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Standard Operating Procedure for On-Chip Porous Silicon Surface Functionalization

by Nathan A Banek and Wayne A Churaman

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14. ABSTRACT
A standard operating procedure for a Schlenk line, degassing solvents by the freeze–pump–thaw method, and porous silicon (pSi) functionalization is detailed. On-chip pSi devices were prepared by anodic etching in 3:1 hydrofluoric acid: ethanol (v/v) solution and subsequently functionalized with 1-octene by thermal hydrosilylation. The chips demonstrated good protection from ambient air moisture.

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Contents

List of Figures

1. Introduction

Porous silicon (pSi) research has received much attention for its potential use in a variety of applications including sensors, imaging, biological drug delivery, antireflective coatings, lithium-ion battery anodes, and energetic materials.[1–6] One of the most common ways to produce pSi is through galvanic or anodic etching in fluorinated electrolytes.[7] Specifically, when using 3:1 hydrofluoric-ethanol solutions, etching p-type wafers ($<1 \times 10^{-2}$ Ω cm) at low current density ($<1 \times 10^{2}$ mA/cm^2) produces pSi with surface area up to 800 m^2/g and porosities up to 70% with pore sizes ranging from 3 to 4 nm.[8] A byproduct of the etching process in hydrofluoric acid is an H-terminated silicon surface. This termination renders the surface predominantly hydrophobic; however, because the hydrogen is susceptible to hydrolysis it is not a strong barrier against long-term ambient moisture exposure. The hydrogen on the surface can be substituted for other hydrophobic molecules by oxidative addition of silicon-hydride (Si-H) across an unsaturated carbon bond—known as hydrosilylation—which has been shown to protect the silicon surface from moisture.[9] The hydrosilylation process has been demonstrated by methods including photo, thermal, and catalytic initiation. Commonly used compounds include alkyl groups of 8–12 carbons in length. Of interest to on-chip pSi energetic devices, these nonpolar and hydrophobic molecules attached to the silicon surface could prevent unwanted moisture exposure during long-term storage. This technical report establishes the standard operating procedure for operating a Schlenk line including the freeze–pump–thaw technique to degas solvents and how to perform pSi functionalization chemistry. Bolded words in text refer to objects highlighted in figures. The operating procedure was followed for a pSi functionalization experiment. This report is designed to assist scientists who have no previous Schlenk experience.

2. Standard Operating Procedures

2.1 Equipment

2.1.1 Vacuum Pump

The vacuum pump, or roughing pump, achieves a vacuum of 10^{-3} Torr. It is typically used alone or as a first stage to an ultrahigh vacuum setup. The pump oil should be changed every 3–6 months depending on the frequency of pump use. Never expose the vacuum to solvents without using a liquid nitrogen trap.

2.1.2 Schlenk Line

The dual-manifold vacuum line is often referred to as a Schlenk line. It allows for air-free synthesis by utilizing an inert gas flowing through one manifold and exhaust to vacuum through the other. The ports are connected with adapters and grease-free Teflon O-rings. The inert gas exit port is fed through an oil bubbler to maintain positive pressure to prevent unwanted air from entering the line.

2.2 Schlenk Line Operation

2.2.1 Start-Up

1) Assemble **VACUUM TRAP** to the Schlenk line vacuum manifold and ensure vacuum pump is properly exhausted into a hood.

2) Confirm that all **MANIFOLD PORT** valves are closed on the vacuum manifold.

3) Connect the vacuum hose to **VACUUM VALVE** and open the valve to the Schlenk **VACUUM TRAP**.

4) Turn on vacuum pump to evacuate manifold and trap until a minimum value is obtained on the vacuum gauge.

5) Situate the Dewar on a mechanical lift with the trap sheathed by the Dewar. Fill the Dewar with 4 L of liquid molecular nitrogen (N_2) and raise Dewar to top of the trap. Wait 5 min for a vacuum to stabilize. Vacuum gauge pressure should read <100 mTorr.

6) (IMPORTANT) Check for vacuum leaks by closing off the **VACUUM VALVE** and look for a rise in pressure on the gauge that would represent a vacuum leak. If a leak is present, ensure the **VACUUM VALVE** is closed, lower the Dewar, vent the line using a **MANIFOLD PORT** valve, wait for the trap to come to room temperature, and reconnect any hardware that you suspect may have a poor connection.

7) If no leaks are present, open the **INERT GAS INLET VALVE** and ensure all inert gas **MANIFOLD PORT** valves are closed. There should now be a free pathway from **INERT GAS INLET** to **INERT GAS OUTLET** to **BUBBLER**.

8) Slowly open the inert gas supply valve to the Schlenk **INERT GAS INLET VALVE**. Monitor the flow rate to the **BUBBLER**. Adjust for flow rate to 1–2 bubbles evolved per second out of the inert gas manifold. Let the manifold purge with inert gas for 15 min. See Fig. 1 for the Schlenk/vacuum line setup.

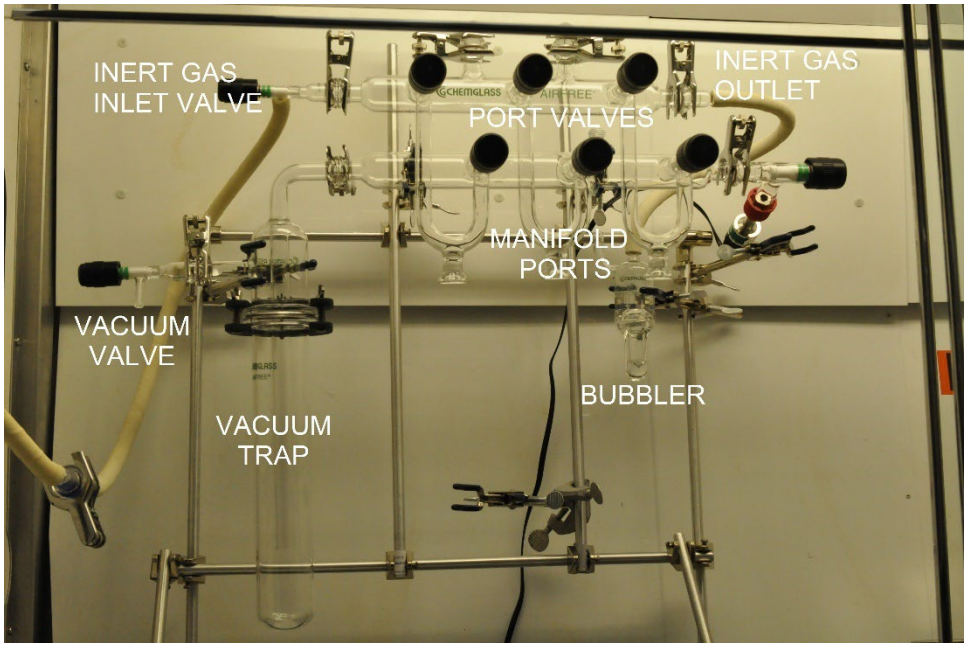
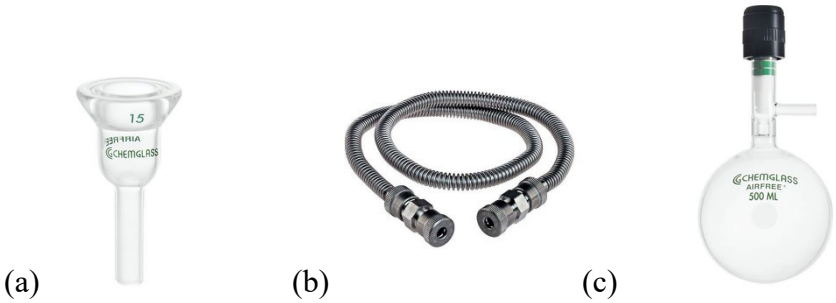


Fig. 1 Schlenk/vacuum line setup

2.2.2 Freeze–Pump–Thaw Technique for Degassing Solvents

1) Fill the round-bottom flask *no greater than half-full* of the desired solvent to degas. If the flask is greater than half-full, it *will* crack when the solvent begins to melt.

2) Attach a connecting adapter (Fig. 2a) to a **MANIFOLD PORT** and use a Cajon ultra-Torr hose (Fig. 2b) to connect the adapter to a Cajon style round-bottom flask (Fig. 2c). The final assembly should appear as in Fig. 3.



