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The Effects of Storing Porous Silicon Produced from Magnesium Silicide (Mg_2Si) in Inert Gas and Ambient Air

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14. ABSTRACT Porous silicon was synthesized by reacting magnesium silicide with aluminum chloride. Samples were aged separately under both nitrogen gas and ambient air for up to 29 days. No discernable change was observed for the sample stored in nitrogen when analyzed by X-ray diffraction, Fourier transform infrared spectroscopy, and thermogravimetric analysis while the sample stored in air had increased oxidation and silicon–hydrogen bond loss. Energetic performance for the sample stored in nitrogen was 880 m/s while the sample stored in air failed to propagate when ignited.					
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1. Introduction

The reaction between porous silicon (pSi) and sodium perchlorate (NaClO_4) has produced flame speeds recorded up to 3000 m/s upon ignition for on-chip devices due to the high porosity and small average pore size of pSi.¹ Traditionally, pSi has been produced by anodic-etching of p-type silicon (Si) wafers. With the relatively high flame speed of pSi compared with other energetic materials, a powder form of pSi is desirable for expanded use; however, the cost of p-type wafers is a significant limitation. Previously, pSi when prepared from the reaction between magnesium silicide (Mg_2Si) and aluminum chloride (AlCl_3) was shown to be a scalable and low-cost alternative to anodic etching of p-type wafers.² The energetic performance of pSi particles produced from Mg_2Si is comparable to pSi particles produced by anodic etching of p-type Si wafers (906 ± 63 m/s vs. 969 ± 14 m/s for pSi from Mg_2Si and pSi from anodic etching, respectively) and could open potential applications to larger propellant and explosive formulations.

Despite relatively similar flame average speed rates, the particles produced from Mg_2Si were more susceptible to oxidation compared to the anodically etched particles, likely due to their smaller size. This raises the question of whether or not pSi produced from Mg_2Si will have long-term stability when stored under inert conditions and what the effects of ambient air exposure are. Degradation of the hydrogen surface termination could be detrimental to the energetic performance when combined with an oxidizer and ignited.³

This technical report details the surface functionalization, oxide content, crystallinity, and energetic performance of pSi produced from Mg_2Si after extended storage in both ambient air and inert gas.

2. Experimental

2.1 Porous Si from Mg_2Si and AlCl_3

A modified synthesis method was followed from a previous report.⁴ The minor impurities of the bulk Si in the Mg_2Si starting material were not considered to have an impact on the study, thus the material was used as is. Powders of 0.367 g (4.79 mmol) of Mg_2Si (99.9%, Alfa Aesar), 10.85 g (81.4 mmol) of AlCl_3 (Alfa Aesar, 99.985%), and 2.38 g (40.7 mmol) of sodium chloride (NaCl) (99.9% previously dried at 300 °C, Fisher Scientific) were combined into a 80-mL hardened steel ball mill cup with ten 1-cm hardened steel balls for a ball-to-powder ratio of 10:1. The cup was sealed with a Viton O-ring and lid, and then sealed additionally

with electrical tape to help prevent air and moisture from contaminating the contents.

The materials were lightly milled for 30 min at 200 rpm, after which the cup was brought back into the dry box and the contents were removed. Then, 13 g of the powder were transferred into a round bottom flask and sealed with a rubber septum.

The contents were placed under a flowing argon stream through the flask septum with a needle to ensure any generated pressure would not dislodge the septum from the flask and expose the contents to air atmosphere. The flask was then submerged in an oil bath, preheated to 125 °C, to allow the AlCl₃ and NaCl contents to become molten. After the contents were liquid, the stir plate was turned on to mix the reactants for 5 min. Then, the flask was removed from the oil bath and let to cool naturally.

The flask was then placed into an ice bath, and 200 mL of degassed methanol (99.8%, Fisher Scientific) was added to the flask and stirred until gas ceased to evolve. Ten milliliters of concentrated hydrochloric acid (VWR Life Science) were added and stirred for an additional 10 min.

