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Laser-Induced Hierarchically Structured Materials from Block Copolymer Self-Assembly

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ABSTRACT

Hierarchically porous structured materials with multifunctional properties and higher order complexities are highly desirable for many applications such as separation and energy storage. Here we describe the generation of hierarchically porous organic and inorganic structures coupling block copolymer self-assembly with spatially- and temporally-controlled laser irradiation. A simple and rapid laser irradiation of block copolymer-directed hybrid films with a continuous wave laser in the sub-millisecond timescales enabled synthesis of 3D mesoporous polymer structures and shapes. Backfilling the polymer template with amorphous silicon followed by pulsed laser annealing enabled transient melt transformation of amorphous precursors into 3D mesoporous crystalline silicon nanostructures. Mechanistic studies on laser-induced crystalline silicon nanostructure formation during the nanosecond silicon melt-crystallization process and polymer template stability at temperatures above 1250 degrees Celsius are highlighted.

Keywords: Self-assembly, Hierarchical nanostructures, laser heating, block copolymers, silicon, single crystal epitaxy,

1. INTRODUCTION

Hierarchically porous structures and materials with high surface area, fast mass transport and other multifunctional properties, are highly sought-after in many applications, ranging from energy storage, separation to tissue engineering.[1–4] Bottom-up self-assembly provides a direct pathway to synthesize three-dimensional (3D) structures with multiple length scale features. For example, amphiphilic molecular surfactants and block copolymers have been utilized to structure-direct organic/inorganic additives into periodically ordered hybrid mesostructures (5–50 nm length scale).[5–10] To access higher order features, block copolymers can be combined with other macroporous templates such as colloidal crystals to form hierarchical structures,[11] amidst with increasing complexities in terms of processing time and cost. Recently, block copolymer self-assembly under non-equilibrium conditions is being explored to directly generate hierarchically porous polymer and inorganic nanostructures.

The first approach is termed as combined block copolymer self-assembly with non-solvent–induced phase separation, or SNIPS. Peinemann *et al.*[12] first demonstrated SNIPS by dissolving a AB diblock copolymer (*e.g.*, polystyrene–*block*–poly(4-vinylpyridine)) in an organic solvent and blade-casting the mixture as a film (~100–200-μm-thickness) on a glass substrate. The wet film was permitted to evaporate for some time (~10–90 sec), resulting in a solvent concentration gradient across the film thickness. As the organic solvent evaporation rate is highest at the film/air interface, the block copolymer began to self-assemble into well-ordered domains where the polymer concentration is the highest. Finally, the film and substrate were plunged into an anti-solvent bath (e.g., water), enabling the exchange of organic and water solvents as well as precipitation of a phase-inverted asymmetric porous structure with a 100–200 nm mesoporous block copolymer skin layer (pore size of 5–50 nm) at the film/air interface, self-supported on the macroporous film substructure (pore size of 0.1-10 μm). The SNIPS approach has been expanded to other block copolymers as well as combining with organic and inorganic additives to generate asymmetrically porous metals, metal oxides and carbon membrane films.[13–17]

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A second “one-pot” approach is to induce non-equilibrium spinodal decomposition of a solution mixture of block copolymer and organic/inorganic additives into hierarchically porous composites.[18,19] Termed as the spinodal-decomposition–induced macro- and mesophase separation plus extraction (SIM^{2}PLE) method, a homogenous solution blend of block copolymer with small molecular organic additives was heated at elevated temperatures to induce macroscopic immiscibility, thereby generating macroscopic additive-rich domains and mesoscopic block copolymer-additive periodic nanodomains.[18] Subsequent removal of either block copolymer or additives yielded hierarchical porous structures with well-ordered nanodomains. Tuning faster solvent evaporation at higher temperatures enable variation in the nanodomain morphology. The SIM^{2}PLE method is generalizable for many different materials, for example, polymers, carbon, metal oxides and nitrides, as well as different shapes such as spherical particles, powders and monoliths.[18–22]

A more recent advancing non-equilibrium approach is to combine rapid laser heating with soft materials to generate hierarchical functional nanostructures. Here we will describe the coupling of block copolymer self-assembly with transient laser-induced heating to enable direct formation hierarchical single crystal, polycrystalline and amorphous organic and inorganic nanostructures.[23–25]

2. RESULTS AND DISCUSSIONS

Routinely deployed in many industries such as semiconductor manufacturing and cutting of metals and composites, transient laser heating enable many benefits such as nanopattern transfer on solid and flexible substrates, as well as spatial and temporal control from femto- to tens of second time scales (10^{-15} to 10^{2} s).[26–32] Figure 1 shows the coupling block copolymer self-assembly with transient laser heating can further enable direct synthesis of advanced hierarchical functional organic and inorganic nanostructures.

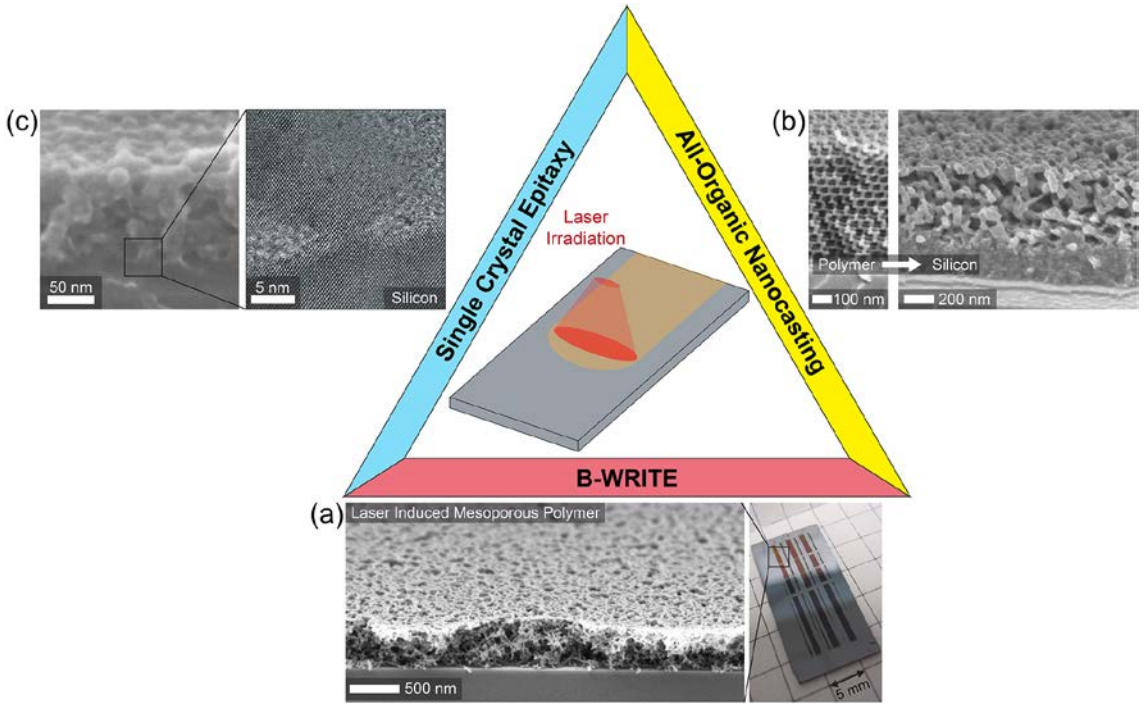

Figure 1. Transient laser heating-induced hierarchical structured materials. (a) Hierarchical mesoporous polymer nanostructures derived by B-WRITE.[24] (b) All-organic block copolymer templating of laser-induced 3D periodic silicon nanostructures.[24] (c) Excimer laser annealing of block copolymer templated single crystal epitaxial silicon nanostructures.[23]

Previous studies had mainly focused on transient laser heating of neat organic block copolymer thin films to generate long-range ordered periodic morphologies for nanolithography applications.[27–29,33] In particular, Jung *et al*. established the thermal stability of a block copolymer resist under transient laser heating was greatly enhanced by more than 400 °C as the heating dwells were reduced from 60 s to 0.5 ms.[31] We extended the process and system space by conducting transient laser heating on all-organic block copolymer thin films to synthesize hierarchical meso- and macroscopic porous polymer structures and shapes (Figure 1a). Figure 2 shows the process schematic of block copolymer-induced writing by transient heating experiments (B-WRITE) method.[24]

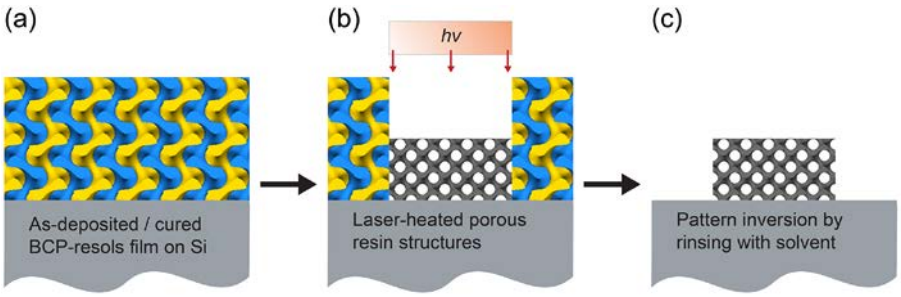

Figure 2. Schematic of block copolymer-induced writing by transient heating experiments (B-WRITE).[24]

For the B-WRITE process,[24] an all-organic hybrid film was formed on a silicon substrate by mixing the self-assembling block copolymer with oligomeric resols additives (Figure 2a). The hybrid film was then scanned by a continuous wave carbon dioxide laser (10.6 μm) for 0.5 ms in air (Figure 2b). The silicon substrate absorbed most of the far-infrared photons thereby heating the hybrid thin film. The spatially localized transient laser heating induced simultaneous thermal polymerization of resols and block copolymer decomposition, enabling generation of 3D mesoporous continuous resin network structures and shapes (Figure 2c). The remaining film regions were then removed by solvent rinsing, leaving hierarchical mesoporous polymer relief structures on the silicon substrate (see optical image in Figure 1a). Scanning electron microscopy (SEM) in Figure 1a shows highly uniform mesoporous resin structure formation and coverage over large areas. Even more surprisingly, the resultant laser-induced mesoporous resin structures exhibited extraordinary thermal stability over 1000 °C under carbon dioxide laser-induced heating in air (Figure 3).

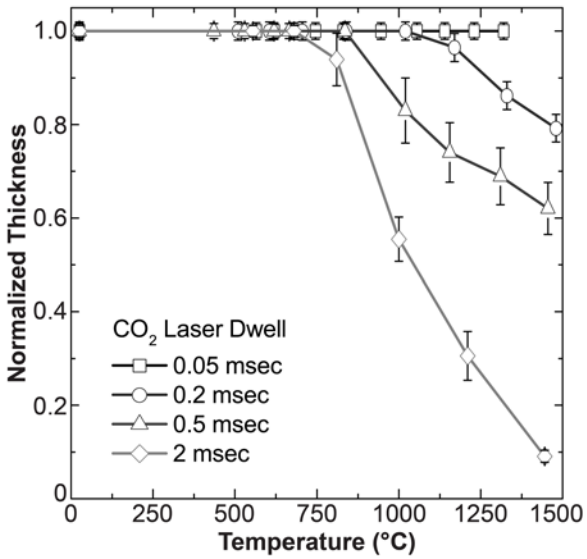

Figure 3. Film thickness plots of mesoporous resin template samples heated by a single laser irradiation for different submillisecond time dwells.[34]

To fully understand the thermal behavior of block copolymer-directed mesoporous resin films under transient laser-induced heating in air, we tracked the remaining film thickness as function of laser-induced temperatures and time dwells.[34] Figure 3 shows the mesoporous resin films became increasingly stable as transient laser heating dwells were reduced into the sub-millisecond dwells. Specifically, there was no observable film thickness loss (Figure 3) or morphological transformation (SEM data not shown) in the mesoporous resin films for 0.05 ms dwell up to 1320 °C under laser heating.

The high thermal stability of mesoporous block copolymer-directed resin structures provides new opportunities to expand laser-induced complex nanostructure generation method to other functional materials classes (Figure 4). To this end, the block copolymer-directed mesoporous resin film was employed as a template and backfilled with amorphous silicon by chemical vapor deposition (Figure 4a). The amorphous silicon/resin composite was then irradiated by a pulsed excimer laser to melt the amorphous silicon into the silicon substrate at temperatures above 1250 °C, followed by rapid solidification within 50–100 ns (Figure 4b). The organic template was then removed by acidic chemical treatments, yielding crystalline silicon nanostructures with high pattern transfer fidelity, as confirmed by SEM (Figure 1b) and grazing incidence small angle X-ray scattering (data not shown). Finally, the removal of the native silicon dioxide layer on the silicon substrate before chemical vapor deposition of amorphous silicon and nanosecond pulsed excimer laser irradiation, enabled generation of ~100 nm thick mesoporous single-crystal epitaxial Si network structures (Figure 1c).

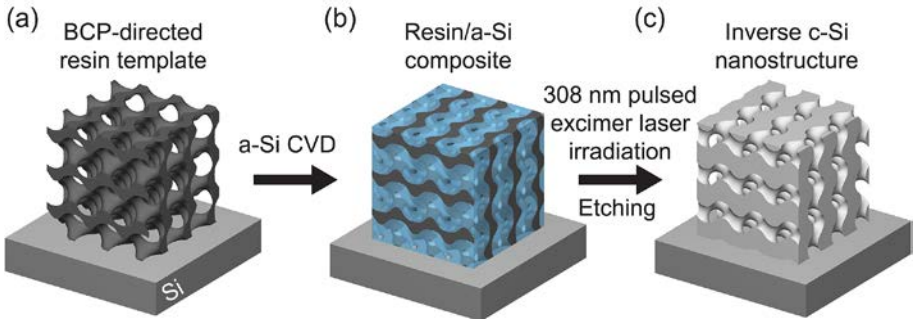

Figure 4. Schematic of complex block copolymer-directed single crystal silicon nanostructure formation by nanosecond pulsed excimer laser annealing.[23,34]

3. CONCLUSIONS

In summary, coupling transient laser heating with block copolymer self-assembly enables a conceptually simple, rapid and scalable approach to form complex 3D porous organic polymers and inorganic single-crystal silicon nanostructures for existing and emerging applications such as sensing, catalysis, energy storage and microfluidic reactors.

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