(a) (b) (c)

Fig. 2 Schlenk line attachments: (a) Cajon ultra-Torr hose, (b) connecting adapter, and (c) round-bottom flask with Cajon-style inlet

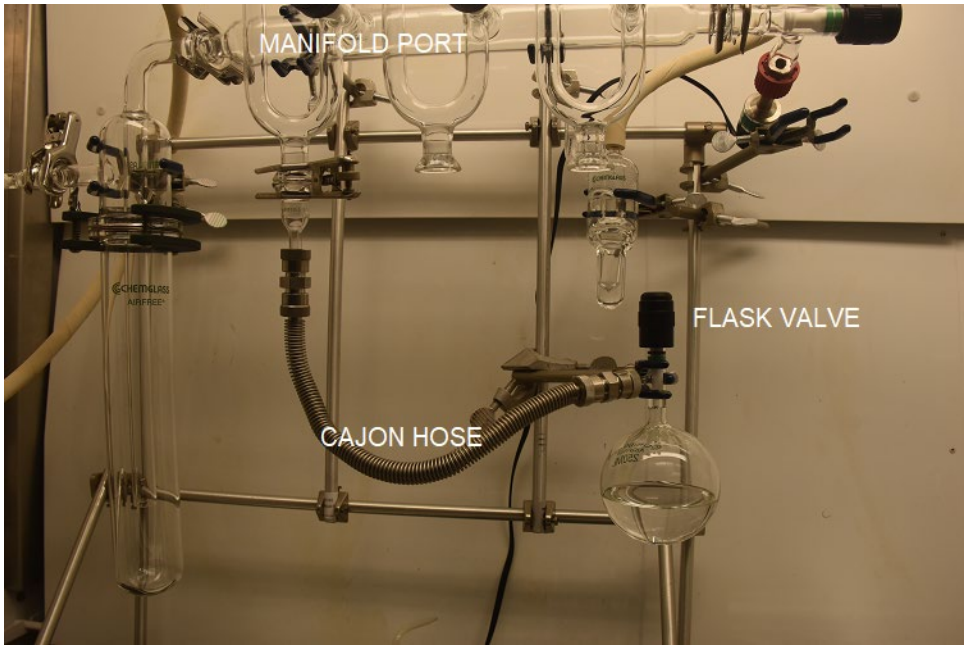


Fig. 3 Storage flask connected to a Schlenk line using a Cajon hose

3) Confirm that the round-bottom **FLASK VALVE** is closed and open the vacuum **MANIFOLD PORT** valve to evacuate the air up to the **FLASK VALVE**.

4) Submerge the flask in a Dewar of liquid nitrogen, a dry ice/isopropyl alcohol bath, or an ice bath contingent on the solvent's freezing temperature.

5) Wait for the solvent to completely freeze, which typically takes 15 min or more.

6) Slowly open the **FLASK VALVE** to evacuate the headspace and continue pumping for 5 min.

7) Close the **FLASK VALVE**, remove the flask from the liquid nitrogen bath, and submerge the flask in a bath of isopropanol to melt the solvent.

8) As the solvent melts, gas bubbles should be evolving to the flask headspace.

9) When the solvent has completely melted, repeat steps 3–7 two more times.

10) If desirable, back flush the round-bottom flask with inert gas from the Schlenk for immediate use.

2.2.3 Porous Silicon Functionalization Procedure

1) Secure a **CONDENSER** to a ring stand and insert it into a **DUAL-NECK ROUND-BOTTOM FLASK** situated in a **HEATING MANIFOLD**.
2) Attach a **24/40 CONDENSER CONNECTOR** to the top of the **CONDENSER**.
3) Attach a rubber hose from the **CONNECTOR** to the Schlenk manifold.
4) Place the pSi chip or powder in the bottom of a **DUAL-NECK ROUND-BOTTOM FLASK**; seal the flask with a rubber septum.
5) Confirm that the respective inert gas **MANIFOLD PORT** valve is closed. Evacuate the **CONDENSER** and **DUAL-NECK ROUND-BOTTOM FLASK** by opening the vacuum **MANIFOLD PORT** valve.
6) After a minimum vacuum is obtained, close the vacuum **MANIFOLD PORT** valve and open the respective inert gas **MANIFOLD PORT** valve to flush the **CONDENSOR** and **DUAL-NECK ROUND-BOTTOM FLASK** with inert gas.
7) Repeat steps 5 and 6 two more times.
8) To transfer solvent from the **STORAGE FLASK**, connect the flask to the connecting adapter on the **MANIFOLD PORT** using the Cajon hose.
9) Evacuate the line up to the **STORAGE FLASK** valve and back flush the line with nitrogen gas.
10) Under flowing N_2 gas remove the valve from the solvent storage flask so that inert gas is flowing out of the flask where the valve was removed.
11) Use a graduated syringe to extract the desired amount of solvent and transfer to the dual-neck round-bottom flask through the septum. Seal the storage flask.
12) Under an inert atmosphere, heat the solvent to reflux for a desired amount of time. Figure 4 shows the solvent reflux reaction under inert gas using a condenser.

