

Contents lists available at ScienceDirect

Journal of Physics and Chemistry of Solids



journal homepage: www.elsevier.com/locate/jpcs

Initiation and reaction tuning of nanoporous energetic silicon

W. Churaman^{a,*}, L. Currano^a, C. Becker^b

^a US Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783-1197, USA ^b University of Colorado, Boulder, CO, USA

ABSTRACT

Nanoporous silicon, well-known for its optical properties, has gained increasing attention in recent years as an energetic material. In this paper, we demonstrate the ability to tune the energy release rate as measured by propagation speed, ranging from a fast burn to speeds that exceed 2000m/s. We also demonstrate tuning the quantity of gas generated by a factor of 3 while keeping the total energy released close to constant. We present the performance characterization data for an improved thermal initiator that is integrated on the nanoporous energetic silicon. The optimization of the hotwire initiator allows ignition with less than 100 ma applied current. Finally, we show integration of the nanoporous energetic silicon on-chip with a MEMS acceleration switch fabricated using standard micromachining techniques.

Published by Elsevier Ltd.

Introduction

For decades, novel microelectro-mechanical systems and devices have been developed using silicon both as a substrate and a functional material. Over time and with significant research efforts, the electrical devices first fabricated in silicon were joined by mechanical, thermal, optical, and fluidic physics on-chip to diversify the design and the application space. The energetic functionality represents a new set of physics, which can be integrated on-chip with these existing MEMS and electronic devices to achieve new capabilities. The silicon manufacturing infrastructure is tremendous, and there is excess unused bulk silicon in virtually every electronic or MEMS device made. Energetic silicon can therefore provide new functionality to chips while using the existing toolsets and available material.

Energetic silicon was first explored in the early 1990s when it was found that porous silicon reacted violently with potassium nitrate and nitric acid [1]. In these and similar experiments [2], the silicon acts as a fuel and requires a dense solid or liquid source of oxygen inside the nanopores to overcome diffusion limitations. The nanoporous silicon material remains inert until the porous network is infused by any one of a number of oxidizers [3]. The reaction can be triggered using heat, friction, or focused light [4]. The strength of the exothermic reaction is thought to be dependent on a number of structural characteristics of the pores that can be controlled during the anodization process. These characteristics, including the porosity, pore diameter, and surface area of the porous silicon, depend on the concentration of HF/ ethanol electrolyte solution used during the electrochemical etch, the dopant level and type of the silicon, the current density, and the etch time.

Fabrication

The nanoporous energetic material used in this study is fabricated using a double-side polished, 1–20 ohm cm, p-type boron-doped wafer. An electrode is deposited on the backside of the wafer by sputtering Ti/Pt layers of 200 and 800 Å. The wafer is annealed in nitrogen to reduce the electrical contact resistance between the electrode and silicon. The wafer is placed inside a Teflon-etch chamber designed to protect the backside of the wafer while providing access to the topside. Electrical contact is made to the backside of the wafer using a sheet of aluminum foil. The chamber is then filled with an electrolyte solution composed of HF and ethanol. A gold electrode, which serves as the cathode, is lowered into the electrolyte solution. Application of current between the cathode and the anode (wafer) causes localized etching of the silicon, creating nanopores in the wafer. The samples are usually rinsed with pentane to ensure the structural stability of the pores [5]. The finished nanopores have a random structure and a hydrogen-passivated surface [6].

The oxidizer is applied to the sample as a liquid solution consisting of an oxidizer salt solute and methanol solvent. Since the porous silicon surface is organophilic, the solution is drawn down inside the pores by capillary forces. The samples are allowed to dry in a humidity-controlled environment; and as the methanol evaporates the oxidizer salt precipitates into the interior surface

^{*} Corresponding author. Tel: +3013940952; fax: +3013941559. E-mail address: wayne.churaman@arl.army.mil (W. Churaman).

of the pores. The work presented here used 3.2 M solution of sodium perchlorate dissolved in methanol. Each section of the porous layer is coated evenly with the oxidizer three consecutive times, while the sample remains wet, to ensure sufficient oxidizer impregnates the pores. Energy dispersive X-ray (EDX) analysis of 1 cm² porous silicon samples was done to confirm the penetration of an equivalent solution of an inert salt (NaCl) into the porous network. Further analysis must be done to quantify the filling of the pores.

Tuning of gas generation

The proposed reaction of the porous silicon/sodium perchlorate system is [7]

$$n\operatorname{SiH}_2 + (1 - n)\operatorname{Si} + \frac{(2 + n)}{4}\operatorname{NaClO}_4 \rightarrow \operatorname{SiO}_2 + \operatorname{NaCl} + n\operatorname{H}_2O + \operatorname{heat}$$

where SiH_2 arises from the hydrogen surface termination of the pore surface. It has been shown that there is a significant gas generation from this system and hypothesized that the majority of the gas generation is the formation of water vapor [7]. If this is the case, it should be possible to tune the quantity of gas generated by changing the quantity of hydrogen present on the surface. Clement et al [3] suggested that stabilization of the porous surface against aging can be accomplished by thermal annealing at low temperatures in an oxygen environment. The oxygen forms bonds with silicon, and we propose that it displaces some of the hydrogen molecules on the surface. We therefore undertook a series of experiments to determine the effect on the pressure output when the samples were annealed and hydrogen was removed from the surface.

The control samples were produced using 18.44 mA/cm^2 etch current and a 1:1 solution of HF/ethanol. Oxidizer was applied to the samples as described above and the samples were allowed to dry for 15 min in a nitrogen environment with relative humidity less than 4%. The samples were placed in a 23 mL pressure bomb and the bomb was sealed at atmospheric pressure. We connected a pressure gauge to a tap on the bomb to observe in real-time the pressure change due to the reaction. Upon ignition of the samples, the pressure immediately jumped to 30 psi, before quickly settling to 7.5 psi. Based on initial calibration measurements, and application of a correction factor shown in [7], a pressure of 8.18 psi was generated. The active mass of the sample was determined using a method described in [8], weighing samples before and after removal of the porous layer in dilute KOH. The total mass of the energetic used was estimated assuming a stoichiometric match of silicon to NaClO4, with 1 mole of NaClO4 to each 2 moles of Si. For an active mass of 43.9 mg, the gas generation per gram of active mass was 0.0129 mol/g.

The same pressure measurement was run using samples etched under the same conditions, but were annealed at 250 °C for 1 min in an oxygen environment. The total active mass was assumed to be the same, 43.9 mg. The real-time pressure measurement showed an immediate jump to 35 psi, before the pressure quickly settled to 2.5 psi. Applying the same correction factor, the pressure was 2.73 psi. Based on the volume of the bomb and the pressure generated at room temperature, we use the ideal gas law to determine the moles of gas generated per gram. The gas generation per gram of active area was 0.004 mol/g. We can therefore tune the amount of gas generated by the reaction by annealing the nanoporous Si.

In order to correct for any possible change in the mass participating in the energetic reaction that might result from the annealing process, we performed a series of bomb calorimetry experiments to compare the heat of reaction between the asgenerated and annealed recipes. A Parr 6275 semimicro-calorimeter was used, with the same 23 mL pressure bomb sealed at ambient pressure. The non-annealed samples produced 310J of energy. The estimated mass was 54.1 mg for an energy yield of 5.74 kJ/g. The annealed samples etched at 18.44 mA/cm² in 1:1 HF/ethanol produced 294J of energy, only about a 5% difference from the as-prepared samples. Using the same estimated mass of 54.1 mg, the annealed samples produce an energy yield of 5.433 kJ/g. Fig. 1 shows a temperature versus time profile for the annealed and non-annealed samples where time T = 0 corresponds to the ignition time of the sample. Therefore low-temperature annealing in an oxygen environment can have a dramatic effect on the quantity of gas generated by the reaction with almost no effect on the net energy output.

Tuning of propagation velocity

The propagation rate of the reaction can be tailored from a fast burn (40 m/s) to one where the reaction front propagates at a velocity higher than the speed of the sound in the material. The variation in velocity as a function of the porosity of the sample has been thoroughly explored in [9]. High-speed video analysis was conducted on several samples to determine whether we can effectively tailor the reaction speed. To capture the reaction front, we etched porous silicon samples that measured 77 mm in length by approximately 10 mm in width. A monolithically integrated initiator was deposited at the very far left edge of the sample [10], and the device was wire-bonded to an electronic package. The reaction is initiated by applying voltage across the hotwire initiator. For the first case, the experiment uses a sample cleaved from a <100> oriented, boron-doped 1 to 10Ω cm silicon wafer that was etched at a current density of 18.44 mA/cm² in 1:1 HF/ethanol. We performed gravimetric porosimetry measurements on separate samples made under the same conditions and found a porosity of 67%. The sample was ignited with 3 V across the initiator, and the propagation was captured at a frame rate of 17.045 frames per second. Three consecutive frames from the video are shown in Fig. 2. The reaction propagation calculated from the video is 230 m/s.

In subsequent experiments, we initiated the hotwire with a 21 V signal to ensure ignition the first time, given the expense of high-speed videography. We have found no dependence of the propagation velocity on the voltage applied to the initiator over this range. We also used an ultra-high speed video camera, triggered using a microphone, which detects the pressure wave produced by the reaction. Fig. 3 shows the propagation velocity of



Fig. 1. Temperature versus time profile for annealed and non-annealed samples, where time T = 0 corresponds to the ignition time of the sample.



Fig. 2. High-speed frame capture at a frame rate of 17,045 frames per second showing reaction propagating at 230 m/s.



Fig. 3. Propagation velocity measurement for sample etch in 1:1 HF/ethanol showing high velocity peak.

a sample etched at 18.44 mA/cm² for 30 min in an electrolyte solution of 1:1 HF/ethanol. Based on previous volumetric analysis of the sample, the porosity is 67% and the surface area is $4.0762 \text{ m}^2/\text{g}$. The propagation event was captured at 250,000 frames per second (fps), and analyzed using an image processing GUI developed in MATLAB, which allows us to find the pixel location of the reaction front. A scale positioned beneath the sample was used to convert pixel measurements extracted from the video to m/s. For this particular sample, we see an average velocity of about 1590 m/s, with a peak velocity of 5000 m/s, which would indicate a propagation velocity greater than the speed of sound in the porous material. Fig. 4 shows the completion of the reaction front as it propagates from left to right. In this reaction, the peak velocity is seen between frames 49 and 50, as the reaction front jumps 2 cm between frames. It appears that the reaction is moving faster underneath the porous network, closest to the Si substrate.

The jump that is seen in the reaction front is most likely due to the manner in which the longitudinal wave is traveling within the porous silicon film [9]. This varies depending on the physical properties of the columnar structures formed during the anodization process. Because the porosity of these two samples is the same, we cannot deduce a direct correlation between porosity and propagation velocity. We do however observe a variation in the propagation velocity at a fixed porosity, which may indicate the dependence of propagation velocity on other factors such as ambient humidity and pore filling, and an extended timeframe (days) between experiments. More dramatic evidence of this jump can be seen in Figs. 5 and 6, where the peak is measured at 6710 m/s and a jump of 2.68 cm is seen.

To further explore the dependence of porosity on propagation velocity, additional tests were done where the porosity is varied across sample sets. One set of samples was prepared in 1:1 HF/ethanol at 105 mA for 30 min, and rinsed in pentane for 1 min.



Fig. 4. Sequence of high-speed propagation frame captures showing a 2 cm jump in the flame as the reaction front propagates from left to right.



Fig. 5. Propagation velocity measurement for sample etch in 1:1 HF/ethanol showing high velocity peak of 6710 m/s.

The porosity was 67%, with a surface area of $4.0762 \text{ m}^2/\text{g}$, and a pore diameter measuring 3.39 nm. The second sample set used in this test was formed using a texturing process, where the silicon is textured in sodium hydroxide solution at 85 °C [11]. The sample was etched in a 2:1 mixture of HF and ethanol, and the etch was tapered from 110 down to 70 mA/cm² over the course of 30 min. The associated porosity is 74.5%, with a surface area of 757 m²/g, and a pore diameter of 3.8 nm. Fig. 7, shows the dependency of the propagation speed on the porosity of the sample. Fig. 8

The propagation measurements taken under similar environmental conditions indicate that the lower porosity samples exhibited faster propagation speeds. This is consistent with the porosity and the sound velocity trend shown in [9].

