) and was recorded at frame rates between 80000-250000 fps. To minimize the geometric distortion, the high speed camera was focused sharply on the object plane. While no shadowgraph effect should be observed in this condition, shock waves will still be resolvable due to the extreme gradient in the refractive index across the shock. An object of known dimensions was imaged before each test, and used to set scale.
2.4 Microfabrication methods

One of the objectives of this study was to control the reactive wave propagation in PS samples, and the approach used for this involved exploiting standard silicon micromachining techniques to create controlled microscale structures on the silicon wafers. Microfabrication techniques provide a high degree of control, and a large number of precise features can be efficiently created on silicon substrates. The various processes used are briefly described below, and further information can be found elsewhere [7, 97].

2.4.1 Photolithographic patterning

Photolithography is a process which allows the transfer of small features, even up to the sub-micron scale onto a photo sensitive material with great accuracy [97]. Virtually all of the modern integrated circuits are manufactured using optical lithographic techniques.

To achieve the patterning, the substrate is first coated with a thin layer of a photosensitive material, known as a photoresist. A uniform thin layer of the photoresist is obtained by depositing the photoresist on the surface of the wafer and spinning it at high speeds to spread the photoresist. The photoresist is a mixture of solvents and photoactive components (PACs) and the solvents evaporate during the spin process leaving behind a uniform
coating of the PACs. The thickness of the photoresist layer is controlled by the spin rate. The wafer is then baked on a hot plate to evaporate away the residual solvents, in a step known as pre-exposure baking.

When the photoresist layer is exposed to UV light, the PACs undergo chemical changes, which affect the dissolution rate of the PACs in specific solvents known as the developers. Positive resists respond to light by becoming more soluble, whereas negative resists become insoluble when exposed. To imprint a desired pattern on the photoresist layer, they are exposed to UV light using a template known as a mask. These masks, which are typically made by depositing a thin chrome layer on glass, expose selective regions of the photoresist to the UV light. This is followed by a post exposure bake (PEB), which provides the heat for the completion of reactions. This step is particularly important for chemically amplified resists, such as the ones used in this study, which derive their high sensitivity to the UV light and provide excellent resolution by initiating catalytic reactions upon exposure to UV light. The PEB provides the energy required to complete these catalytic reactions, and also the required mobility to the reacting species. Following the PEB, the substrates are immersed in a developer solution, typically a metal free alkaline solution, till the soluble portion of the photoresist dissolved. The wafers are then again held at an elevated temperature, a step known as the hard bake, which hardens the resist and improves its ability to withstand chemical attacks. These photoresist templates remaining on the surface of the wafer serve as masks, and facilitate selective removal of material in the exposed regions.

An i-line aligner (EVG-620, EV Group, USA), utilizing 365 nm UV light, and capable of providing 1 \( \mu \text{m} \) resolution was used to expose the photoresists. Different resists were used for different processes, as described below

1. Microposit S1811: This is a positive photoresists which can be spun to create thin photoresist layers. This resist provide excellent resolution, but they is only able to withstand anisotropic plasma etch processes for short durations.

2. SPR-220-7, and SPR-955 (Positive photoresists), KMPR-1010 (Negative photoresist):
These photoresists are capable of forming stable films with thicknesses in excess of 10 µm. These resists are capable of withstanding extended durations of etch processes. The thicker layers, however, come at an expense of the resolution. Further, the exposure and development of the resist are very sensitive processes which are strongly dependent on the exposure and development times, and the bake temperatures.

### 2.4.2 Deep Reactive ion Etching (DRIE)

The developed and hard baked wafers from the previous step were etched anisotropically using plasma etch processes such as DRIE. While wet chemical etching can be used to produce anisotropic structures, plasma processes are superior due to their faster etch rates and better directionality.

A basic plasma etch system consists of a chamber evacuated to low pressures, across which a high electric field is applied. This causes the gases to ionize and create a plasma consisting of free electrons, ionized molecules, neutral molecules, free radicals, and ionized fragments of broken molecules. The gases used typically consist of halides such as CF₄, which provide the reactive species capable of etching silicon surfaces. The fluorine free radicals react with silicon to produce a volatile product (SiF₄), which leaves the surface and facilitates continuous etching. These free radicals provide the chemical component of the etching, which is non-directional. However, the chemical etching is very selective, i.e., etches the exposed silicon surface preferentially compared to the photoresist mask.

The other species participating in the etch process are the ions, which can be accelerated by the electric fields within the plasma. The flux of ions striking the surface provides the physical component of the etching, which is highly directional due to the directionality of the electric field. However, the material removal due to ion bombardment offers very little selectivity, i.e., it erodes the photoresist mask and etches the silicon surfaces at comparable rates. To obtain high aspect ratio structures, the chemical and physical components must act synergistically. By a suitable choice of the gases in the plasma, inhibiting polymer molecules can be deposited on the surfaces, which prevent the anisotropic chemical etch
processes. The highly directional ionic species then strike the bottom surfaces preferentially, and remove the inhibiting layer from the bottom surface, while leaving the side walls still covered in a protective layer. Exposure to the reactive neutral species now etches the bottom of the etch pit, while the side walls are only attacked minimally. This process is known as reactive ion etching (RIE), and can be used to etch anisotropically, producing high aspect ratio structures. The process used consists of alternating passivation and etch cycles, by flowing C$_4$F$_8$ for the passivating cycle and SF$_6$ and O$_2$ for the etch cycle.

2.4.3 Preparation of PS samples with micro/nanoscale features

As discussed later in Chapter 5, multiscaled PS samples were used to study the effect of structure on reactive wave propagation. Photolithographic patterning followed by DRIE was used to create microscale patterns on the silicon substrates (pillars and microchannels), which were then electrochemically etched to create the nanoscale features (pores). The process flow is shown in Figure 2.3. It should be noted that the photolithographic patterning and DRIE are performed on the silicon wafer before the electrochemical etch process, as the porous layers can be dissolved away by the basic solutions used to develop the photoresist, due to the high reactivity of PS. Further, etching silicon wafers with PS on the top requires recalibration of the DRIE processes to account for the change in the low thermal conductivity of PS, which can cause the top surface of the wafer (which is exposed to the plasma) to be at a higher temperature, resulting in changed etch conditions. Also, removal of the polymeric inhibition layer deposited during the DRIE process may not be possible, as PS cannot be exposed to harsh oxygen plasmas like a bare silicon wafer.
Figure 2.3. Schematic showing the process for preparing PS samples with microscale features etched using Photolithographic patterning followed by DRIE.
Chapter 3

Combustion analysis of porous silicon-oxidizer composites

A parametric study of reactive wave propagation in heavily doped P-type PS-oxidizer composites is presented in this chapter. The role of the composite equivalence ratio and the choice of the oxidizer are examined. The reactive wave speed and structure for energetic PS composites formed by depositing sodium, magnesium, or calcium perchlorates within the nanoscale pores were analyzed with high speed video recordings and spectroscopic temperature measurements. The findings indicate that heavily doped samples that do not yield a microscale structure result in slow propagation speeds. A systematic study of the mixture composition revealed very wide flammability limits and flame speed and temperature measurements independent of the global equivalence ratio, consistent with thermochemical equilibrium calculations. Also, while all the composites considered in this study are fuel rich with equivalence ratios greater than 1.76, the composites with equivalence ratios closer to unity exhibited lower temperatures and propagation speeds than more fuel rich composites. This unusual behavior of the composites is attributed to the inhomogeneity of the system even though the reactants are mixed at the nanometer scale. This was illustrated by developing a phenomenological model describing the interaction of silicon and the oxidizer within a single nanometer scale pore, which revealed that the reactive wave propagation is
more strongly controlled by the specific surface area than the global equivalence ratio, due to the transport length scales involved. The results presented in this chapter have appeared as a publication by Parimi et al. [98].

3.1 Analysis of oxidizer deposition within the pores

Previous work on PS assumed that the void space was completely filled with the oxidizer. However, experimental measurements indicated that such a model is inadequate and the actual amount of oxidizer deposited is lower, as the void space is not completely filled with an oxidizer [85]. Thus, a simple model incorporating the solubility of the oxidizer in organic solutions was developed to predict the oxidizer deposition in the pores more accurately. The composite equivalence ratio ($\varphi$), defined as the ratio of the fuel to oxidizer ratio in the mixture to that of a stoichiometric mixture, can be expressed as

$$
\varphi = \left( \frac{\frac{m_f}{m_{ox}}}{(\frac{m_f}{m_{ox}})_{st}} \right)
$$

(3.1)

where $m_f$ and $m_{ox}$ are the masses of the fuel and oxidizer respectively, and the subscript “st” indicates the stoichiometric composition. The stoichiometric reaction between silicon and the perchlorate salts used in this study, ignoring the surface hydrogen atoms, is described in equation 2.3.

In practice, it is not possible to deposit solid oxidizer such that the oxidizer crystals completely fill the void space. In an ideal case, the oxidizer solutions in an organic solvent such as the methanol solutions used in this work can be expected to completely fill the pores. Once the pores are completely filled with the oxidizer solution, when the solvent is evaporated, the maximum amount of oxidizer deposited within the pores will be the amount of oxidizer dissolved in the solution in the void space. A schematic explaining this assumption is shown in Figure 3.1.

Assuming the pore is completely filled with the oxidizer solution, the volume of the solution within the pore is $V$, the same as the pore volume. Upon the evaporation of the
solvent, the mass of oxidizer residue in the pore will be $Vs$ where $s$ is the concentration of the oxidizer solution (g/L). The lower bound of the equivalence ratio ($\varphi_{\text{min}}$), described by this situation is

$$\varphi_{\text{min}} = \left( \frac{m_{\text{ox}}}{m_f} \right)_{st} \cdot \left( \frac{m_f}{Vs} \right)$$  \hspace{1cm} (3.2)

The porosity $P$ is related to the pore void volume $V$ as

$$P = \frac{V_{\text{void}}}{V_{\text{total}}} = \frac{V}{V + \frac{m_f}{\rho_{\text{Si}}}}$$  \hspace{1cm} (3.3)

where $\rho_{\text{Si}}$ is the density of bulk silicon. Thus, $\varphi_{\text{min}}$ can be expressed as

$$\varphi_{\text{min}} = \left( \frac{m_{\text{ox}}}{m_f} \right)_{st} \left( \frac{1 - P}{P} \right) \frac{\rho_{\text{Si}}}{Ps}$$  \hspace{1cm} (3.4)

**Figure 3.1.** Schematic showing the maximum permissible oxidizer deposition within the pores. If the pore is completely filled with the oxidizer solution as shown in the middle figure, upon the evaporation of the solvent, only a thin layer of the oxidizer can be expected to remain in the pore, as depicted in the rightmost figure.

Due to the low solubility of perchlorate salts (and most common oxidizers, which are usually ionic salts), it is not possible to obtain a stoichiometric composite even when the hydrogen termination of the PS surfaces is neglected and saturated solutions are used, due to:

1. An upper limit on the porosity of the samples that can be prepared, which is dictated by the stability of the porous film formed. It was found that attempting to etch PS with a porosity greater than 0.75 resulted in delamination of the porous films.
2. Limited solubility of perchlorate salts in organic solvents. A detailed list of the solubility of perchlorate salts in various solvents can be found elsewhere [99], and the solubility data for selected perchlorate salts in methanol are presented in section 3.4.

3. While soaking the samples in the oxidizer solution and evaporating the solvent multiple times can increase the oxidizer deposition within the pores in theory, experiments have shown that the porous layer tends to delaminate during the second drying process, leading to ignition of the sample.

The low sensitivity and stability of PS etched from the heavily doped P-type substrates was exploited to measure the oxidizer deposition within the pores. As seen from equation 3.4, the concentration of the oxidizer solution can be varied to change the composite equivalence ratio. Thus, PS samples were soaked in methanol solutions of the oxidizer of varying concentrations to impregnate the porous layers with varying amounts of the oxidizer. The samples were then removed from the oxidizer solution and dried, and then their surfaces were carefully cleaned with a tissue dampened with methanol to remove the oxidizer residues from the surface. The difference in the weights of the samples before and after soaking them in the oxidizer was used to determine the amount of oxidizer deposited. The actual amount of fuel on each sample was estimated using the weight change of a representative test strip from the same wafer when the porous layer was completely dissolved using aqueous 1 M NaOH solution. Experimental measurements indicate that the oxidizer mass deposited exceeded the predicted maximum mass deposition. This is attributed to the highly hygroscopic nature of the oxidizer, coupled with the elevation of the boiling point of methanol and the absorbed water, which is a colligative property [100]. Further details regarding the experimental measurements of the oxidizer deposition are presented in Appendix B, and it can be inferred from these measurements that the assumption that the oxidizer solution completely fills the void space is appropriate.
3.2 Effect of the composite equivalence ratio on the reactive wave propagation

To study the effect of mixture composition on the reactive wave propagation, PS samples prepared from heavily doped P-type substrates were used. The PS etched from heavily doped P-type substrates was chosen for this study as

- Heavily doped P-type substrates permit the etching of thick porous layers without any micro-crack patterns. The presence of micro-crack patterns results in a change in the reactive wave propagation mechanism as discussed in Chapter 5, which precludes a simple analysis. Based on the experimental results presented in this section, the reactive wave propagation in heavily doped P-type PS can be considered to be a purely conductive heat transfer driven propagation.

- The PS etched from heavily doped substrates is less sensitive (qualitatively) than the PS with micro-crack patterns, and is less reactive than the PS etched on low doped P-type substrates. These samples permit reasonable handling of the samples even after oxidizer deposition, which can be exploited to quantify the oxidizer fill within the pores.

3.2.1 Combustion analysis of porous silicon - magnesium perchlorate composites

The FE-SEM images of the PS layers etched on heavily doped P-type substrates indicate pore diameters around 30 nm at the surface, and porous layer thicknesses about 140 µm as seen in Figure 3.2. The gravimetrically measured porosities for these samples were between 0.71 and 0.75, and BET measurements indicate SSA of ≈ 310 m²/g. Based on the porosity of the samples, and the solubilities of various perchlorate salts in methanol, magnesium perchlorate was chosen as the oxidizer to investigate the effect of composite equivalence ratio on the reactive wave propagation speed. The equivalence ratios of the composites prepared, and the reactive wave propagation speeds and temperatures measured
are shown in Table 3.1. The measured reactive wave propagation speeds and temperatures are indicated as a range (minimum – maximum) of values measured, as no specific trend was observed in either the speeds or the temperatures with respect to the equivalence ratio. At least three samples were tested at each composite equivalence ratio shown in Table 3.1. The spectroscopic temperatures were estimated using data collected from 450.12 to 650.64 nm, as shown in Figure 3.3, and the standard deviation for the temperature data calculated over six measurements was 92 K. To test the fuel rich flammability limits for PS-magnesium perchlorate composites, PS samples soaked in dilute oxidizer solutions were tested. The samples soaked in a 0.1 M solution yielded $\varphi_{min} = 80$ and failed to ignite while the samples soaked in 0.15 M solution, with $\varphi_{min} = 56$, ignited at the spot heated by the laser but failed to propagate, indicating that they were beyond the fuel rich extinction limit.

**Figure 3.2.** (a) Top view of the porous layer showing pores with diameters ~30 nm. (b) Low magnification cross sectional view showing bulk silicon with porous layer on the top. The thickness of the porous layer is 140 μm.
Figure 3.3. (a) Collected raw spectrum, and the corrected spectrum accounting for the collection efficiency of the optics. (b) $Z$ vs $1/\lambda$ plot for estimating the temperature of the reaction zone, for the case $\varepsilon = \text{constant}$, for PS-magnesium perchlorate composite with an equivalence ratio ($\varphi_{\text{min}}$) of 6.7, described in Table 3.1. The flame temperature is $C$/slope, where $C = 1.44 \times 10^{-2}$, which yields a temperature of 1901 K.
Table 3.1. Equivalence ratio, reactive wave propagation speeds, and spectroscopically determined temperatures for porous layers etched on heavily doped P-type substrates impregnated with magnesium perchlorate. The reported ranges of the temperature and the reactive wave propagation speed (\(\vartheta\)) are measurements over several samples. \(\varphi_{\text{min}}\) is the theoretical equivalence ratio as described in equation 3.4. The spectroscopic temperatures were estimated using a gray body assumption, as described in section 2.3.1.1 on page 31.

<table>
<thead>
<tr>
<th>(\varphi_{\text{min}})</th>
<th>(\vartheta) (m/s)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.8 or 4.2(^a)</td>
<td>5 - 7.7</td>
<td>2044(^b)</td>
</tr>
<tr>
<td>4.6</td>
<td>2.6 - 7.7</td>
<td>1869 - 2184</td>
</tr>
<tr>
<td>6.7</td>
<td>2.5 - 3.3</td>
<td>1844 - 1930</td>
</tr>
<tr>
<td>8.3</td>
<td>3.9 - 4.9</td>
<td>1706 - 2043</td>
</tr>
<tr>
<td>13.5</td>
<td>2.4 - 2.8</td>
<td>1792 - 1870</td>
</tr>
<tr>
<td>16.5</td>
<td>3.2 - 4.0</td>
<td>2002(^b)</td>
</tr>
<tr>
<td>33.1</td>
<td>2.6 - 3.0</td>
<td>1886 - 1993</td>
</tr>
</tbody>
</table>

\(^a\) Test samples from two different PS substrates with different porosities were soaked in saturated solutions, resulting in two different \(\varphi_{\text{min}}\) values (see Table B.1).

\(^b\) Successful temperature measurements were obtained on only one sample tested at these equivalence ratios.

3.3 Thermochemical equilibrium calculations for silicon - magnesium perchlorate system

The flame speed and temperature data from Table 3.1 indicate that the composite equivalence ratio does not have a significant effect on either the temperature or the propagation speed. The trends of the temperature and reactive wave propagation speeds are similar, indicating a strong coupling between the two, consistent with the significant role the reaction zone temperature plays in the propagation of a conductive wave. To understand the equivalence ratio independent behavior of the composites, thermochemical equilibrium calculations were performed to study the effect of the equivalence ratio on temperature. These calculations were performed using the CHEETAH 4.0 equilibrium code [91] and the JCZS library [92], and the surface hydrogen termination was ignored. The heat of formation values used for the calculation are included in the Appendix (Table B.3). The interaction between PS and the oxidizer occurs at the PS-oxidizer interface within the nanometer scale.
pores, which results in the release of hot gaseous products (primarily from the hydrogen termination on the surface silicon atoms) within the pores. The high temperature of the gases coupled with the fast reaction results in a pressure rise within the pores. From high speed videos of the reactive wave propagation, it was observed that the porous layers just behind the reactive wave disintegrate. This disintegration of the porous layers would allow the gaseous products to at least partially expand. Thus, the reaction that occurs in the experiments lies somewhere between a constant pressure and a constant volume system. The constant pressure calculation was chosen to calculate the adiabatic flame temperature, as it represents the lower bound for the temperature predicted by thermochemical equilibrium calculations. The measured reactive wave temperatures were compared to the calculated temperatures as shown in Figure 3.4. Figure 3.5 shows the variation in the product species as a function of equivalence ratio for equilibrium calculations performed at a constant pressure (1 atmosphere).

The first sudden drop followed by the plateau in temperature at 2000-2100 K is due to the equilibrium between SiO (gas) and liquid Si and SiO$_2$. The second temperature drop and plateau is due to the phase change of silicon, which melts at 1687 K. The spectroscopically measured temperatures plotted against the adiabatic flame temperature predicted by the equilibrium calculations agree except for very fuel rich samples. This indicates that the multiwavelength pyrometry algorithm employed here over-predicts the temperatures, since the actual reaction zone temperature has to be lesser than the adiabatic equilibrium temperature.

### 3.4 Influence of the oxidizer

Two other oxidizers with widely different solubilities in methanol (sodium perchlorate and calcium perchlorate) were chosen to study the effect of the choice of oxidizer and equivalence ratio on the reactive wave propagation. The solubility of the oxidizers used, and the theoretical minimum equivalence ratios obtainable for PS samples with porosity of 0.6 are
Figure 3.4. Adiabatic flame temperatures calculated using CHEETAH 4.0 equilibrium code and spectroscopically measured flame temperatures as a function of equivalence ratio for PS-magnesium perchlorate composites. The predicted minimum equivalence ratio ($\phi_{min}$) described by equation 3.4 is used to represent the composite equivalence ratio in this plot.

shown in Table 3.2. Thermochemical equilibrium calculations for PS composites with each of these oxidizers show very similar variation of the adiabatic temperature with equivalence ratio as shown in Figure 3.6, indicating that the oxidizers do not change the overall energy content of the composites sufficiently enough to change the flame temperature. The heat of formation values used for the calculation are included in the Appendix (Table B.3).

From the data presented in Table 3.1 and Figure 3.4, it can be reasonably expected that the low reactive wave propagation speeds recorded are a consequence of the behavior of the PS - perchlorate system, as the adiabatic flame temperature is limited by the equilibrium reaction $Si_{(liq)} + SiO_{2(liq)} \rightleftharpoons 2SiO_{(gas)}$. The recorded slow speeds are consistent with conductively driven reactive wave propagation speeds observed in other systems.
Figure 3.5. Thermochemical equilibrium calculations showing the Concentrations of product species and the adiabatic temperature as a function of equivalence ratio for PS – magnesium perchlorate composites. The first plateau in temperature between 2000-2100 K is due to the equilibrium between SiO (gas), Si (liquid), and SiO$_2$ (liquid). The second plateau at 1683 K in temperature is due to phase change of silicon.

Table 3.2. Solubilities of selected perchlorate salts in methanol, grams per 100 grams of solvent at 25 °C (From [99]). $\varphi_{\text{min}}$ was calculated for saturated solutions and porous layers with $P = 0.60$, ignoring the surface hydrides as described in equation 3.4.

<table>
<thead>
<tr>
<th>Oxidizer</th>
<th>Solubility in methanol (g/100g$_{\text{methanol}}$)</th>
<th>$\varphi_{\text{min}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium perchlorate</td>
<td>51.36</td>
<td>8.32</td>
</tr>
<tr>
<td>Magnesium perchlorate</td>
<td>51.84</td>
<td>7.52</td>
</tr>
<tr>
<td>Calcium perchlorate</td>
<td>237.38</td>
<td>1.76</td>
</tr>
</tbody>
</table>

Nanolamintes prepared by depositing alternating Ni and Al nanolayers can be considered to be closest analogue for the PS - perchlorate systems described in this work, and the reactive wave propagation speeds observed in these nanolaminate systems are on the order of 10 m/s [101]. The important differences between PS based nEMs and other nEMs are discussed further in Chapter 6. For a purely conductive heat transfer driven reactive wave
Figure 3.6. Thermochemical equilibrium calculations for the reaction between PS and the oxidizers used in this study. The three perchlorate salts used to test the effect of mixture composition on the reactive wave propagation exhibit similar adiabatic flame temperature dependence on the equivalence ratio.

propagation, the driving force is expected to scale with the maximum temperature, and thus, preparing leaner composites with higher predicted adiabatic temperatures is expected to yield composites with higher reactive wave propagation speeds.

This hypothesis was tested by using leaner composites prepared by using saturated calcium perchlorate solutions to deposit more oxidizer within the pores. However, the samples soaked in calcium perchlorate exhibited slower reactive wave propagation speeds than the samples soaked in saturated sodium perchlorate solutions, despite the potential to form nearly stoichiometric mixtures as shown in Table 3.3. These tests were repeated several times, and produced consistently slower propagation speeds. Further, to rule out the oxidizer as a possible cause for the results, a dilute solution of calcium perchlorate was prepared to yield samples with the same theoretical equivalence ratio ($\varphi_{\text{min}}$) as saturated
sodium perchlorate solution. These solutions were prepared both by dissolving a fresh sample of the oxidizer in methanol, and carefully diluting the previously prepared saturated solutions. It was found that the samples soaked in dilute calcium perchlorate solutions designed to prepare composites with the same $\varphi_{\text{min}}$ as the saturated sodium perchlorate solutions yielded higher propagation speeds compared to the samples soaked in saturated calcium perchlorate solution. The measured flame speeds and temperatures over several samples (at least three samples for each case) are shown in Table 3.3 as the range of values (minimum – maximum) from all experiments.

Table 3.3. Reactive wave propagation speeds and temperatures for PS composites prepared using porous layers etched on a heavily doped P-type substrate with a porosity of 0.6. The dilute calcium perchlorate solution was prepared to yield composites with the same theoretical equivalence ratios as a saturated sodium perchlorate solution. The measured flame speeds and temperatures over several samples (at least three samples for each case) are shown as the range of values (minimum – maximum) from all experiments.

<table>
<thead>
<tr>
<th>Oxidizer solution</th>
<th>$\varphi_{\text{min}}$</th>
<th>$\vartheta$ (m/s)</th>
<th>Temperature (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium perchlorate (saturated)</td>
<td>8.32</td>
<td>3.2 - 3.3</td>
<td>1772 - 1956</td>
</tr>
<tr>
<td>Calcium perchlorate (saturated)</td>
<td>1.76</td>
<td>0.7 - 1.2</td>
<td>1650$^a$</td>
</tr>
<tr>
<td>Calcium perchlorate (dilute)</td>
<td>8.32</td>
<td>4.2 - 4.3</td>
<td>1826 - 2031</td>
</tr>
</tbody>
</table>

$^a$Due to the low intensity of the spectrum, multiwavelength pyrometry could only be applied successfully to one of the several samples tested.

3.4.1 Discussion

The oxidation reactions in heterogeneous systems such as the PS - perchlorate system occur in two steps: The fast initial oxidation of the PS-oxidizer interface, followed by a slower oxidation of silicon atoms away from the pore walls by diffusive mechanisms. Hence, the interfacial contact area between PS and the oxidizer can have a stronger effect on the flame propagation than the overall equivalence ratio of the composite. A similar effect of specific surface area was reported previously by du Plessis [78] who explored the competing effects of surface area and oxidizer deposition on the energetic properties as a function of pore diameter. His analysis indicated that small pore sizes ($\approx 3.4$ nm) yield the most reactive composites. In this work, the oxidizer deposition in the pores was studied for a fixed pore
distribution, isolating the effect of oxidizer deposition from surface area and pore size. The results presented in Table 3.3 indicate that increasing the oxidizer deposition within the pores can offset the improvement of the overall equivalence ratio. A possible cause for this is that the heat generated at the silicon - oxidizer interface can also diffuse into the now increased amount of oxidizer in the pore, resulting in the excess oxidizer acting as a diluent over the time scales associated with the fast propagating reactive wave. This hypothesis is tested by developing a phenomenological reaction model to describe the thermal behavior of the PS composites.

3.5 Phenomenological reaction model

For the conductive heat transfer driven reactive wave examined in this study, the behavior of the energetic composite is controlled by the interaction of the silicon and oxidizer within the pores, which generates the heat required to sustain the propagation. Thus, the behavior of the composite itself can be described by developing a phenomenological model examining the interaction between silicon and the oxidizer within a single pore. Further, the reactive wave propagation speed behavior can be expected to scale with the peak temperature of the system, as described previously. The thermochemical equilibrium calculations presented previously assume that all the silicon in the system can interact with all the oxidizer present, which is not necessarily always true, especially when considering a high speed reactive wave propagation. This is important because as the silicon and oxidizer start reacting at the interface, a diffusion barrier consisting of the product species forms, inhibiting the oxidizer away from the interfacial layer from reacting with silicon atoms away from the pore wall. The purpose of this model is to incorporate the physics of the system, the role of transport phenomena, to isolate and study the interfacial silicon - oxidizer reactions which do not depend on transport phenomena, and the interaction between silicon atoms and oxidizing species away from the interface. The assumptions and approximations used in this model are:
1. While the porous layers contain a filamentous porous network and the pore diameters may vary with depth, the porous layer can be treated as a matrix of cylindrical pores extending throughout the thickness of the porous layer as shown in Figure 3.7(a), consisting of single, repetitive elements as shown in Figure 3.7(b).

2. The oxidizer deposited within the pores is assumed to form a uniform layer along the inner pore wall, as depicted in Figure 3.7(b).

3. The porosity of each repetitive cell is the same as the porosity of the porous layer (obtained from gravimetric measurements), and the pore diameters \(d_p\) used are the average pore diameters obtained from gas adsorption measurements. For the heavily doped P-type PS, \(d_p \approx 10\) nm.

4. A large Damköhler number \((Da)\). The Damköhler number is defined as

\[
Da = \frac{\text{Reaction rate}}{\text{Transport rate}} \tag{3.5}
\]

the large \(Da\) assumption means that the time scale associated with the chemical interaction between the silicon atoms and the oxidizer molecules is assumed to be much smaller than the time scale associated with the transport phenomena.

5. As a consequence of the large \(Da\) assumption, the interaction between the silicon atoms and the oxidizer will be diffusion limited. Thus, similar to the thin flame in a gas phase diffusion flame with fast chemistry, a thin layer of the oxidizer reacts stoichiometrically with a thin layer of silicon (of thickness \(\Delta r\)), as shown in Figure 3.7(b).

6. The Lewis number \((Le)\) is large. The Lewis number is defined as

\[
Le = \frac{\alpha}{D} \tag{3.6}
\]

where \(\alpha\) is the thermal diffusivity, and \(D\) is the coefficient associated with the mass transport phenomena. Due to the small length scales involved, nanoscale reactive
materials can interact by phenomena other than pure Fickian diffusion, such as deformation and flowing, which are not significant in macroscale systems. Thus, for the case of both large $Da$ and $Le$, it is more appropriate to use a combined transport phenomena coefficient specific to the system than simply a diffusion coefficient.

7. The heat released from the thin reaction zone heats up the remaining unreacted silicon and any remaining oxidizer. As a consequence of assumptions 4 and 5, it can be assumed that in the time scale associated with a fast reactive wave propagation, only a thin layer of silicon reacts, and the cell quickly attains thermal equilibrium. The final temperature of the cell is calculated by an iterative method.

![Figure 3.7](image)

**Figure 3.7.** Schematic of the model used to describe the reaction between porous silicon and the oxidizer on the basis of a single pore. Figure 3.7(a) represents how the porous layers were approximated to consist of repeating cells with a cylindrical void surrounded by silicon. Figure 3.7(b) depicts a uniform layer of oxidizer coating the pore wall, and the thin reaction zone where the silicon and oxidizer react stoichiometrically. The silicon and the oxidizer beyond this region as assumed to be unable to react on the time scales associated with the reactive wave propagation, and only absorb the heat generated by the reaction zone.

The simplified energy balance for each unit cell can be written as

$$Q_{R,Tf} = [\Delta H_{Si}]_{T_o}^{T_f} + [\Delta H_{O_2}]_{T_o}^{T_f}$$

(3.7)
where $Q_{R,T_f}$ is the total heat flow from the reaction zone at the final temperature ($T_f$) to the unreacted silicon and oxidizer in the cell and $\Delta H_{Si}$ and $\Delta H_{ox}$ are the total change in the enthalpies of the unreacted silicon and oxidizer remaining in the cell. This unreacted silicon and the oxidizer are separated by the diffusion barrier, and act only as heat sinks over the time scale considered by this model. The change in enthalpy for the unreacted silicon is calculated as

$$[\Delta H_{Si}]_{T_o}^{T_f} = (m_{si} - m_{si,r}) \left[ \int_{T_o}^{T_m} C_{si}(T)\,dT + h_{fus} + \int_{T_m}^{T_b} C_{si}(T)\,dT + h_{vap} + \int_{T_b}^{T_f} C_{si}(T)\,dT \right]$$

(3.8)

where $m_{Si}$ is the total mass of silicon in the cell, $m_{Si,t}$ is the mass of silicon that participates in the chemical reaction at the interface, $C$ is the specific heat, $T_m$ is the melting temperature of silicon, $h_{fus}$ is the enthalpy of fusion, $T_b$ is the vaporization temperature of silicon, and $h_{vap}$ is the enthalpy of vaporization of silicon. The change in enthalpy for the oxidizer is calculated as

$$[\Delta H_{ox}]_{T_o}^{T_f} = (m_{ox} - m_{ox,r}) \left[ \int_{T_o}^{T_d} C_{ox}(T)\,dT + \Delta H_{dec} \right] + m_{MCl_x} \int_{T_d}^{T_f} C_{MCl_x}(T)\,dT + m_{O_2} \int_{T_d}^{T_f} C_{O_2}(T)\,dT$$

(3.9)

where $m_{ox}$ is the total mass of the oxidizer in the cell, $m_{ox,r}$ is the mass of the oxidizer that participates in the chemical reaction at the interface, $C$ is the specific heat, $T_d$ is the temperature at which the oxidizer decomposes, $\Delta H_{dec}$ is the heat of decomposition for the oxidizer, $m_{MCl_x}$ and $m_{O_2}$ are the masses of the metal chloride and the gaseous oxygen formed upon the decomposition of the oxidizer, respectively. The thermodynamic quantities were obtained from the National Institute of Standards and Technology WebBook [102]. The heat flow term, $Q_{R,T_f}$ was calculated for every 10 K between 800 K and 3190 K (included in Appendix B.4), and an iterative calculation was performed to calculate $T_f$ such that the heat released equals the change in enthalpy.
3.5.1 Si - Mg(ClO$_4$)$_2$ system (P = 0.75)

The reaction model developed was first tested by applying it to the Si - Mg(ClO$_4$)$_2$ system described in Section 3.2.1. As a first step, the calculations were performed assuming that all the oxidizer deposited within the pores reacts stoichiometrically with a thin layer of silicon. In this case, the thickness of the annulus of silicon that participates in the chemical reaction ($\Delta r_r$) is given by

$$\Delta r_r = \frac{d_p}{2} \left( \sqrt{1 + \frac{(1 - P)}{\varphi_{min} P}} - 1 \right)$$

(3.10)

where $d_p$ is the diameter of the pore. For the leanest compositions described in Table 3.1, $\varphi_{min} = 3.8$, for which $\Delta r_r = 0.21$ nm. The growth of ultra-thin oxide films on silicon has been extensively studied computationally, to understand and improve the thin film oxide formation processes for electronics and to predict the behavior of silicon based electronic devices in outer space. While the growth of thick silicon oxide films is well know, and can be accurately predicted, for example, by the Deal-Grove model [103], the initiation and the growth of very thin layers is still poorly understood. This is because the growth of thick films is diffusion controlled, while the growth of thin oxide layers at the interfaces is kinetically controlled, with the kinetics differing significantly compared to the kinetics within the bulk material which presents a Si/SiO$_2$ interface. Since the interfacial reaction being studied here is essentially the growth of an ultra-thin oxide layer, some of the published work utilizing molecular dynamics can be used to draw some important conclusions. A relevant study is the work by Khalilov et al. [104] which examines the formation of ultra-thin oxide films by hyperthermal oxidation using molecular/monoatomic oxygen with kinetic energies up to 5 eV. The findings indicate that the penetration of the oxygen atoms is limited to less than 1 nm over very short time scales. Since the PS-oxidizer system presented here involves the interaction of silicon atoms with complex perchlorate molecules, the interaction distance in this case ($\Delta r_r$) can be reasonably expected to be even lesser. The temperature of the cell predicted by the model and the thermochemical equilibrium calculations as a function of equivalence ratio are shown in Figure 3.8.
Figure 3.8. Temperatures predicted by the phenomenological model and thermochemical equilibrium calculations as a function of equivalence ratio.

The temperature predicted by the model closely agrees with the equilibrium prediction for a wide range of equivalence ratios. While the agreement over a wide range is due to the temperature being limited to the melting point of silicon due to the phase change, the model prediction agrees with the equilibrium calculations for fuel rich composites with temperatures lower than the melting point. However, the model starts to deviate from the equilibrium calculations for $\varphi < 10.5$, when the model predicts temperatures higher than the equilibrium calculation, but the temperature predicted by the model does not exceed the peak temperature predicted by the thermochemical equilibrium calculations. Upon examining the composition of the reactive zone, it is revealed that the difference in the behavior of the model compared to the thermochemical equilibrium calculations arises due
to the constraint on the transport processes imposed in the model. As explained previously, thermochemical equilibrium calculations performed under the same constant pressure (1 atm) were used to set up the iterative calculation for the model. However, while the equivalence ratio was varied in the thermochemical equilibrium calculations first presented in Figure 3.5, and again plotted in Figure 3.8, the thermochemical equilibrium calculations for estimating $Q_{R,T_f}$ were always performed for a stoichiometric mixture. This is to account for the assumption that all the chemical reactions occur at a thin, stoichiometric reaction zone at the silicon–oxidizer interface. When the thermochemical equilibrium calculations are performed for a stoichiometric mixture, the reaction products are almost exclusively $\text{SiO}_2$ and $\text{MCl}_x$. For the $Q_{R,T_f}$ calculations performed at high temperatures close to 3000 K, only a small amount of disassociation of $\text{SiO}_2$ into $\text{SiO}$ was observed. However, in case of thermochemical equilibrium calculations for fuel rich mixture, the product species transitioned to $\text{SiO}$ from $\text{SiO}_2$ as the equilibrium temperature approached 1900 K. This is a consequence of the $\text{SiO}_2$ reacting with liquid silicon to form gaseous $\text{SiO}$, which does not occur in the stoichiometric reaction zone in the model. The temperature predicted by the model, and the spectroscopically measured temperatures are shown in Figure 3.9. When compared to the model, the spectroscopically estimated temperatures for $\varphi_{\text{min}} < 10$ are even lower than when compared to the thermochemical equilibrium calculations. Also, since the measured temperatures in the fuel rich region are higher than both the thermochemical equilibrium and model temperature predictions, the measured temperatures can be expected to be overestimated, as discussed previously on page 50. Thus, the lower measured temperatures for $\varphi_{\text{min}} < 10$ indicate that only a fraction of the silicon and the oxidizer in the cell react, at least in the time scale associated with the reactive wave propagation, as expected from the work on ultra-thin oxide film formation on silicon substrates [104].

### 3.5.2 Si–Ca(\text{ClO}_4)_2 system (P = 0.60)

From section 3.5.1, it is inferred that all the oxidizer is not consumed by the silicon in the cell during the fast reactive wave propagation. Based on the experiments conducted using
calcium perchlorate, it was hypothesized that the excess oxidizer deposited within the pores acts as a diluent, negatively affecting the reactive wave propagation speed and temperature, despite the equivalence ratio being closer to unity. For the silicon - calcium perchlorate composites described in Table 3.3 with equivalence ratios closer to unity, the thickness of the silicon layer required to completely consume the oxidizer increases significantly. The thickness of the silicon layer needed to completely consume the oxidizer is \( \approx 0.88 \text{ nm} \) at \( \varphi_{\text{min}} = 1.76 \), which is significantly thicker than the silicon - magnesium perchlorate system. In the previous section, the calculations were performed assuming that all the oxidizer reacts, to test the model against the thermochemical equilibrium calculations. In

**Figure 3.9.** Spectroscopically measured and predicted temperatures as a function of equivalence ratio. The predicted minimum equivalence ratio (\( \varphi_{\text{min}} \)) described by equation 3.4 is used to represent the composite equivalence ratio for the spectroscopically measured temperatures.
case of calcium perchlorate, due to the lower $\varphi_{\text{min}}$, it is possible to vary the amount of silicon and oxidizer that are allowed to stoichiometrically react. This was accomplished by placing an upper bound on the thickness of the silicon layer ($\Delta r_r$) that can interact with the oxidizer. Any remaining oxidizer does not participate in the chemical reaction, and only absorbs the heat. The effect of maximum permissible $\Delta r_r$ being limited to 0.1, 0.2, and 0.3 nm on the temperature predicted by the model is shown in Figure 3.10.

![Figure 3.10](image)

**Figure 3.10.** Comparison of the temperatures predicted by thermochemical equilibrium calculations and the model for Si - Ca(ClO$_4$)$_2$ system with a porosity ($P$) of 0.60. The maximum allowable thickness of the silicon layer ($\Delta r_r$) that can react with the oxidizer was fixed to be 0.1, 0.2, and 0.3 nm. It can be seen that the temperature predicted by the model can reduce as the equivalence ratio approaches unity, based on the maximum allowable $\Delta r_r$, while the temperature predicted by the thermochemical equilibrium calculations increases. This is due to the excess oxidizer within the pores at lower equivalence ratios acting as a diluent over the time scale associated with the reactive wave propagation.

From the data presented in Figure 3.9 and Figure 3.10, it can be seen that only a very
small amount of the silicon present in each repetitive cell needs to react stoichiometrically with the oxidizer to raise the temperature to the melting point of silicon and above. This indicates that the fast propagating reactive wave can be sustained by the consumption of only a small fraction of the silicon atoms. For example, to produce the temperature curve depicting the reaction zone thickness being limited to 0.1 nm only requires 6% of the total silicon in the repetitive cell to react stoichiometrically with the oxidizer. This small fraction of reacted silicon still releases enough heat to raise the temperature of the whole cell to the melting temperature of silicon. The remaining silicon and oxidizer can react after the high speed reactive wave propagates to release more heat, which neither supports nor is necessary to sustain the fast propagating reactive wave. Phenomenologically, this indicates that higher temperatures, which in turn are expected to result in higher reactive wave propagation speeds, can be obtained if the $\Delta r_r$ required to consume all the oxidizer is as small as possible. This condition dictates that the porosity be as high as possible, and the pore diameters as small as possible. According to the geometry described in Figure 3.7, higher $P$ and smaller $d_p$ also results in higher SSA, as $\text{SSA} \propto \frac{P}{d_p (1 - P)}$.

In order to match the temperatures predicted by the model to the experimentally obtained data, the thickness of the reacted silicon layer needs to be unphysically small (< 0.1 nm). These unphysical thicknesses arise due to two of the approximations required for the phenomenological model:

1. The approximation that the silicon and oxidizer are in the form of uniform layers, which was used to calculate the volume, and thus the thin layers which react, is no longer applicable at the small length scales considered. At these sub-nanometer length scales which approach the dimensions of the silicon atoms and oxidizer molecules itself, the continuum assumption is no longer valid.

2. The approximation that the thin reaction zone is a uniform annulus is similarly not valid at these length scales. Multiple atomic layers of the silicon and oxidizer could
react at isolated spots, but averaging this reaction zone all over the pore wall results in a reduced value for the average thickness of the annulus.

Thus, while the data in Figure 3.10 is presented as a thickness of the silicon layer, which is below the Si-Si bond length, it is an artifact of the continuum assumption. Physically, the small thicknesses can be interpreted as describing the fraction of silicon atoms that participate in the chemical reaction. Further, the purpose of this phenomenological model is not to match the experimental results presented in the previous sections, but to illustrate the significance of inhomogeneity of this system and to show that the SSA is more important than the global equivalence ratio. While the global equivalence ratio calculated from the total amount of oxidizer deposited within the pores can be a metric to describe the overall combustion performance in terms of total energy obtainable from the composite, due to the inhomogeneity and finite rate of transport phenomena, the reactive wave propagation speed itself is more strongly affected by the SSA and the reactivity of the interface.

3.6 Summary and conclusions

The reactive wave propagation in PS composites prepared heavily doped P-type silicon substrates and impregnated with three different oxidizers (magnesium, sodium, and calcium perchlorates) was characterized using high speed imaging and multiwavelength pyrometry. The experimental results indicate that the reactive wave propagation speeds in the heavily doped P-type substrates are slow (< 8 m/s), and showed no specific dependance on composite equivalence ratio. Similarly, the spectroscopically measured temperatures also were found to have no specific dependance on the composite equivalence ratio. Experimental measurements indicate wide flammability limits for PS - perchlorate composites, and thermochemical equilibrium calculations show nearly constant temperature over a wide range of equivalence ratios. Further, due to the poor solubility of perchlorate salts in organic solvents and limitations on maximum porosity and number of time the pores can be filled, only fuel rich composites could be prepared even with the perchlorate salt most soluble in
organic solvents, calcium perchlorate. However, in contrast to the thermochemical equilibrium calculations, experimental combustion analysis of the leanest composites ($\varphi_{\text{min}} = 1.76$) indicated that the increased oxidizer deposition resulted in a reduction in the reactive wave propagation speeds and the spectroscopically determined temperatures. This is attributed to some of the oxidizer within the pores not contributing to the reactive wave front propagation, but instead acting as a heat sink. A phenomenological model incorporating constraints representing the limitations of the mass transport phenomena on the thermochemical equilibrium calculations was developed. This model shows that only a small fraction of the silicon atoms need to react to sufficiently raise the temperature to sustain a reactive wave propagation, and the global equivalence ratio is not a good metric to describe the combustion performance of PS composites. This is a consequence of the inhomogeneity of the system despite the small length scales (on the order of 10 nm) involved.
Chapter 4

Effect of substrate properties on energetic porous silicon composites

A study of the substrate doping atom type and concentration on the behavior of energetic porous silicon composites prepared by impregnating various oxidizers within the pores is presented in this chapter. Specifically, the influence of the substrate doping properties on the reactive wave propagation speeds and the interaction of PS and the oxidizer at the silicon - oxidizer interface is discussed. Two P and two N-type silicon substrates with a wide range of doping concentrations were used to prepare PS substrates, and energetic composites were prepared using sodium, magnesium, calcium, or lithium perchlorate salts, or sulfur. The PS samples and the behavior of the energetic composites were characterized using TGA/DSC and reactive wave propagation speed measurements, SEM imaging, and gas adsorption measurements. The work presented in this chapter has appeared in peer reviewed publications by Parimi et al. [84,98,105,106]. The energetic composites prepared from PS etched on heavily doped P and N-type substrates yielded reactive wave propagation speeds on the order of 10 m/s, whereas the composites prepared from PS etched on low doped N or P-type substrates exhibited reactive wave propagation speeds on the order of 100 m/s and 1000 m/s, respectively. The interaction between the silicon atoms and the perchlorate salts at the PS - oxidizer interface was found to be unaffected by the substrate
doping properties, whereas the low temperature exothermic interfacial reactions between PS and sulfur were influenced by the substrate doping properties. This is attributed to the effect of substrate doping on the microstructure of the PS formed.

