

CONTROL OF REACTIVE WAVE PROPAGATION IN ENERGETIC NANOPOROUS SILICON COMPOSITES

V.S. Parimi^{1*}, R.A. Yetter¹, and S.A. Tadigadapa²

¹Department of Mechanical and Nuclear Engineering

²Department of Electrical Engineering

The Pennsylvania State University, University Park, PA, USA

Abstract: This paper reports on the various factors that affect reactive wave propagation in porous silicon (PS) – oxidizer composites using high speed imaging and spectroscopically estimated temperature measurements. In particular, the effects of the mixture composition, substrate properties, deposition of the oxidizer within the nanoscale pores, and presence of randomly forming micro-crack patterns on the reactive wave propagation behavior are analyzed. Also, control of the reactive wave using multiscaled structures containing nanometer and micrometer scale features and how the propagation speeds can be tuned are described. Finally, this paper aims to provide both the fundamental understanding of the various processes and demonstrate how PS composites can be engineered to provide desired energy release profiles.

Keywords: Micropyrotechnics, nanoenergetic materials, multiscaled structures, porous silicon

INTRODUCTION

Miniaturization of devices provides several advantages such as increased performance and efficiency coupled with lower masses and production costs. However, this poses several new challenges associated with reduced length scales. While many efficient actuation methods for macroscale devices are readily available, they are impractical on MEMS platforms due to scale effects. An attractive solution to this problem is utilizing the energy released upon the combustion of energetic materials (EMs), which can provide very high energy densities. While modern day batteries are capable of energy densities of only ~ 0.5 MJ/kg, combustion of EMs can yield greater than 5 MJ/kg. For applications requiring mechanical actuation, the efficacy of the energy source is best described by actuation pressure, which is essentially the volumetric energy density. Thus, the integration of EMs, which provide the highest actuation pressures, into multifunctional microsystems, to exploit the thermal, mechanical, and chemical energy released has attracted significant attention recently, and is known as micropyrotechnics [1]. However, the greatly increased surface/volume ratios in microscale devices result in enhanced heat losses, which render most traditional EMs incapable of sustaining chemical reactions.

Quenching at small length scales can be overcome by using nanoenergetic materials (nEMs), which are capable of sustaining combustion reactions even at the micrometer scale due to the high reactivity of their nanoscale constituents [2]. One such attractive nEM is porous silicon (PS), which is essentially a crystalline

form of silicon with missing crystal atoms, formed by simple electrochemical/galvanic processes. These missing atoms create nanometer scale pores, resulting in specific surface areas (SSA) up to 1,000 m²/g. The high SSA of PS can be exploited to form highly reactive composites by depositing an oxidizer within the nanoscale pores. Since silicon is the base material, PS also has the advantage of easy integration as an on-board energy source and utilization of the already well developed low cost batch processing technology used silicon microfabrication.

PS-oxidizer composites have demonstrated high energy densities up to 10 MJ/kg [3] and reactive wave propagation speeds (v) up to 3,000 m/s [4]. However, the properties of the energetic composites strongly depend on several factors, such as the substrate type and dopant concentration, the micro and nanoscale structure, oxidizer deposition etc, which are poorly understood. This work examines how the various parameters affect the energy release from PS-oxidizer composites, and demonstrate how it can be tuned so that PS-oxidizer composites can be successfully integrated and used as on-board energy sources for microscale devices.

EXPERIMENTAL METHODS

The PS used in this work was prepared by electrochemical dissolution of silicon using electrolytes consisting of equal volumes of hydrofluoric acid and ethanol. The etch process was carried out in a Teflon etch cell capable of holding 250 ml of electrolyte and exposing only the top side of 4" silicon wafers to the electrolyte. During the etch

