## Induced patterning of organic and inorganic materials by spatially discrete surface energy

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Many nanotechnology applications require the fabrication of discrete but spatially organized nanostructures both in organic and inorganic materials. Available methods are mainly divided into "bottom-up" self-assembly and "top-down" nanolithography in conjunction with pattern transfer methods such as etching and liftoff processes. However, for self-assembly, the control of uniformity, 3D geometry, and transfer to substrate are difficult. For lithography, patterning functional organic materials is a challenge. Pattern transfer using liftoff will involve strong solvents, which is not applicable for organic materials. Pattern transfer with etching will damage or change functionality of materials as well. Here we developed another pattern transfer method for nanolithography, which can be applied to pattern discrete organic or inorganic materials in a controlled manner. It is based on patterning substrates to have spatially different surface energies via nanolithography and selective surface treatment. Then the discrete surface energies on the substrate induce microfluidic self-patterning of materials that are deposited on the surface. It can also be used for additive deposition methods, such as atomic layer deposition (ALD), to pattern structures in the areas of particular surface energy.

Figure 1 illustrates the process flow of this pattern transfer method. First, nanoimprint, electron beam lithography, or photolithography is used to define openings in the resist. Then trichlorosilane such as FDTS is covalently bonded to OH- on the surface of the openings. After resist removal, organic or inorganic films can be deposited via evaporation, spincoating, or ALD, etc. Heating the deposited film at a certain temperature range allows the material to re-flow and self-organize to the areas of high surface energy, leaving empty space at the areas of low surface energy. Figure 2 demonstrates patterning of PEG-PLA copolymers into residue-free discrete micro-structures without damaging its bio-functionality by heating the polymer-coated Si to 100 °C. In addition, biopolymer formed interesting wave-like substructures after the re-flow, which seemed to only depend on material properties, such as viscosity. These sub-structures are uniform in various shapes and are about a half micron in width. We have also patterned Al microstructures by heating the deposited Al film to 700 °C for 10 min. The Al layer will re-flow to the patterned areas of high surface energy (Fig. 3). Fig. 4 demonstrated using ALD to deposit high-K material HfO<sub>2</sub> on the similar substrates at 0.5 Torr. The ALD process consisted of a 0.2/0.05sec for the Hf precursor/H<sub>2</sub>O pulse time and a 7 sec for the purging time with N<sub>2</sub>. The temperature of the substrate and the container of the Hf precursor were chosen at 180°C and 130°C, respectively. HfO<sub>2</sub> only grew on the areas with high surface energy, with no deposition on the areas treated with FDTS.

We will further demonstrate nanoscale patterning of organic and inorganic materials using this spatially discrete surface energy induced pattern transfer method in the paper. This simple method is another pattern transfer technique other than liftoff and etching. It provides advantages of ease of processing and is widely applicable to both organic and inorganic materials. The selective ALD method can be used to make nanoimprint molds. We believe this method will allow more flexibility of nanofabrication for future nanotechnology products.

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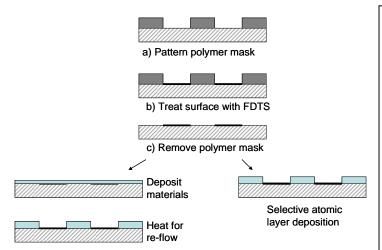


FIG 1: Schematics illustrates fabrication process

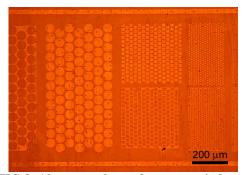


FIG 3: Al patterns by surface energy induced patterning. Light areas are Al, dark are Si.

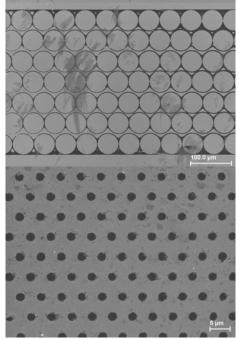


FIG 4: SEMs of selective ALD of HfO<sub>2</sub> (dark areas ) on Si substrate (light areas).



FIG 2: Optical images of biopolymer patterns formed by heating polymer to re-flow to patterned hydrophilic areas