### 4.1 Background

As described in Chapter 1, much of the work on PS based energetic composites is aimed at micropyrotechnic applications exploiting the material compatibility of PS with microfabrication methods. While silicon is the building material for most microscale devices, intrinsic silicon by itself is a poor conductor, and dopant atoms are required to control the electrical properties to be able to form functional devices. The dopant atoms introduced into the silicon crystal lattice introduce additional charge carriers, and the concentration of the dopant atoms controls the electrical properties of silicon, which is exploited in modern day semiconductor devices. While the effect of dopant atoms on electrical properties of silicon is precisely known, the effect of the dopant atoms and their concentrations on the chemical reactions between porous silicon and oxidizers has not been studied. Since the reactions of interest are essentially solid-solid redox reactions, the dopant atoms, which affect the electron density can be expected to affect the reactive properties, as evidenced from the available literature on PS and other reactive systems described below. The aim of the work presented in this chapter is to examine the effect of the substrate doping type and concentration on the reactions between PS and the oxidizer, with the goal to aid the design of functional microscale systems with on-board PS energy sources.

### 4.2 Review of the effect of dopant atoms on reactivity

#### 4.2.1 Effect of dopant atoms on other reactive systems

The effect of doping on solid state reactions was first investigated by Schwab and Gerlach [107], who studied the oxidation of germanium by molybdenum trioxide. The powdered reactants were pressed into pellets and heated to temperatures between 460 °C to 620 °C,
and the degree of conversion after a specified time was used as a metric to study the reaction described below.

\[
\text{Ge} + 2\text{MoO}_3 \rightarrow \text{GeO}_2 + 2\text{MoO}_2 \tag{4.1}
\]

It was found that samples prepared using N-doped germanium powders exhibited a higher degree of conversion than the intrinsic germanium samples, whereas the P-doped samples exhibited a lower degree of conversion. Further, the reaction rates for N-doped substrates were found to increase with an increase in the dopant atom concentrations, while increasing the concentration of the P-type dopant atoms slowed down the reactions. The change in the reaction rates with the addition of dopant atoms was attributed to the higher electron count of N-doped Ge which was hypothesized to reduce the oxygen concentration at the Ge/MoO$_3$ interface, resulting in faster diffusion times through the products. Altham et al. [108] studied the complimentary system, the effect of doping the oxidizer, nickel oxide, on reactions with boron, germanium, and silicon.

\[
\text{Ge} + 2\text{NiO} \rightarrow \text{GeO}_2 + 2\text{Ni} \tag{4.2}
\]

An examination of the DSC traces revealed a lower onset temperature for the P-doped oxidizer compared to the N-doped and undoped oxidizer (up to 200 °C lower). A redox reaction involves the transfer of electrons, where the oxidizing agent is the electron acceptor and the reducing agent is the electron donor. Based on this, McLain [109] explained the observed effect of the dopant atoms using a P-N junction semiconductor analogy. Since an N-type crystal creates space charge potential by donating electrons to the P-type crystal, it should be a stronger reducing agent, and consequently more reactive than a P-type reducing agent. Also, introducing N-type dopant atoms into the semiconductor crystal lattice increases the number of electrons in the Fermi level, increasing the potential energy compared to the undoped material. This results in a reduction in the activation energy \((E_a)\), as shown in Figure 4.1.
Figure 4.1. Potential energy diagram for the Ge-MoO$_3$ system, adapted from [109]. The addition of the N-type dopant atoms results in an increase of the potential of the Ge-MoO$_3$ system, resulting in the activation energy reducing from $E_a$ to $E_a^*$. 

All the reactive systems described above involve slow reactions, which take place over time scales on the order of several days, which means that slow processes such as transport phenomenon can be expected to have a strong effect on the behavior of the systems. The effect of doping on such combustion systems has been sparsely studied, and only one relevant study is available in the literature, in which Yarrington et al. [110] studied the effect of dopant atoms on the combustion performance of pellets prepared by pressing micron silicon powders and PTFE into pellets. It must be noted that the silicon formulations used by Yarrington et al. and the PS considered in this work differ in several ways (size, hydrogen termination, oxidizer), which precludes a direct comparison of the behavior of the two systems. Yarrington et al. found that the addition of dopant atoms resulted in a decrease in the activation energy (from 130 kJ/mol to up to 110 kJ/mol) coupled with an increase
in the burning rates from 2 mm/s to up to 3 mm/s. However, in contrast to Schwab and Gerlach, and Altham et al.'s work, the effect of the dopant atoms was independent of the dopant type. The burning rates increased as the dopant atom concentrations were increased, and the activation energy reduced as the dopant atom concentration increased, irrespective of whether the dopant atoms were P-type or N-type. While the germanium systems involve only solid-solid redox reactions, the reactions in the Si-PTFE system studied by Yarrington et al. do not necessarily occur in the solid state. In Si-PTFE systems, the liquid/gas phase oxidizing species produced upon the melt-decomposition of PTFE can react with the silicon at the surface heterogeneously. In this case, the diffusion of the oxidizing species to the silicon surfaces is also important.

4.2.2 Effect of dopant atoms on thermal oxidation of porous silicon

The examination of the effect of doping on PS reactions is limited to the slow thermal oxidation of PS films aimed at understanding the stability of PS, which affects its luminescence properties and degrades PS based optoelectronic devices [111]. Salonen et al. [112] found that the activation energy for the oxidation near room temperature was found to be lower for N-doped PS (0.4 eV) compared to P-doped samples (0.5 eV). However, unlike the germanium systems described previously, PS presents an additional parameter, the microstructure. Since the pore walls in PS, which present the reactive Si atoms to the oxidizer are formed by crystalline silicon planes, the reactivity of the Si atoms at the surface can also be affected by the crystallographic orientation of the pore walls, as it affects the structure and composition of the surface. Such dependance of the reactivity as a function of crystallographic planes exposed has also been demonstrated in other systems [113]. Thus, based on Munder et al.'s study [114], which showed that the microstructure of P-type PS differs from that of N-type PS, Salonen et al. attributed the difference in the activation energies to the difference in the microstructure. Another difference between P and N-type PS is the hydrogen termination at the surface, and an examination of hydrogen desorption
in an inert environment by DSC showed a dihydride terminated surface for P-type PS and monohydride termination for N-type PS [112].

4.3 Results and discussion

The effect of dopant atoms on the behavior of PS composites was studied by analyzing the thermal analysis of PS and PS composites, which is described in the next section. The effect of the substrate doping levels on the reactive wave propagation speeds obtained in PS composites is tabulated in this chapter, and further discussed in Chapters 5 and 6.

4.3.1 Preparation and characterization of PS

PS etched on four different silicon substrates and nanoscale silicon powder was used in this study. The silicon wafers were all obtained from El-Cat Inc., and the nanoscale silicon powder (diameter < 100 nm, SSA between 70 – 80 m$^2$/g) used was obtained from Sigma Aldrich Inc. The PS was prepared by an electrochemical etch process as described in Chapter 2, with a few differences as described below. The low doped N-type substrates could only be etched under strong illumination (provided by a 10 W LED lamp), and the maximum achievable current density was limited by the intensity of the LED. For the heavily doped substrates (both P and N-type) and the low doped P-type substrates, an electropolishing step was used at the end of the etch process to release free standing porous layers. The electropolishing step consisted of replacing electrolyte with a dilute electrolyte consisting of 16.7% (vol) hydrofluoric acid and 83.3% (vol) ethanol followed by a 30 second etch at a higher current density (100 mA/cm$^2$). For the low doped substrates on which an electropolishing step could not be performed, samples were prepared for thermal analysis by scraping off the porous layers using a knife edge. The substrate properties, current density for the electrochemical etch, and the measured SSA, porosity, and average pore diameter (using Micrometrics ASAP 2020) of the PS etched are shown in Table 4.1.
Table 4.1. Substrate dopant type and resistivity of the silicon wafers used to prepare porous silicon for thermal analysis, the current density for the electrochemical etch, and the specific surface area (SSA), porosity, and average pore width of the etched samples determined using a multi-point BET measurement.

<table>
<thead>
<tr>
<th>Dopant atom and type</th>
<th>Dopant atom concentration (atoms/cm$^3$)</th>
<th>Resistivity (Ω-cm)</th>
<th>Current density (mA/cm$^2$)</th>
<th>Etch duration (min)</th>
<th>SSA (m$^2$/g)</th>
<th>Porosity</th>
<th>Average pore width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron (P)</td>
<td>2.1×10$^{19}$ - 1.2×10$^{20}$</td>
<td>0.001-0.005</td>
<td>80/40</td>
<td>60/90</td>
<td>284/271</td>
<td>0.75/0.73</td>
<td>18.9/17.1</td>
</tr>
<tr>
<td>Boron (P)</td>
<td>6.7×10$^{14}$ - 1.3×10$^{15}$</td>
<td>10-20</td>
<td>40/60</td>
<td>30/60</td>
<td>644/528</td>
<td>-/0.62</td>
<td>-/-5.2</td>
</tr>
<tr>
<td>Arsenic (N)</td>
<td>1.2×10$^{19}$ - 7.4×10$^{20}$</td>
<td>0.001-0.005</td>
<td>40</td>
<td>90</td>
<td>439</td>
<td>0.74</td>
<td>11.2</td>
</tr>
<tr>
<td>Phosphorus (N)</td>
<td>2.7×10$^{15}$ - 7.0×10$^{15}$</td>
<td>2-5</td>
<td>20</td>
<td>60</td>
<td>236</td>
<td>0.42</td>
<td>5.4</td>
</tr>
</tbody>
</table>
4.3.2 Thermal oxidation of PS

The PS samples were thermally oxidized in the TGA to estimate the active content of the silicon within the samples, as the presence of inert silicon dioxide affects energy density and reactivity of the PS composites prepared, which are important for micropyrotechnic applications. The PS samples were oxidized in an oxygen environment (20 ml/min helium + 20 ml/min oxygen) in the TGA/DSC to 1200 °C at a rate of 20 °C/min, and held at that temperature for 60 minutes. For the complete oxidation of pure silicon, the final mass of the sample will be 2.14 times the mass of the silicon \( \frac{\text{MW}_{\text{SiO}_2}}{\text{MW}_{\text{Si}}} \). However, if the sample already contains some oxide, the final mass will be

\[
(1-x)\text{Si} + x\text{Si} \rightarrow \text{SiO}_2 \ (m_f = m_i + 2.14 \times (1 - x))
\]

(4.3)

where \( m_f \), \( m_i \), and \( x \) are the final mass of the sample, initial mass of the sample, and the fraction of oxide initially in the sample, respectively. Once the final mass of the sample is known upon complete oxidation within the TGA/DSC furnace, the active content of the PS sample can be calculated. The TGA traces for the PS samples described in Table 4.1 are shown in Figure 4.2. The TGA traces of both the heavily doped PS samples attained a final value followed by no additional mass gain, indicating complete oxidation of all the silicon present in the sample, enabling the estimation of the active silicon content of the samples. The high mass gain upon oxidation indicates that the PS samples contained only a small amount of oxide initially, and the amount of pure silicon in the PS, estimated from oxidizing several samples from different batches (all of which were between 4 – 6 months old), was found to be 93.6 ± 3.2% and 88.4 ± 6.2% (by mass, given as the average ± standard deviation) for the heavily doped P and N-type substrates, respectively. The TGA traces for the PS from both the low doped substrates (PS scraped off low doped N-type substrates, and PS obtained from low doped P-type substrates by scraping with a knife edge or electropolishing) show a continuous slow mass gain throughout the duration of the experiment. However, both low doped PS samples had DSC traces similar to those of the
heavily doped PS including the characteristic peaks observed upon the thermal oxidation of PS. The trends observed in the TGA traces can be attributed to:

1. Inclusion of non-nanostructured microscale silicon crystals: The non-porous silicon crystals would oxidize much slower than PS due to formation of thick oxide layers, which would result in a TGA profile as shown in Figure 4.2, while exhibiting DSC traces similar to PS. Inclusion of silicon crystals can be expected in the PS samples scraped off from silicon substrates.

2. Differences in the porous structure: Different pore morphologies would mean that the growth of the oxide layer would be different, and in the low doped P-type samples, this could cause a difference in the diffusion of oxygen to the unoxidized regions and result in the trends seen in Figure 4.2.

To test for the inclusion of non-nanostructured silicon crystals, the PS samples were dissolved in a 1 M aqueous sodium hydroxide solution after the surfaces were wetted with methanol. The PS from both heavily doped substrates, and the PS obtained by delamination from low doped P-type substrates quickly dissolved (in ~ 30 s) without leaving a residue, indicating they did not contain large microscale silicon crystals. However, the scraped off PS samples from low doped N-type substrates left a silicon residue, which explains the low weight gain and the slow increase in weight at elevated temperatures observed in the TGA trace.

4.3.3 DSC analysis of the effect of dopant atoms on PS - oxidizer composites

4.3.3.1 PS - perchlorate composites

The PS samples were loaded with a small amount of oxidizer using solutions of the oxidizer in methanol to impregnate the pores with the oxidizers. Dilute solutions of the oxidizer were used to yield very fuel rich composites incapable of sustaining a reactive wave propagation, thus preventing ignition of the samples within the TGA/DSC. DSC traces of PS treated with
Figure 4.2. Thermogravimetric analysis (TGA) traces for PS samples prepared from the four different kinds of substrates described in Table 4.1. The PS was heated to 1200 °C at a rate of 20 °C/min, which was followed by a 1 hour isotherm at the same temperature, in an oxygen environment.

A 0.4 M solution of sodium perchlorate heated in an inert helium environment are shown in Figure 4.3. Before the start of each experiment conducted in an inert environment, the TGA/DSC was purged with helium, and evacuated and backfilled with helium thrice to minimize the fraction of oxygen within the furnace. Further, a constant flow of helium was maintained over the sample through the furnace. All samples exhibit two distinct exothermic peaks, with the first low temperature exothermic peak below 400 °C, which is attributed to backbond oxidation. As described in Chapter 1, the Si-H bond is stronger than the Si-Si bond, and the presence of the surface hydrides also weakens the Si-Si bond between the surface silicon atom and the skeletal Si atom one layer deeper. Thus, the oxygen atom attaches itself first between the silicon atoms, resulting in the formation of Si-O-Si-H structure. This insertion of the oxygen between the surface and the skeletal silicon atoms...
is referred to as the backbond oxidation. This low temperature exothermic peak occurs at a temperature significantly below the temperature at which the oxidizer exothermically decomposes, as seen from the DSC trace of the pure oxidizer in Figure 4.3, and similar exothermic peaks before the oxidizer decomposition were also observed by Becker et al. [85]. Becker et al., who studied low doped P-type PS (1 - 20 Ω-cm) attributed the occurrence of this low temperature exothermic peak to the P-type dopant atoms, based on Wydeven’s work [115] or to the presence of unsaturated reactive sites at the surface. Wydeven studied the decomposition of perchlorate salts, and found that an electron acceptor, such as an electron deficient P-doped material, facilitate the decomposition by accepting an electron from the ClO$_3^-$ ion. However, in the work presented here, the low temperature exothermic peak is found even in the most electron rich sample, the heavily doped N-type PS, indicating that the low temperature reaction between PS and the oxidizer is a result of the solid oxidizer reacting with unsaturated silicon atoms/defects, rather than the dopant atoms aiding the decomposition of the oxidizer. Similar results were obtained when magnesium perchlorate was used as the oxidizer too, with the low temperature exothermic peak occurring at a lower temperature ($\approx 200^\circ$C), which is well below the onset temperature for decomposition of the perchlorate salt, which is above 400 $^\circ$C.

Since the low temperature exothermic peak can be attributed to the defects and unsaturated sites, further experiments were conducted to study the effect of annealing PS in an inert environment (helium in this case). During these inert annealing experiments, no mass gain or exothermic peaks were observed, indicating that the samples were not exposed to any appreciable amount of residual oxygen. These annealed samples were then treated with a dilute perchlorate salt solution as described before, and thermal analysis was conducted. Samples annealed to temperatures below 700 $^\circ$C behaved similar to the samples shown in Figure 4.3. However, when the PS samples were annealed to temperatures 700 $^\circ$C or higher, the low temperature exothermic peak was no longer observed. However, the second exothermic peak, which occurs at a higher temperature, was unaffected, and the onset of the second peak was close to the onset of the melting of the oxidizer salt as in the previous experiments.
Figure 4.3. The DSC traces of PS samples etched from four different substrates treated with a 0.4 M sodium perchlorate solution and heated in an inert helium environment.

The DSC traces of PS samples annealed above 700 °C and treated with perchlorate salts is shown in Figure 4.4, along with the DSC trace of silicon nanoparticles for comparison. Thermal annealing in an inert environment can cause dehydrogenation of the PS [112] and can also affect the internal structure of PS [116], both of which can affect the reactivity of PS.

From the DSC trace of the silicon nanoparticles shown in Figure 4.4, it can be seen that the nSi - NaClO$_4$ system does not exhibit a low temperature exothermic peak similar to the unannealed PS, but the higher temperature exothermic peak still occurs just after the melting temperature of the oxidizer despite the silicon core being encapsulated inside an oxide layer in the silicon nanoparticles. A DSC scan of the perchlorate salts with silica nanoparticles (< 10 nm diameter, obtained from Sigma Aldrich Inc.) showed no difference compared to the pure salt itself, indicating that the high surface areas presented by silicon
Figure 4.4. DSC traces of annealed and fresh heavily doped P-type PS samples, and silicon nanoparticles treated with 0.4 M NaClO₄ solution. Only the fresh PS exhibits a low temperature exothermic reaction, but all three samples start reacting with the oxidizer below the decomposition temperature of the oxidizer. The exothermic reaction initiates shortly after the oxidizer melts, which can be seen as an endothermic kink in the DSC trace.

dioxide and the oxide layer on the nanoscale silicon particles do not aid the decomposition of the perchlorates. In the case of sodium and magnesium perchlorates, there is no clear distinction between the melting of the salt and the onset of decomposition. To examine the effect of the phase change of the salt on the reaction, lithium perchlorate, which melts at 247 °C and decomposes only above 400 °C [99] was used. The DSC traces of heavily doped P-type PS treated with a dilute solution of lithium perchlorate indicated the onset of an exothermic reaction upon the melting of the salt, which accelerated close to the decomposition temperature of the salt.
4.3.3.2 PS - Sulfur composites

The interaction between the perchlorate salts and PS requires some degree of decomposition of the perchlorate salt in order to produce the oxidizing species which can interact with the silicon atoms. The decomposition of the oxidizer, and subsequent reaction with the silicon atoms can be expected to be coupled, at least in relation to the low temperature exothermic peak which is a solid - solid redox reaction. Thus, a simpler oxidizer molecule, sulfur was used to further examine the effect of substrate doping properties on the reactivity of PS. The DSC traces of the two high doped PS samples impregnated with sulfur (using a saturated solution of sulfur dissolved in carbon disulfide) are shown in Figure 4.5. The first two endothermic peaks are associated with the phase change and melting of sulfur respectively. The N-type PS reacts with sulfur resulting in an exothermic peak immediately after the sulfur melts, while the P-type substrates do not show this low temperature exothermic reaction. The low temperature exothermic reaction is not prominent in either low doped N or P type PS. When heavily doped N-type PS samples annealed to 700 °C were treated with sulfur, the low temperature exothermic peak immediately following the melting of sulfur was no longer observed. During the inert environment anneal, the pore walls can undergo surface reconstructions, during which the concentration of defects and unsaturated atoms can be reduced, and the internal structure, i.e., the crystallographic planes forming the pore walls can change. However, the concentration of the dopant atoms present in the silicon substrate does not change, and thus the electron density remains unchanged. This indicates that the observed low temperature exothermic reaction is a consequence of the defects and unsaturated silicon atoms, and the difference in the reactivity of the crystallographic planes in the N-type PS.

4.3.4 Influence of substrate doping properties on reactive wave propagation speeds

In the previous section, the effect of substrate doping properties on the reactivity of PS was examined via TGA/DSC analysis which involved slow heating rates. The reactions between
Figure 4.5. DSC traces of heavily doped N and P substrates heated in an inert environment after being impregnated with sulfur. The N-doped PS exhibits a low temperature exothermic reaction with sulfur immediately after the melting point of sulfur, while the P-doped PS does not.

PS and perchlorate salts were not affected by the dopant atom type or concentration as seen in Figure 4.3. However, the substrate doping properties affect the structure of PS, which can have an effect on the reactive wave propagation speeds, and thus the energy release profiles. To elucidate the effect of substrate doping levels and the nano and microscale structure on the reactive wave propagation, porous layers were etched on N and P-type substrates with widely different doping levels and impregnated with sodium perchlorate and tested. The porous layers etched on all the substrates were impregnated with sodium perchlorate using a saturated solution in methanol. The substrate properties, porous layer characteristics, and the reactive wave propagation speeds are shown in Table 4.2. The reactive wave propagation
speeds are presented as a range (minimum – maximum) of values measured over at least three samples for each case.

**Table 4.2.** Porosity, SSA, and Reactive wave propagation speeds measured on PS etched from four different silicon substrates.

<table>
<thead>
<tr>
<th>Dopant atom</th>
<th>Resistivity (Ω-cm)</th>
<th>Porosity</th>
<th>SSA (m²/g)</th>
<th>( \vartheta ) (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron (P)</td>
<td>0.001-0.005</td>
<td>0.6(^a)</td>
<td>312</td>
<td>3-3.3</td>
</tr>
<tr>
<td>Arsenic (N)</td>
<td>0.001-0.005</td>
<td>0.62(^a)</td>
<td>423</td>
<td>5.4-11.0</td>
</tr>
<tr>
<td>Phosphorus (N)</td>
<td>2-5</td>
<td>0.40(^b)</td>
<td>145</td>
<td>314-372</td>
</tr>
<tr>
<td>Boron (P)(^c)</td>
<td>10-20</td>
<td>0.67(^b)</td>
<td>730</td>
<td>1098-1261</td>
</tr>
</tbody>
</table>

\(^a\)From gravimetric measurements  
\(^b\)From gas adsorption measurements  
\(^c\)The data presented here is from PS samples with the highest SSA

Broadly, the reactive wave propagation speeds appear to be in one of the three regimes, \(~1\) m/s, \(~100\) m/s, and \(~1000\) m/s. Both the heavily doped substrates were found to yield PS devoid of any microscale patterns, and they consistently exhibited low reactive wave propagation speeds. The low doped N-type substrates, etched under illumination, yielded PS substrates with randomly forming microscale crack patterns (micro-crack patterns), and exhibited significantly higher reactive wave propagation speeds than the heavily doped PS substrates, despite having a lower SSA, which is expected to be the controlling parameter. As discussed in the next chapter, the higher speeds despite the lower SSA in case of the low doped N-type substrates is a consequence of the microscale structure, which results in a change in the reactive wave propagation mechanism. The highest reactive wave propagation speeds, \(~1000\) m/s, were observed on low doped P-type substrates, consistent with the literature presented in Chapter 1. However, not all PS samples etched on low doped P-type PS yielded composites exhibiting high speed reactive wave propagation speeds. The low doped P-type PS samples described in Table 4.2 were etched using a recipe similar to that described by Churaman *et al.* [80], which typically resulted in SSA around 700 m²/g. However, PS samples etched at higher current densities, with SSA around 600 m²/g resulted in significantly lower reactive wave propagation speeds, between 4.1 m/s and 4.9 m/s. This change in the behavior of PS is further discussed in Chapter 6, where the effect of SSA on
the DSC traces of several PS samples is examined. As seen from Table 4.2, the reactive wave propagation speeds observed in heavily doped N-type PS are consistently higher than the speeds observed in the heavily doped P-type PS composites. While the heavily doped N-type PS has a higher SSA than the heavily doped P-type PS, the low doped P-type PS samples with higher SSA ($\approx 600 \text{ m}^2/\text{g}$) exhibited lower reactive wave propagation speeds. This indicates that the reactive wave propagation speeds in heavily doped N-type PS may be influenced by factors other than the SSA, such as the reactivity of the crystallographic planes exposed to the oxidizer, as described previously. While thermal analysis at low heating rates did not show an effect of the dopant atoms on reactions with perchlorate salts, the heating rates experienced during the reactive wave propagation are several orders of magnitude higher, which could lead to different reaction mechanisms.