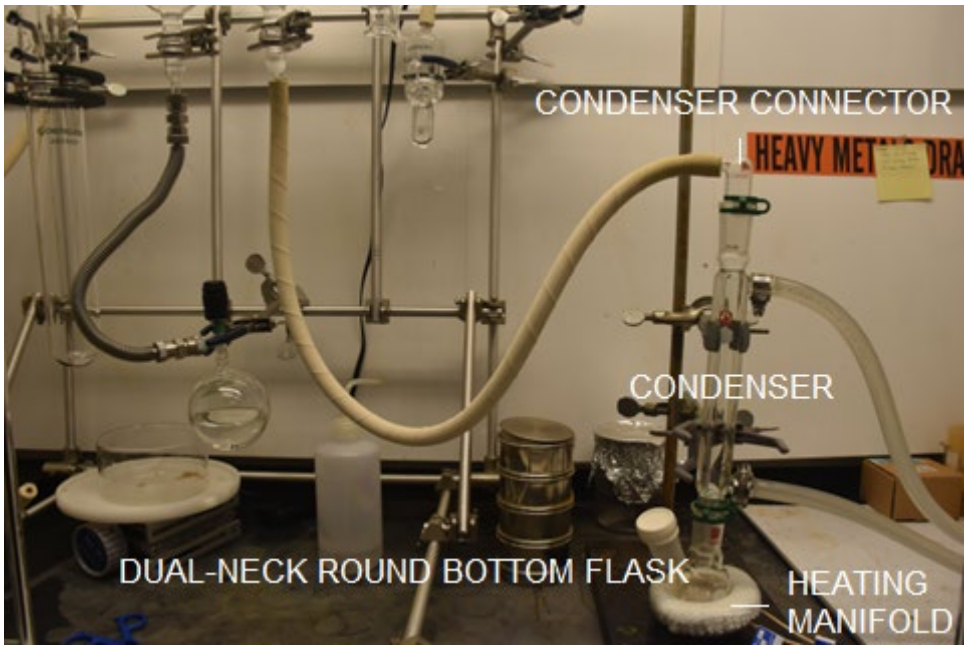


Fig. 4 Solvent reflux reaction under inert gas using a condensor

3. Experimental

Prior to use, 1-octene was let stand on 3-Å molecular sieves for 72 h to remove traces of water and 200 mL of 1-octene (99+%, Thermo Scientific) were transferred to a 500-mL air-free round-bottom storage flask (Cajon connector, Chemglass). The flask was connected to a Schlenk manifold and then submerged in liquid nitrogen until the solvent solidified. The gas-occupied headspace was evacuated by vacuum (10^{-3} Torr) under dynamic vacuum. The flask was backfilled with nitrogen gas, removed from the liquid nitrogen, and placed in a shallow isopropanol bath to melt the 1-octene. The freeze–pump–thaw process was repeated two more times to ensure the gas was removed; then, the headspace was filled with inert nitrogen for further use.

A 4-inch {100} p-type silicon wafer, platinum-backed (170 nm), was masked with silicon-nitrogen to expose an array of 2-mm-diameter silicon islands for a total silicon surface area of 10.94 cm^2. Gold bridge wires were patterned on the devices prior to etching. The wafer was put into a Teflon etching holder with aluminum foil in contact with the platinum back. The power supply leads were connected to a platinum mesh (anodic) and the aluminum foil (cathodic). A current density of 18 mA/cm^2 was applied for 25 min. The wafer was washed thoroughly with methanol and dried under a gentle nitrogen gas stream. The etch depth was

determined to be approximately 30 μm measured with a stereoscope.[*] The wafer was then stored under dry nitrogen for 24 h.

