

Silicon Phononic Crystals for High Efficiency Thermoelectrics

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Abstract:

Thermoelectric materials can generate an electric current in response to an applied temperature gradient (Seebeck effect), or cause cooling in response to an applied current (Peltier effect). For thermoelectrics to be useful in application, higher efficiencies must be attained. This project focused on developing phononic crystals with a feature size of roughly 20 nanometers, utilizing a phononic band gap to decrease thermal conductivity, in order to achieve never before attained thermoelectric efficiencies.

Introduction:

Thermoelectrics devices can use a temperature gradient to produce an electric current. The effectiveness of these devices is often measured by the dimensionless figure of merit, ZT , as described by this equation:

$$ZT = \frac{S^2 \sigma}{\kappa} T$$

For thermoelectric devices to become commercially viable, ZT needs to be three times larger, ($ZT > 3$) than is currently available in the best thermoelectric materials. To accomplish this, the electrical (σ) and thermal (κ) conductivities must be varied independently, which is challenging since they are interdependent in bulk materials. The proposed method for decreasing thermal conductivity without impacting electrical conductivity was the use of nanostructured phononic crystals. Phononic crystals are materials that are created with periodic variations, which allow for the presence of a phononic band gap. A phononic band gap is a region of frequencies in which phonons are impeded or stopped from moving through the crystal, which decreases lateral heat transfer. A phononic band gap in the terahertz (THz) range will decrease thermal conductivity without affecting electrical conductivity. To accomplish this effect, periodic holes 10-50 nm in size needed to be created—much smaller than holes in previous phononic crystals [1]. Block copolymers could create an array with this feature size due to phase separation. The two polymers polystyrene and poly(methyl methacrylate) or PS/PMMA that were investigated, separate into periodic rods, 20 nm in diameter [2]. This template, with a wet etch process, should allow for the small feature diameters and high aspect ratios required for phononic crystals with hole depths in the micron range.

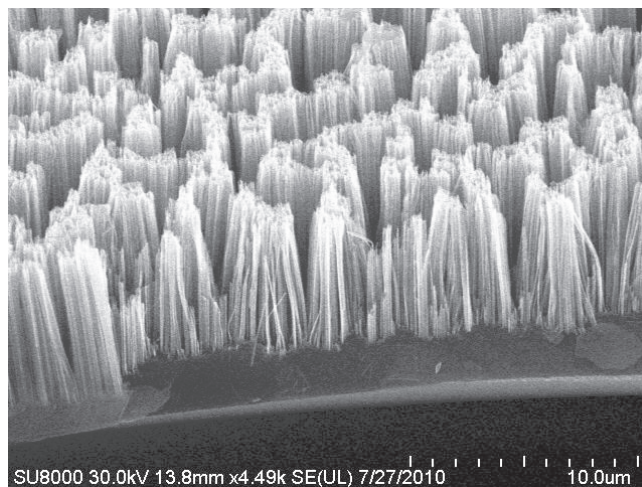


Figure 1: SEM of a 15 minute undirected HF etch on silicon.

Methods and Results:

A wet etch technique was explored using a solution of silver nitrate (AgNO_3 , 1.87g), 48% hydrofluoric acid (HF, 100 mL) and distilled water (451 mL). Ag nanoparticles formed out of solution from the AgNO_3 onto the surface of the silicon (Si) substrate. The Ag oxidized the Si surface forming SiO_2 , which was readily etched by the HF. This process was repeated, allowing for the high aspect ratios necessary. When not directed, this solution provided randomly etched Si nanowires (Figure 1). The targeted pattern was achieved on a thin film of Si, but to create phononic crystals, the wet etch process had to be used (Figure 2). While the polymer could provide the pattern of small diameter holes required, the polystyrene (PS) could not withstand the etching process long enough to obtain the high aspect ratios.

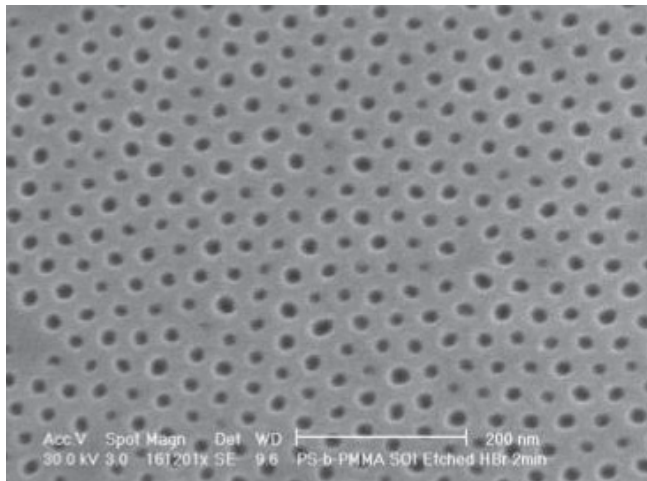


Figure 2: Ideal pattern for crystal, shown on a thin film using reactive ion etching.

Metals were examined based on the ability to evaporate onto the block copolymer easily. The first step was to make a pattern with larger features for testing. Photolithography was used to create an array with 3-8.5 μm features. Chromium (Cr), titanium and nickel were evaporated at a thickness of 50 nm to examine durability during the etching process. Cr was the most promising metal tested; lasting 15 minutes with no etching present where the Cr was shielding the Si (Figure 3). Optical microscopy was used to view the integrity of the overall array with scanning electron microscopy (SEM) performed to determine if there was any etching under the Cr mask. The next step was to use the block copolymer as the template for the Cr.

The PS/PMMA copolymer was developed by a member of the Boukai/Tuteja lab. The PMMA was removed, yielding the desired polystyrene array of hexagonally close-packed holes. The Enerjet evaporator was used to evaporate varying thicknesses of Cr (7-15 nm) over the PS-coated Si. The PS was then lifted off by first soaking in benzene for 24 hours, and then using a syringe to spray benzene for 20 minutes at a sharp angle from the edges of the sample.

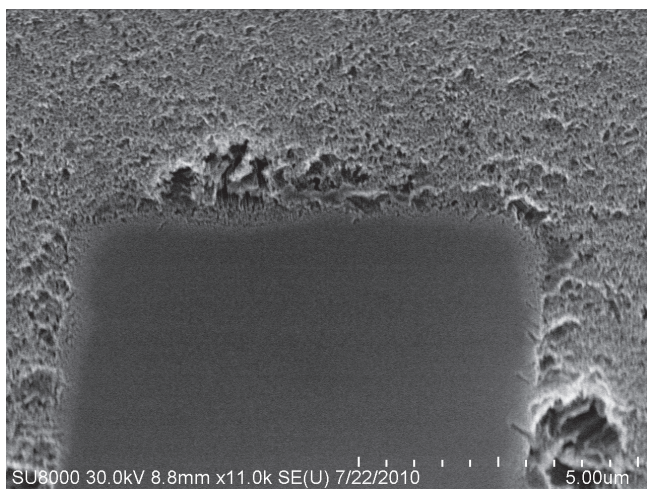


Figure 3: SEM of successful shielding of Si by Cr after HF etch.

These samples were then etched with the HF technique for various times, and images were obtained using SEM. The images showed the PS had not completely peeled off in the removal process—most likely due to the Cr forming a layer shielding the PS from the benzene. The 10 minute etch cracked the pattern, and where Si was visible, the Cr was left in the desired pattern of 20 nm sized features (Figure 4).

Conclusions and Future Work:

Cr completely shielded the Si underneath for 15 minutes, making it the most effective mask tested. The hydrofluoric acid and Ag nitrate solution proved to be capable of the high aspect ratios needed, while the polystyrene template was shown to provide features of the necessary size.

The polystyrene removal and thickness of deposited Cr need to be optimized before phononic crystals can be etched. A PDMS copolymer is also being examined as a possible replacement for the PS/PMMA. Once a crystal is assembled, a device will be required to test the thermoelectric capabilities. A testing device is being developed which will allow for ZT values to be calculated for the sample materials.

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References:

- [1] Gorishnyy et al, Physical Review Letters, 2005, 94, 11, 115501.
- [2] Jung and Ross, Small, 2009, 5, 14, 1654-1659.

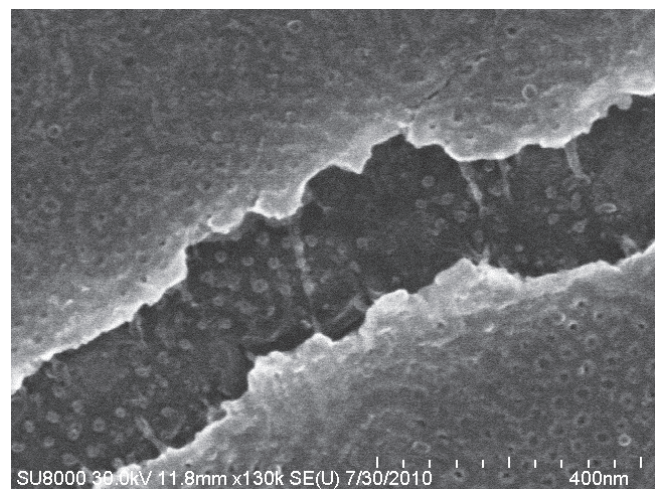


Figure 4: SEM image of 10 minute etched sample.