Amplification of soft lithographic patterning of Si

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Pattern formation of micrometer and submicrometer features on a solid substrate directed by desired design rules is of great interest in modern technology. Today, the majority of such patterning for the production of microelectronics is accomplished by photolithography.[1] Fabrication by projection-based lithography, however, has disadvantages such as diffraction-limited resolution and a limited selection of substrates available for the technique.[1] Soft lithography, a collection of fabrication methods that use an elastomeric medium to transfer patterns, has been developed as an alternative to conventional photolithography.[2] The basis of surface modifications by soft lithography is the self-assembly of molecules into organized domains at the substrate-adsorbate interface.

The work described here utilizes a soft lithographic technique called microcontact printing (μCP) to form self-assembled monolayers (SAMs) on silicon substrates.[2] In μCP, a patterned poly(dimethylsiloxane) (PDMS) stamp is used to transfer the ink molecules from the stamp to the substrate. Patterned SAMs of alkanethiols and alkylsiloxanes prepared by μCP have been used as templates for polymer patterning,[3,4] metal and metal oxide deposition,[5-7] and cell engineering.[8,9] Further processing of the films has led to the production of optical waveguides,[10,11] sensors,[9,12] and other microelectronic devices.[13,14] Although alkanethiols are capable of forming well-defined SAMs on Au, it is often convenient to use alkyltrichlorosilane SAMs, which can be formed on variety of oxide-coated substrates, including Si and glass. We have investigated the properties of microcontact printed SAMs derived from octadecyltrichlorosilane (OTS), a methyl-terminated reagent, and 7-octenyltrichlorosilane (OCT), an alkene-terminated reagent, and the applications of these films in microfabrication.

The film growth mechanism of a given alkyltrichlorosilane depends on the concentration of water in the reaction environment, and deposition temperature. An excessive amount of water results in undesirable deposition of highly polymerized alkylsiloxane on the SAM films as permanent defects. Insufficient hydration of the substrates results in incomplete films. Using OTS films prepared by immersion, researchers have shown that films consisting of densely packed, well-organized OTS molecules can be prepared only below an intrinsic threshold temperature T_c (~28 °C).[15,16] The molecules are believed to be mobile on the thin layer of water adsorbed on the oxide surface, where they form crystalline islands by surface diffusion and aggregation below T_c, or a more liquid-like phase above T_c.

Film formation of alkyltrichlorosilanes by contact printing is complicated by the presence of additional water in the ambient. The trichlorosilane molecules are hydrolyzed and cross-linked while being cast and dried on the elastomeric stamp, before they are brought into contact with the substrate. Films prepared by contact printing a 5 mM OCT solution contained a large number of polysiloxane defects; however, increasing the solution concentration to 50 mM resulted in reproducible preparation of relatively smooth films. In contrast, the same strategy when applied to OTS, did not result in smooth films. The morphologies of OTS films prepared at 25 °C and 45 °C (~20 °C

above T_c) were nearly identical, despite the large difference in the deposition temperature. These observations led us to conclude that film formation in contact printing involves permeation of ink molecules into the PDMS stamp, which serves as a reservoir of these molecules. Low molecular weight species with high mobility can diffuse out the stamp and adsorb to the substrate first, while highly cross-linked species either remain on the stamp, or adsorb to the substrate at late stages of the deposition process. Thus, by increasing the concentration of OCT in the ink, we increased the ratio of OCT monomers with respect to cross-linked species, which resulted in preferential deposition of low molecular weight species to produce smooth films. OTS however, is much larger than OCT, and the extent of permeation into the PDMS stamp is expected to be lower compared to OCT. Therefore, a high concentration of OTS accumulates near the surface of the stamp, where the molecules are hydrolyzed and polymerized. Ordered domains of OTS must be forming at the ink-air interface as well, while OTS is exposed to air at room temperature (~T_c). OTS deposition from the stamp results in adsorption of both low and high molecular weight species, generating OTS films containing some polymer defects.
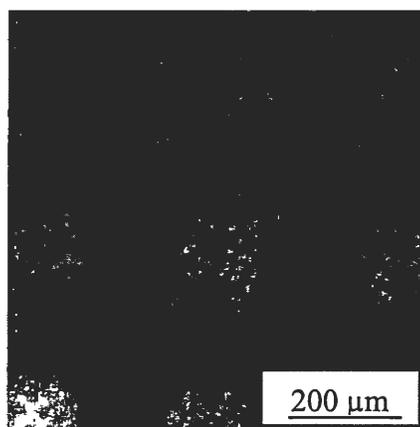

Figure 1. XPS image of patterned polymer film consisting of pixel arrays ~150 µm in diameter.

Two examples are given here as applications for microcontact printed SAMs. Figure 1 shows an XPS image of a sample in which patterned OTS was used as a template to direct polymer patterning. The general fabrication procedure involves patterning OTS by µCP to protect the underlying substrate, orthogonal printing of OCT to activate the areas not coated with OTS, anchoring of a polymerization catalyst through OCT, and finally, ring-opening metathesis polymerization of a strained olefin in the OCT derivatized regions. Figure 2 shows a fluorescence micrograph and a corresponding spectrum of a patterned porous silicon sample. In this sample, an OTS layer was used as a template for selective deposition of a Pt catalyst that assisted the dissolution of Si to generate porous silicon.
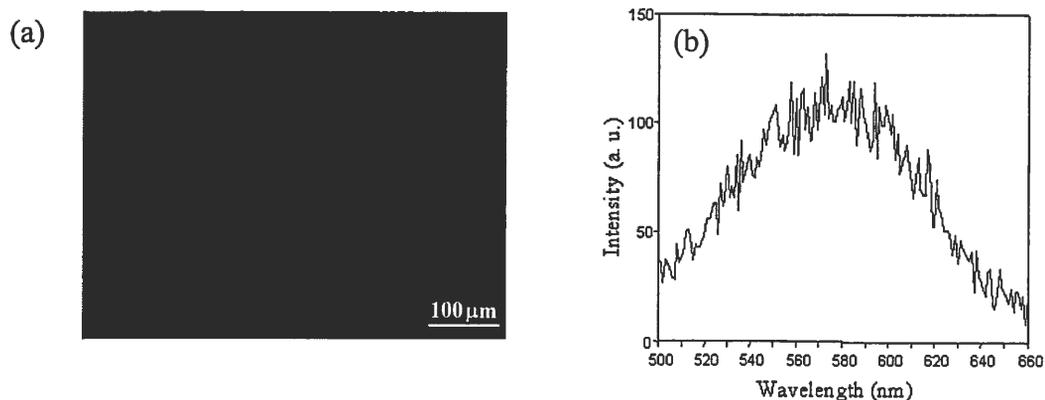
Figure 2. (a) Fluorescence micrograph of patterned porous silicon pixel arrays ~150 μm in diameter. Bright spots are the photoluminescent porous silicon areas. (b) Emission spectrum of a patterned porous silicon sample at λ_{ex} = 360 nm.

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