Colloidal Self-Assembly-Directed Laser-Melt-Induced Crystalline Silicon Nanostructures

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Principal Investigator: Ulrich Wiesner
User: Kwan Wee Tan

Affiliation: Department of Materials Science and Engineering, Cornell University
Contact: ubw1@cornell.edu, kwt32@cornell.edu

Abstract:
We describe a rapid, facile technique coupling colloidal crystal templating with laser thermal processing to fabricate crystalline Si nanostructures with deterministic non-close-packed symmetry. Two- and three-dimensional (2D, 3D) colloidal crystals are grown as porous templates on a single-crystal Si substrate. Pulsed excimer laser irradiation is used to induce a transient melt-crystallization conversion of the amorphous silicon filled in the templates to the crystalline phase. The pattern transfer yields are high and long-range hexagonal order is maintained. The method is highly adaptable as an alternative strategy to generate silicon nanostructures of other symmetries for use in applications such as energy generation and storage.

Summary of Research:
Ordered nanostructures based on silicon grown by colloidal self-assembly have been extensively studied and widely adapted for nanofabrication and many potential applications, for example, photonic crystals and solar cells [1-7]. In particular, non-close-packed crystalline silicon nanostructures are highly desirable for their enhanced electrical conductivity, photonic and other surface properties [5-10].

In this work, we combined colloidal crystal template formation with laser thermal processing to generate crystalline silicon (c-Si) nanostructures with non-close-packed symmetry [11]. Figure 1 schematically shows the experimental procedure.

We began by growing a hexagonally arranged close-packed (hcp) monolayer colloidal crystal of 350 nm or 530 nm polystyrene (PS) spheres surrounded by silica (SiO₂) using the vertical deposition method. The latex beads were calcined in air at 500°C, leaving behind a highly ordered SiO₂ inverse monolayer. The SiO₂ template was subsequently filled with a 100 nm thick amorphous Si (α-Si) overlayer and irradiated with a 40 ns full-width-half-maximum pulsed XeCl excimer laser (308 nm wavelength) in air to induce the transient melt conversion of α-Si to the crystalline phase (~ 20-100 ns).

Finally, the template was removed in concentrated hydrofluoric (HF) acid solution, leaving hexagonally arranged non-close-packed (hncp) Si nanostructured array as seen in Figure 1c.

Using the 530 nm PS colloidal template with a single laser irradiation pulse at 600 mJ/cm², we grew 2D hnp arrays of c-Si nanostructures with an average width and height of around 410 and 300 nm, respectively.

Figure 2 shows the hncp c-Si nanostructures generated from a smaller, 350 nm PS colloidal template and four sequential
laser pulses at 500-700 mJ/cm², with an average width of 170 nm and height of 60-70 nm height. Atomic force microscopy analysis indicated a ~100% hexagonal pattern transfer from the (350 nm) cp SiO₂ inverse colloidal template to the ncp c-Si nanostructures.

The method is easily adaptable to generate more complex 3D ordered macroporous c-Si inverse opals with hncp symmetry. We began with a ~150 nm thick plasma enhanced chemical vapor deposited (PECVD) α-Si in a (350 nm) multilayered SiO₂ inverse colloidal crystal template. The SiO₂/α-Si core-shell composite inverse opal was subsequently irradiated with a total of 43 sequential laser pulses at fluences from 5-550 mJ/cm². Selective HF etching of the SiO₂ template results in a ~1.3 µm thick c-Si single interconnected network of hncp inverse opal morphology, see Figure 3.

In conclusion, we have demonstrated a rapid and highly versatile method using colloidal crystal templates coupled with pulsed excimer laser-induced melting to obtain ncp c-Si arrays of varying scales at ambient conditions. In analogy to results on block copolymer templates, this approach may also be applied to form not only single-crystal homoepitaxial but also heteroepitaxial ncp nanostructured arrays on Si, enabling new functionalities and the engineering of novel device prototypes [12].

References: