



Investigating aging effects for porous silicon energetic materials



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ABSTRACT

When infused with an oxidizer, on-chip porous silicon (PS) shows tremendous potential as an energetic material. However, applications such as fuzing and propulsion require long-term material stability. The present work utilizes accelerated lifetime testing for PS samples with sodium perchlorate (NaClO_4) oxidizer. Devices were exposed to elevated temperatures for various time intervals, then subjected to an electrical pulse through an integrated bridgewire to test for ignition. The pass/fail data from ignition testing was then analyzed to determine the mean and median failure point at each temperature using an Arrhenius aging model and a lognormal probability density function (PDF). Samples were heated over a temperature range of 185–300 °C for up to 46 h with median failure times ranging from 0.4–20 h. Differential scanning calorimetry (DSC) and Fourier transform infrared (FTIR) spectroscopy were used to evaluate chemical changes of PS/ NaClO_4 during aging. Comparison of DSC traces for aged samples showed differences for heating above and below 250 °C, suggesting two different aging mechanisms. FTIR results suggest that for low temperature aging (below ~250 °C) the hydrogen termination layer of the porous silicon was still intact, but backbond oxidation did occur. Above ~250 °C the hydrogen termination layer was no longer evident in FTIR and considerable oxidation occurred, suggesting reaction or dissociation of the hydrogen layer. This corresponds with an exothermic peak shown during DSC at 300 °C. Thermogravimetric analysis/mass spectroscopy (TGA/MS) was also performed, and confirmed hydrogen gas release beginning at ~280 °C. A DSC peak at ~400 °C is evident for fresh samples, but is greatly reduced or not evident for all aged samples. We attribute this peak to backbond oxidation, which is shown to occur in FTIR for all aged samples. Variable heating rate DSC experiments were also performed to determine activation energy of fresh and aged samples. Activation energy was calculated using the Kissinger Method for the first two exothermic peaks in DSC experiments. For the first peak, corresponding to hydrogen desorption (~300 °C), activation energy for fresh and aged samples was 132.1 kJ/mol and 132.7 kJ/mol, respectively. The activation energy of the second exothermic peak, corresponding to backbond oxidation, for fresh and aged samples was 183.8 kJ/mol and 159.6 kJ/mol, respectively. Device failure during accelerated aging tests was also used to predict the mean lifetime of porous silicon/sodium perchlorate at room temperature (25 °C) as 100 years with a 90% confidence interval of 31 to 328 years.

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1. Introduction

Porous silicon (PS) has been widely investigated due to its high surface area, optical properties, and compatibility with microelectromechanical systems (MEMS) fabrication processes, which makes it an attractive material for a number of applications including, optical biosensors, solar cells, or energetic materials [1–6]. For the application of energetic materials, PS is very unique when infiltrated with an appropriate oxidizer, as it has a high energy density and highly tunable reaction rate that can be initiated

with a very small energy input [7]. Due to these qualities, porous silicon has the potential to provide significant improvements or new capabilities in the areas of fuzing, propulsion, or delay timers [4,5]; however, these applications typically require long term material stability. Although much research has been performed on the basic combustion properties of porous silicon [4,5,7–16], little has been done to investigate the stability, lifetime, and failure mechanism of a porous silicon energetic material.

In general, long term material stability is investigated using accelerated aging tests at elevated temperatures. Exposure to higher temperature will accelerate the chemical processes and mimic the environments experienced over the lifetime of a material. Often these tests are used to determine a point of “failure”, or a point

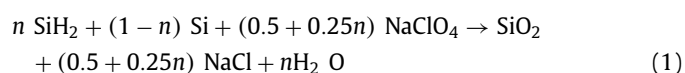
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where a significant change has occurred in the material that is detrimental to its desired performance. This type of study has not been performed for PS energetic materials, but has been done for a number of other energetics including PETN, HMX, and double-base propellants, where measurement of mass loss or change in specific area was used to characterize aging [17–19]. Failure points found through accelerated aging can then be fit with a kinetic model such as the Arrhenius equation to predict the lifetime of the material at a given temperature [17,19].

Although aging studies have not been previously performed on porous silicon energetic materials, some studies have investigated decomposition and reaction mechanisms for non-energetic porous silicon (porous silicon with no added oxidizer). When considering decomposition or reaction of porous silicon, there are a few major material features to consider; the silicon pores, a hydrogen termination layer on the surface of the porous silicon, and the surrounding environment (air, nitrogen, solid oxidizer, etc.). The hydrogen termination layer is a result of the hydrofluoric acid used in typical porous silicon fabrication, and can be considered similar to SiH₂ [20]. This is the initial passivation layer for the porous silicon, rather than SiO₂ for bulk silicon. Identified reaction steps for porous silicon include backbond oxidation, reaction or dissociation of the hydrogen termination layer, and oxidation of the silicon. Backbond oxidation occurs as the Si-Si bonds at the surface are weaker than the surface Si-H bonds, and therefore oxidize first. Fukuda et al. probed porous silicon surface reactions using FTIR spectroscopy and transmission electron microscopy (TEM) for samples aged at room temperature for up to 192 days. [21] Their results show an increase in Si-O bond intensity for FTIR spectroscopy indicating oxidation occurs. This may have been primarily backbond oxidation as there is no significant change for Si-H bonding, suggesting the hydrogen termination layer is still intact. Several studies at elevated temperature have also investigated the surface reactions for porous silicon, however explanations vary as to how, and at what temperature backbond oxidation and hydrogen reaction/desorption occur. [10,12,21–23] Studies using differential scanning calorimetry typically show two primary exothermic peaks, at ~300 °C and >450 °C. [10,12,22] The peak at higher temperature is attributed to the bulk oxidation of the porous silicon, while the low temperature peak is often reported to be due to backbond oxidation. [10,12,22] However, others note that hydrogen is released from the termination layer at >250 °C [23,24,28] suggesting that the low temperature DSC peak could be due to oxidation related to removal of hydrogen. This allows formation of O_xSiH_y and SiO_x species, including backbond oxidation. [5,22,23,25] Lastly, investigation of activation energies of non-energetic PS using DSC was done to study oxidation events for the exothermic event occurring near 250–300 °C, reporting an activation energy of 116–134 kJ/mol. [22,26]