Hotwire optimization

We first demonstrated ignition of the nanoporous energetic silicon using a lithographically patterned hotwire in [10]. We present here a hotwire design with smaller dimensions and improved performance. The electrical testing was done by



Fig. 6. Sequence of high-speed propagation videos showing 2.68 cm jump in the reaction front, indicating progression of the reaction underneath the silicon network.



Fig. 7. Graph showing propagation velocity as a function of porosity of the nanoporous Si.



Fig. 8. Bomb calorimeter data showing temperature versus time profile, where the ignition of the samples resulted in the production of 310J of energy.



Fig. 9. Top-down view of original design of lithographically patterned hotwire that is 25 µm wide by 500 µm long.



Fig. 10. Top-down view of original design of lithographically patterned hotwire that is $12.5 \,\mu$ m wide by $75 \,\mu$ m long.

applying a voltage across the hotwire terminals and monitoring the voltage and current with voltage and current probes connected to an oscilloscope.

The original design of the lithographically patterned hotwire was 25 μ m wide by 500 μ m long as shown in Fig. 9. The time from the onset of the 2.8 V DC applied voltage to ignition of the energetic was approximately 475 μ s. The optimized design, shown in Fig. 10, takes advantage of reducing the hotwire dimensions to improve the efficiency. We tested number of different dimensions to evaluate their performance. Fig. 11 shows the voltage and the current curve for a 15 μ m by 75 μ m hotwire with the DC power supply set to 5 V. The resistance of the hotwire was 12 ohms. The hotwire fails at the point of ignition; approximately 120 μ s after the power supply is turned on. The ignition occurred so quickly that the power supply had not yet reached the 5 V setpoint.

Another sample was tested with a 15 μ m by 125 μ m hotwire to determine the effects of increasing the length while holding the width constant. The results are shown in Fig. 12. The response time measured was approximately 88 μ s. Due to the similarity



Fig. 11. Voltage and current electrical characterization for hotwire 15 μm wide and 75 μm long.



Fig. 12. Voltage and current electrical characterization for hotwire 15 μ m wide and 125 μ m long.

between the response time of the $75 \,\mu\text{m}$ and the $125 \,\mu\text{m}$ long hotwires, and the limited quantity of samples tested, we cannot draw a correlation between the electrical performance and these two specific dimensions.

In comparison to the previously designed hotwires electrically characterized in [10], we can conclude that reducing the length of the center section does indeed lower the response time and the measured peak current, which was originally 475 μ s and 840 mA, respectively. Clearly there is an advantage in shrinking the hotwire dimensions for improved electrical performance.

Integration

In order to fully demonstrate the potential of nanoporous silicon as an energetic material, we have demonstrated monolithic integration with a MEMS sensor. We use traditional MEMS bulk micromachining tools, including standard photolithography and deposition techniques, to fabricate both the MEMS device and the energetic material in the same process run to reduce cost and increase device yield. Our goal proof of concept device is a MEMS acceleration switch, designed to close an electrical circuit and ignite the nanoporous energetic silicon upon sensing acceleration above the designed threshold. Fig. 13 shows a fully fabricated integrated system including nanoporous silicon, a hotwire initiator, and an MEMS sensor. The acceleration switch is a mass-spring design fabricated using 2-µm-thick gold structures deposited on top of a sacrificial photoresist layer. Electrical contacts are patterned underneath the mass, so that the mass itself must move a distance equivalent to the thickness of the sacrificial layer in order to make electrical contact with the pads.



Fig. 13. SEM of MEMS acceleration switch integration alongside nanoporous energetic Si.



Fig. 14. Indentations on the mass of the acceleration switch, showing presence of dimples to reduce contact resistance.



Fig. 15. Electrical discontinuity between the device and the energetic due to delamination.

The energetic region on the chip is a nanoporous layer of 2 mm diameter. The device consists of 1° of freedom with out-of-plane motion. In order to integrate both devices during the same processing sequence, we first fabricate the MEMS acceleration switch and then protect the device using a polymer-like material that is resistant to the HF electrochemical etchant. Once the anodization process is complete, we remove the polymer protective layer from the device and finally release the mass-spring structures on the wafer.

Our initial fabrication run resulted in a device yield of ~30%, due to adhesion problems between the protective polymer and the nitride film. The surviving devices had very poor contact resistance, on the order of several M Ω . Because of this, we were unable to ignite the nanoporous energetic silicon through the acceleration switch. We later applied NaClO₄ to the nanoporous silicon to ensure that the sample would ignite after being subjected to post-etch processing. We successfully ignited the sample using a spark as our ignition method. To reduce the contact resistance, we attempted to incorporate dimples in our mass, shown in Fig. 14, which would increase the contact force between the mass and the bottom electrical contacts. Further optimization of the dimple structures is still needed to minimize the contact resistance.

Further evaluation of the MEMS contact switch indicates potential adhesion problems and delaminating of the contact metals. The device is fabricated on an LPCVD nitride wafer, which is then patterned to open up windows in silicon to allow for the electrochemical etch of the nanoporous silicon. The MEMS device is situated directly on the nitride layer. Fig. 15 shows delamination of the hotwire from the contact pad located on the MEMS accelerometer. To eliminate the problems associated with low-device yield and delaminating films, we have redesigned the device mask to allow for the mass-spring structure and contact pads to be patterned directly on a silicon substrate, rather than having the structure sitting on a nitride film. The results from this fabrication run are pending.

Conclusions

Silicon has moved into a new and ever evolving design space, where it holds great potential in merging electrical, mechanical, optical, and fluidic physics with energetics on the same platform. We have demonstrated some ability to tune the propagation rate of the exothermic reaction that appears to have an inverse correlation with sample porosity. We have shown electrical characterization of an improved fully integrated hotwire, with ignition occurring as quickly as 88 µs at currents as low as 80 mA. We have also provided a proof of concept for monolithic integration of energetic silicon with on-chip sensing and actuation mechanisms.

References

- [1] P. McCord, S.-L. Yau, A.J. Bard, Science 257 (1992) 68-69.
- [2] M. du Plessis, Materials Science and Engineering B 147 (2008) 226-229.
- [3] D. Clement, J. Diener, E. Gross, N. Kunzner, V. Yu Timoshenko, D. Kovalev, Physica Status Solidi (a) 202 (8) (2005) 1357-1364.
- [4] W. Churaman, L. Currano, A.K. SinghU.S. Rai, M. Dubey, P. Amirtharaj, P.C. Ray, Chemical Physics Letters 464 (2008) 198–201.
- [5] D. Bellet, Drying of porous silicon, in: L. Canham (Ed.), Properties of Porous Silicon, INSPEC, London, 1997, pp. 38–43.
- [6] A. Grosman, C. Ortega, Chemical composition of 'fresh' porous silicon, in: L. Canham (Ed.), Properties of Porous Silicon, INSPEC, London, 1997, pp. 145–153.
- [7] L. Currano, W. Churaman, C. Becker, Proceedings of the Transducers, Denver, CO, June 21–25, 2009, pp. 2172–2175.
- [8] A. Halimaoui, Porous silicon formation by anodisation, in: L. Canham (Ed.), Properties of Porous Silicon, INSPEC, London, 1997, pp. 12–22.
- [9] H.J. Fan, M.H. Kuok, S.C. Ng, R. Boukherroub, J.-M. Baribeau, J.W. Fraser, D.J. Lockwood, Physical Review B 65 (2002) 165330-1–165330-8.
- [10] L. Currano, W. Churaman, Journal of Microelectromechanical Systems 18 (4) (2009) 799–807.
- [11] S. Sharma, R.K. Sharma, G. Bhagavannarayana, S.B. Samanta, K.N. Sood, S.T. Lakshmikumar, Materials Letters 60 (2006) 1166–1169.