The sample was recovered by vacuum filtration and then placed into 150 mL of degassed H₂O and agitated by sonication for 30 s to dissolve the remaining salts, and then recovered immediately by vacuum filtration and further washed with methanol. The product was dried under dynamic vacuum and stored in a nitrogen (N₂)-filled drybox until further use.

2.2 Environment Exposure Time Study

The dried pSi powder was halved by mass and stored in different conditions. Half of the sample was stored in an N₂ drybox (<1 ppm oxygen [O₂] and H₂O) and the remaining half was stored in ambient atmosphere on a benchtop at 23 °C and approximately 30% relative humidity. Initial data were collected at day 1, including powder X-ray diffraction, thermal gravimetric, and Fourier transform infrared (FTIR) spectroscopy analysis. Subsequent data were collected at day 4, 7, 12, 19, 26, and 29.

2.3 Power X-Ray Diffraction

Powder X-ray diffraction patterns were collected for the samples on a Bruker D2 Phaser X-ray diffractometer. Copper was used as the X-ray source with a nickel filter (CuK α λ = 1.5406 Å). Patterns were obtained using an Si low = background sample holder from a continuous scan of 8 s per step and a step width of 0.1° 2 θ .

2.4 Thermal Gravimetric Analysis

Thermogravimetric oxidation measurements were collected on a PYRIS 1 thermogravimetric analyzer (Perkin Elmer) using a platinum crucible. Samples were heated from 30 to 1000 °C at 20 °C/min.

2.5 Fourier Transform Infrared Spectroscopy

Infrared absorption spectra were collected on a Spectrum One (Perkin Elmer) using a molecular liquid N₂ cooled mercury–cadmium–telluride detector in attenuated-total-reflection mode on a diamond reflection crystal.

2.6 Flame Speed Tests

Flame speed measurements were performed by placing a small quantity (5 mg) of pSi powder into a 3-D-printed trench with a cavity measuring 20 mm × 1.5 mm × 1 mm. The trench was then placed into a N₂-containing chamber with a nichrome (NiCr) wire embedded into the pSi powder at one end of the trench. Enough oxidizer (3.2 M sodium perchlorate in methanol) was added to the trench to saturate the pSi powder and was dried for 15 min under N₂ flow in the chamber. Ignition was triggered by a 4-A square wave current pulse (0.100 s) delivered from a Quantum Composers 9730 series pulse generator with the trigger signal split to a Photon FASTCAM SA5 to record the ignition. Flame speed measurements were performed using ImageJ (www.imagej.net) by measuring the flame propagating along the trench gap opening with respect to the time evolved per ensuing frame recorded. Camera data were recorded at 192 × 32 pixels at a frame rate of 500000 s⁻¹.

3. Results and Discussion

The region of interest for the powder X-ray diffraction pattern pSi powder from Mg₂Si consisted of a broad peak from 18 to 30° 2θ. The sample is mostly amorphous or has no long-range crystalline domains but a sharp peak occurring at 28.44° 2θ, which was determined to be a crystalline Si “impurity” from the Mg₂Si starting material, non-appreciable to approximately 1% of its total mass. There was no large change in the diffraction pattern for the pSi when stored in a N₂ for 29 days (Fig. 1). The diffraction patterns for the sample exposed to ambient air in the laboratory revealed a gradual peak shift to lower angles with the pattern’s intensities normalized to the crystalline Si peak (Fig. 2). After only 4 days of air exposure, a significant shift in the peak position occurred from approximately 25° to 22° 2θ. This indicates the sample has oxidized. The low-angle peak for nano

silicon dioxide (SiO_2) broadly appears between 20° and 25° 2θ representing the (100) reflection of silica.⁵ Visually, the color of the sample changes gradually from a reddish brown to a light brown. The high-surface-area pSi is highly susceptible to oxidation when stored in ambient air.

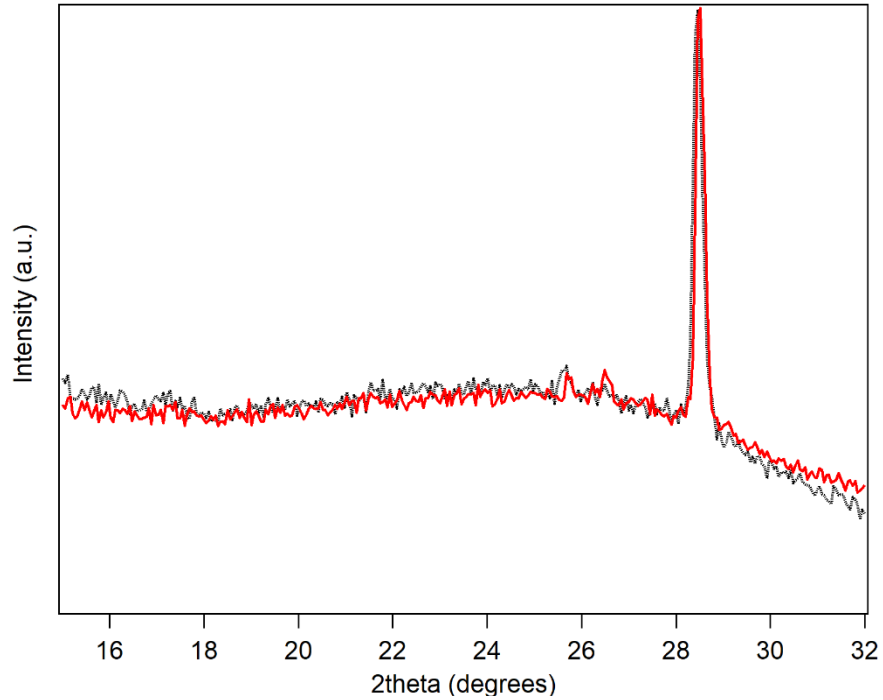


Fig. 1 Powder X-ray diffraction patterns for pSi stored in N_2 after (black) 1 day and (red) 29 days

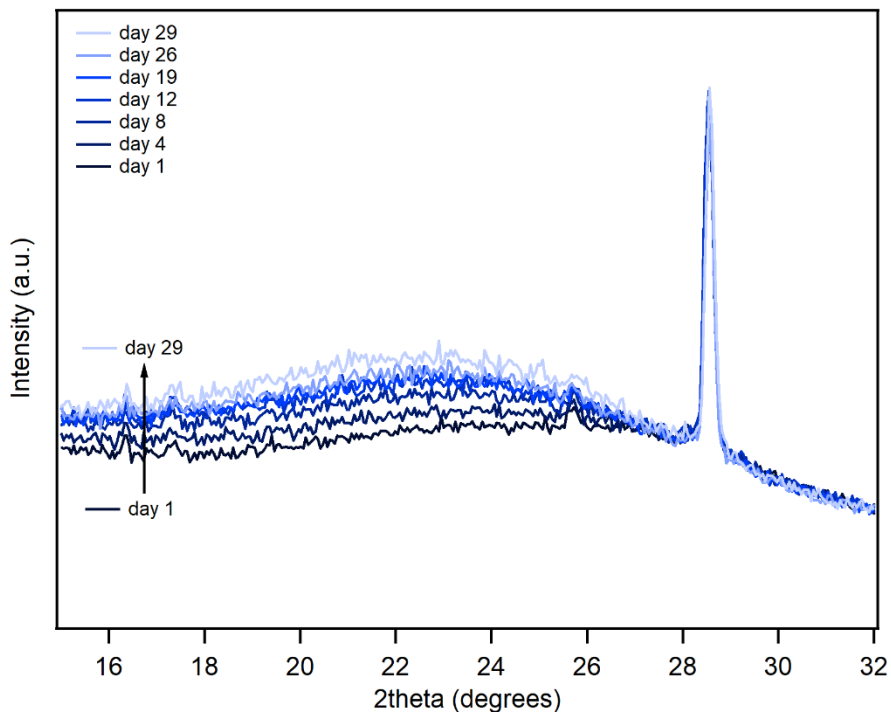


Fig. 2 Powder X-ray diffraction patterns for pSi stored in ambient air. The day of scan progresses upward from (black) day 1 to (light blue) day 29, as indicated on the plot.