For porous silicon energetic materials, the chemical effects of aged samples, particularly on the surface of porous silicon, are thought to be critical to performance. If we consider the reaction for porous silicon with NaClO₄ in Eq. (1), the primary fuels are silicon and the hydrogen termination layer SiH₂. The hydrogen from SiH₂ contributes significantly to the reaction [10,27], therefore any hydrogen dissociation or reaction will be detrimental to the material's energy production.



Likewise, backbond oxidation can also affect reactivity. Backbond oxidation only affects the surface atoms of the porous silicon, but with the high surface area of porous silicon and nanoscale pores, this surface layer is actually a considerable amount of material. Several studies have investigated thermal effects on energetic porous silicon using DSC and FTIR spectroscopy, primarily with

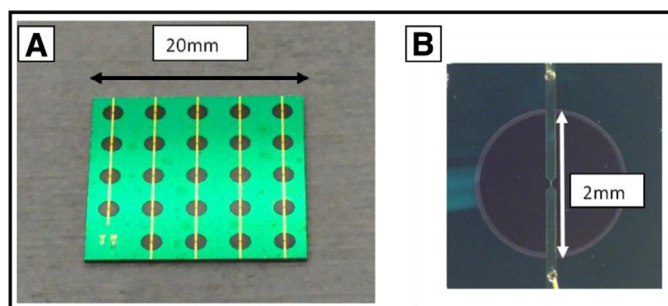


Fig. 1. A. PS pattern used in the study showing the black, 2 mm PS regions, green LPCVD Si₃N₄ layer, and gold bridgewires. B. A single 2 mm PS device used for aging tests and material characterization. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

sodium perchlorate (NaClO₄) as the oxidizer [10,12,28]. Porous silicon with sodium perchlorate has been shown to ignite at or below 200 °C, but typically when heated in a relatively inert environment (N₂, H₂, etc.) DSC studies show exothermic peaks at ~300 °C and >450 °C as shown with neat porous silicon [22], but also an exothermic peak between 350 and 400 °C. There is some inconsistency in the attribution of the peaks at ~300 °C and between 350 and 400 °C where one study states that backbond oxidation occurs at the lower temperature peak [10], and the other states this as occurring between 350 and 400 °C [12]. More recently, Plummer *et al* attribute the peak at 300 °C to hydrogen desorption and subsequent silicon reaction [28].

Because applications such as fuzing and propulsion require a long material lifetime, it is of utmost importance to gain a better understanding of the aging mechanism for porous silicon energetic materials. The present study investigates the long term reactions and lifetime of a porous silicon/sodium perchlorate system. The aging temperature ranged from 185–300 °C, with a maximum aging time of 46 h at 185 °C. Through comparison of DSC, FTIR and TGA/MS results for samples aged at different temperatures, we conclude that there are two different aging mechanisms for PS energetic materials; excessive backbond oxidation, and removal of the hydrogen termination layer. Aging data was also extrapolated with statistical software that utilizes the Arrhenius acceleration model and lognormal PDF, predicting a mean material lifetime at room temperature of 100 years with a 90% confidence interval (CI) of 31 to 328 years.

2. Experimental setup

2.1. Sample preparation

Porous silicon was fabricated using a galvanic electrochemical etch method that is detailed elsewhere [4,9,29,30]. A 1–10 Ω-cm, <100> orientation, P-type, boron doped silicon wafer was used as the starting material. The front side of this wafer was coated with LPCVD silicon nitride (Si₃N₄) layer, and the back side was coated with sputter deposited platinum [4,13,14]. Using standard photolithography techniques, the Si₃N₄ was selectively removed in 2 mm circular regions to expose the underlying silicon, which later undergoes the galvanic etch to form porous silicon. A tri-layer chrome/platinum/gold bridgewire, used for ignition of the energetic material, was also patterned atop the nitride and exposed silicon through an evaporation deposition. Following patterning and bridgewire deposition, wafers were diced with a Disco DAD3240 dicing saw into 20 × 20 mm squares containing up to 25–2 mm circular regions of exposed silicon as shown in Fig. 1A.

Following dicing, the device coupons were placed in the galvanic etch solution of 3:1 volumetric ratio of hydrofluoric acid

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