process, the silicon wafer acts as the anode, and a silver mesh, placed at a fixed distance from the surface of the wafer acts as the cathode. Electrical contact was established with the low doped P-type wafers (10 – 20 Ω -cm, Boron doped) by depositing a 20 nm thick layer of titanium on the backside of the wafer followed by a rapid thermal anneal in an Argon environment. The low doped N-type wafers (2 – 5 Ω -cm, Phosphorus doped) were etched under illumination. Uniform porous layers could be etched on the heavily doped wafers (0.001 – 0.005 Ω -cm, Boron or Arsenic doped) without the need of illumination or backside titanium deposition. Thick and stable porous layers were etched on the substrates using an etch-stop-etch method with several minute relaxation times between etch cycles. The etched wafers were cut into test samples 5 mm wide, which were used to study the reactive wave propagation. The porosity was estimated by gravimetric methods, by dissolving the porous films in a 1M aqueous sodium hydroxide (NaOH) solutions [5]. The etched PS was further characterized using scanning electron microscope (SEM) imaging and BET measurements. Energetic composites were prepared by impregnating these test strips of PS with sodium, magnesium, or calcium perchlorate salts using methanol solutions. The test strips were then mounted on glass slides using double sided adhesive tape and ignited using a 10 ms pulse from a 200 W CO₂ laser. The reactive wave propagation was characterized by means of a high speed video (recorded using a Phantom V 7.3 high speed camera) and a single time integrated (50 ms) spectrum (acquired using an Ocean Optics HR-2000 spectrometer). The temperature of the reactive wave was estimated using a multiwavelength pyrometry algorithm [6] after correcting the collected spectrum for the collection efficiency of the optics.

Controlled microscale structures were created on heavily doped P-type substrates using standard microfabrication techniques. The wafers were patterned using thick positive photoresist (Megaposit SPR-220-7) and etched by deep reactive ion etch (DRIE) using a modified BOSCH process. The photoresist was then stripped off and the wafers were electrochemically etched to create PS. This process results in multiscaled structures with the nanoscale constituent (PS) arranged in controlled micrometer scale patterns. These patterned samples were prepared such that only half the length of the sample contained microscale structures. Samples were ignited in the unpatterned region and the reactive wave was allowed to achieve a steady propagation rate before reaching the patterned region.

RESULTS AND DISCUSSION

Using the etch-stop-etch technique, stable porous layers up to 150 μ m thick were etched on the heavily doped P-type substrates. It was found that PS etched on heavily doped substrates is smooth and uniform, and is stable enough to withstand slight manipulation post impregnation with the oxidizers. In contrast, the low doped substrates form highly unstable porous layers which disintegrate and explode upon contact. This insensitivity of heavily doped silicon substrates was exploited to clean the surfaces of the samples and gravimetrically determine the oxidizer deposition within the pores. Samples were soaked in solutions of magnesium perchlorate (Mg(ClO₄)₂), and the amount of oxidizer deposited was controlled by changing the concentration of the oxidizer solutions. The composite equivalence ratio (ϕ), is defined as the ratio of the fuel to oxidizer ratio in the mixture, to that of a stoichiometric mixture. Assuming that the void space is completely filled with the oxidizer solution, which upon evaporation deposits the oxidizer in the pores, the theoretical lower bound on the equivalence ratio can be expressed as

$$\phi_{\min} = \left(\frac{m_{ox}}{m_f} \right)_{st} \left(\frac{(1-P)\rho_{Si}}{Ps} \right) \quad (1)$$

where P is the porosity, ρ_{Si} is the density of bulk silicon, and s is the strength of the solution (g/L). Reactive composites with a wide range of equivalence ratios were prepared using saturated to very dilute solutions of Mg(ClO₄)₂ were prepared using PS with a porosity of 0.71 – 0.75 and the reactive wave propagation was studied. It was found that the propagation speeds obtained were always low, between 2 – 8 m/s, with consistent nearly constant spectroscopic temperatures as shown in Table-1. The fuel rich extinction limit was found to be close to $\phi_{\min} = 56$ ($\phi_{\text{measured}} = 39$), at which composition the samples could be ignited but could not sustain a self propagating reaction.

Thermodynamic equilibrium calculations using CHEETAH 4.0 equilibrium code [7] indicate that liquid silicon is one of the major condensed phase species, whose spectral emissivity has a very weak dependence on wavelength. Thus, a gray body approximation was used for the multiwavelength pyrometry algorithm. Also, the thermodynamic calculations indicate that the equilibrium temperature remains nearly constant over a wide range of equivalence ratios as shown in Figure 1. 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 SiO₂. The second drop and plateau is due to the phase change of silicon, which melts at 1683 K.

Table 1: Equivalence ratio, flame propagation speeds and spectroscopically determined temperatures for porous layers etched on heavily doped p-type substrates impregnated with magnesium perchlorate.

Φ_{\min}	Φ_{measured}	v (m/s)	Temperature (K)
3.8	1.2-1.24	5-7.7	2044
6.7	2.4-3.4	2.5-3.3	1844 - 1930
13.5	3.9-5.2	2.4-2.8	1792 - 1870
33.1	20.4-20.8	2.6-3.0	1886 - 1993

The role of the oxidizer used was examined using sodium and calcium perchlorates, which have very different solubilities in methanol. To achieve lower equivalence ratios, saturated solutions of calcium perchlorate (Ca(ClO₄)₂) in methanol were used to prepare energetic composites. It was found that increasing the oxidizer deposition in the pores reduced the propagation velocity (v) despite the mixture composition being closer to stoichiometric. However, using a dilute solution of Ca(ClO₄)₂ to prepare composites with the same ϕ as NaClO₄ resulted in higher v as shown in Table 2. This indicates that heavily doped substrates which form smooth and uniform porous layers always result in low speed propagations regardless of the oxidizer deposition within the pores. The reduction in v with increased oxidizer deposition indicates that the reaction is perhaps more strongly controlled by the PS-oxidizer interface than the composition. Increased oxidizer within the pores with a fixed SSA can act as local diluents during the time scales associated with the initial reactive wave, thereby reducing v [8].

The reactive composites prepared from low doped P and N type substrates, however, exhibited $v \sim 300$ m/s. An SEM examination of these substrates showed a naturally forming micro-crack pattern, as shown in Figure 2. These samples with microscale features were always found to yield high propagation rates due to transition from a conductive heat transfer based mechanism to a much faster convective heating of the reactants by hot gaseous products flowing through the microscale cracks, known as convective burning.

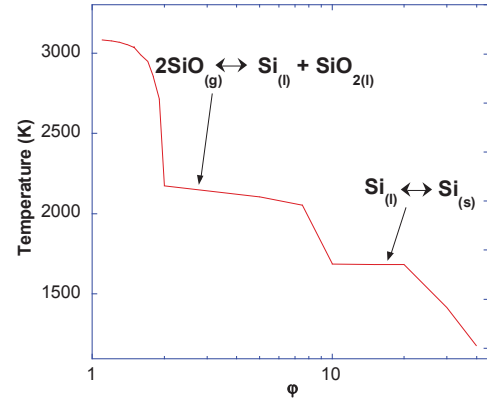


Figure 1: Thermodynamic equilibrium calculations using showing the effect of composite equivalence ratio on reaction zone temperature

Table 2: Reactive wave propagation as a function of theoretical composite equivalence ratio (Φ_{\min})

Oxidizer solution	Φ_{\min}	v (m/s)
NaClO ₄	8.32	3.2-3.3
Ca(ClO ₄) ₂	7.52	0.7-1.2
Ca(ClO ₄) ₂	1.76	4.2-4.3

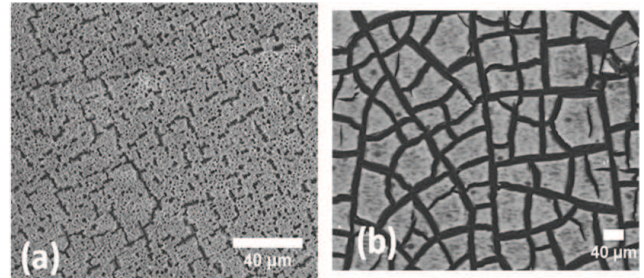


Figure 2: random micro-crack patterns formed during the electrochemical dissolution process for (a) low doped N-type substrates (Phosphorous doped, 2-5 Ω -cm) and (b) low doped P-type substrates (Boron doped, 10-20 Ω -cm). These samples exhibited propagation rates > 300 m/s.

This property of microscale structures can be exploited to tune v . In our previous work [9], we described how multiscaled structures formed by arranging nanoscale PS in microscale square pyramids increased v on slow propagating heavily doped substrates from ≈ 2 m/s up to 500 m/s. From the various configurations tested of pillared samples tested, the reactive wave was found to be affected the most by gas permeation, spacing between structures and the initial surface area of the microscale patterns.