The FTIR pattern for the pSi as synthesized consisted of Si–hydrogen (H) bonding present at approximately 625 cm^{-1} attributed to Si–H bending, at approximately 660 cm^{-1} attributed to Si–H wagging, and at approximately 2100 cm^{-1} attributed to Si–H stretching; and Si–H–O back-bond oxidation at approximately 2250 cm^{-1} attributed to $\text{O}_3\text{–SiH}$ stretching, Si–O bending at approximately 880 cm^{-1} , and Si–O stretching between 1000 and 1200 cm^{-1} . The S–H bonding is presumed to form during the removal of aluminum when significant amounts of molecular H_2 evolved. As synthesized, some oxidation of the sample is largely unavoidable when salt is removed from the raw product during washing.

By this synthesis method, there is still an appreciable amount of S–H bonds present on the powder surface (Fig. 3). After 29 days of sample storage in a N_2 , the FTIR pattern remains unchanged. Conversely, the sample stored in ambient air for 29 days saw a reduction in the Si–H bonding in the wavenumber regions between 620 and 670 cm^{-1} and at 2100 cm^{-1} .

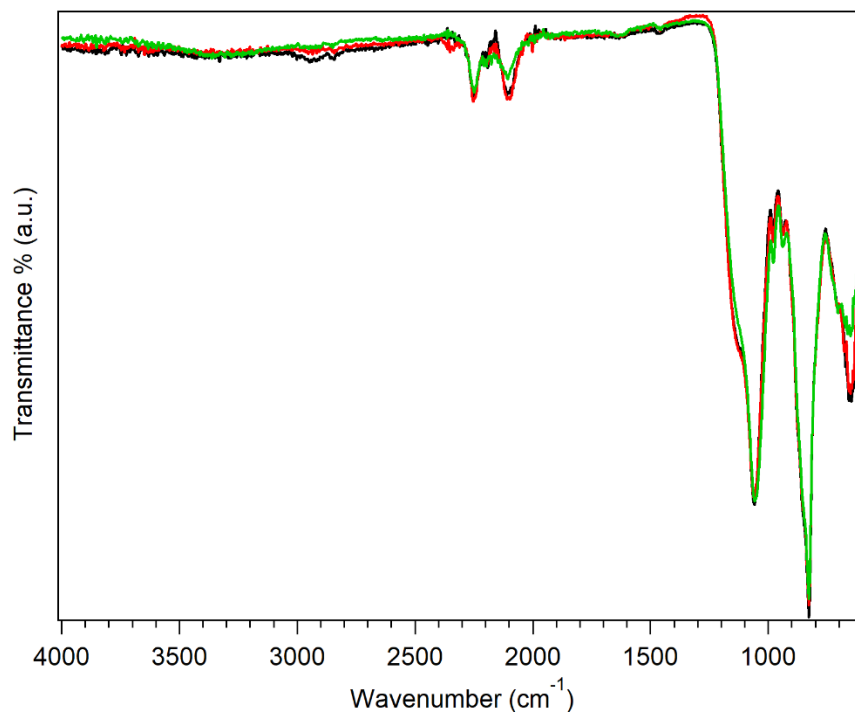


Fig. 3 FTIR spectra for (black) freshly prepared pSi, (red) pSi stored in N₂ for 29 days, and (green) pSi stored in ambient air for 29 days

Thermogravimetric analysis was used to determine the amount of oxide present prior to heating using the final mass gain value. A fully oxidized sample would not have a mass increase, while the mass of an unoxidized sample would increase 2.14 times (214% from 100%). Partially oxidized Si would exist as $\text{Si}_x + (\text{SiO}_2)_{1-x}$ ($0 \leq x \leq 1$).

Both samples, freshly prepared, had an identical mass gain of 1.44 times the original mass giving the stoichiometric equivalent of $\text{SiO}_{0.85}$. After 4 days, the stoichiometric ratios between Si and O were $\text{SiO}_{0.95}$ and $\text{SiO}_{0.83}$ for storage in ambient air and N₂ atmosphere, respectively (Fig. 4). The sample stored in air continued to oxidize. At day 29 of air storage, the ratio was $\text{SiO}_{1.15}$, which is a significant increase in oxide content and corroborates the data collected with the X-ray diffractometer.

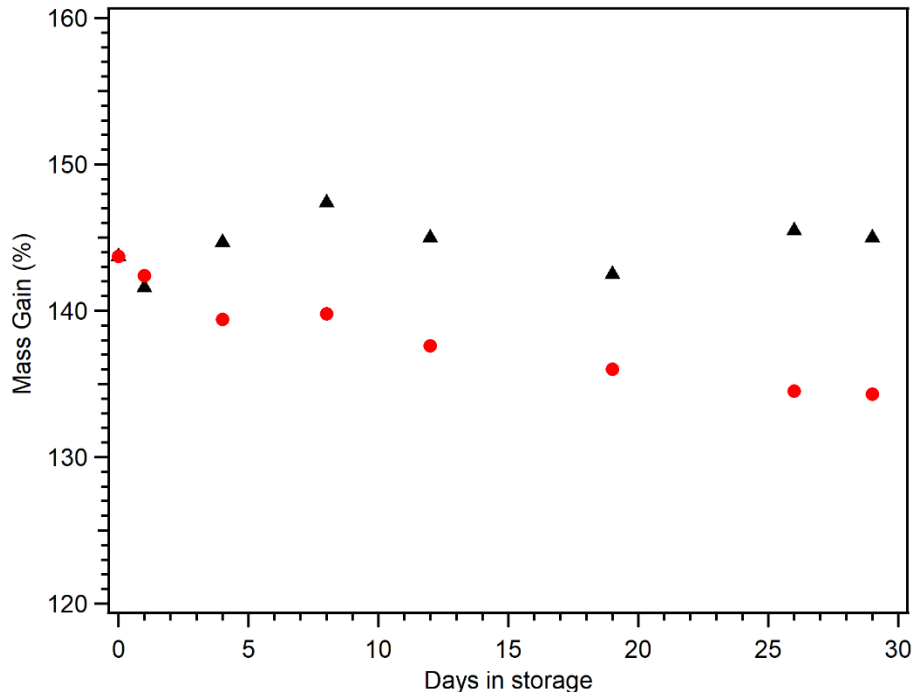


Fig. 4 Mass change from 100% on a thermogravimetric analyzer heated when stored in (red) air and (black) N₂

Flame speed tests were initiated by heating a NiCr wire that was embedded into the pSi powder prior to adding the oxidizer. A stock reference photo was taken for each test to determine the pixel-to-distance ratio of 7.4 pixels/mm. The flame propagation for pSi from Mg₂Si was recorded at 1.9- μ s intervals with the frame containing the first visible light set as 0 μ s (Fig. 5). Velocity measurements were calculated using the slope of the propagation data from the flame speed front pixel location versus time (Fig. 6). A flame speed was measured at 880 m/s for pSi powder stored after 29 days of storage in N₂ atmosphere. The sample stored in air after 29 days failed to ignite and propagate, likely due to excessive oxidation and Si-H bond loss.

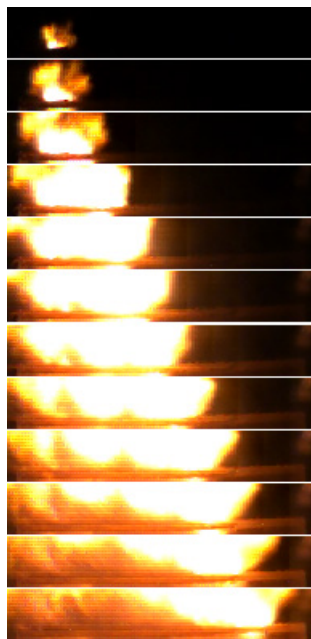


Fig. 5 Flame propagation frame captures (1.9 μs) for pSi after 29 days stored in N_2 then oxidized with sodium perchlorate and ignited

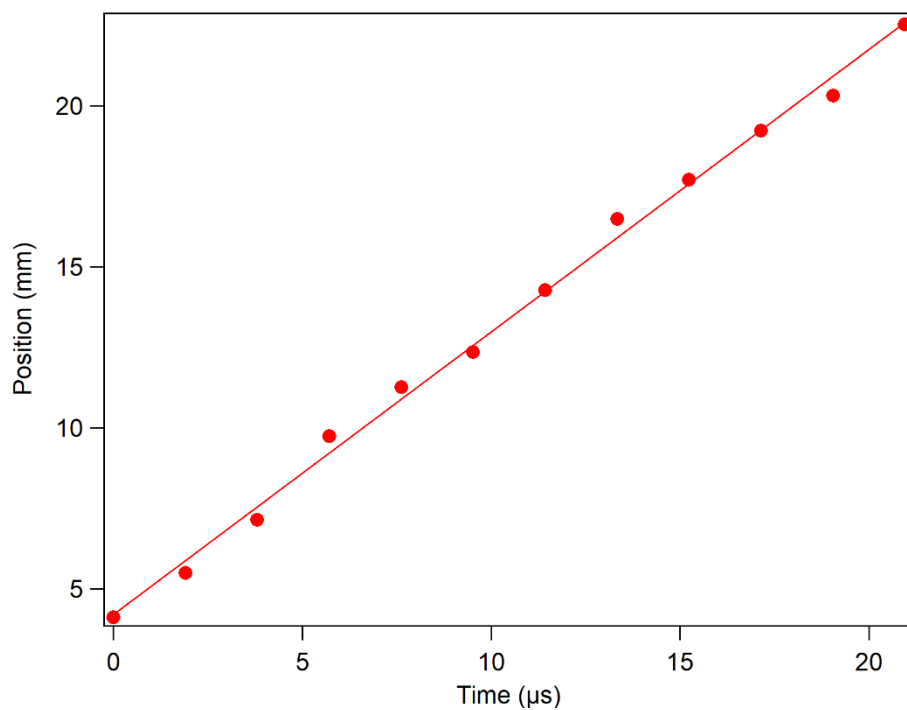


Fig. 6 Flame-speed velocity calculation for pSi from Mg_2Si after 29 days of storage in N_2

4. Conclusion

Powder X-ray diffraction, FTIR, and thermogravimetric analysis data showed that pSi prepared from Mg₂Si stored under N₂ for at least 29 days at less than 1 ppm O₂ and H₂O did not change and was still energetic when oxidized with sodium perchlorate and subsequently ignited. The flame speed measurement was 880 m/s, a value within the standard deviation of the average flame speed previously reported for pSi from Mg₂Si.¹ Storing the sample in ambient air caused an increase in oxide mass and a reduction in the S–H bond quantity, thus inhibiting its ability to ignite and propagate. Minor (ppm) O₂ and H₂O impurities, which are often present in some inert gas sources, could cause oxidation when stored on the order of years. Further studies on long-term storage (years), and in dry air and under vacuum are encouraged.

5. References

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List of Symbols, Abbreviations, and Acronyms

AlCl ₃	aluminum chloride
FTIR	Fourier transform infrared spectroscopy
H	hydrogen
H ₂ O	water
Mg ₂ Si	magnesium silicide
NaCl	sodium chloride
NiCr	nichrome
O	oxygen
pSi	porous silicon
Si	silicon
SiO ₂	silicon dioxide

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