4.4 Conclusions

The effect of dopant atoms on the reactivity of PS was explored by studying the chemical reactions between PS and oxidizers. In slow reacting Ge-MoO$_3$ systems, the dopant type was found to affect the conversion rates and onset temperatures, while the faster, high temperature combustion processes in Si-PTFE systems were found to depend only on the dopant atom concentration. The work presented here indicates that the dopant atoms have minimal effect on the interaction between PS and oxygen or complex oxidizer molecules such as perchlorate salts, at least at low heating rates $\sim 10 \text{ K/s}$. The low temperature backbond oxidation with these oxidizers was found to depend on the surface defects and internal structure, as the low temperature exothermic reaction was observed in both P and N-type substrates, but was no longer observed upon annealing the PS samples above 700 $^\circ\text{C}$ in an inert environment prior to treating them with the oxidizer. This indicates that the low temperature reaction is only a function of the reactive sites in PS, and not a consequence of the boron atoms accepting an electron and aiding the decomposition of perchlorate salts. The reaction with perchlorate salts requires the breakdown of the
perchlorate ion to oxidize the silicon. However, when a simple elemental oxidizer (sulfur) was considered, the difference in the substrate doping type and concentration manifested in the form of the reactivity of the surface sites, as a low temperature exothermic reaction was observed only with the heavily doped N-type substrates. While this observation is consistent with the effect observed in other solid-solid systems, the elimination of this low temperature exothermic reaction by an inert environment anneal to 700 ℃ indicates that it is a consequence of the difference in the internal structure and reactive sites of the PS, and not the difference in the electron concentration. For the PS-oxidizer systems described in this chapter, the internal structure of PS was found to have a strong effect on its reactivity with sulfur, and the substrate doping properties influence the internal structure of the PS formed.

In terms of the combustion performance of PS composites, PS etched from heavily doped substrates (P or N-type) was found to yield composites which always exhibit low reactive wave propagation speeds on the order of 1 m/s. PS samples with a microscale structure (low doped N-type substrates) exhibited reactive wave propagations two orders of magnitude faster, despite having lower SSA, which is attributed to the microscale patterns affecting the reactive wave propagation mechanism. Consistent with previously published literature, the PS etched from low doped P-type PS yielded composites with reactive wave propagation speeds on the order of 1000 m/s. However, these high speeds are strongly dependent on the SSA, as PS samples with SSA around 600 m²/g exhibited significantly lower reactive wave propagation speeds.
Chapter 5

Enhancement of reactive wave propagation speeds by organized microscale structures

As seen from Table 4.2, the slowest reactive wave propagation speeds were observed in PS composites prepared from heavily doped P or N-type substrates, and the highest reactive wave propagation speeds were observed on PS prepared from the low doped P-type substrates. Intermediate reactive wave propagation speeds, on the order of 100 m/s, were observed on PS prepared from low doped N-type PS, attributed to the microscale structure of PS. In this chapter, the random micro-crack patterns, and their effect on the reactive wave propagation speeds is discussed. The random micro-crack patterns which are formed during the electrochemical dissolution process create a microscale structure, which effectively organizes the nanostructured PS-oxidizer composites in random geometries. This organization of reactive PS composites is hypothesized to result in enhanced reactive wave propagation speeds by a change in the reactive wave propagation mechanism from a conductive heat transfer driven process described in Chapter 3 to a convective heat transfer driven process. This hypothesis is tested by using standard microfabrication processes described
in Chapter 2 to create controlled multiscale structures, consisting of micro/nanoscale features on heavily doped P-type substrates, which yielded composites exhibiting low reactive wave propagation speeds. The microscale structures examined include square pillars and microchannels, which resulted in an increase in the reactive wave propagation speeds by up to two orders of magnitude. The behavior of these multiscaled PS samples is studied by characterizing the reactive wave propagation using regular high speed imaging and high speed focused shadowgraphy. The work presented in this chapter is the first demonstration of the control of the reactive wave propagation speeds in PS composites exploiting microfabrication techniques, and appears in publications by Parimi et al. [84, 105].

5.1 Background

5.1.1 Hierarchical micro/nanoscale structures in other systems

The work presented later in this chapter examines the effect of multiscale structures consisting of micro and nanoscale features on the reactive wave propagation in PS composites. While the reactive wave propagation mechanism discussed here primarily depends on the ability of PS composites to generate large volume of gaseous combustion products as described in Chapter 1 and elsewhere [79, 80], it is interesting to note that many naturally occurring biological and physical objects derive their unique properties through a similar hierarchical organization of their constituent nano and microscale structures. The strength of calcified bones [117], the gravity defying stickiness of the feet of geckos [118], the color and hydrophobicity of butterfly wings [119], and the color of opal gemstones [120] are some of the examples of functional manifestations arising from the hierarchical organization of nanostructures. Such multiscaled structures are being increasingly exploited to engineer devices such as adhesives mimicking spatulae of a gecko [121], porous silicon drug delivery systems [122], etc.
5.1.2 Low doped N-type PS composites

Low doped N-type substrates (phosphorus doped, with resistivity between 2 and 5 Ω-cm) were etched under the illumination provided by a 10 W LED lamp, and a current density of 40 mA/cm² for 60 minutes. The etched silicon wafers were scribed and cleaved to yield test samples, which were impregnated with magnesium perchlorate. Energetic composites prepared from these samples were found to be more susceptible to accidental ignition compared to the heavily doped PS samples, and thus a drop casting method was used to impregnate the PS samples with the oxidizers. The PS samples were mounted on the test block using double sided adhesive tape, and then a few drops of saturated magnesium perchlorate solution (in methanol) were applied on the surface of the sample. The test chamber was purged with argon, and the samples were dried by heating under vacuum, and then ignited. As seen in Table 4.2, reactive wave propagation speeds around 300 m/s were observed on these samples. The micro-crack patterns that randomly form during the electrochemical etch process, and the resultant microscale structure can be seen in the SEM image of the low dope N-type PS shown in Figure 5.1.

5.1.3 Convective burning

Based on the behavior of other macroscale systems, it is known that the spatial arrangement of reactive compositions can significantly affect the reactive wave propagations. Dremin et al. [123], in their review of the behavior of condensed phase explosive charges, indicate the possibility of obtaining average propagation rates greater than those of compact charges of a given explosive for certain spatial arrangement of the charges. Other examples for fast propagations created due to uncontrollable geometric factors are dust explosions where dispersion of particulate combustible materials can result in strong explosions [124], detonations in damaged propellants containing undesirable cracks or porous beds with significant permeability [125,126], and the high speed reactive wave propagations in nanothermite systems which are inversely proportional to the packing densities [127–129]. In the case of solid propellant systems, combustion within the voids accompanied by the release of hot
gaseous products results in increased localized pressures, which reduces the flame stand-off distance from the propellant surface, which results in further increased burning rates within the voids. This positive feedback results in a transition from deflagrations to detonations. One of the phenomena leading to the transition from a deflagration to a detonation (known as DDT) is a transition from a conductive burning mode to a convective burning mode, wherein enhanced heat transfer by the pressure driven upstream flow of hot gaseous combustion products results in a several-order-of-magnitude enhancement in the reactive wave propagation speeds [130]. A schematic detailing the convective burning mechanism, obtained from [125], is shown in Figure 5.2. An examination of Figure 5.1 shows that such permeation is possible in the low doped N-type PS, indicating that the high speed reactive wave propagations are a consequence of transition from a conductive to a convective burning mechanism.

Figure 5.1. SEM image of the porous silicon etched on low doped N-type substrates with resistivity between 2 and 5 Ω-cm showing the random micro-crack pattern formed during the electrochemical etch process (top view).
product gases being generated in the porosity faster than venting could occur. For porous materials and narrow cracks, the escape of gas from reactions inside the porosity can be constrained due to viscous effects and gas-dynamic choking. With sufficient confinement, the contained product gases locally elevate the porosity pressure and drive the hot products ahead of the deflagration and into unreacted explosive. They may even precede the conductive preheat zone. The degree of convection penetration is currently not fully resolved and, in all likelihood, depends on the porosity of the explosive [6].

In this situation, thermal and frictional losses to the walls quickly slow and cool the product gases and preheat the unreacted explosive in the process, decreasing the amount of heating required by conduction. In some cases, the preheating of the product gases is sufficient to induce ignition by itself. So, in contrast to conductive burning, where propagation of the chemical reaction is primarily due to conduction of heat, the propagation rate of this new mode is augmented by the convection of hot product gases. Thus, it is referred to as convective burning.

It is important to note that, in a convective burn, conductive heating is still present and plays a major role in the ongoing reaction of the ignited material, as heat still propagates ahead of the deflagration via thermal conduction. The convection simply enhances the burn rate by providing additional energy transport ahead of the front. The key identifying characteristics of a convective burn are penetration of porosity by the flame and preheating of the porosity by hot gases driven ahead of the flame front. A schematic of the convective burn process is shown in Fig. 5.7.

Some authors [22] have gone as far as to classify two modes of convective penetration: “spontaneous” and “forced.” Spontaneous burning occurs where the reaction front penetrates porosity smoothly with a definite velocity. Forced penetration is when the reaction spreads in a highly nonsteady fashion, with fingers of reaction shooting ahead of the main front into pockets of...
and side views of the microscale patterns are shown in Figure 5.3. Figure 5.4 shows higher magnification images of a single pillar, and the diameters of the pores at the surface are ~30 nm, similar to the PS samples described in Chapter 3.

![Figure 5.3](image1.png)

**Figure 5.3.** Top view of the etched pillar structures, showing square bases with a side of 8 µm separated by 8 µm. (b) Side view of the pillared structures showing the sidewall profile. These pillars are about 35 µm tall.

![Figure 5.4](image2.png)

**Figure 5.4.** (a) SEM image of a single pillar showing the nanoscale features. (b) High magnification image of a single pillar showing pores with diameters ~30 nm, similar to the PS samples shown in Figure 3.2.

The current density used in Chapters 2, 3, and 4 to describe the electrochemical etch process is based on the initial surface area of the silicon wafer exposed to the electrolyte.
Based on the literature review presented in Chapter 1, the current density can be expected to affect the pore morphology. In case of the silicon wafers with microscale patterns etched on them, the initial surface area of the silicon exposed to the electrolyte at the beginning of the etch process is several fold higher, and reduced current densities had to be used to electrochemically etch the wafers to avoid overheating the small volume of electrolyte used in the etch cell. Thus, the electrochemical etch was carried out using the same electrolyte composition and total current as the samples used in chapter 3. To account for the effect of the reduced current density, only one half of each silicon wafer was patterned with the microscale features before the electrochemical etch process. The test samples were then cut such that each test sample contained an unpatterned PS section and a patterned PS section with the microscale features. It must be noted that due to the nature of the electrochemical etch process, there is always a porous layer on the underneath surfaces that connect the microscale patterns. Thus, patterned PS samples were prepared in four configurations as shown in Figure 5.5 to obtain a variation in the micron size pillars versus the nanometer scale features.

Energetic composites were prepared by impregnating the porous layers with sodium or magnesium perchlorate salts (using saturated methanol solutions). The patterned samples were ignited in the half containing only nanoporous silicon and the reaction was allowed to achieve a steady propagation rate before encountering the patterned region. Since the purely nanoporous region and the multiscaled region have been treated similarly (i.e., etched with the same current density and treated with the same oxidizer fill procedure), the purely nanoporous region served as the control sample, and the reactive wave propagation speeds in this section can be used as a baseline to analyze the effect the microscale patterns have on the reactive wave propagation. In samples with thick porous layers (I and III), the flame speeds in the non-patterned region were between 1 and 3 m/s, consistent with the work presented in Chapters 3 and 4. However, when the reactive wave reached the patterned region, an abrupt transition resulting in a bright reaction front propagating much faster was observed. Figure 5.6 shows the reactive wave propagation in samples with tall pillars.
Figure 5.5. The four different configurations of patterned PS substrates prepared. The shaded region in the images represents the nanoporous region. The thickness of the substrates used in all these cases was 525 µm. Note that the image is not to scale.

and thick porous layers (I). The large variation of the propagation rates in Figure 5.6 is shown by means of a distance-time plot in Figure 5.7. The samples with thick porous layers and tall pillars (I) exhibited post transition speeds up to 500 m/s, while the samples with thick porous layers and short pillars exhibited speeds up to 150 m/s. Based on the high speed camera images post transition, the reactive wave propagates at a much higher speed between the pillars on the surface, while the thick porous layer underneath the pillars burns longer. Thus, the propagation speed was measured along the surface of the sample, as indicated by the circles in Figure 5.6.

Samples with thin porous layers (II and IV) showed no transition. While slow propagations ~ 0.5 m/s were observed with IV, flame speeds of 1 – 3 m/s were observed for II. BET measurements on substrates III and IV indicated surface areas of 284 and 361 m²/g, respectively. The porosities calculated from the BET void space measurement were 0.76 for
Figure 5.6. Reactive wave propagation on patterned substrate with only nanopores on the bottom half and nanoporous pillars ~35 µm tall on the top half. Note the non linear time change between photographs. The reactive wave propagation speed exhibited a sudden transition from ~2.5 m/s to ~ 360 m/s as shown in the following x-t plot.

substrates III and IV. No significant difference was observed between the estimated temperatures using the spectrum from a point post transition from I and II and non-patterned substrates soaked in saturated solutions. While the temperatures were determined to be between 1700 and 2000 K for the unpatterned samples, the spectrum collected from the fast propagating region in samples I and II indicated temperatures near 2250 K. The similarity of the temperatures despite two orders of magnitude difference in the propagation rate indicates a difference in the reactive wave propagation mechanism, as similar temperatures indicate a similar thermal driving force. Further, if the PS - oxidizer is to be approximated to be a one-dimensional premixed system, the reactive wave propagation rate varies as

$$\vartheta \propto \sqrt{\frac{\alpha \omega}{\rho}}$$  (5.1)

where $\alpha$, $\omega$, and $\rho$ are the thermal diffusivity, reaction rate, and density of nanoporous
silicon, respectively. Since the local reaction rate is based on the chemical kinetics for the chosen fuel and oxidizer reactants, the temperature of the reaction zone, and the available surface area between the fuel and oxidizer components in the nanoscale pores, it is expected to be unchanged between the patterned and unpatterned regions. However, the effective transport properties can be changed if the heat transfer process changes from a condensed phase conductive mechanism to convective mechanism.

### 5.2.1 Shadowgraph analysis of the reactive wave propagation in patterned PS composites

Reactive wave propagation by a convective burning mechanism requires the upstream permeation of hot gaseous reaction products to achieve a convective preheat zone thicker than the conductive preheat zone as shown in Figure 5.2. Thus, the behavior of the hot gaseous reaction products was visualized using the high speed focused shadowgraphy system described in Chapter 2. Test samples with square pillar geometry similar to the samples used
in the previous section were prepared. However, due to a change in the doping properties of the silicon substrates provided by the manufacturer, the etch recipes used in the previous work could not be replicated, and new electrochemical etch parameters had to be developed, which included a 50% reduction in the current densities used. Thus, there are differences between the work presented in the preceding section and the current section, specifically in terms of the enhancements observed in the reactive wave propagation speeds by the microscale patterns. However, the phenomenological behavior discussed in this section is expected to be applicable to the previous section too. Figure 5.8 shows the square pyramidal structures etched on one half of the silicon wafers, with better control over the side wall profiles, while using the same mask. A series of high speed shadowgraph images from a single video depicting several phenomena that occur as the sample is ignited in the unpatterned region and the reactive wave is allowed to propagate into the patterned region are shown in Figure 5.9.

Figure 5.8. SEM images of the square cylindrical pillars etched on heavily doped P-type substrates. (a) Top view showing 12 μm × 12 μm square bases separated by 7 μm. (b) The silicon-PS interface (c) Side view of the square cylindrical pillars and the PS layer etched on the silicon substrate. The PS layer below the pillars is 133 μm thick, and the initial thickness of the silicon wafer was 525 μm. (d) Side view of a pillar showing the sidewall profile arising due to the plasma etch process (DRIE). The pillars are 57 μm tall. The curvature in the side wall profile is due to the isotropic component of the DRIE.
Figure 5.9. Series of images from the high speed side view shadowgram captured for samples in which the non patterned PS was ignited and the reactive wave was allowed to propagate into the patterned region. The high speed video was recorded at a frame rate of 80590 fps, with an exposure of 1.02 μs. Note the non linear time scales used. The dark strip seen on the left side in each of the images in the panel is the side view of the silicon wafer and the mounting block placed in the shadowgraph system depicted in Figure 2.2. (a) and (b): Consecutive images acquired following the ignition of the PS sample by a spark. The arrows point to the location of the weak shock that was generated upon ignition. (c) and (d) depict the formation and growth of a localized ignition front resulting in a “flame jump”. (e) and (f) show the steady state propagation, and (f) is the frame right before the reactive wave encounters the patterned region. In (a)-(f), the plume containing the hot gaseous products is directed away from the direction the reactive wave propagates. (g) shows the shock formation when the reactive wave enters the patterned region. In (g)-(l), gas permeation ahead of the luminous flame front can be seen.
The sample is ignited on the unpatterned PS by means of an electrical spark, and the transient ignition process results in the formation of a weak spherical shock as seen in Figure 5.9 (a) and (b). During the reactive wave propagation in the unpatterned region, as seen in Figure 5.9 (a) – (f), it can be seen that the plume comprising of the hot gaseous products is directed away from the direction that the reactive wave propagates. However, when the reactive wave enters the patterned region, there is a clear permeation of the hot gases ahead of the luminous flame front, as shown in Figure 5.9 (g) – (l). The permeation of the hot gaseous products ahead of the luminous flame front indicates that the reactive wave propagation is occurring by means of convective heat transfer, and that the enhancement of the reactive wave propagation speed is due to transition from a conductive burning mechanism to convective burning. For the sample shown in Figure 5.8, the reactive wave propagation speed in the non-patterned and patterned regions was 4.3 m/s and 137 m/s, respectively. Further, it can be seen from Figure 5.9 (g) – (k) that the luminous front does not follow the shock wave, indicating that the enhancement in the reactive wave propagation speeds is not due to the interaction of the shock with the PS surface. The spherical shock front expands with a nearly constant speed of 419 m/s, and is driven by the disturbances generated by the reactive wave propagation. The gas velocity behind the moving shock wave is with respect to a stationary reference frame ($V_g$), for the sample shown in Figure 5.9 is 115 m/s, which is close to the reactive wave propagation speed, indicating that the moving shock wave is driven by the reactive wave propagation.

This directionality of the plume arises from the fact that the combustion of PS occurs heterogeneously at the surface and the gaseous reaction products are generated at a solid surface. The solid boundary forces the gases to be ejected in a direction away from the reactive wave propagation direction as shown in Figure 5.10. However, in the case of the pillars protruding above the PS surface, it can be expected that they disintegrate and burn rapidly, that is explode, causing the hot gaseous products to be ejected in all directions. This process is believed to be the mechanism responsible for the permeation of the gases ahead of the luminous reaction zone. Plummer et al. attributed the erratic and infrequent “flame
jump” observed in Figure 5.9 (c) and (d) to the detachment of the PS film from the silicon substrate due to the pressure build up within the porous layer. Such skipping has been observed at speeds ranging from < 10 m/s in our work to speeds above 3000 m/s in Piekiel et al.’s work. While the mechanism for the flame skipping might be different between the vastly different propagation speeds, the crystalline nature of PS and the underlying silicon substrate makes it possible for the PS film to crack and ignite due to mechanical stresses generated from temperature gradients near the reaction zone and the thrust experienced by the sample.

![Diagram](image)

**Figure 5.10.** Schematic explaining the directionality of the gaseous product plume seen in Figure 5.9. In the non patterned region, the gaseous products formed at the reaction zone are confined in the upstream direction by the silicon substrate and the PS layer, forcing the gases to be ejected in a direction away from the reactive wave propagation. However, the small micrometer sized pillars are expected to disintegrate and burn, or explode, resulting in the gaseous products being ejected ahead of the reaction zone, resulting in convective burning.

### 5.2.2 Reactive wave propagation in PS composites with microchannels

Based on the shadowgraph analysis and the reactive wave propagation speeds observed in the four different configurations of samples with microstructures presented in Figure 5.5,
the parameters controlling the reactive wave propagation speed enhancement by convective burning can be summarized as:

1. **The permeability of the microscale structure.** The permeability depends on the geometry of the microscale patterns etched, and indicates the degree of resistance to the flow of the gaseous reaction products in the upstream direction.

2. **The spacing between the microscale features.** An enhancement in the burning rate is observed as long as the convective heat transfer to the adjacent microscale PS element from the reaction zone occurs faster than the time taken for the purely conductive reactive wave in the underlying PS film to cover the same distance. When the spacing between the microscale structures is too large or too small, it can be expected that there will be no convective burning, and the reactive wave propagation will approach the purely conductive burning attained in unpatterned PS.

3. **The height of the microscale features above the PS base,** which controls the surface area and the volume of the microscale feature. This controls the heat transfer by convection and also the volume of gas phase reaction products generated. The height and spacing also affect the permeability of the microscale patterns.

In case of the square pillars, the three parameters cannot be independently varied. To obtain better control over the three parameters described, PS samples with a different geometry of microscale pattern, that is, microchannels were prepared. Reactive wave propagation perpendicular to the microchannels restricts the upstream gas flow, as any gases generated at the reaction zone cannot travel any further than the next side wall they encounter. The spacing and the height can thus be varied independently, by changing the feature size on the mask and changing the DRIE duration. When the reactive wave propagates along the direction of the microchannels, a fraction of the gases generated from the reaction zone can travel along the microchannel and heat the side walls. This provides a pathway with high permeability for the gaseous products. Three different microchannel configurations were used in this study, and the feature sizes on the mask used to pattern the microchannels
had a fixed sidewall thickness of 15 μm, with channel widths of 5 μm, 15 μm and 25 μm. A representative SEM image of the microchannel patterns etched on the silicon substrates is shown in Figure 5.11.

Figure 5.11. Representative SEM image of the microchannels etched on PS samples. For the PS sample shown in this figure, the spacing between the sidewalls is 8 μm, and the thickness of the sidewalls is 12 μm. The height of the sidewalls is 82 μm, and the thickness of the PS layer below is 118 μm.

As in the previous sections, the patterned PS samples were impregnated with sodium perchlorate using a saturated solution of the salt in methanol, and the test samples were ignited in the unpatterned region, and the reactive wave was allowed to propagate into the patterned region. The reactive wave propagation speed observed in the non-patterned region was 4.6 ± 0.5 m/s (average ± standard deviation) between the several samples tested. The effect of the microchannels on the reactive wave propagation was:

1. When the reactive wave propagation was perpendicular to the microchannels, a slight increase in the reactive wave propagation speeds was observed, and the maximum observed speed was 15.1 m/s.

2. When the reactive wave propagation was parallel to the microchannels, a larger enhancement in the reactive wave propagation speeds was observed. The maximum
observed speed was 51.2 m/s.

3. No specific dependence of the reactive wave propagation speed on just the depth or the width of the microchannels was observed.

However, when the reactive wave propagation speed in the patterned region were plotted as a function of the channel aspect ratio (distance between the sidewalls/height of the side walls), the reactive wave propagation speeds show a dependence on the aspect ratio as defined in Figure 5.12. The influence of the void aspect ratio and the direction of the reactive wave propagation with respect to the orientation of the microchannels is shown in Figure 5.13, which indicates that the higher propagation speeds were observed at lower aspect ratios. The low enhancement of the reactive wave propagation speeds in the perpendicular configuration indicates that the gas permeation has the strongest effect on the enhancement. The pillar structures in which the gases could permeate ahead of the reaction zone exhibited speeds above 100 m/s, whereas the maximum speed observed in the perpendicular configuration was limited to 15.1 m/s. Further, the parallel configuration showed higher enhancements than the perpendicular configuration, despite only a fraction of the gas being driven ahead of the reaction zone. The aspect ratio of the microchannels is phenomenologically the inverse of the ratio of the flow resistance to the gas flow to escape through the top opening and to be driven in the upstream direction. Thus, as the aspect ratio reduces, a higher fraction of the gaseous products can be expected to be driven along the microchannels (especially in the parallel configuration), resulting in higher reactive wave propagation speeds. This interpretation is consistent with the observations on pressure driven flow in Al/CuO nanothermites by Sullivan *et al.* [132,133], who examined the effect of film thickness on pressure driven flows in nanothermite systems.

5.3 Conclusions

The work presented in this chapter examines the effect of the microscale structure of PS on the reactive wave propagation in energetic PS composites. SEM examination of PS etched
on low doped N-type substrates, which exhibit reactive wave propagation speeds of several hundreds of meters per second, revealed the presence of microscale features. The microscale features on PS etched on low doped N-type substrates under illumination are formed due to uncontrollable micro-crack patterns that arise during the electrochemical etch process. The microscale features on low doped N-type substrates were hypothesized to be responsible for the higher reactive wave propagation speeds observed in these samples compared to the PS composites from heavily doped substrates, despite the low doped N-type PS having a lower SSA than the heavily doped PS. This hypothesis was tested by using microfabrication techniques to create controlled microscale features on silicon substrates (pillars and microchannels), which resulted in up to two orders of magnitude enhancement in the reactive wave propagation speeds. The mechanism for the enhancement is a transition from a conductive heat transfer based propagation mechanism to a convective heat transfer based
Figure 5.13. Reactive wave propagation speeds parallel and perpendicular to the microchannels etched on heavily doped P-type PS as a function of the void aspect ratio. No specific dependence of the reactive wave propagation speed on the channel width or height was observed. The highest speeds were obtained when the reactive wave propagation was along the microchannels, and at low void aspect ratios.

propagation mechanism, which is supported by existing literature on convective burning, and flow visualization using high speed focused shadowgraphy which showed permeation of hot gaseous combustion products ahead of the luminous reaction zone. The parameters expected to affect the enhancement in the reactive wave propagation speeds, the permeability of the microscale structure, the spacing between the microscale features, and the height of the microscale structures were examined by studying the reactive wave propagation parallel and perpendicular to microchannels. Experimental results indicated that the permeability of the structure has the strongest effect on the enhancement obtained, and the reactive wave propagation speed depends on the aspect ratio of the microchannels etched.
Chapter 6

Mechanistic investigation of reactive wave propagation in low doped P-type PS composites

In this chapter, a mechanistic investigation of propagating reactive waves through porous silicon (PS) – sodium perchlorate composites prepared from low doped P-type substrates (resistivity 10 - 20 $\Omega$-cm) is presented. While high speed reactive wave propagations in low doped P-type PS composites have been reported previously by other researchers [80,81,134], the work presented in this chapter is aimed at understanding the mechanism by which the reactive wave front propagates at speeds on the order of thousands of meters per second, and how these PS composites differ from the heavily doped PS composites discussed in Chapters 3 and 4, and the low doped N-type PS composites discussed in Chapter 5. Speed of sound measurements using acoustic microechography and high speed shadowgraph imaging reveal that the high speed reactive wave propagations are not a consequence of a detonation in the condensed phase (as hypothesized elsewhere [134]), nor the interaction of the shock in the gaseous medium with the condensed phase composite. Thermal analysis showed that the heat release from exothermic reactions between PS and the oxidizer within the pores shifted
to lower temperatures as the SSA of PS increased, which was accompanied by a reduction in the activation energy associated with the lowest temperature exothermic reaction between PS and the oxidizer. The combined experiments indicated that a combination of conductive and convective burning, possibly assisted by fast crack propagation within the silicon/porous silicon substrate, was responsible for the observed difference in propagation speeds and was the mechanism by which the reactive wave propagated with speeds on the order of a km/s within the porous layers.

6.1 Background

Reactive wave fronts propagate by heat transfer by conductive or convective mechanisms, or by detonation phenomenon. A detonation is a shock wave that propagates through a medium, which is driven by an exothermic reaction behind the shock front. Unlike conductive and convective burning mechanisms, shock heating of the medium sustains the detonation wave. Typically, conductively driven reactive wave propagations are slow reactive waves propagating with speeds on the order of a meter per second, and convective wave propagations approach speeds on the order of hundreds of meters per second, and the fastest reactive wave propagations are detonations, which propagate at speeds of several thousands of meters per seconds. The PS used in this chapter was prepared using the same electrochemical etch parameters as Churaman et al. [80]. The etched porous layers were 35 μm thick, and gas adsorption measurements indicated a SSA of 730 m²/g, and a porosity of 0.67. The samples were impregnated by sodium perchlorate by drop-casting the saturated oxidizer solution on the sample surface, and were ignited by an electric spark, and exhibited reactive wave propagation speeds on the order of 1000 m/s. The PS etched on the low doped P-type substrates did not show any micro-crack patterns, similar to PS etched from heavily doped silicon substrates, indicating that convective burning similar to the low doped N-type PS is not the mechanism responsible for the high speed reactive wave propagations. Thus, detonations, and shock assisted reactive wave propagations are examined
in this chapter as other possible mechanisms responsible for the high speed reactive wave propagations observed in low doped P-type PS composites.

6.2 Results and discussion

6.2.1 Speed of sound measurements

Piekiel et al. [134] applied the technique demonstrated in Chapter 5 to low doped P-type PS by etching microchannels onto the silicon substrates, which resulted in an enhancement in the reactive wave propagation speeds up to 4 km/s, which are the fastest reactive wave propagation speeds observed among all nanoenergetic materials. Piekiel et al. observed that the reactive wave propagation speeds approached, and in some cases slightly exceeded the predicted speed of sound in their PS samples, and concluded that the high speed reactive wave propagations observed are detonations in the condensed phase. Since the speed of sound in PS strongly depends on the pore morphology, and the substrate doping properties and the electrochemical etch properties strongly affect the pore morphology, the speed of sound for the PS used in this study was measured using an acoustic microscope. The longitudinal speed of sound in PS (LA) was measured by microechography using a scanning acoustic microscope, similar to the method previously used to measure the speed of sound in PS [135]. The PS samples were placed in water below an immersion type ultrasound resonator with a central frequency of 75 MHz, and the time taken for the reflections from the PS/water and the PS/Si interfaces to return to the transducer was measured. The thickness of the PS layer measured from SEM images was used to calculate the longitudinal wave speed in PS.

The speed of sound measured for the samples used in this work and the values found in the literature for the speed of sound in low doped P-type PS [135–137] are shown in Figure 6.1. It must be noted that the longitudinal velocity measured was for the sound wave propagating in a direction perpendicular to the reactive wave propagation in the PS samples. Due to the slightly anisotropic nature of the porous layer, as seen in Figure 5.8 (b), the
speed of sound can be expected to depend on the direction of propagation. The anisotropy in the structure arises from the fact that the pore growth during the electrochemical etch process is fastest in the \(<100\) direction \([64,138]\). However, the measurements by Aliev et al. on PS etched on differently oriented silicon substrates show that the measured speed of sound for a given porosity between (100), (110) and (111) oriented substrates are very similar, despite the differences in the orientation of the pores within the porous layer. Thus, the experimentally measured sound speeds can be assumed to be similar to the speed of sound along the direction of the reactive wave propagation within the porous layers. The reactive wave propagation speeds measured \((\approx 1500 \text{ m/s})\) are smaller than the measured speed of sound in PS \((2169 -2479 \text{ m/s})\), indicating that the high speed propagations are not detonations.

6.2.2 Interaction with the shock above the PS surface

Since the reactive wave propagation speeds observed in the low doped P-type PS composites are faster than the speed of sound in the air, the medium in which the samples are tested, a shock driven by the reactive wave front was observed in the shadowgrams. A small stand-off distance \((\sim 1 \text{ mm})\) was observed between the luminous reactive wave front and the location where the shock touches the PS surface, as shown in Figure 6.2. At the surface of the PS sample, the shock orientation was normal to the surface, and the static temperature and pressure jump conditions across the shock are

\[
\frac{P_2}{P_1} = \frac{2\gamma M_s^2}{\gamma + 1} - \frac{\gamma - 1}{\gamma + 1} \quad (6.1)
\]

\[
\frac{T_2}{T_1} = \frac{\left(1 + \frac{\gamma - 1}{2} M_s^2\right)\left(\frac{2\gamma}{\gamma - 1} M_s^2 - 1\right)}{M_s^2 \left(\frac{2\gamma}{\gamma - 1} + \frac{\gamma - 1}{2}\right)} \quad (6.2)
\]

\[
M_s = \frac{\vartheta}{\sqrt{\gamma RT_1}} \quad (6.3)
\]
Figure 6.1. Longitudinal speed of sound in low doped P-type PS from literature and the values measured by acoustic microscopy. For the low doped P-type PS samples used in this work, the measured speed of sound was between 2169 m/s and 2479 m/s, while the reactive wave propagation speeds measured were below 1500 m/s, indicating that the reactive wave propagation was subsonic.

where $M_s$ is the Mach number of the shock, $P_2$ and $T_2$ are the static pressure and temperature behind the shock, $P_1$ and $T_1$ are the static pressure and temperature in the undisturbed medium ahead of the shock, $\gamma$ is the ratio of specific heats of the gaseous medium, $R$ is the universal gas constant, and $\vartheta$ is the speed of the reactive wave front. The stand-off distance observed in Figure 6.2 is interesting, as it indicates the possibility of the reactive wave front in the condensed phase being coupled to the shock observed in the gas phase in two ways:
1. The high static temperature behind the shock can heat the PS and cause thermal ignition.

2. The high pressure behind the shock can cause mechanical damage to PS and result in the formation of localized ignition fronts as described previously [71].

![Figure 6.2. Side view shadowgram image of the reactive wave propagation in low doped P-type PS samples impregnated with sodium perchlorate. The reactive wave front moves supersonic with respect to the air, and drives the shock. A small stand-off distance was observed between the shock-PS surface and the luminous reactive wave front on the PS surface.](image)

The interaction between the condensed phase reactions and the gas phase compressible flow phenomena was investigated by preparing samples with a section in the middle which was not filled with the oxidizer. This sample fabrication was accomplished by masking a section of the PS (10 mm long) in the middle of the test sample with a tape and drop-casting the oxidizer solution on the other two halves. A section of the masked region remained unfilled with the oxidizer, as verified by the unburnt PS remaining on the middle of the sample strips after the combustion experiments. When the samples were ignited, the shock remained coupled with the luminous front, which is the supersonic disturbance driving the
shock for the length of the first reactive segment. When the reactive wave front reached the end of the first reactive segment, the shock decouples from the luminous front, and propagates over the inert region onto the second reactive region, while continuously decaying. In a small number of experiments (2 of >10), the decayed shock was capable of igniting the second reactive PS region, as shown in Figure 6.3. Since the decayed shock was capable of igniting PS, and the shock appeared coupled to the reactive wave for propagation speeds greater than ~1000 m/s as indicated by the relative positions of shock and luminous zone, the interaction between the shock and the reactive wave was examined further, to examine whether the high speed reactive waves propagate by the interaction of the shock in the gaseous medium with the condensed phase. The reignition of PS depends on the strength of the shock wave traveling above the PS surface, and the variations in the reactive wave propagation speeds mean that only the fastest reactive wave propagations can generate shocks strong enough to reignite the samples, resulting in the unrepeatability of the reignition experiments. Strategies to achieve repeatable reignition, focusing on achieving a shock - PS interaction are discussed in Chapter 7.

**Figure 6.3.** (a) Schematic (not to scale) of the test samples prepared to study the interaction of the gas phase shock with PS. The PS in the top and bottom regions of the test sample is impregnated with sodium perchlorate while the PS in the middle is not. (b), (c), (d) and (e) are a series of images from a high speed shadowgraph recording, and the time delay between each image is 12.5 µs. (b) shows the reactive wave front in the first PS region impregnated with the oxidizer. In this image, the shock is driven by the reactive wave front. (c) shows the propagation of the decaying shock upon the complete combustion of the reactive PS in the first filled region. (d) and (e) show the ignition and combustion of the second reactive PS region as the shock from the first region passes over it.
6.2.2.1 Influence of the pressurizing gas on the high speed reactive wave propagation

From equations 6.3, 6.2, and 6.1, the jump conditions across the shock depend on the ratio of specific heats of the gas around the sample, and the strength of the moving shock. The moving shock itself is coupled to the reactive wave front, and the strength of the shock depends on the shock Mach number, which depends on the speed of sound of the gas. Based on this, the effect of the shock front on the reactive wave propagation was studied by varying the gaseous medium in which the experiments were conducted. The reactive wave propagation was studied in air at 1 atm and 0.1 atm, and in helium at 1 atm. Between the experiments in air at different pressures, the strength of the shock, and thus, the ratio of static pressures and temperatures across the shock remain the same. While the static temperature behind the shock remains the same, heat transfer to the sample is different due to the difference in density of air over the surface of the sample. Also, the actual pressure behind the shock and the resulting force on the PS sample are lesser than those in the experiments conducted at 1 atm. The moving shock wave creates an abrupt change in pressure and temperature above the PS surface, and also creates a gas flow along the direction the shock wave propagates (at a velocity $V_g$). Thus, the shock wave can interact with the surface by means of heat transfer, shear forces (which depend on $V_g$, the temperature, and the pressure), and the normal force exerted on the PS surface due to the sudden change in the pressure behind the shock. The force exerted by the pressure jump behind the moving shock can be expected to be important in this case due to the porous nature of the samples. The pores are initially at atmospheric pressure, and the increased pressure behind the shock above the PS surface can lead to mechanical damage due to the pressure difference. For experiments conducted in helium, the Mach number of the shock coupled with the reactive wave front is significantly smaller, as the speed of sound in helium is much higher (1008 m/s in helium versus 343 m/s in air at 293 K), and consequently, the temperature and pressure jumps across the shock are smaller compared to air. The reactive wave propagation speeds in air and helium are shown in Table 6.1.
Because the reactive wave propagation speeds did not slow down in air at low pressure or in helium, it can be concluded that the compressible flow phenomena above the PS surface are not the mechanism responsible for the high speed of the reactive wave. Further, these results indicate that the high speed reactive wave propagation depends on what happens within the PS sample, and not on the gaseous medium surrounding the PS composites.

<table>
<thead>
<tr>
<th>Test conditions</th>
<th>Reactive wave propagation speed (m/s)</th>
<th>Average</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air (1 atm)</td>
<td>1162</td>
<td>94</td>
<td></td>
</tr>
<tr>
<td>Air (0.1 atm)</td>
<td>1324</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>Helium (1 atm)</td>
<td>1279</td>
<td>177</td>
<td></td>
</tr>
</tbody>
</table>

### 6.3 Possible reactive wave propagation mechanisms

#### 6.3.1 Conductive and convective burning

Both conductive and convective burning within the porous layers are examined in this section. While these phenomenon are discussed in separate sections below to better organize each section, it might not possible to experimentally distinguish between the two different phenomena that can simultaneously occur within the nanoporous material. Thus, it is important to consider both processes together for an unbiased analysis.

#### 6.3.1.1 Conductive burning

High speed reactive wave propagations in most conventional EMs and nEMs are a consequence of convective burning (for example, nanothermites) or detonations (RDX, HMX etc). The slow deflagration processes in EMs typically involve combustion in the gas phase, and the reactive wave propagates by heat transfer from the gas to the solid such as in low speed propellant combustion. As a consequence of the poor heat transport from the
reaction zone through the gaseous medium into the condensed phase reactants, conductive burning is typically discounted as a possible mechanism for high speed reactive wave propagations. However, PS - oxidizer composites studied in this work are unique in several aspects described below, and no other comparable reactive systems are known.

1. The oxidation of silicon takes place heterogeneously \[^{[58]}\], and the heat release occurs at the solid surface.

2. While PS has poor thermal transport properties compared to bulk crystalline silicon, the thermal diffusivity of PS is higher (0.02 - 0.09 cm\(^2\)/s) \[^{[139]}\] than that of nanothermite formulations (0.001 - 0.005 cm\(^2\)/s) \[^{[140]}\] or typical composite propellants (~10\(^{-4}\) - 10\(^{-3}\) cm\(^2\)/s) \[^{[141]}\]. Since the reactive wave propagation speed scales with the thermal diffusivity for a purely conductive propagation, and the heat release in PS occurs directly at the solid surface, PS can be expected to have a higher purely conductive component of the reactive wave propagation speed than most EM/nEMs.

3. The hydrogen termination of PS prevents the formation of a passivating native oxide layer, as previously discussed in Chapter 4. A passivating layer such as a native oxide prevents the effective mixing of the reactants, as it also acts as a barrier for transport phenomenon. While the Si-H bond being stronger than the Si-Si bond means that back-bond oxidation takes place before the Si-H bond is attacked, oxidation of the Si-H bond is still exothermic unlike in the case of an inert passivating layer.

4. Another consequence of the stability of the PS surfaces due to the hydrogen termination is that reactive composites with transport length scales smaller than those associated with any other nanoenergetic material formulation are possible with PS. While the metal particle diameters in nanothermite formulations are several tens of nanometers, the pore diameters and the silicon crystallite skeleton thickness in PS can be below 10 nm. As discussed in section 1.1.2.1, the reactive properties of nanoscale materials change significantly with respect to the length scales, with a more pronounced dependance on the dimensions at single nanometer length scales.
Reactive systems in which the reactive wave propagation can be expected to be driven purely by conductive heat transfer are intermetallic alloying reactions. These exothermic alloying reactions have been exploited to form nanoscale laminates with alternating Ni and Al layers [101]. The fastest reactive wave propagations observed in the Ni/Al nanolaminates have approached 100 m/s. However, the thicknesses of the metal layers in the Ni/Al laminates are on the order of 10 nm, as the laminates suffer from a passivating alloy layer that forms as metal interfaces during the deposition process itself; reducing the thicknesses of the layers would result in a complete alloying of the metals during the deposition itself. The fact that reactive wave propagation speeds on the order of several tens of meters per second to a few hundreds of meters per second have been observed in Ni/Al system can be used to support the argument that a faster purely conductive heat transfer driven reactive wave can be sustained in PS composites. However, a quantitative substantiation of this argument requires the knowledge of the kinetics for the interaction of the silicon atoms and the oxidizer molecules at the interface, the data for which is not available.

6.3.1.2 Estimation of reaction kinetics for PS composites using thermal analysis

While the direct and complete estimation of the kinetic parameters for PS composites is complicated, a method to address the importance of the conductive component of the high speed reactive wave propagation is to compare the two different PS composites used in this work: the heavily doped P-type PS composites which exhibit reactive wave propagation speeds ~1 m/s, and the low doped P-type PS composites which exhibit reactive wave propagations ~1000 m/s. For a purely conductive reactive wave propagation, closely following Semenov’s analysis, and assuming that the transport properties are unchanged between the two differently doped PS composites, the reactive wave propagation speed scales as

$$\vartheta \sim \sqrt{\frac{A}{E_a}} \exp \left(\frac{-E_a}{RT}\right)$$

(6.4)
where $E_a$ is the activation energy and $A$ is the pre-exponential factor.

The activation energy was estimated for the heavily doped P-type substrates and the low doped P-type substrates using Kissinger’s method as described in Chapter 2. The first exothermic peak was used to determine the activation energy for the purely solid – solid reaction, and the data presented in Table 6.2 shows that the low doped P-type PS – sodium perchlorate reaction has the lower activation energy. Also, DSC traces of different PS samples with different SSA are shown in Figure 6.4. At a fixed heating rate, the first exothermic peak, which is associated with a solid – solid reaction, as well as the overall exothermicity, are observed to shift to lower temperatures, indicating increased reactivity of the PS. However, assuming that the pre-exponential factor scales with the SSA, the difference in the activation energies measured at low heating rates itself cannot explain the difference in the reactive wave propagation speeds observed, and falls short by an order of magnitude. The activation energies for the reaction pathways associated with the high heating rates experienced by PS in the preheat zone during combustion could be significantly different than the low heating rates used in the DSC, and thermal analysis of PS composites in micro-differential scanning calorimeters [142] is required to emulate such high heating rates. Activation energies for other energetic materials measured using Kissinger’s analysis at low heating rates have been reported to be much lower than activation energies estimated at high heating rates [142]. However, in the absence of this data for both heavily doped and low doped P-type PS composites, the inability to account for the difference in the reactive wave propagation rates also needs to be considered to indicate coupling with a different mechanism such as convective burning.

Table 6.2. Estimated activation energies for the first exothermic reaction between PS and sodium perchlorate for PS etched from heavily doped and low doped P-type substrates.

<table>
<thead>
<tr>
<th>SSA (m²/g)</th>
<th>Average pore diameter (nm)</th>
<th>Activation energy (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>284</td>
<td>18.9</td>
<td>124.5</td>
</tr>
<tr>
<td>730</td>
<td>4.8</td>
<td>72.1</td>
</tr>
</tbody>
</table>
Figure 6.4. DSC traces of PS samples with different SSA treated with a dilute (0.4 M) NaClO$_4$ solution and heated 20 °C/min in an inert helium environment. The temperature of the first exothermic peak was found to shift to lower temperatures as the SSA increases, with most of the heat release from the PS samples with the highest SSA used in this work (730 m$^2$/g) being associated with the lowest temperature exothermic peak.

6.3.1.3 Convective burning by gas permeation within the nanoscale pores

As discussed previously, the high speed reactive wave propagations in nanothermite formulations are attributed to convective burning based on experimental evidence. While this can be thought to indicate that it is possible for gaseous combustion products to permeate through the nanoscale voids between the nanoparticles, recent studies might be inferred to indicate otherwise. Typically, the reactive wave propagation speeds are estimated by following the luminous front as it propagates through the nanothermite mixture. However,
Densmore et al. [143] recently showed that the luminous front propagation could be affected strongly by dispersion of the reactive material and does not necessarily correspond to a propagating reactive wave. One of the important conclusions of the study was that the luminous front could correspond to the dispersion of unburnt material by the gas generation from an initial small volume of reactive material, which disperses hot reaction products and still reacting material along with the unburnt material. Thus, it is not possible to correlate the luminous front with a reactive wave, or estimate a degree of conversion to correspond to the reactive wave propagation. While the lack of structural integrity of powdered nanothermite systems can possibly favor dispersion of the unburnt material versus a pressure driven permeation of gaseous products through the nanoscale matrix, the structural integrity of PS can prevent dispersion, as it can be inferred from Figure 6.3. This also means that in order for a gas flow driven reactive wave propagation, the gaseous products need to actually permeate ahead of the reaction front through the nanoscale pores. Interconnectivity within the porous layers is by very small pores with diameter ~ 2 nm [144], which makes effective gas permeation difficult, and the hot gaseous products can be expected to permeate only short distances.

As in the previous section, the low doped P-type PS composites can be compared with the heavily doped P-type PS composites to understand the factors leading to the three-order-of-magnitude difference in the reactive wave propagation speeds. While increasing SSA was found to reduce the activation energies and shift the exothermic reactions to lower temperatures, higher SSA also means increased amount of hydrogen is present within the pores in the form of surface hydrides. A threefold increase in the SSA from the heavily doped P-type PS to the low doped P-type PS also means a threefold increase in the gas production within the pores. The increased gas production and pressure generated within the pores can result in improved permeation through the pores in the pressure driven flow, which in conjunction with the change in activation energies could explain the difference in the reactive wave propagation speeds between the heavily doped and the low doped P-type PS samples.
6.3.2 Other mechanisms leading to high speed reactive wave propagations

In addition to the classical conductive and convective reactive wave propagation mechanisms described in the previous section, the unique physical properties of PS can result in mechanisms not possible in other reactive systems. Despite its nanoscale structure, porous silicon retains its crystallinity, and remains as single crystal silicon with missing silicon atoms [64,145]. Thus, cracks along crystallographic directions can be easily initiated in the PS sample, and can propagate at very high speeds [146]. The oxidation of silicon atoms in the nanoporous structure results in a volume expansion, which can initiate cracks. Also, the enhanced gas production in low doped P-type PS due to higher SSA can increase the stresses experienced by the PS, which can also result in initiation and growth of cracks. The cracks can generate free radicals which act as localized ignition fronts. Furthermore, the openings created by the cracks can also act as conduits for the permeation of the hot gaseous products, which offer significantly lesser flow resistance and higher permittivity than the nanoscale pores within the porous layers, contributing to the high speed reactive wave propagation speeds observed.

6.4 Conclusions

The mechanisms responsible for the high speed reactive wave propagations observed in low doped P-type PS composites are examined in this chapter. Experimental speed of sound measurements using ultrasonic microechography on the PS samples used in this study confirm that the reactive wave propagation is subsonic, and the observed high speeds are not due to detonation phenomenon. Thermal analysis of the PS impregnated with NaClO⁴ shows that the heat release from the exothermic solid - solid reactions shifts to lower temperatures as the SSA increases. The activation energy measured at heating rates between 10 to 40 °C/min for the first exothermic peak corresponding to the solid - solid reaction was also lower for the low doped P-type PS compared to the high doped P-type PS. However, following Semenov’s analysis for purely conductive reactive wave propagation, the difference
in the activation energy is insufficient to explain the three-order-of-magnitude difference in
the reactive wave propagation speeds observed. Thus, a combination of conductive and
convective burning, which could be assisted with material specific phenomena such as crack
propagation is believed to be the mechanism responsible for the observed high speed reactive
wave propagations.
Chapter 7

Conclusions and future work

7.1 Summary of research and conclusions

This dissertation presents a quantitative and mechanistic investigation of reactive wave propagations in PS based energetic composites, which are potential candidates for integration onto MEMS platforms as on-board energetic materials. Porous layers were etched on silicon substrates with different substrate doping properties, and the etched PS was characterized using SEM imaging, gravimetric porosity measurements, gas adsorption measurements, and thermal analysis techniques (simultaneous TGA/DSC). Energetic composites were prepared by depositing oxidizers (sodium perchlorate, magnesium perchlorate, calcium perchlorate, or sulfur) within the pores. The behavior of the energetic composites was characterized by simultaneous high speed imaging multiwavelength pyrometry to measure the reactive wave propagation speeds and the corresponding reaction zone temperatures, DSC to examine the interaction between PS and the oxidizer at the interface, and high speed focused shadowgraphy to study the interaction between the condensed phase reactive material and compressible flow phenomenon in the gaseous medium above.
7.1.1 Effect of composite equivalence ratio and inhomogeneity of the system

Thick uniform porous layers were etched on heavily doped P-type substrates, on which the effect of the composition equivalence ratio on the reactive wave propagation was studied. The amount of oxidizer deposited within the pores was varied by changing the concentration of the oxidizer solutions used to deposit the oxidizer within the pores. Combustion experiments revealed that neither the reactive wave propagation speeds or the spectroscopically determined temperatures showed a dependence on the composite equivalence ratio, and revealed that PS composites have wide flammability limits. While lean composites cannot be realized due to the limitations on the oxidizer deposition within the pores (due to the low solubility of the oxidizers in organic solvents), the fuel rich flammability was found to be between composite equivalence ratios of 33 and 56. Thermochemical equilibrium calculations also revealed similar equivalence ratio independent temperature behavior for a wide range of fuel rich compositions, due to phase changes and chemical equilibrium conditions. However, the behavior of less fuel rich composites prepared by depositing calcium perchlorate within the pores differs significantly from the behavior expected based on the thermochemical equilibrium calculations. While the thermochemical equilibrium calculations predict temperatures approximately 1000 K higher for the PS - calcium perchlorate composites (\(\varphi_{\text{min}} = 1.76\)), experiments revealed that the reaction zone temperature, and the reactive wave propagation speed reduced despite the the composite equivalence ratio approaching closer to unity. To explain this behavior, a reaction model incorporating thermochemical equilibrium calculations and diffusion considerations was developed. This phenomenological reaction model showed that despite pore diameters on the order of a few nanometers, the inhomogeneity of PS-oxidizer composites is important. Further, one of the significant problems associated with PS composites, the deposition of oxidizer within the pores, was shown to be less important than the specific surface area and microstructure of PS in terms of the reactive wave propagation.
7.1.2 Effect of substrate properties on PS composites

The influence of substrate doping properties was studied by preparing energetic composites from porous layers etched on four different silicon substrates encompassing the four extremes dopant configurations: heavily doped P and N-type, and low doped P and N-type. The heavily doped substrates yielded porous layers without any microscale features, and the reactive wave propagation speeds observed on the heavily doped PS composites were always low, on the order of 1 m/s. Between the two heavily doped PS samples, the reactive wave propagation speeds on the N-doped substrates were higher than the P-doped substrates, which is due to the differences in the reactivity of the silicon surfaces arising from the differences in the microstructures. The reactive wave propagations on the low doped N-type substrates were on the order of 100 m/s despite lower SSA than the heavily doped substrates. The low doped P-type substrates yield PS with the highest SSA, which also exhibited the highest reactive wave propagation speeds, on the order of 1000 m/s.

DSC studies of the PS - perchlorate composites reveal that the first low temperature exothermic reaction between PS and the oxidizer occurs at temperatures well below the temperature the oxidizers start to decompose, indicating that this is a solid-solid reaction. This low temperature exothermic reaction occurs in both P and N-type PS composites, indicating that this reaction is not a consequence of the electron deficient P-type material facilitating the decomposition of the perchlorate ion at low temperatures by accepting an electron, as hypothesized before. Further, annealing the PS samples to temperatures above 700 °C before treating them with the oxidizer eliminates the low temperature exothermic reaction. Thus, it can be concluded that the low temperature exothermic reaction is a consequence of the reactive sites arising from the defects in the PS.

While no difference was observed in DSC analysis between P and N-type PS samples with perchlorate salts, heavily doped N-type PS samples were found to react differently with sulfur compared to the other PS samples. Only the heavily doped N-type PS exhibited a low temperature exothermic reaction with sulfur close to the melting temperature of sulfur, while the other PS samples did not. While this appears to be consistent with the previous
literature on the effect of dopant atoms on solid-solid redox reactions, the low temperature exothermic reaction between sulfur and heavily doped N-type PS is no longer observed upon annealing the PS samples in an inert environment, which indicates that this reaction is also a consequence of the microstructure of heavily doped N-type PS and not the change in electron density.

7.1.3 Control of the reactive wave propagation through microfabrication techniques

SEM examination of the porous layers etched on low doped N-type substrates revealed the presence of random micro-crack patterns which develop during the electrochemical etch process. The low doped N-type PS samples have lower SSA than the heavily doped PS samples, but exhibit reactive wave propagations two orders of magnitude faster. This was hypothesized to be a consequence of a transition to convective burning due to permeation of hot gaseous products through the voids formed by the micro-crack patterns. This hypothesis was verified by using microfabrication techniques to create controlled microscale features on heavily doped P-type silicon substrates, which resulted in an enhancement in the reactive wave propagation speeds by up to two orders of magnitude. High speed shadowgraph analysis of the reactive wave propagation in the heavily doped P-type PS samples with microscale patterns (pillars) showed that the luminous front was decoupled from the shock generated upon the transition, and revealed permeation of gaseous combustion products ahead of the luminous front. This indicates that the enhancement in the reactive wave propagation speeds is by a transition to convective burning, as hypothesized. Studying the reactive wave propagation in PS samples with different microscale structures (pillars and microchannels) revealed that the permeability of the microscale features has the strongest effect on the enhancement in the reactive wave propagation speeds.
7.1.4 High speed reactive wave propagation in low doped P-type PS composites

While the low doped P-type PS composites are known to yield the highest reactive wave propagation speeds, these composites were studied to understand the mechanism by which the reactive wave propagation at speeds on the order of 1000 m/s in PS composites. PS etched from low doped P-type substrates exhibited the highest reactive wave propagation speeds (~1000 m/s) and were capable of driving strong shock waves in the gaseous medium above the PS. Speed of sound measurements in the PS samples using acoustic microechography revealed that the high speed reactive wave propagations are not detonations in the condensed phase. Also, repeating the experiments in air at different pressures and helium revealed that the high speed reactive wave propagations are not a consequence of the compressible flow phenomenon above the PS surface. Thus, the possible mechanisms for the high speed reactive wave propagations are PS specific mechanisms such as formation of free radicals associated with high speed crack propagations in crystalline PS, or a combination of fast conductive burning coupled with gas permeation within the nanoscale pores.

The importance of conductive burning was further explored by comparing heavily doped P-type PS with low doped P-type PS, using activation energies estimated using Kissinger’s method. It was found that the activation energies, and the temperature at which the low temperature exothermic peak occurs are reduced as the SSA of PS increases, which indicates an enhancement in the reactivity of PS at higher SSAs. However, the reduced activation energies are still insufficient to account for the three-order-of-magnitude difference in the reactive wave propagation speeds assuming a purely conductive reactive wave propagation. It must be noted that the heating rates used in this work are between 10 and 40 °C/min, which are several orders of magnitude lower than the heating rates experienced during the reactive wave propagation itself. As the activation energies are known to depend on heating rates, thermal analysis at high heating rates is required to further establish the prominence of the conductive component of the high speed reactive wave propagations observed in low doped P-type PS.
7.2 Recommendations for future work

7.2.1 Further analysis of low doped P-type PS composites

As discussed previously, the high speed reactive wave propagations in low doped P-type PS composites are not a consequence of detonations or compressible flow phenomena above the PS surface. While convective burning by effective permeation of gaseous products through the small interconnection pores with diameters ~ 2 nm is unlikely, the extent of gas permeation at such length scales needs to be examined further using computational techniques (such as MD simulations). As described in section 6.3.1.1, it is possible for conductive heat transfer to sustain a high speed reactive wave propagation in PS, unlike other reactive systems. The first step towards testing the possibility of this hypothesis would be conducting thermal analysis in micro-differential scanning calorimeters, to enable estimation of the kinetic parameters at heating rates comparable to those experienced during the reactive wave propagations. Both the heavily doped and low doped PS composites have to be analyzed at high heating rates to verify whether the difference in the activation energies can account for the difference in propagation speeds using a purely conductive model such as Semenov’s analysis.

The other mechanism discussed for the high speed reactive wave propagations is crack propagations leading to the formation of free radicals which act as localized ignition fronts, which can be further studied by combining high speed imaging with X-ray imaging. This would permit looking beyond the luminous reactive wave front to check for crack patterns. Potentially, PS samples etched on low doped P-type polycrystalline silicon samples could also be used to study the possibility of crack propagation resulting in high speed reactive wave propagations. However, this also requires modeling crack propagations across grain boundaries in polycrystalline silicon.

In terms of practical research problems focused at tuning PS composite performance for on-chip applications, exploring methods to push the reactive wave speeds to steady burn rates above 4 km/s and also to achieve low speed – long duration “simmering” burn profiles
are other interesting research avenues. While Piekiel et al. [134] obtained reactive wave speeds up to 3600 m/s in low doped P-type PS by etching microchannels on the silicon substrates, the mechanism for the enhancement in low doped P-type PS appears to be incorrectly identified in the publication, and consequently, the microscale patterns are not optimized for high speeds. Identifying the mechanisms responsible for the enhancement in the reactive wave propagation speeds in low doped P-type PS can help optimize the microscale patterns to attain faster reactive wave propagations. While the work presented in Chapter 6 shows that the reactive wave propagation is not driven by the shock above the PS surface, another possible strategy to achieve high speeds is to couple the gas phase shock wave with the condensed phase PS to achieve shock-assisted burning regimes. In the current work, PS samples have been tested without any confinement. However, by conducting the same experiments with appropriate confinements, it may be possible to approach a 1-D system similar to a piston - cylinder configuration, resulting in a stronger shock above the PS surface compared to an unconfined system. The pressurizing gases can be changed to provide stronger jump conditions across the shock. If the gaseous medium above the PS samples is changed to a high molecular weight gas with a significantly lower speed of sound, such as xenon or sulfur hexafluoride, the Mach number of the shock coupled with the reactive wave front is higher for the same shock speed. As the pressure and temperature spikes across the shock wave increase in this case, it is interesting to examine if shock assisted reactive wave propagations can be realized, which could result in higher reactive wave propagation speeds. Such systems can be used to create PS based microinitiators, which could potentially be batch fabricated to reduce costs and reliability.

One of the main issues with the PS composites discussed in this dissertation is that even the slow reactive wave front propagations are too violent, presenting significant challenges in terms of building energy harvesters to exploit the energy released. Long burn times for PS composites, on the other hand, can be realized by creating microchannels of reactive PS on heavily doped P-type silicon substrates. This can be treated as a heat transfer problem to calculate the minimum permissible width and pitch of the microchannels to
keep the reactive wave propagation beyond the quenching limit and achieve the maximum burn time for a given area. Some aspects of this approach to extend the energy release times were explored by creating microscale channels of PS on silicon substrates. This was accomplished by using photolithography to pattern microchannels on silicon wafers with silicon nitride protective layer. The silicon nitride is then etched away exposing bare silicon, and electrochemically etching the silicon wafers for short duration creates microchannels of PS as shown in Figure 7.1. Patterns with reducing channel spacing were used to investigate the minimum separation between adjacent channels. No cross-talk was observed for the smallest separation (300 µm) tested, while the reactive wave propagation was sustained for 120 ms compared to 10 ms on an unpatterned silicon substrate. Other strategies to slow down the reactive wave propagation speeds include depositing materials within the pores to act as a diffusion barrier and/or heat sinks to limit the temperature. Both ideas proposed can be further improved upon by combining them flash ignition [147] as a means to achieve distributed ignition or as a non-intrusive and safe ignition mechanism, and can be used towards designing and fabricating microscale devices powered and/or actuated by controlled energy release from integrated reactive PS composites.
Figure 7.1. PS microchannels etched on silicon wafers masked with silicon nitride. The dark regions are PS while the reflective regions are silicon nitride. The width of the PS microchannels was approximately 200 μm, and the smallest separation between the microchannels was approximately 300 μm, as seen in the inset (post combustion image). No cross-talk between the PS microchannels was observed at this separation, and the reactive wave front propagated for 120 ms.
Appendix A

Electrochemical etch and photolithography recipes

A.1 Details of the electrochemical etch process

The reactive wave propagation speeds in PS composites were measured using samples with PS layer on top of the silicon substrate. Based on the literature survey presented in section 3.1, PS composites can be expected to be always fuel rich. Thus, prior to the combustion analysis presented in Chapter 3, electrochemical etch recipes were developed to etch porous layers on heavily doped silicon substrates with the highest possible porosity without causing the porous layers to delaminate. The recipes developed for the various silicon substrates are included below to facilitate the reproduction of the samples used in this work.

1. Heavily doped substrates with resistivity ~ 0.001 Ω-cm

- Current density: 40 mA/cm²
- Electrolyte composition: 50% (by vol.) aqueous 48% hydrofluoric acid and 50% (by vol.) anhydrous ethyl alcohol
- Backside electrical contact with the silicon wafer was established using an aluminum foil
Etch process:

(a) The electrochemical etch is carried out for three 15 minute intervals. The electrolyte was stirred every 5 minutes. The duration of the relaxation step is chosen such that the evolution of hydrogen bubbles from the PS surface slows down significantly/stops. Gaps of 5 minutes were found to be sufficient.

(b) The three 15 minute etch steps are followed by three 5 minute etch steps, with gaps of 15 minutes. Additional relaxation steps and shorter etch steps after 45 minutes have been found to prevent delamination of the porous layers.

(c) After the completion of the one hour etch process, the electrolyte needs to be drained from the etch cell, and the wafer needs to be dried. When the electrolyte is removed, care should be taken to avoid drying the PS immediately. Typically, a thin layer of electrolyte was left above the PS surface which was then diluted with ethanol, and then drained. This process is repeated two times to ensure that the HF concentration in the electrolyte drops, and then the samples are left under the methanol layer for 10 minutes. The samples are then dried under a gentle stream of nitrogen.

2. Low doped N-type substrates

- Electrolyte composition: 50% (by vol.) aqueous 48% hydrofluoric acid and 50% (by vol.) anhydrous ethyl alcohol
- Illumination was provided by a 10 W LED lamp
- Backside electrical contact with the silicon wafer was established using an aluminum foil
- The maximum current density obtained is a function of the intensity of the illumination. The current density used to etch the samples used in this work was 20 mA/cm²
• The silicon substrates were etched continuously without any gaps during the etch process

3. Low doped P-type substrates

• Forming an ohmic contact with the silicon wafer requires deposition of a thin layer of platinum on the backside followed by an anneal to form platinum silicide. 150 nm thick platinum layers were deposited on the backside of the silicon wafer by evaporation, which was followed by a RTA at 350 °C for 2 minutes in a nitrogen/argon environment. The native oxide on the silicon wafers was removed using a 10:1 BOE solution just before the evaporation.

• Electrolyte composition: 50% (by vol.) aqueous 48% hydrofluoric acid and 50% (by vol.) anhydrous ethyl alcohol

• Current density: 20 mA/cm²

• The electrochemical etch duration was 30 minutes, and no gaps were used in this process

• After the removal of the electrolyte solution and rinsing with ethanol, the etched wafers were also rinsed with n-Pentane before being dried under nitrogen. The low surface tension of n-Pentane prevents the porous layers from cracking and delamination during the drying step.

A.2 Recipes for Photolithographic patterning

1. Megaposit SPR 220-7.0 positive photoresist

   (a) Clean silicon wafers with acetone/IPA and rinse with DI water.

   (b) Bake the wafers for 10 minutes at 120 °C (dehydration bake), and let the wafers col for at least 1 minute.

   (c) Spin hexamethyldisilazane (HMDS) (speed: 500 rpm, ramp: 100 rpm/s, duration: 10 s, followed by speed: 4000 rpm, ramp: 500 rpm/s, duration: 10 s).
(d) Heat the wafer at 120 °C for 1 minute, and let the wafer cool down.

(e) Due to the high viscosity of SPR 220-7.0, it is optimal to use 3/4 droppers and cover about half of the surface of the wafer with closely wound spiral patterns. This improves the uniformity of the photoresist covering. Spin parameters: speed: 500 rpm, ramp: 100 rpm/s, duration: 10 s, followed by speed: 1500 rpm, ramp: 500 rpm/s, duration: 30 s.

(f) Heat the wafer at 120 °C for 3.5 minutes.

(g) After the wafer cools down, the photolithographic patterning is performed. It was found to be optimal to split the total dose of UV radiation into four steps. The exposure and relaxation times were maintained the same (9 s exposure followed by 9 s gap, repeated 4 times).

(h) After the exposure, the wafer needs to be stored in the dark for 1 hour.

(i) Heat the wafer at 120 °C for 3.5 minutes.

(j) Develop using Microposit MF-CD-26 solution. The typical development time is around 2.5 minutes.

2. **Megaposit SPR-955 positive photoresist**

(a) Clean silicon wafers with acetone/IPA and rinse with DI water.

(b) Bake the wafers for 10 minutes at 120 °C (dehydration bake), and let the wafers cool for at least 1 minute.

(c) Spin hexamethyldisilazane (HMDS) (speed: 500 rpm, ramp: 100 rpm/s, duration: 10 s, followed by speed: 4000 rpm, ramp: 500 rpm/s, duration: 10 s).

(d) Heat the wafer at 105 °C for 1 minute, and let the wafer cool down.

(e) The photoresist is dispensed onto the wafer using a dynamic process: speed: 900 rpm, ramp: 1000 rpm/s, duration: 10 s (the photoresist needs to be dispensed at the center of the rotating wafer during the 10 s window), followed by: speed:
100 rpm, ramp: 10000 rpm/s, speed: 2000 rpm, ramp: 10000 rpm/s, duration: 45 s.

(f) Heat the wafer 105 °C for 1 minute, and let the wafer cool down.

(g) Exposure: 15 s total (5 s exposure with a 15 s gap, repeated thrice).

(h) Develop using Microposit MF-CD-26 solution. The typical development time is around 1.5 minutes.

(i) Before performing the DRIE process, the photoresist layer is hard baked at 105 °C for 5 minutes to improve the etch resistance of the photoresist film.
Appendix B

Supplementary data

B.1 Gravimetric porosity measurements for heavily doped P-type PS samples

Table B.1. Gravimetric porosity calculations for PS etched on heavily doped P-type substrates with resistivity between 0.001 – 0.005 Ω-cm.