The dried wafer was scribed by hand using a tungsten carbide scribe and cleaved into chips consisting of 4 × 5 devices (~16 × 20 mm); the size was chosen based on the ability to fit in a 24/40 round-bottom glass joint. A 4 × 5 device chip was placed into a 50-mL double-neck round-bottom flask equipped with a condenser, and then a septum was connected to seal the contents to the Schlenk line. The flask atmosphere was purged and backfilled with nitrogen three times. Five milliliters of the octene were transferred to the flask using a graduated syringe. Chips were heated under 1-octene reflux (boiling point 121 °C) for 2 and 4 h. After letting cool naturally, the chips were removed and rinsed with toluene, dried under a nitrogen stream, and stored in an N_2 dry box.

4. Results and Discussion

Porous silicon chips were analyzed by Fourier-transform infrared (FTIR) to determine the degree of functionalization and their moisture resistance (Fig. 5). After 2 h of treatment, an FTIR scan revealed characteristic peaks between 2856 and 2960 cm^{-1} for carbon-hydrogen (C-H) stretching from alkyl surface termination as a result of treatment with 1-octene. Silicon-hydrogen bonding around 2100 cm^{-1} was not present; however, some back bond oxidation appeared at 2250 cm^{-1}. There was a broad absorption peak at 3400 cm^{-1}, which is characteristic of hydroxyl surface termination groups and a broad peak around 1600 cm^{-1} that would represent moisture. After 4 h of treatment, surface hydroxyl absorption was observed as significantly reduced. The C-H stretching was present between 2856 and 2960 cm^{-1}, no Si-H or Si-H-O bonds were present and the OH stretch was minimal, supporting that the longer reflux time improved surface moisture oxidation resistance through additional hydrophobic functional groups.

[*] Nikon SMZ 1000, Leica.

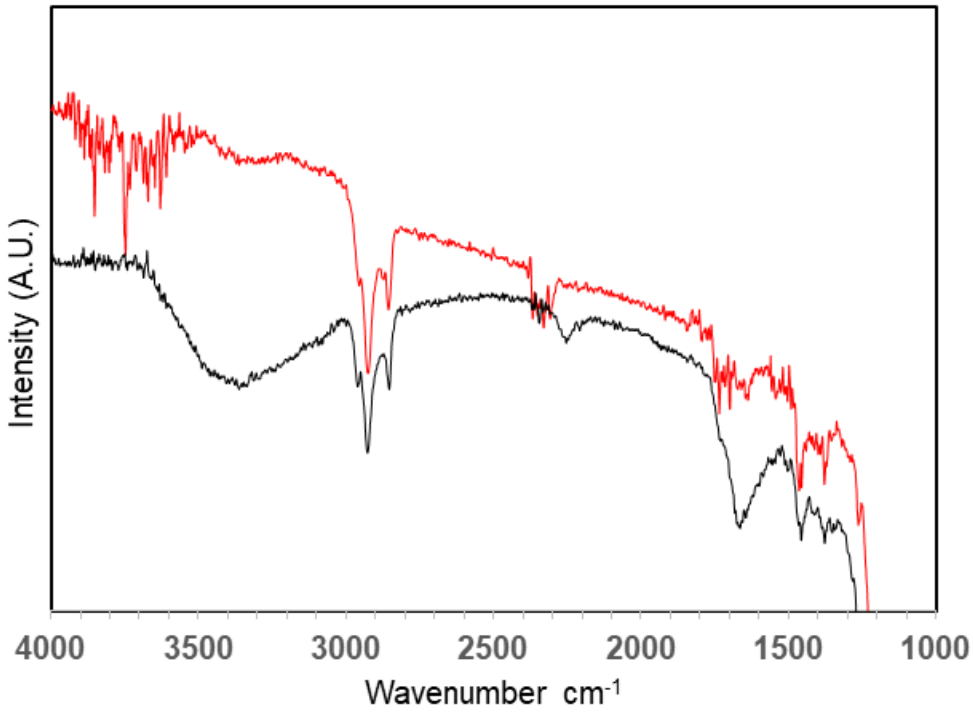


Fig. 5 FTIR absorption spectra of a pSi wafer treated in 1-octene for 2 h (black) and a pSi wafer treated in 1-octene for 4 h (red)

5. Conclusion

The surface of anodically etched pSi was functionalized with 1-octene by thermal hydrosilylation under reflux in inert atmosphere. Four hours of treatment time was determined to be superior to 2 h of treatment time when the surface was analyzed by FTIR. The surface was shown to have improved resistance to ambient moisture and oxidation. Readers should be able to reproduce this process using the detailed standard operating procedure and experimental steps.

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