Block Copolymer Self-Assembly-Directed
Single Crystal Homo- and Heteroepitaxial Nanostructures

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Abstract:

The report describes a novel technique coupling bottom-up self-assembly structure formation with pulsed laser irradiation to fabricate single-crystal epitaxial nanostructured thin films. Organic block copolymers are used as structure-directing agent for the added inorganic sol nanoparticles to form the nanoporous templates on a single-crystal Si substrate. Pulsed excimer laser irradiation induces a transient melt-crystallization conversion of the amorphous overlayer material filled in the templates. The pattern transfer yields of the resulting single-crystal nanostructures grown epitaxially from the Si substrate are high. The approach to generate these single-crystal epitaxial nanostructured thin films is highly adaptable which may be used in a wide host of applications such as energy generation and storage devices.

Summary of Research:

Block copolymer self-assembly hybrid materials utilize the spontaneous phase separation of the different components of a blocked linear macromolecule to drive added inorganic sol nanoparticles into ordered structures at the nanoscale [1-4]. A bottom-up self assembly approach combined with laser to induce a transient melt and solidification conversion (~ 20-100 ns) with the molten Si recrystallizing epitaxially from the single-crystal Si substrate. Finally the template was etched away in hydrofluoric acid leaving porous single-crystal epitaxial nanostructures behind.

Figure 1: Schematic illustration of (A-E) single-crystal epitaxial nanostructure fabrication and (F) laser irradiation of the template covered Si substrate [6].
The hexagonal pattern transfer yields of the single-crystal Si homoepitaxial nanopillars were high and long-range ordering was maintained. Atomic force microscopy analysis indicated a pattern transfer of approximately 90%. High-resolution transmission electron microscopy (HRTEM) in Figure 2 confirms the single-crystal epitaxy of the pillar to the substrate.

The method is easily adaptable to generate single-crystal epitaxial nanostructures of more complex three-dimensional (3D) architectures. To this end, we used a triblock terpolymer directed niobia template to grow a 100 nm thick single-crystal homoepitaxial Si nanoporous film with a 3D interconnected network structure; see Figure 3. Confinement of the interface area to nanoscopic dimensions further allows growth of heteroepitaxial nanostructures. To this end, we generated single-crystal heteroepitaxial nanopillars of moderately lattice mismatched NiSi on Si. Finally, we combined top-down lithography with bottom-up self assembly using a TEM grid as a mask to generate micro- and nano-patterned hierarchical Si nanostructures.

In conclusion, we have demonstrated a proof-of-concept experiment using block copolymer template formation coupled with pulsed laser annealing to grow single-crystal nanostructures with epitaxial relation to the Si substrate. The lack of grain boundaries in these single-crystal materials and the ability to epitaxially grow along specific crystal axes relative to the substrate may allow, e.g. optimal charge transport and enhance the performance of energy storage and generation devices.

References: