

Controlling and Understanding the Effects of Reactive Colloids' Packing on Silicon Etching Patterns

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Abstract:

Previous research found that amidine-functionalized polystyrene latex (APSL) adsorbed to a silicon substrate and heated produces nanowells whose sizes are dependent on the size of APSL particles. These surface features have applications to mechanical, optical, and electrical devices as well as many procedures in which mask-less fabrication is desirable. This study focused on understanding what effect a highly dense particle packing would have on the etching process and the observable features. A dense monolayer was achieved through spin-coating APSL directly onto the silicon. After heating and toluene cleaning to remove the layer of glassed polystyrene that formed, there was observed an assumed silicon re-deposition covering the nanowells and appearing to coat favorably to particles resting within the nanowells. Preliminary results showed the surface to become more hydrophilic with the presence of the deposited material. Further research aims to confirm the identity of this re-deposition as well as control the formation and removal of the deposited material through an understanding of the formation mechanism. Research will also be conducted examining the effect of the deposited material on the physical properties, such as the hydrophobicity and reflectance, of the sample.

Introduction:

Nanofabrication of materials is important to the creation of many mechanical, optical, and electrical devices. Traditional fabrication techniques, such as lithography, require expensive, harmful materials and must be carried out in expensive, well-maintained cleanrooms. In contrast, the mask-less fabrication method described by Chaturvedi uses inexpensive, harmless materials and can be performed under desktop conditions [1]. This technique uses an amidine-functionalized polystyrene latex (APSL) adsorbed to the surface of a silicon substrate and heated to 150°C to produce a hydroxide particle, a known etchant of silicon. The hydroxide is produced locally beneath the polystyrene bead, and the etched area is therefore, for silicon <100>, in the shape of an inverted square pyramid the size of the polystyrene bead. Normal fabrication using this technique sets the inter-particle distance based off the

particles' Debye length. This experiment aimed to decrease the inter-particle distance through spin-coating and observe the changes to the etching pattern seen previously.

Experimental Procedure:

To a plasma-cleaned silicon <100> wafer was spin-coated a solution of 4% wt/v 500 nm APSL at 400 RPM. The sample was then placed in a 23 mL Parr bomb containing 15 mL of DI water. The bomb was then placed in an oven pre-heated to 150°C and cooked for three hours. The sample was allowed to cool inside the bomb, and then placed in toluene for 30 minutes, three times. Imaging of samples was performed with field-emission scanning electron microscopy (FESEM).

Results and Conclusions:

Though the etching formation process — the creation of an inverted square pyramid — remained the same, the high-density array caused a variation from the expected result. Because of the close proximity of one bead to the next and because the sample was heated above the glass-transition temperature, the polystyrene glassed, forming a hydrophobic layer over the silicon surface. Although the glassed polystyrene did affect and possibly hinder the etching, it did not halt it. Some areas, termed under-etched and shown in Figure 1, had etching formations similar to that of 50 minutes of heating rather than three hours. Other areas, termed over-etched and shown in Figure 2, appeared to have fully etched with the etchings overlapping. In areas where etching was formed fully and correctly, a re-deposition was observed, as seen in Figure 3.

The re-deposition favored, but was not limited to, the etched areas. It appeared similar to the polystyrene bead expected to still be present in the nanowell, giving the appearance that formation was coating the polystyrene. Repeated toluene cleaning did not remove this deposition, shown in Figure 4, and sample surface was found to be more hydrophilic than an un-etched silicon surface. This seemed to suggest that

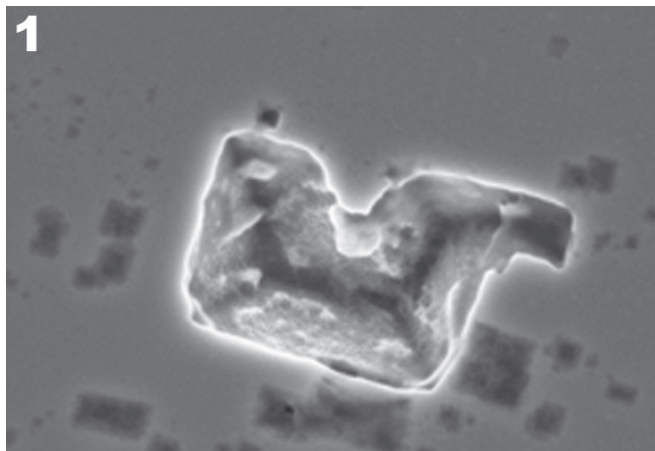


Figure 1: Under-etched 500 nm nanowells.

