Transient Laser Heating Derived Mesoporous Materials Directed by Gyroidal Templates from Block Copolymer Self-Assembly

CNF Project Number: 1356-05

Principal Investigator(s): Ulrich Wiesner

User(s): Qi Zhang, Fei Yu

Affiliation(s): Department of Materials Science and Engineering, Cornell University

Primary Source(s) of Research Funding: National Science Foundation (DMR-1719875)

Contact: ubw1@cornell.edu, qz224@cornell.edu, fy84@cornell.edu

Website: http://wiesner.mse.cornell.edu/

Primary CNF Tools Used: TFT N+/P+ Polysilicon Furnace - A4, Oxford 81 etcher

Abstract:

Equilibrium thin-film gyroidal carbon was fabricated from co-assembly of an amphiphilic triblock terpolymer and resorcinol-formaldehyde resols through solvent vapor annealing. Upon crosslinking the resols and carbonizing the thin films, mesoporous carbon templates were obtained. Low-pressure chemical vapor deposition (LPCVD) was utilized to deposit amorphous silicon into the templates. Pulsed excimer laser irradiation melted and crystallized the deposited silicon through a non-equilibrium nanosecond-scale process that preserves the underlying organic template. Finally, after removing the carbon template, we successfully prepared 3D continuous crystalline silicon with the inverse gyroidal nanostructure.

Summary of Research:

Templates enable the manufacturing of objects with intricate and complicated structures. Templates at the nanoscale allow for fabrication of nanomaterials that could find applications in catalysis or microelectronics. Block copolymer self-assembly offers bottom-up pathways to complex nanostructured templates, which can be combined with laser annealing for pattern transfer to produce porous ordered nanomaterials after template removal.

We first prepared such nanoscale organic templates derived from block copolymer in co-assembly with carbon precursors. To this end, poly(isoprene)-*block*-poly(styrene)-*block*-poly(ethylene oxide) (PI-*b*-PS-*b*-PEO, or ISO) was synthesized via sequential anionic polymerization as described elsewhere [1]. The resorcinol-formaldehyde resols, i.e. the carbon precursors, are hydrogen bonded to the PEO block of the amphiphilic ISO terpolymer. Through solvent vapor annealing, the resols were structure-directed by ISO and they formed an equilibrium co-continuous structure known as alternating gyroids on silicon wafers [2]. After the resols were crosslinked and carbonized at high temperatures, mesoporous carbon thin-film templates with gyroidal nanostructures were prepared (Figure 1).

These thin films derived from organic precursors are stable and amenable to nanomaterials fabrication and processing techniques, a prerequisite for any structure-directing template. We used LPCVD in the A4 Polysilicon Furnace at CNF to backfill the mesopores with undoped Si (Figure 2). Following TFT MOS cleaning procedures, the native oxide layer between the carbon templates and silicon wafers was removed by dipping them in diluted 20:1 hydrofluoric acid (HF) without compromising the ordered mesostructure of the organic templates. The resulting thin films have small grains of silicon filling the pores with a silicon overlayer on top.

In order to achieve conformal backfilling with crystalline materials, carbon templates with amorphous silicon deposited were subject to pulsed laser annealing at ambient atmosphere. Previous research [3] has demonstrated that shortening heating times promotes the thermal stability of organic materials. Transient excimer laser irradiation for 40 ns delivered enough energy to melt the silicon (melting temperature around 1250°C). The resulting crystallized silicon displayed polycrystallinity, with the carbon template remaining intact after the heating process.

A combination of dry and wet etching was utilized to remove the carbon template from the carbon/silicon hybrid. Using the Oxford 81 etcher at CNF, reactive ion etching was carried out with CF_4 and oxygen, and brief dipping in HF exposed the carbon template to the outside.

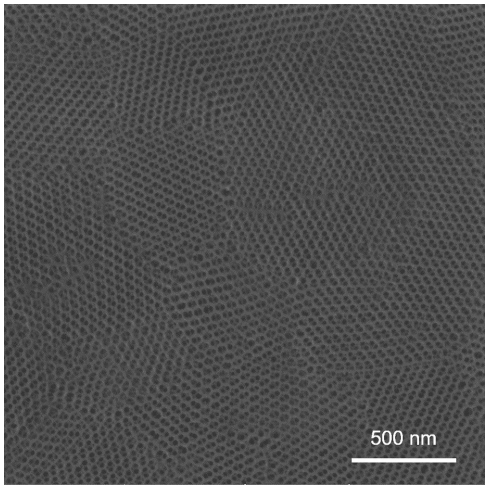

Figure 1: Scanning electron microscopy (SEM) plan view of the mesoporous gyroidal carbon template, derived from ISO-resols hybrid carbonized at 450°C.

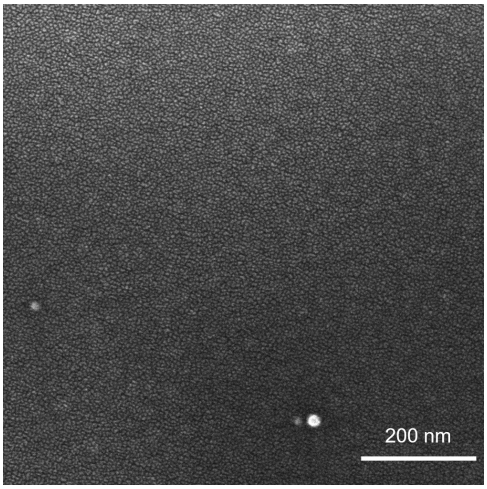

Figure 2: SEM plan view of the carbon template with Si deposited through LPCVD. There is a Si overlayer on top of the template, showing grains of silicon.

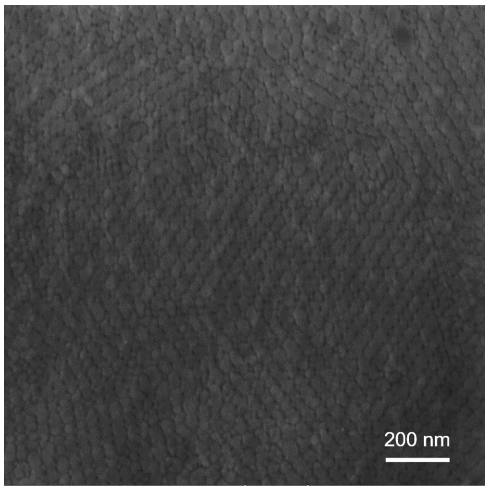

Figure 3: SEM plan view of crystalline silicon nanostructures after template removal, leaving behind interconnected trenches.

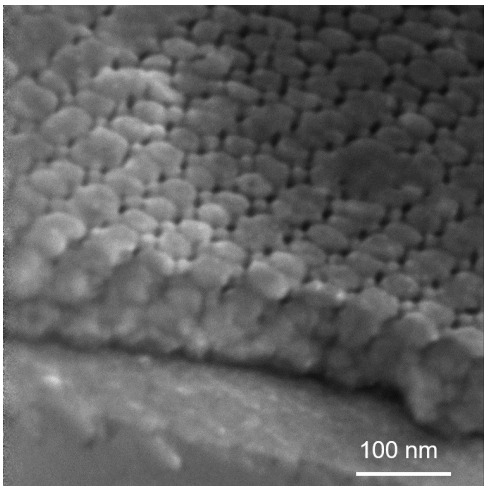

Figure 4: SEM cross-section view of crystalline silicon nanostructures after template removal, leaving behind interconnected trenches.

We subsequently immersed the samples in piranha solution at elevated temperatures to decompose the carbon template. The 3D continuity of gyroids ensures complete removal of the template. Periodically ordered crystalline silicon with the inverse nanostructure of the carbon template was finally obtained via brief dipping in HF to remove silicon oxide (Figures 3 and 4).

Our fabrication route makes compatible the processing of organic soft materials and inorganic semiconductors and capitalizes on the highly non-equilibrium nature of transient laser heating. This same strategy can be expanded to other materials, such as metals and compound semiconductors, to be backfilled into the template.

The resulting mesoporous crystalline materials could allow us to explore interesting functionalities in areas including sensing, catalysis, and microelectronics.

References:

[1] Bailey, T. S. et al. A Noncubic Triply Periodic Network Morphology in Poly (Isoprene-b-Styrene-b- Ethylene Oxide) Triblock Copolymers. Macromolecules 35, 7007-7017 (2002).

[2] Zhang, Q. et al. Pathways to Mesoporous Resin/Carbon Thin Films with Alternating Gyroid Morphology. ACS Nano 12, 347-358 (2018).

[3] Jung, B. et al. Kinetic Rates of Thermal Transformations and Diffusion in Polymer Systems Measured during Sub-millisecond Laser-Induced Heating. ACS Nano 6, 5830-5836 (2012).