To isolate and study the effect of each of these parameters independently to better understand and control the reactive wave propagation, samples were prepared with plates along the width of the sample normal to the propagation as shown in Figure 3.

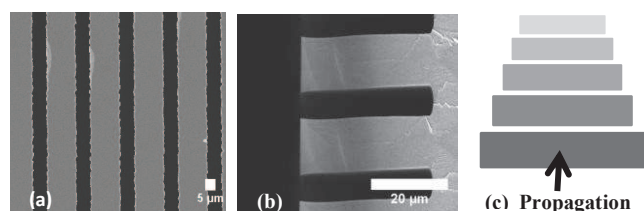


Figure 3: Microscale patterns etched on heavily doped P-type substrates. (a) and (b) Top and side views showing 15 μm plates with a spaced 5 μm apart. (c) Direction of reactive wave propagation relative to the plate orientation.

This configuration eliminates the gas permeation and the spacing and surface area (controlled by the height of the plates) can be independently varied. From these structures, it was found that the initial surface area did not have a strong effect on the gas phase heat transfer, and the gap between the structures was found to have a very strong effect. While gaps of 25 μm resulted in no transition, 15 μm gaps accelerated the reactive wave from 4 m/s to 6 m/s whereas 5 μm gaps resulted in a transition from 4 m/s to 30 m/s. Such multiscaled structures can be used to design energetic materials with precisely controlled energy release profiles, making PS a suitable nEM for a range of micropyrotechnic applications.

CONCLUSIONS

This work provides a fundamental understanding of the various factors that affect the reactive wave propagation, and thus the energy release from PS based reactive composites. A detailed study on the mixture composition and the effect of substrate properties reveals that the oxidizer fill process has a small effect on the reactive wave propagation speeds, due to the various equilibrium processes that hold the adiabatic temperature constant over a wide range of equivalence ratios. Also, the interfacial contact area between PS and oxidizer was found to be an important factor affecting the propagation speeds. The low doped samples with randomly forming micro-crack patterns were found to always result in high propagation speeds of hundreds of m/s. Also, this work identifies the important parameters for organizing the reactants into controlled microscale structures, which can be used to precisely control the

propagation speeds and the energy release, such that PS based nEMs can be engineered to actuate/power specific devices.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the support and funding from the Defense Threat Reduction Agency (DTRA), Counter-WMD basic research program, under grant number HDTRA1-08-1-0006.

REFERENCES

- [1] Rossi C, Esteve D. 2005 Micropyrotechnics, a new technology for making energetic microsystems: review and prospective. *Sensor Actuat A-Phys* **120** 297-310.
- [2] Rossi C., Kaili Z., Esteve D., Alphonse P, Tailhades P, Vahlas C. 2007 Nanoenergetic Materials for MEMS: A Review. *J. Microelectromech. S.*, **16** 919-931.
- [3] Becker C.R., Currano L.J., Churaman W.A., Stoldt C.R. 2010 Thermal Analysis of the Exothermic Reaction between Galvanic Porous Silicon and Sodium Perchlorate. *ACS Appl. Mater. Interfaces* **2** 2998-3003.
- [4] Becker C.R., Apperson S., Morris C.J., Gangopadhyay S., Currano L.J., Churaman W.A., Stoldt C.R., 2011 Galvanic Porous Silicon Composites for High-Velocity Nanoenergetics. *Nano Lett.* **11** 803-807.
- [5] Canham L. (Ed) 1997 Properties of Porous Silicon. (London, Institution of Engineering and Technology).
- [6] Ng D., Fralick G. 2001 Use of a multiwavelength pyrometer in several elevated temperature aerospace applications. *Rev. Sci. Instrum.* **72(2)** 1522-1530.
- [7] Fried L.E., Glaesemann K.R., Howard W.M., Souers P.C., Vitello P.A. 2004 CHEETAH 4.0. (Lawrence Livermore National Laboratory, Livermore, CA.).
- [8] Parimi V.S., Bermudez A., Tadigadapa S.A., Yetter R.A., 2012 Reactive wave propagation in energetic porous silicon composites. *To be submitted.*
- [9] Parimi V.S., Tadigadapa S.A., Yetter R.A. 2012 Control of nanoenergetics through organized microstructures. *J. Micromech. Microeng.* **22** 055011.