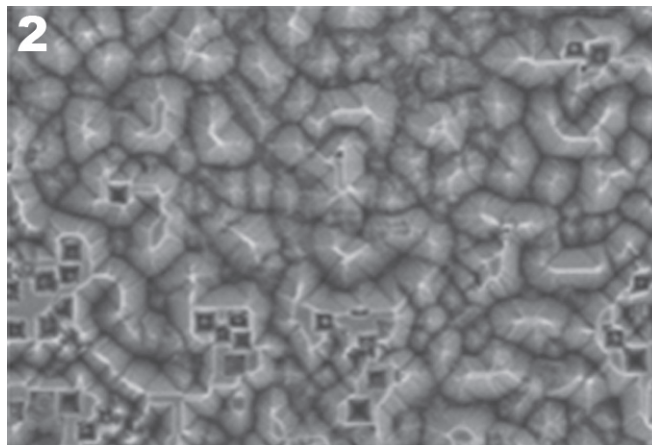


Figure 2: Over-etched 500 nm nanowells.

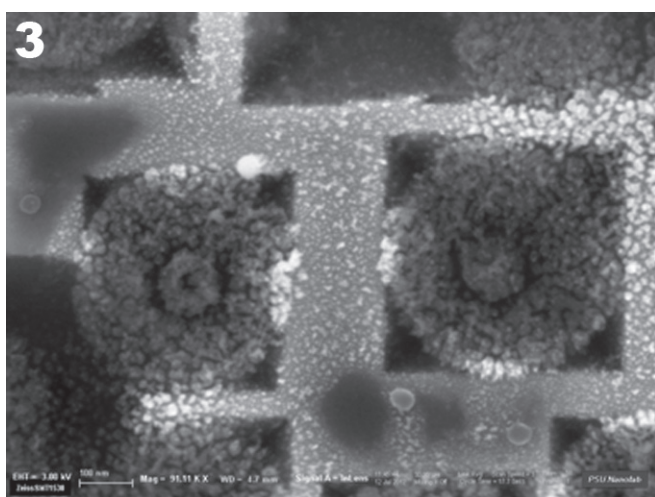


Figure 3: Re-deposited material on top of 500 nm nanowells.

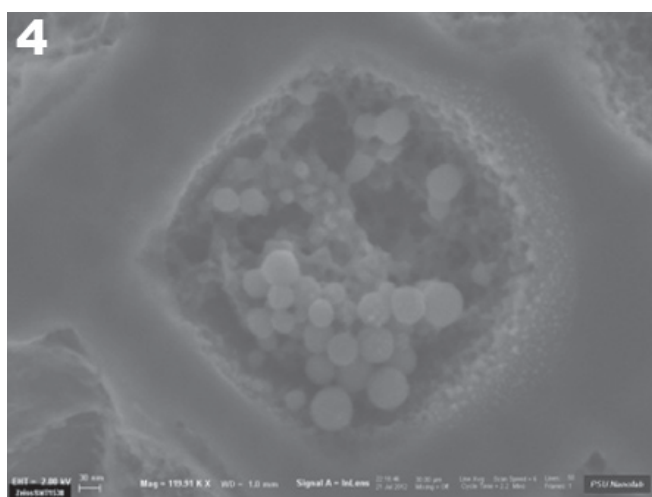


Figure 4: Thrice toluene-cleaned sample with 500 nm nanowells.

the formation was due to a re-deposition of etched silicon. Before the toluene cleaning, most of the deposition appeared to be smaller particles with a small number of larger beads. As the number of toluene cleanings increased, the frequency of the larger beads, seen in Figure 4, increased. This seems to indicate the deposition, while inorganic, was interacting with organic matter. As more of the organic matter was removed through toluene cleaning, the deposited material was left to interact with itself, creating larger beads.

Future Work:

It is assumed that the areas of over-etching are due to multi-layering. As such, the spin-coating method needs to be adjusted to ensure the polystyrene layer is indeed a monolayer. The identity of the deposited material needs to be identified, possibly through x-ray diffraction could also help determine the structure of the deposited material before and after toluene cleaning. In addition, FESEM imaging does not reveal clearly whether the deposition is occurring as a coating of the

remaining polystyrene or if the material is a residue within the nanowell that has replaced the particle.

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References:

- [1] Chaturvedi, N.; "Maskless Fabrication of Nanowells Using Chemically Reactive Colloids"; *Nano Lett.*, 11 (2), pp 672–676 (2011).