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Force-Controlled Inorganic Crystallization Lithography

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Lithography plays a key role in integrated circuits, optics, information technology, biomedical applications, catalysis, and separation technologies.[1] However, inorganic lithography techniques remain of limited utility for applications outside of the typical foci of integrated circuit manufacturing. Many of these techniques though require multistep patterning to fabricate etch masks or templates for structuring the inorganic materials. Therefore, alternate technologies have evolved, including soft lithography,[2] nanoimprint lithography,[3] microcontact printing,[4] and capillary lithography.[5] One of the common features of many of these techniques is that they utilize a mold of either silicon or a polymer, which is brought into contact with an underlying mask containing essential fabricated features. These techniques have made significant advances in the field and also are improvements for patterning a range of materials at the small scale with relatively low cost and high efficiency. Expanding on this approach in creating gradient patterns provides freedom in studying many processes, which are often limited to binary control in the presence versus absence of a material. Venkateswar et al.[6] previously used electrodes to establish a gradient of charged molecules within a liquid. Also, Bhangale et al.[7] used a metal-transfer process to form arbitrarily shaped surface-conjugated protein gradients. Both of these stamping methods are limited by the gradient patterns, sizes, and shapes that they can fabricate.

In this communication, we propose a novel stamping method that applies pressure on the upper surface of the stamp to regulate the dewetting process of the inorganic buffer and the evaporation rate of the solvent in this buffer between the substrate and the surface of the stamp. We focus on developing inorganic microstructures with specific locations and also on enabling the ability to pattern gradients during the crystallization of the inorganic salts. This approach utilizes a combination of lithography with bottom-up growth and assembly of inorganic crystals.

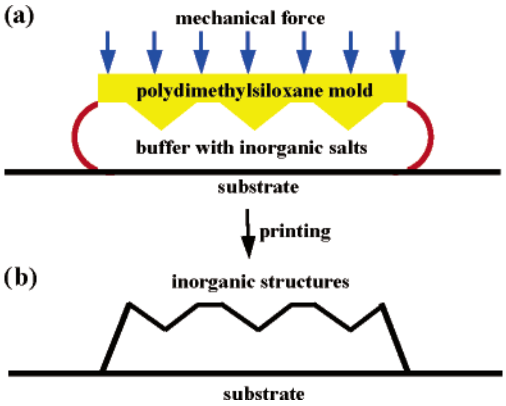

Figure 1. Schematic of the stamping method for fabricating inorganic microstructures through balancing the dewetting of an inorganic buffer and the evaporation rate of the solvent. (a) A manual mechanical force is placed on the PDMS mold, which results in (b) controlled inorganic microstructures after removing the stamp.

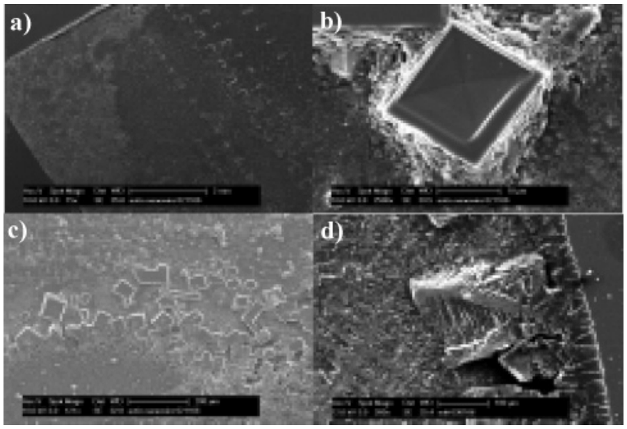

Figure 2. (a and b) Scanning electron microscope images of the highly regular inorganic microstructures with a large area through application of manual force. (c and d) Images of the process when not applying force. In (d), this microscale structure was formed through multiple applications of the organic layers.

Figure 1 shows a schematic of this microstamping method. Briefly, a mold was made for inverted pyramid structures and was immersed in an inorganic buffer for enabling the transfer. We first fabricated the pyramid stamp using ⟨100⟩-oriented, 4 in. p-doped (1−100 Ωcm) silicon wafers. A masking layer of thermal oxide with a thickness of 0.6 μm was employed for passivation. Arrays of grating elements were patterned in a SiO_2 mask by photolithography to evaluate the surface roughness and the rate of etching of the (100) plane. The etching windows were generated by removing SiO_2 with a buffered hydrofluoric acid solution. The KOH etchant was a 25 wt % aqueous solution without isopropyl alcohol (IPA). The etching experiments were conducted at a temperature of 60−100 °C.[8] After fabrication, PDMS [poly(dimethylsiloxane), Dow Corning, Sylgard 184] reverse molds were created from the silicon master using conventional photolithography to create the flexible microstructures. The PDMS stamp with the inorganic buffer was brought into contact with the surface of the glass substrate under a manual force for 40 min. The inorganic buffer contained 25−150 mM KCl, 1 mM $MgCl_2$, and 1 mM ATP with a pH of 7.0−8.0 (polymerization buffer from Cytoskeleton, No. BSA02-001).

Figure 2 displays scanning electron microscope images of the inorganic microstructures through applying a manual mechanical force as well as the structure that evolves when there is no force. The highly regular features are often explained in terms of a diffusion-limited aggregation model.[9] In a solidification or crystallization process, this model assumes that the velocity of the solidification front is proportional to the concentration gradient of the material which solidifies. Our process is also influenced by the dewetting process of the inorganic solution on the hydrophilic stamped (PDMS) surface. We assume that the mass transport during the dewetting process for a defined evaporation rate of the inorganic

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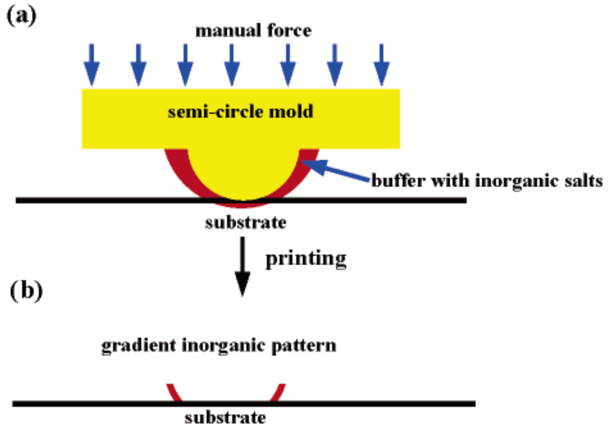

Figure 3. Schematic for creating a gradient inorganic pattern using a semicircle microstamping method. The semicircle mold was fabricated using photocuring, and then a gradient pattern is created through applying a manual force before lifting off the stamp.

solvent will increase the concentration gradient in front of the solidification boundary. This likely leads to a higher growth velocity of the crystallizing structures when a mechanical force is applied. Regular inverted pyramid patterns can be obtained over a large area by applying this manual force (Figure 2a and b). When using a stamp, but not applying a continuous force, the behavior of this system is governed by the evaporation rate of the inorganic buffer, forming structures that conformed to the original stamp (Figure 2c and d). The relative positions between the structures is also shown to be irregular when the initial manual forces on the stamp between the glass substrate and the inorganic buffer is varied. In addition, the effect of other factors, such as the concentration of the buffer and the immersion time, affects this process.[10]

While most lithographic processes are planarly constrained, we are able to fabricate a semicircle mold; this is accomplished using photocuring.[11] We use this stamp to create a gradient inorganic pattern through the process shown in Figure 3. To create this stamp, after spinning liquid SU-8 resin (Shell Chemical) on a substrate, we heated the system at 75 °C for 30 min. We utilized a microscope to expose the SU-8 to UV excitation with an epifluorescence microscope (Zeiss Axiovert) with a light source spectrum between 365 and 410 nm. We then developed the system in propylene glycol methyl ether acetone (PGMEA), rinsed it in water, and the air-dried the system.

Through this method, a gradient inorganic pattern is created, as demonstrated in Figure 4. As the amount of force applied on the stamp is regulated, the contact area of the semicircle regions with the surface is consequentially controlled. This simple process directly correlates the force to the patterns of inorganic material that are generated (i.e., the greater the quantity of the force applied, the greater the contacted surface area and the gradient pattern transfer).

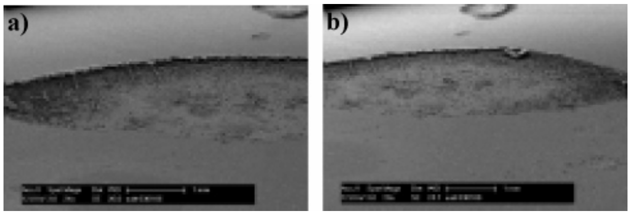

Figure 4. (a and b) Scanning electron microscope images of the inorganic gradient pattern created through our method.

In summary, we developed a novel method to build inorganic microstructures through a mechanics-based approach. Through applying a manual force to a polymer stamp, we regulated the interactions between the inorganic buffer and the substrate. This allowed us to fabricate uniform microstructures over a large area. We also can create multiple sizes and distributions of the inorganic material using a single stamp combined with analogue patterning through this force-contact control; this could alleviate issues with mask-based systems. This work has potential applications in a variety of fields, including studying inorganic material patterning and small-scale fabrication technology.

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