<table>
<thead>
<tr>
<th>Mass of wafer before etching (mg)</th>
<th>Mass of wafer after etching (mg)</th>
<th>Mass of test sample before dissolution (mg)</th>
<th>Mass of test sample after dissolution (mg)</th>
<th>Change in mass (mg)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9719.4</td>
<td>8910.4</td>
<td>585.8</td>
<td>545.2</td>
<td>40.6</td>
<td>71.06</td>
</tr>
<tr>
<td>9583.4</td>
<td>8282.4</td>
<td>978.7</td>
<td>910.6</td>
<td>68.1</td>
<td>74.41</td>
</tr>
<tr>
<td>9707.0</td>
<td>8402.2</td>
<td>480.8</td>
<td>456.1</td>
<td>24.7</td>
<td>75.06</td>
</tr>
<tr>
<td>9570.4</td>
<td>8269.4</td>
<td>357.1</td>
<td>333.9</td>
<td>23.2</td>
<td>72.82</td>
</tr>
</tbody>
</table>

*The samples cut from these wafers were soaked in a saturated solution of magnesium perchlorate in methanol which are described in Table 3.1.

B.1.1 A note on the oxidizer deposition within the pores

The measured equivalence ratios were found to be slightly fuel leaner than the estimated minimum possible equivalence ratios. This may be attributed to the highly hygroscopic
nature of the oxidizer, as any water absorption by the salt deposited within the nanoscale pores increases the measured weight change, erroneously indicating a higher than actual oxidizer deposition. While the samples and oxidizer solutions were stored in a humidity free chamber, the samples had to be cleaned and weighed in ambient conditions, which exposed the samples to ambient conditions (relative humidity $\approx 20\%$ at $21^\circ C$) for a short duration ($\approx 5$ minutes). Also, any small amount of the oxidizer present on the surface of the porous layers, which cannot be removed due to the possibility of unintentional ignition due to friction, can skew the equivalence ratio measurements. This surface residue does not contribute to the oxidation unlike the oxidizer deposited in the pores, which is intimately mixed with the fuel at the nanometer scale. However, most samples could be cleaned to remove most of the surface residue, and measuring the weight of the surface residue on non porous silicon substrates indicated that the weight of the residue is negligibly small. Another likely reason for the observed discrepancy in the measured oxidizer deposition is the elevation of boiling point, which is a colligative property [100]. Heating the saturated methanol – Mg(ClO$_4$)$_2$ solutions showed that the salt dissolution significantly increases the boiling point of the concentrated solutions resulting in the formation of a thick paste instead of crystalline salt at temperatures far exceeding the boiling point of pure methanol. Any methanol left within the pores also can erroneously indicate a higher than actual deposition of oxidizer. The three factors mentioned above skew the estimated equivalence ratios towards leaner values. Some samples, whose oxidizer deposition and reaction zone temperature were not measured, were treated such that they were not exposed to ambient conditions. These samples were dried in the test chamber under vacuum, and exhibited similar reactive wave propagation speeds as the data described in Table 3.1.

These measurements indicate that the pores can be efficiently filled by the oxidizer solution, since the hydrogen terminated oraganophilic pore walls can be expected to draw in the oxidizer solution into the pores. Due to the low solubility of the oxidizer solutions in organic solvents (with the solubility in methanol being the highest), it is not possible to prepare a stoichiometric composite at porosities which yield stable porous layers. Further,
using saturated solutions results in methanol being left behind in the pores even after heating the samples. This methanol does not participate in the oxidation of silicon, and can act as a diluent, affecting the performance of the composite.

B.2 Gravimetric estimation of the oxidizer deposition within the pores

Table B.2. Sample data for magnesium perchlorate deposition and equivalence ratio estimations described in section 3.2.1. The data presented in the following table are for sample #3 from the above table, with a calculated porosity of 75.06 %. Oxidizer solutions in methanol of varying concentrations are used to deposit the oxidizer within the pores.

<table>
<thead>
<tr>
<th>Initial mass of the sample (mg)</th>
<th>Final mass of the sample (mg)</th>
<th>Calculated equivalence ratio ((\varphi))</th>
<th>Theoretical minimum equivalence ratio ((\varphi_{min}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidizer solution concentration: 0.51 M</td>
<td>413.5</td>
<td>419.0</td>
<td>3.86</td>
</tr>
<tr>
<td>371.6</td>
<td>375.3</td>
<td>5.16</td>
<td>13.5</td>
</tr>
<tr>
<td>Solution concentration: 1.02 M</td>
<td>406.0</td>
<td>412.1</td>
<td>3.42</td>
</tr>
<tr>
<td>351.7</td>
<td>358.7</td>
<td>2.58</td>
<td>6.73</td>
</tr>
<tr>
<td>414.7</td>
<td>423.7</td>
<td>2.37</td>
<td>6.73</td>
</tr>
<tr>
<td>Saturated oxidizer solution</td>
<td>505.8</td>
<td>527.5</td>
<td>1.20</td>
</tr>
<tr>
<td>518.3</td>
<td>539.8</td>
<td>1.24</td>
<td>3.3</td>
</tr>
<tr>
<td>377.8</td>
<td>393.4</td>
<td>1.24</td>
<td>3.3</td>
</tr>
</tbody>
</table>

B.3 Heat of formation values used for thermochemical equilibrium calculations

The heat for formation values used for the thermochemical equilibrium calculations and the source for the data are shown in Table B.3.
Table B.3. Heat of formation data used for thermochemical equilibrium calculations (from [99])

<table>
<thead>
<tr>
<th>Oxidizer</th>
<th>Heat of formation (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium perchlorate</td>
<td>-385.7</td>
</tr>
<tr>
<td>Magnesium perchlorate</td>
<td>-588.3</td>
</tr>
<tr>
<td>Calcium Perchlorate</td>
<td>-744.8</td>
</tr>
</tbody>
</table>

B.4 Heat flow from the reaction zone calculated from thermochemical equilibrium calculations

The raw data used to perform the iterative calculations for the phenomenological model described in section 3.5 is included in Table B.4 below.

Table B.4: Heat flow from the reaction zone from thermochemical equilibrium calculations

<table>
<thead>
<tr>
<th>P (atm)</th>
<th>V (cc/g)</th>
<th>T_f (K)</th>
<th>Si - Ca(ClO_4)_2</th>
<th>Si - Mg(ClO_4)_2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>-Q_{R,T_f} (cal/g)</td>
<td>-Q_{R,T_f} (kJ/kg)</td>
</tr>
<tr>
<td>1</td>
<td>0.87</td>
<td>800.00</td>
<td>-2403.70</td>
<td>-31457.87</td>
</tr>
<tr>
<td>1</td>
<td>0.88</td>
<td>810.00</td>
<td>-2401.27</td>
<td>-31426.07</td>
</tr>
<tr>
<td>1</td>
<td>0.88</td>
<td>820.00</td>
<td>-2398.83</td>
<td>-31394.13</td>
</tr>
<tr>
<td>1</td>
<td>0.89</td>
<td>830.00</td>
<td>-2396.39</td>
<td>-31362.20</td>
</tr>
<tr>
<td>1</td>
<td>0.90</td>
<td>840.00</td>
<td>-2393.94</td>
<td>-31330.14</td>
</tr>
<tr>
<td>1</td>
<td>0.90</td>
<td>850.00</td>
<td>-2391.49</td>
<td>-31298.07</td>
</tr>
<tr>
<td>1</td>
<td>0.91</td>
<td>860.00</td>
<td>-2389.03</td>
<td>-31265.88</td>
</tr>
<tr>
<td>1</td>
<td>0.91</td>
<td>870.00</td>
<td>-2386.58</td>
<td>-31233.82</td>
</tr>
<tr>
<td>1</td>
<td>0.92</td>
<td>880.00</td>
<td>-2384.11</td>
<td>-31201.49</td>
</tr>
<tr>
<td>1</td>
<td>0.93</td>
<td>890.00</td>
<td>-2381.65</td>
<td>-31169.29</td>
</tr>
<tr>
<td>1</td>
<td>0.93</td>
<td>900.00</td>
<td>-2379.18</td>
<td>-31136.97</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>1</td>
<td>0.94</td>
<td>910.00</td>
<td>-2376.71</td>
<td>-31104.64</td>
</tr>
<tr>
<td>1</td>
<td>0.94</td>
<td>920.00</td>
<td>-2374.23</td>
<td>-31072.19</td>
</tr>
<tr>
<td>1</td>
<td>0.95</td>
<td>930.00</td>
<td>-2371.76</td>
<td>-31039.86</td>
</tr>
<tr>
<td>1</td>
<td>0.95</td>
<td>940.00</td>
<td>-2369.28</td>
<td>-31007.41</td>
</tr>
<tr>
<td>1</td>
<td>0.96</td>
<td>950.00</td>
<td>-2366.79</td>
<td>-30974.82</td>
</tr>
<tr>
<td>1</td>
<td>0.97</td>
<td>960.00</td>
<td>-2364.30</td>
<td>-30942.23</td>
</tr>
<tr>
<td>1</td>
<td>0.97</td>
<td>970.00</td>
<td>-2361.81</td>
<td>-30909.64</td>
</tr>
<tr>
<td>1</td>
<td>0.98</td>
<td>980.00</td>
<td>-2359.32</td>
<td>-30877.06</td>
</tr>
<tr>
<td>1</td>
<td>0.98</td>
<td>990.00</td>
<td>-2356.82</td>
<td>-30844.34</td>
</tr>
<tr>
<td>1</td>
<td>0.99</td>
<td>1000.00</td>
<td>-2354.32</td>
<td>-30811.62</td>
</tr>
<tr>
<td>1</td>
<td>1.00</td>
<td>1010.00</td>
<td>-2351.82</td>
<td>-30778.90</td>
</tr>
<tr>
<td>1</td>
<td>1.00</td>
<td>1020.00</td>
<td>-2349.31</td>
<td>-30746.05</td>
</tr>
<tr>
<td>1</td>
<td>1.01</td>
<td>1030.00</td>
<td>-2346.80</td>
<td>-30713.20</td>
</tr>
<tr>
<td>1</td>
<td>1.01</td>
<td>1040.00</td>
<td>-2344.29</td>
<td>-30680.35</td>
</tr>
<tr>
<td>1</td>
<td>1.02</td>
<td>1050.00</td>
<td>-2341.77</td>
<td>-30647.37</td>
</tr>
<tr>
<td>1</td>
<td>1.02</td>
<td>1060.00</td>
<td>-2339.25</td>
<td>-30614.39</td>
</tr>
<tr>
<td>1</td>
<td>1.03</td>
<td>1070.00</td>
<td>-2336.73</td>
<td>-30581.41</td>
</tr>
<tr>
<td>1</td>
<td>1.04</td>
<td>1080.00</td>
<td>-2315.85</td>
<td>-30308.15</td>
</tr>
<tr>
<td>1</td>
<td>1.05</td>
<td>1090.00</td>
<td>-2313.17</td>
<td>-30273.08</td>
</tr>
<tr>
<td>1</td>
<td>1.06</td>
<td>1100.00</td>
<td>-2310.55</td>
<td>-30238.79</td>
</tr>
<tr>
<td>1</td>
<td>1.06</td>
<td>1110.00</td>
<td>-2307.93</td>
<td>-30204.50</td>
</tr>
<tr>
<td>1</td>
<td>1.07</td>
<td>1120.00</td>
<td>-2305.31</td>
<td>-30170.21</td>
</tr>
<tr>
<td>1</td>
<td>1.07</td>
<td>1130.00</td>
<td>-2302.68</td>
<td>-30135.79</td>
</tr>
<tr>
<td>1</td>
<td>1.08</td>
<td>1140.00</td>
<td>-2300.05</td>
<td>-30101.37</td>
</tr>
<tr>
<td>1</td>
<td>1.08</td>
<td>1150.00</td>
<td>-2297.42</td>
<td>-30066.95</td>
</tr>
<tr>
<td>1</td>
<td>1.09</td>
<td>1160.00</td>
<td>-2294.79</td>
<td>-30032.53</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.10</td>
<td>1170.00</td>
<td>-2292.16</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>------</td>
<td>---------</td>
<td>----------</td>
</tr>
<tr>
<td>1</td>
<td>1.10</td>
<td>1180.00</td>
<td>-2289.52</td>
<td>-29963.56</td>
</tr>
<tr>
<td>1</td>
<td>1.11</td>
<td>1190.00</td>
<td>-2286.88</td>
<td>-29929.01</td>
</tr>
<tr>
<td>1</td>
<td>1.11</td>
<td>1200.00</td>
<td>-2284.23</td>
<td>-29894.33</td>
</tr>
<tr>
<td>1</td>
<td>1.12</td>
<td>1210.00</td>
<td>-2281.59</td>
<td>-29859.78</td>
</tr>
<tr>
<td>1</td>
<td>1.13</td>
<td>1220.00</td>
<td>-2278.94</td>
<td>-29825.10</td>
</tr>
<tr>
<td>1</td>
<td>1.13</td>
<td>1230.00</td>
<td>-2276.29</td>
<td>-29790.42</td>
</tr>
<tr>
<td>1</td>
<td>1.14</td>
<td>1240.00</td>
<td>-2273.64</td>
<td>-29755.74</td>
</tr>
<tr>
<td>1</td>
<td>1.14</td>
<td>1250.00</td>
<td>-2270.99</td>
<td>-29721.06</td>
</tr>
<tr>
<td>1</td>
<td>1.15</td>
<td>1260.00</td>
<td>-2268.33</td>
<td>-29686.25</td>
</tr>
<tr>
<td>1</td>
<td>1.15</td>
<td>1270.00</td>
<td>-2265.67</td>
<td>-29651.43</td>
</tr>
<tr>
<td>1</td>
<td>1.16</td>
<td>1280.00</td>
<td>-2263.01</td>
<td>-29616.62</td>
</tr>
<tr>
<td>1</td>
<td>1.17</td>
<td>1290.00</td>
<td>-2260.34</td>
<td>-29581.68</td>
</tr>
<tr>
<td>1</td>
<td>1.17</td>
<td>1300.00</td>
<td>-2257.68</td>
<td>-29546.87</td>
</tr>
<tr>
<td>1</td>
<td>1.18</td>
<td>1310.00</td>
<td>-2255.01</td>
<td>-29511.92</td>
</tr>
<tr>
<td>1</td>
<td>1.18</td>
<td>1320.00</td>
<td>-2252.34</td>
<td>-29476.98</td>
</tr>
<tr>
<td>1</td>
<td>1.19</td>
<td>1330.00</td>
<td>-2249.66</td>
<td>-29441.91</td>
</tr>
<tr>
<td>1</td>
<td>1.20</td>
<td>1340.00</td>
<td>-2246.99</td>
<td>-29406.96</td>
</tr>
<tr>
<td>1</td>
<td>1.20</td>
<td>1350.00</td>
<td>-2244.31</td>
<td>-29371.89</td>
</tr>
<tr>
<td>1</td>
<td>1.21</td>
<td>1360.00</td>
<td>-2241.63</td>
<td>-29336.82</td>
</tr>
<tr>
<td>1</td>
<td>1.21</td>
<td>1370.00</td>
<td>-2238.95</td>
<td>-29301.74</td>
</tr>
<tr>
<td>1</td>
<td>1.22</td>
<td>1380.00</td>
<td>-2236.26</td>
<td>-29266.54</td>
</tr>
<tr>
<td>1</td>
<td>1.22</td>
<td>1390.00</td>
<td>-2233.58</td>
<td>-29231.46</td>
</tr>
<tr>
<td>1</td>
<td>1.23</td>
<td>1400.00</td>
<td>-2230.89</td>
<td>-29196.26</td>
</tr>
<tr>
<td>1</td>
<td>1.24</td>
<td>1410.00</td>
<td>-2228.19</td>
<td>-29160.92</td>
</tr>
<tr>
<td>1</td>
<td>1.24</td>
<td>1420.00</td>
<td>-2225.50</td>
<td>-29125.72</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>------</td>
<td>------</td>
<td>----------</td>
<td>----------</td>
</tr>
<tr>
<td>1</td>
<td>1.25</td>
<td>1430.00</td>
<td>-2222.80</td>
<td>-29090.38</td>
</tr>
<tr>
<td>1</td>
<td>1.26</td>
<td>1440.00</td>
<td>-2218.72</td>
<td>-29036.99</td>
</tr>
<tr>
<td>1</td>
<td>1.27</td>
<td>1450.00</td>
<td>-2195.41</td>
<td>-28731.92</td>
</tr>
<tr>
<td>1</td>
<td>1.28</td>
<td>1460.00</td>
<td>-2192.54</td>
<td>-28694.36</td>
</tr>
<tr>
<td>1</td>
<td>1.28</td>
<td>1470.00</td>
<td>-2189.70</td>
<td>-28657.19</td>
</tr>
<tr>
<td>1</td>
<td>1.29</td>
<td>1480.00</td>
<td>-2186.86</td>
<td>-28620.03</td>
</tr>
<tr>
<td>1</td>
<td>1.30</td>
<td>1490.00</td>
<td>-2184.02</td>
<td>-28582.86</td>
</tr>
<tr>
<td>1</td>
<td>1.30</td>
<td>1500.00</td>
<td>-2181.17</td>
<td>-28545.56</td>
</tr>
<tr>
<td>1</td>
<td>1.31</td>
<td>1510.00</td>
<td>-2178.31</td>
<td>-28508.13</td>
</tr>
<tr>
<td>1</td>
<td>1.32</td>
<td>1520.00</td>
<td>-2175.46</td>
<td>-28470.83</td>
</tr>
<tr>
<td>1</td>
<td>1.32</td>
<td>1530.00</td>
<td>-2172.60</td>
<td>-28433.40</td>
</tr>
<tr>
<td>1</td>
<td>1.33</td>
<td>1540.00</td>
<td>-2169.73</td>
<td>-28395.84</td>
</tr>
<tr>
<td>1</td>
<td>1.33</td>
<td>1550.00</td>
<td>-2166.87</td>
<td>-28358.41</td>
</tr>
<tr>
<td>1</td>
<td>1.34</td>
<td>1560.00</td>
<td>-2164.00</td>
<td>-28320.85</td>
</tr>
<tr>
<td>1</td>
<td>1.35</td>
<td>1570.00</td>
<td>-2161.12</td>
<td>-28283.16</td>
</tr>
<tr>
<td>1</td>
<td>1.35</td>
<td>1580.00</td>
<td>-2158.25</td>
<td>-28245.60</td>
</tr>
<tr>
<td>1</td>
<td>1.36</td>
<td>1590.00</td>
<td>-2155.37</td>
<td>-28207.91</td>
</tr>
<tr>
<td>1</td>
<td>1.37</td>
<td>1600.00</td>
<td>-2152.48</td>
<td>-28170.09</td>
</tr>
<tr>
<td>1</td>
<td>1.37</td>
<td>1610.00</td>
<td>-2149.60</td>
<td>-28132.39</td>
</tr>
<tr>
<td>1</td>
<td>1.38</td>
<td>1620.00</td>
<td>-2146.71</td>
<td>-28094.57</td>
</tr>
<tr>
<td>1</td>
<td>1.39</td>
<td>1630.00</td>
<td>-2143.82</td>
<td>-28056.75</td>
</tr>
<tr>
<td>1</td>
<td>1.39</td>
<td>1640.00</td>
<td>-2140.92</td>
<td>-28018.80</td>
</tr>
<tr>
<td>1</td>
<td>1.40</td>
<td>1650.00</td>
<td>-2138.02</td>
<td>-27980.84</td>
</tr>
<tr>
<td>1</td>
<td>1.41</td>
<td>1660.00</td>
<td>-2135.12</td>
<td>-27942.89</td>
</tr>
<tr>
<td>1</td>
<td>1.42</td>
<td>1670.00</td>
<td>-2132.22</td>
<td>-27904.94</td>
</tr>
<tr>
<td>1</td>
<td>1.42</td>
<td>1680.00</td>
<td>-2129.31</td>
<td>-27866.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1</td>
<td>1.43</td>
<td>1690.00</td>
<td>-2126.40</td>
<td>-27828.77</td>
</tr>
<tr>
<td>1</td>
<td>1.44</td>
<td>1700.00</td>
<td>-2123.49</td>
<td>-27790.69</td>
</tr>
<tr>
<td>1</td>
<td>1.45</td>
<td>1710.00</td>
<td>-2120.57</td>
<td>-27752.47</td>
</tr>
<tr>
<td>1</td>
<td>1.46</td>
<td>1720.00</td>
<td>-2117.66</td>
<td>-27714.39</td>
</tr>
<tr>
<td>1</td>
<td>1.47</td>
<td>1730.00</td>
<td>-2114.74</td>
<td>-27676.17</td>
</tr>
<tr>
<td>1</td>
<td>1.48</td>
<td>1740.00</td>
<td>-2111.81</td>
<td>-27637.83</td>
</tr>
<tr>
<td>1</td>
<td>1.49</td>
<td>1750.00</td>
<td>-2108.89</td>
<td>-27599.61</td>
</tr>
<tr>
<td>1</td>
<td>1.50</td>
<td>1760.00</td>
<td>-2105.96</td>
<td>-27561.27</td>
</tr>
<tr>
<td>1</td>
<td>1.51</td>
<td>1770.00</td>
<td>-2103.03</td>
<td>-27522.92</td>
</tr>
<tr>
<td>1</td>
<td>1.52</td>
<td>1780.00</td>
<td>-2100.10</td>
<td>-27484.57</td>
</tr>
<tr>
<td>1</td>
<td>1.53</td>
<td>1790.00</td>
<td>-2097.16</td>
<td>-27446.10</td>
</tr>
<tr>
<td>1</td>
<td>1.54</td>
<td>1800.00</td>
<td>-2094.22</td>
<td>-27407.62</td>
</tr>
<tr>
<td>1</td>
<td>1.55</td>
<td>1810.00</td>
<td>-2091.28</td>
<td>-27369.14</td>
</tr>
<tr>
<td>1</td>
<td>1.57</td>
<td>1820.00</td>
<td>-2088.34</td>
<td>-27330.67</td>
</tr>
<tr>
<td>1</td>
<td>1.58</td>
<td>1830.00</td>
<td>-2085.39</td>
<td>-27292.06</td>
</tr>
<tr>
<td>1</td>
<td>1.60</td>
<td>1840.00</td>
<td>-2082.44</td>
<td>-27253.45</td>
</tr>
<tr>
<td>1</td>
<td>1.61</td>
<td>1850.00</td>
<td>-2079.49</td>
<td>-27214.85</td>
</tr>
<tr>
<td>1</td>
<td>1.63</td>
<td>1860.00</td>
<td>-2076.54</td>
<td>-27176.24</td>
</tr>
<tr>
<td>1</td>
<td>1.65</td>
<td>1870.00</td>
<td>-2073.58</td>
<td>-27137.50</td>
</tr>
<tr>
<td>1</td>
<td>1.67</td>
<td>1880.00</td>
<td>-2070.62</td>
<td>-27098.76</td>
</tr>
<tr>
<td>1</td>
<td>1.69</td>
<td>1890.00</td>
<td>-2067.66</td>
<td>-27060.02</td>
</tr>
<tr>
<td>1</td>
<td>1.72</td>
<td>1900.00</td>
<td>-2064.70</td>
<td>-27021.28</td>
</tr>
<tr>
<td>1</td>
<td>1.74</td>
<td>1910.00</td>
<td>-2061.73</td>
<td>-26982.42</td>
</tr>
<tr>
<td>1</td>
<td>1.77</td>
<td>1920.00</td>
<td>-2058.76</td>
<td>-26943.55</td>
</tr>
<tr>
<td>1</td>
<td>1.80</td>
<td>1930.00</td>
<td>-2055.79</td>
<td>-26904.68</td>
</tr>
<tr>
<td>1</td>
<td>1.83</td>
<td>1940.00</td>
<td>-2052.82</td>
<td>-26865.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1</td>
<td>1.87</td>
<td>1950.00</td>
<td>-2049.84</td>
<td>-26826.81</td>
</tr>
<tr>
<td>1</td>
<td>1.91</td>
<td>1960.00</td>
<td>-2046.86</td>
<td>-26787.81</td>
</tr>
<tr>
<td>1</td>
<td>1.95</td>
<td>1970.00</td>
<td>-2043.87</td>
<td>-26748.68</td>
</tr>
<tr>
<td>1</td>
<td>2.00</td>
<td>1980.00</td>
<td>-2040.89</td>
<td>-26709.68</td>
</tr>
<tr>
<td>1</td>
<td>2.05</td>
<td>1990.00</td>
<td>-2037.90</td>
<td>-26670.55</td>
</tr>
<tr>
<td>1</td>
<td>2.11</td>
<td>2000.00</td>
<td>-2034.90</td>
<td>-26631.28</td>
</tr>
<tr>
<td>1</td>
<td>2.18</td>
<td>2010.00</td>
<td>-2031.91</td>
<td>-26592.15</td>
</tr>
<tr>
<td>1</td>
<td>2.25</td>
<td>2020.00</td>
<td>-2028.90</td>
<td>-26552.76</td>
</tr>
<tr>
<td>1</td>
<td>2.34</td>
<td>2030.00</td>
<td>-2025.89</td>
<td>-26513.37</td>
</tr>
<tr>
<td>1</td>
<td>2.44</td>
<td>2040.00</td>
<td>-2022.88</td>
<td>-26473.98</td>
</tr>
<tr>
<td>1</td>
<td>2.56</td>
<td>2050.00</td>
<td>-2019.86</td>
<td>-26434.45</td>
</tr>
<tr>
<td>1</td>
<td>2.70</td>
<td>2060.00</td>
<td>-2016.83</td>
<td>-26394.80</td>
</tr>
<tr>
<td>1</td>
<td>2.86</td>
<td>2070.00</td>
<td>-2013.79</td>
<td>-26355.01</td>
</tr>
<tr>
<td>1</td>
<td>3.06</td>
<td>2080.00</td>
<td>-2010.74</td>
<td>-26315.10</td>
</tr>
<tr>
<td>1</td>
<td>3.30</td>
<td>2090.00</td>
<td>-2007.68</td>
<td>-26275.05</td>
</tr>
<tr>
<td>1</td>
<td>3.61</td>
<td>2100.00</td>
<td>-2004.59</td>
<td>-26234.61</td>
</tr>
<tr>
<td>1</td>
<td>4.01</td>
<td>2110.00</td>
<td>-2001.47</td>
<td>-26193.78</td>
</tr>
<tr>
<td>1</td>
<td>4.56</td>
<td>2120.00</td>
<td>-1998.30</td>
<td>-26152.29</td>
</tr>
<tr>
<td>1</td>
<td>5.33</td>
<td>2130.00</td>
<td>-1995.06</td>
<td>-26109.89</td>
</tr>
<tr>
<td>1</td>
<td>6.53</td>
<td>2140.00</td>
<td>-1991.68</td>
<td>-26065.65</td>
</tr>
<tr>
<td>1</td>
<td>8.60</td>
<td>2150.00</td>
<td>-1988.02</td>
<td>-26017.75</td>
</tr>
<tr>
<td>1</td>
<td>13.09</td>
<td>2160.00</td>
<td>-1983.60</td>
<td>-25959.91</td>
</tr>
<tr>
<td>1</td>
<td>29.98</td>
<td>2170.00</td>
<td>-1975.23</td>
<td>-25850.37</td>
</tr>
<tr>
<td>1</td>
<td>512.65</td>
<td>2180.00</td>
<td>-1819.07</td>
<td>-23806.66</td>
</tr>
<tr>
<td>1</td>
<td>515.10</td>
<td>2190.00</td>
<td>-1816.28</td>
<td>-23770.15</td>
</tr>
<tr>
<td>1</td>
<td>517.55</td>
<td>2200.00</td>
<td>-1813.49</td>
<td>-23733.63</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1</td>
<td>520.01</td>
<td>2210.00</td>
<td>-1810.69</td>
<td>-23696.99</td>
</tr>
<tr>
<td>1</td>
<td>522.49</td>
<td>2220.00</td>
<td>-1807.89</td>
<td>-23660.34</td>
</tr>
<tr>
<td>1</td>
<td>524.96</td>
<td>2230.00</td>
<td>-1805.08</td>
<td>-23623.57</td>
</tr>
<tr>
<td>1</td>
<td>527.45</td>
<td>2240.00</td>
<td>-1802.26</td>
<td>-23586.66</td>
</tr>
<tr>
<td>1</td>
<td>529.95</td>
<td>2250.00</td>
<td>-1799.44</td>
<td>-23549.76</td>
</tr>
<tr>
<td>1</td>
<td>532.46</td>
<td>2260.00</td>
<td>-1796.61</td>
<td>-23512.72</td>
</tr>
<tr>
<td>1</td>
<td>534.98</td>
<td>2270.00</td>
<td>-1793.77</td>
<td>-23475.55</td>
</tr>
<tr>
<td>1</td>
<td>537.52</td>
<td>2280.00</td>
<td>-1790.93</td>
<td>-23438.38</td>
</tr>
<tr>
<td>1</td>
<td>540.06</td>
<td>2290.00</td>
<td>-1788.08</td>
<td>-23401.08</td>
</tr>
<tr>
<td>1</td>
<td>542.62</td>
<td>2300.00</td>
<td>-1785.22</td>
<td>-23363.65</td>
</tr>
<tr>
<td>1</td>
<td>545.20</td>
<td>2310.00</td>
<td>-1782.35</td>
<td>-23326.09</td>
</tr>
<tr>
<td>1</td>
<td>547.79</td>
<td>2320.00</td>
<td>-1779.47</td>
<td>-23288.40</td>
</tr>
<tr>
<td>1</td>
<td>550.39</td>
<td>2330.00</td>
<td>-1776.58</td>
<td>-23250.58</td>
</tr>
<tr>
<td>1</td>
<td>553.02</td>
<td>2340.00</td>
<td>-1773.69</td>
<td>-23212.76</td>
</tr>
<tr>
<td>1</td>
<td>555.66</td>
<td>2350.00</td>
<td>-1770.78</td>
<td>-23174.67</td>
</tr>
<tr>
<td>1</td>
<td>558.32</td>
<td>2360.00</td>
<td>-1767.86</td>
<td>-23136.46</td>
</tr>
<tr>
<td>1</td>
<td>561.01</td>
<td>2370.00</td>
<td>-1764.94</td>
<td>-23098.25</td>
</tr>
<tr>
<td>1</td>
<td>563.71</td>
<td>2380.00</td>
<td>-1761.99</td>
<td>-23059.64</td>
</tr>
<tr>
<td>1</td>
<td>566.44</td>
<td>2390.00</td>
<td>-1759.04</td>
<td>-23021.03</td>
</tr>
<tr>
<td>1</td>
<td>569.20</td>
<td>2400.00</td>
<td>-1756.07</td>
<td>-22982.16</td>
</tr>
<tr>
<td>1</td>
<td>571.98</td>
<td>2410.00</td>
<td>-1753.09</td>
<td>-22943.16</td>
</tr>
<tr>
<td>1</td>
<td>574.79</td>
<td>2420.00</td>
<td>-1750.09</td>
<td>-22903.90</td>
</tr>
<tr>
<td>1</td>
<td>577.63</td>
<td>2430.00</td>
<td>-1747.08</td>
<td>-22864.51</td>
</tr>
<tr>
<td>1</td>
<td>580.51</td>
<td>2440.00</td>
<td>-1744.05</td>
<td>-22824.85</td>
</tr>
<tr>
<td>1</td>
<td>583.42</td>
<td>2450.00</td>
<td>-1741.00</td>
<td>-22784.94</td>
</tr>
<tr>
<td>1</td>
<td>586.37</td>
<td>2460.00</td>
<td>-1737.93</td>
<td>-22744.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>1</td>
<td>589.36</td>
<td>2470.00</td>
<td>-1734.84</td>
<td>-22704.32</td>
</tr>
<tr>
<td>1</td>
<td>592.40</td>
<td>2480.00</td>
<td>-1731.73</td>
<td>-22663.62</td>
</tr>
<tr>
<td>1</td>
<td>595.48</td>
<td>2490.00</td>
<td>-1728.59</td>
<td>-22622.52</td>
</tr>
<tr>
<td>1</td>
<td>598.61</td>
<td>2500.00</td>
<td>-1725.43</td>
<td>-22581.17</td>
</tr>
<tr>
<td>1</td>
<td>601.80</td>
<td>2510.00</td>
<td>-1722.24</td>
<td>-22539.42</td>
</tr>
<tr>
<td>1</td>
<td>605.05</td>
<td>2520.00</td>
<td>-1719.02</td>
<td>-22497.28</td>
</tr>
<tr>
<td>1</td>
<td>608.36</td>
<td>2530.00</td>
<td>-1715.77</td>
<td>-22454.74</td>
</tr>
<tr>
<td>1</td>
<td>611.74</td>
<td>2540.00</td>
<td>-1712.48</td>
<td>-22411.69</td>
</tr>
<tr>
<td>1</td>
<td>615.19</td>
<td>2550.00</td>
<td>-1709.16</td>
<td>-22368.24</td>
</tr>
<tr>
<td>1</td>
<td>618.72</td>
<td>2560.00</td>
<td>-1705.80</td>
<td>-22324.26</td>
</tr>
<tr>
<td>1</td>
<td>622.34</td>
<td>2570.00</td>
<td>-1702.39</td>
<td>-22279.64</td>
</tr>
<tr>
<td>1</td>
<td>626.05</td>
<td>2580.00</td>
<td>-1698.93</td>
<td>-22234.35</td>
</tr>
<tr>
<td>1</td>
<td>629.86</td>
<td>2590.00</td>
<td>-1695.43</td>
<td>-22188.55</td>
</tr>
<tr>
<td>1</td>
<td>633.78</td>
<td>2600.00</td>
<td>-1691.87</td>
<td>-22141.96</td>
</tr>
<tr>
<td>1</td>
<td>637.82</td>
<td>2610.00</td>
<td>-1688.26</td>
<td>-22094.71</td>
</tr>
<tr>
<td>1</td>
<td>641.98</td>
<td>2620.00</td>
<td>-1684.58</td>
<td>-22046.55</td>
</tr>
<tr>
<td>1</td>
<td>646.28</td>
<td>2630.00</td>
<td>-1680.83</td>
<td>-21997.47</td>
</tr>
<tr>
<td>1</td>
<td>650.74</td>
<td>2640.00</td>
<td>-1677.01</td>
<td>-21947.48</td>
</tr>
<tr>
<td>1</td>
<td>655.35</td>
<td>2650.00</td>
<td>-1673.11</td>
<td>-21896.44</td>
</tr>
<tr>
<td>1</td>
<td>660.14</td>
<td>2660.00</td>
<td>-1669.12</td>
<td>-21844.22</td>
</tr>
<tr>
<td>1</td>
<td>665.12</td>
<td>2670.00</td>
<td>-1665.04</td>
<td>-21790.83</td>
</tr>
<tr>
<td>1</td>
<td>670.30</td>
<td>2680.00</td>
<td>-1660.86</td>
<td>-21736.12</td>
</tr>
<tr>
<td>1</td>
<td>675.71</td>
<td>2690.00</td>
<td>-1656.57</td>
<td>-21679.98</td>
</tr>
<tr>
<td>1</td>
<td>681.36</td>
<td>2700.00</td>
<td>-1652.16</td>
<td>-21622.26</td>
</tr>
<tr>
<td>1</td>
<td>687.27</td>
<td>2710.00</td>
<td>-1647.62</td>
<td>-21562.85</td>
</tr>
<tr>
<td>1</td>
<td>693.47</td>
<td>2720.00</td>
<td>-1642.95</td>
<td>-21501.73</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
<td>-------</td>
</tr>
<tr>
<td></td>
<td>699.98</td>
<td>2730.00</td>
<td>-1638.12</td>
<td>-21438.52</td>
</tr>
<tr>
<td></td>
<td>706.84</td>
<td>2740.00</td>
<td>-1633.14</td>
<td>-21373.34</td>
</tr>
<tr>
<td></td>
<td>714.07</td>
<td>2750.00</td>
<td>-1627.97</td>
<td>-21305.68</td>
</tr>
<tr>
<td></td>
<td>721.70</td>
<td>2760.00</td>
<td>-1622.61</td>
<td>-21235.53</td>
</tr>
<tr>
<td></td>
<td>729.78</td>
<td>2770.00</td>
<td>-1617.03</td>
<td>-21162.51</td>
</tr>
<tr>
<td></td>
<td>738.34</td>
<td>2780.00</td>
<td>-1611.23</td>
<td>-21086.60</td>
</tr>
<tr>
<td></td>
<td>747.44</td>
<td>2790.00</td>
<td>-1605.17</td>
<td>-21007.29</td>
</tr>
<tr>
<td></td>
<td>757.12</td>
<td>2800.00</td>
<td>-1598.83</td>
<td>-20924.32</td>
</tr>
<tr>
<td></td>
<td>767.45</td>
<td>2810.00</td>
<td>-1592.19</td>
<td>-20837.42</td>
</tr>
<tr>
<td></td>
<td>778.50</td>
<td>2820.00</td>
<td>-1585.21</td>
<td>-20746.07</td>
</tr>
<tr>
<td></td>
<td>790.33</td>
<td>2830.00</td>
<td>-1577.86</td>
<td>-20649.88</td>
</tr>
<tr>
<td></td>
<td>803.04</td>
<td>2840.00</td>
<td>-1570.10</td>
<td>-20548.32</td>
</tr>
<tr>
<td></td>
<td>816.71</td>
<td>2850.00</td>
<td>-1561.89</td>
<td>-20440.88</td>
</tr>
<tr>
<td></td>
<td>831.47</td>
<td>2860.00</td>
<td>-1553.17</td>
<td>-20326.75</td>
</tr>
<tr>
<td></td>
<td>847.44</td>
<td>2870.00</td>
<td>-1543.88</td>
<td>-20205.17</td>
</tr>
<tr>
<td></td>
<td>864.76</td>
<td>2880.00</td>
<td>-1533.97</td>
<td>-20075.48</td>
</tr>
<tr>
<td></td>
<td>883.61</td>
<td>2890.00</td>
<td>-1523.34</td>
<td>-19936.36</td>
</tr>
<tr>
<td></td>
<td>904.19</td>
<td>2900.00</td>
<td>-1511.91</td>
<td>-19786.77</td>
</tr>
<tr>
<td></td>
<td>926.73</td>
<td>2910.00</td>
<td>-1499.57</td>
<td>-19625.28</td>
</tr>
<tr>
<td></td>
<td>951.50</td>
<td>2920.00</td>
<td>-1486.20</td>
<td>-19450.30</td>
</tr>
<tr>
<td></td>
<td>978.84</td>
<td>2930.00</td>
<td>-1471.64</td>
<td>-19259.75</td>
</tr>
<tr>
<td></td>
<td>1009.15</td>
<td>2940.00</td>
<td>-1455.71</td>
<td>-19051.27</td>
</tr>
<tr>
<td></td>
<td>1042.89</td>
<td>2950.00</td>
<td>-1438.19</td>
<td>-18821.98</td>
</tr>
<tr>
<td></td>
<td>1080.66</td>
<td>2960.00</td>
<td>-1418.82</td>
<td>-18568.48</td>
</tr>
<tr>
<td></td>
<td>1123.18</td>
<td>2970.00</td>
<td>-1397.26</td>
<td>-18286.32</td>
</tr>
<tr>
<td></td>
<td>1171.36</td>
<td>2980.00</td>
<td>-1373.09</td>
<td>-17970.00</td>
</tr>
</tbody>
</table>

145
<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1226.34</td>
<td>2990.00</td>
<td>-1345.80</td>
<td>-17612.85</td>
<td>-1234.20</td>
<td>-15428.42</td>
</tr>
<tr>
<td>1</td>
<td>1289.60</td>
<td>3000.00</td>
<td>-1314.70</td>
<td>-17205.83</td>
<td>-1182.64</td>
<td>-14783.88</td>
</tr>
<tr>
<td>1</td>
<td>1363.08</td>
<td>3010.00</td>
<td>-1278.90</td>
<td>-16737.31</td>
<td>-1123.23</td>
<td>-14041.21</td>
</tr>
<tr>
<td>1</td>
<td>1449.36</td>
<td>3020.00</td>
<td>-1237.22</td>
<td>-16191.83</td>
<td>-1053.99</td>
<td>-13175.66</td>
</tr>
<tr>
<td>1</td>
<td>1551.94</td>
<td>3030.00</td>
<td>-1188.06</td>
<td>-15548.46</td>
<td>-972.25</td>
<td>-12153.85</td>
</tr>
<tr>
<td>1</td>
<td>1675.77</td>
<td>3040.00</td>
<td>-1129.14</td>
<td>-14777.36</td>
<td>-874.28</td>
<td>-10929.15</td>
</tr>
<tr>
<td>1</td>
<td>1827.94</td>
<td>3050.00</td>
<td>-1057.21</td>
<td>-13835.99</td>
<td>-754.75</td>
<td>-9434.94</td>
</tr>
<tr>
<td>1</td>
<td>2019.11</td>
<td>3060.00</td>
<td>-967.38</td>
<td>-12660.36</td>
<td>-605.74</td>
<td>-7572.20</td>
</tr>
<tr>
<td>1</td>
<td>2265.96</td>
<td>3070.00</td>
<td>-852.00</td>
<td>-11150.35</td>
<td>-415.01</td>
<td>-5187.93</td>
</tr>
<tr>
<td>1</td>
<td>2596.16</td>
<td>3080.00</td>
<td>-698.37</td>
<td>-9139.76</td>
<td>-162.74</td>
<td>-2034.37</td>
</tr>
<tr>
<td>1</td>
<td>3059.04</td>
<td>3090.00</td>
<td>-483.84</td>
<td>-6332.14</td>
<td>127.71</td>
<td>1596.47</td>
</tr>
<tr>
<td>1</td>
<td>3751.48</td>
<td>3100.00</td>
<td>-163.95</td>
<td>-2145.66</td>
<td>144.51</td>
<td>1806.48</td>
</tr>
<tr>
<td>1</td>
<td>4887.68</td>
<td>3110.00</td>
<td>359.65</td>
<td>4706.84</td>
<td>162.58</td>
<td>2032.37</td>
</tr>
<tr>
<td>1</td>
<td>5323.83</td>
<td>3120.00</td>
<td>556.05</td>
<td>7277.18</td>
<td>182.12</td>
<td>2276.64</td>
</tr>
<tr>
<td>1</td>
<td>5354.60</td>
<td>3130.00</td>
<td>564.37</td>
<td>7386.06</td>
<td>203.39</td>
<td>2542.53</td>
</tr>
<tr>
<td>1</td>
<td>5385.81</td>
<td>3140.00</td>
<td>572.87</td>
<td>7497.30</td>
<td>226.66</td>
<td>2833.42</td>
</tr>
<tr>
<td>1</td>
<td>5417.47</td>
<td>3150.00</td>
<td>581.56</td>
<td>7611.03</td>
<td>252.30</td>
<td>3153.94</td>
</tr>
<tr>
<td>1</td>
<td>5449.63</td>
<td>3160.00</td>
<td>590.46</td>
<td>7727.51</td>
<td>280.75</td>
<td>3509.58</td>
</tr>
<tr>
<td>1</td>
<td>5482.30</td>
<td>3170.00</td>
<td>599.58</td>
<td>7846.86</td>
<td>312.54</td>
<td>3906.98</td>
</tr>
<tr>
<td>1</td>
<td>5515.52</td>
<td>3180.00</td>
<td>608.93</td>
<td>7969.23</td>
<td>348.34</td>
<td>4354.51</td>
</tr>
<tr>
<td>1</td>
<td>5549.33</td>
<td>3190.00</td>
<td>618.53</td>
<td>8094.87</td>
<td>388.98</td>
<td>4862.54</td>
</tr>
</tbody>
</table>

146
References


[25] Troy W. Barbee Jr., Randall L. Simpson, Alexander E. Gash, and Joe H. Satcher Jr. Nano-laminate-based ignitors, May 2011. U.S. Classification 149/15; International Classification C06B23/00, C06C9/00, C06B33/00, C06B45/14; Cooperative Classification C06B33/00, C06B45/14, C06C9/00; European Classification C06C9/00, C06B33/00, C06B45/14.


[28] Achim Hofmann, Horst Laucht, Dimitri Kovalev, Victor Yu Timoshenko, Joachim Diener, Nicolai Künzner, and Egon Gross. Explosive composition and its use, January 2006. U.S. Classification 149/2, 149/14, 149/109.6; International Classification C06B33/06, B60R22/46, B60R21/26, C06B33/08, C06B45/00, C06C9/00, C06B33/00, C06B33/04, D03D23/00, C06C7/00, C06B21/00;
Cooperative Classification C06B33/00, C06B45/00, C06C9/00; European Classification C06B33/00, C06B45/00, C06C9/00.

[29] Reed J. Blau and Jerald C. Hinshaw. Thermite compositions for use as gas generants, August 1995. U.S. Classification 149/22, 422/165, 149/37; International Classification C06D5/06, C06B5/00, B60R21/26, C06B33/00; Cooperative Classification C06D5/06, C06B33/00; European Classification C06D5/06, C06B33/00.


154


and wet environments under mild temperature conditions. *Journal of Porous 

explosion of nanostructured silicon in microsystem devices. *Semiconductors*, 

Highly explosive nanosilicon-based composite materials. *physica status solidi (a)*, 


[80] W. Churaman, L. Currano, and C. Becker. Initiation and reaction tuning of 
nanoporous energetic silicon. *Journal of Physics and Chemistry of Solids*, 

[81] Collin R. Becker, Steven Apperson, Christopher J. Morris, Shubhra Gangopadhyay, 


Vita

Venkata Sharat Parimi

Venkata Sharat Parimi was born in Nellore, India on February 27th 1985. He received a Bachelor of Technology degree in Mechanical Engineering from the Indian Institute of Technology, Madras in 2007. He developed an interest in thermal-fluid sciences during his undergraduate education, and joined The Pennsylvania State University in 2007 to pursue experimental research on combustion. He joined Dr. Richard Yetter’s group in 2008, and initially worked on measuring the transport properties of nanofluids. Since 2009, his work focused on combustion of nanoporous silicon, and he was co-advised by Dr. Richard Yetter and Dr. Srinivas Tadigadapa. His current research interests are in the area of energy conversion, with emphasis on reactive nanomaterials. A list of his peer-reviewed publications is provided below.

Peer-Reviewed Publications:


