Manipulation of Surface Properties by Patterning of Covalently Bound Polymer Brushes

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While the preparation of patterned spin-cast thin films by photolithographic techniques forms the basis for the entire semiconductor industry and has been the object of intensive study over the past few decades,[1] the patterning of covalently bound thin or ultrathin polymer films has received only scant attention. This is unfortunate since the covalent nature of these polymer brushes opens up a number of possibilities, similar to the patterned wetting of self-assembled monolayers (SAMs),[2] which are not available to traditional spin-cast films. For example, attempts to perform chemistry on patterned spin-cast films, or to employ them in solvating environments, often fail due to their solubility, or swellability, in the reaction media. In contrast, patterned polymer brushes are stable to a wide range of different environments and processing conditions; in the extreme case of good solvents, chemistry can be performed on the covalently attached polymer chains with no dissolution or removal of the film. These advantages may permit the use of these films in technological applications including specialty photoresists, sensors, microfluidic networks, etc.

In examining the synthesis of patterned polymer brushes a number of different approaches have been recently described. Ruhe et al.[3] have reported the patterning of surface-bound initiators by either photoablation or photoinitiation, followed by polymerization to give discrete areas of polymer brushes,[4] while Clark and Hammond have detailed the growth of patterned polymer films using layer-by-layer techniques.[5] A number of groups have also reported the elaboration of microcontact-printed thiol monolayers to patterned polymer brushes.[6−9] The structures produced by these strategies are similar in that the polymer brushes are not continuous over the substrate surface, with areas of polymer brushes being separated by substrate surface/monolayer. While successful, these approaches do not address the alternative and potentially more interesting structure in which a continuous polymer brush is patterned into chemically distinct regions. In this communication we report the successful combination of photolithographic techniques with surface-initiated polymerization to give continuous films in which there are discrete areas of hydrophilic and hydrophobic polymer brushes.

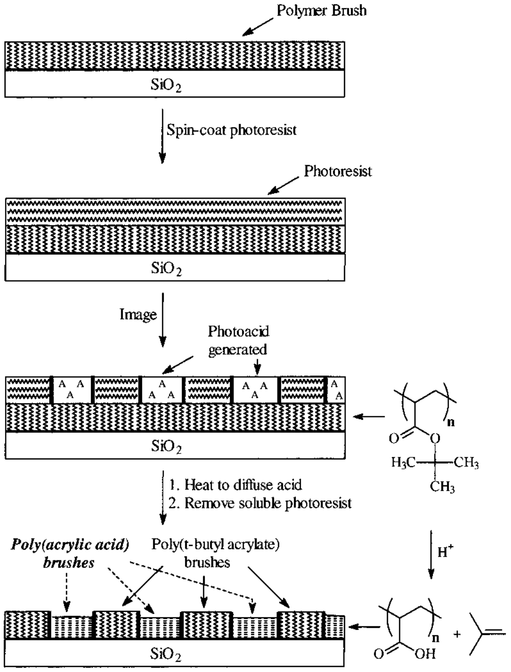
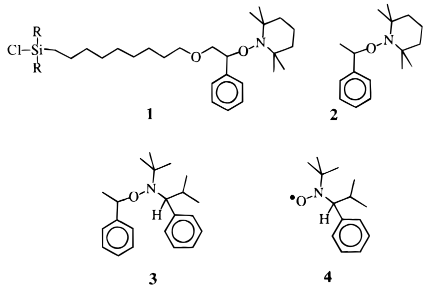


Figure 1. Scheme of strategy for patterning of a polymer brush using a sacrificial photoresist layer and lithographic imaging.

Chart 1



The basic strategy of this novel process is depicted in Figure 1 and relies on the concept of surface-initiated polymerizations.[10] Initially, a layer of initiating groups is formed by the reaction of a trichlorosilyl-functionalized alkoxyamine, **1**, with the surface Si−OH groups of a silicon wafer (Chart 1). The growth of well-defined polymer brushes with controlled thickness from these surface-bound alkoxyamines is a "living" process in the presence of added alkoxyamines.[11] However, initial attempts to control the polymerization of *tert*-butyl acrylate from **1** in the presence of **2** were unsuccessful. This result is not surprising given the demonstrated difficulty in polymerizing acrylates using TEMPO-based systems. To overcome these difficulties, the TEMPO-based alkoxyamine was replaced by the alkoxyamine **3**, which is derived from the α-hydrido nitroxide **4**, which has recently been shown[12] to be an extremely effective initiator for the "living" free radical polymerization of acrylates. Controlled surface-initiated polymerization of *tert*-butyl acrylate could then be effected by heating the wafer at 125 °C under argon in the presence of *tert*-butyl acrylate and a 19:1 mixture of **3** and **4**. The rapid interchange[13] of mediating nitroxides between the surface-bound alkoxyamines and the solution derivatives permitted the controlled growth of poly(*tert*-butyl acrylate) chains from the surfaces. The thickness

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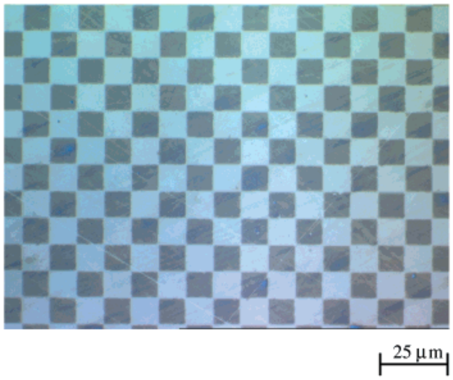

Figure 2. Optical micrograph of 10-μm features in a continuous polymer brush showing regions of poly(*tert*-butyl acrylate) (dark) and poly(acrylic acid) (light).

over the entire wafer was found to be uniform and could be controlled by varying the molar ratio of *tert*-butyl acrylate and **3**.

Having obtained the desired poly(*tert*-butyl acrylate) brushes (100−200 nm in thickness), a solution of polystyrene[14] containing bis(*tert*-butylphenyl)iodonium triflate (8 wt % wrt PSt) was spin-coated onto the top of the brush layer to give a 1-μm-thick sacrificial photoresist layer. Exposure of the surface to 248-nm radiation (10 mJ/cm^2) through a mask resulted in the photogeneration of acid in specific areas of the polystyrene overlayer. To effect image transference into the polymer brush layer, the wafer was heated at elevated temperatures to cause diffusion of the photogenerated acid as well as to promote deprotection of the *tert*-butyl ester groups. This results in conversion of the poly(*tert*-butyl acrylate) chain of the underlying polymer brush to poly(acrylic acid) chains. The sacrificial photoresist layer was then removed by simply washing with the appropriate solvent, in this case dichloromethane. Interestingly, it was found that control of the temperature and heating time was crucial in order to obtain the highest resolution images. For example, heating the wafers at 130 °C for 60 s resulted in distortion of the images and permitted features with a resolution of only 25 μm to be printed. However, decreasing the temperature to 95 °C for 120 s resulted in a significant increase in resolution, with features as small as 1 μm being reproducibly obtained.[15]

Imaging of these features by optical microscopy shows the pattern generation in the polymer brush with 10-μm squares clearly visible in Figure 2. Interestingly, transmission infrared microscopy of the exposed and unexposed regions reveals the expected strong absorbance for the *tert*-butyl ester groups at 1725 cm^{-1} in the unexposed regions, which changes dramatically after pattern generation to a broad peak centered at 1690 cm^{-1} that is fully consistent with essentially complete (>95%) conversion to the carboxylic acid groups of a poly(acrylic acid) chain.

Further evidence for the controlled formation of patterned areas of hydrophilic poly(acrylic acid) and hydrophobic poly(*tert*-butyl acrylate) brushes was obtained from AFM studies. After patterning, the surface is no longer smooth, and distinct topological features are observed which correlate with the original pattern (Figure 3). These features are due to the shrinkage of the poly(*tert*-butyl acrylate) brushes on deprotection of the *tert*-butyl ester to give poly(acrylic acid) brushes.[16] The decrease in film thickness from 130 to 80 nm is directly comparable to the ca. 40% decrease in film thickness that is traditionally observed for photolithographically defined films of spin-cast poly(*tert*-butyl acrylate).

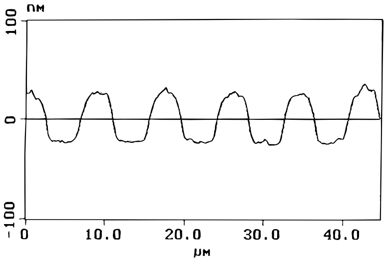

Figure 3. AFM profile of 4-μm features showing thickness change on deprotection of poly(*tert*-butyl acrylate) chains.

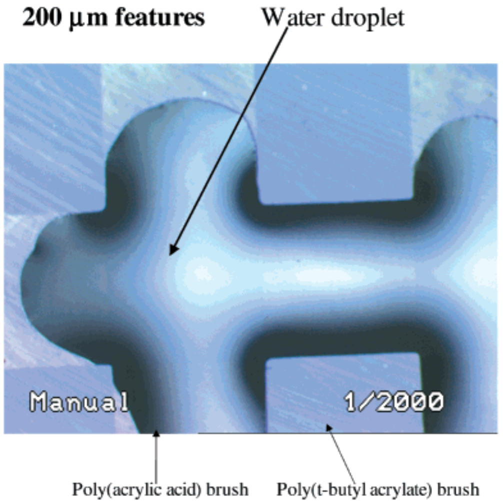

Figure 4. Interaction of a water droplet with 200-μm features showing unusual wetting profile and preferential interaction with poly(acrylic acid) brush domains.

The generation of distinct areas of hydrophilic and hydrophobic polymer brushes also has a dramatic effect on the surface properties of these thin films. The advancing contact angle (water) changes from 92° to 15° on going from the poly(*tert*-butyl acrylate) domains to the poly(acrylic acid) domains. This dramatic difference can be further increased by exposure of the poly(acrylic acid) chains to an aqueous solution of trimethylamine. In this case, the carboxylate groups cause the surface domains to be essentially wetted by water, which can then be used to direct the flow or interaction of fluids with the patterned surface. Figure 4 shows the menisci of a water droplet on top of a 200-μm patterned surface and clearly demonstrates that the underlying patterned polymer brush is directing the menisci shape by unfavorable interactions with the poly(*tert*-butyl acrylate) brush and favorable interactions with the poly(acrylic acid) brush. The dramatic effect of controlled surface functionality has also been recently demonstrated by Aizenberg et al. during crystal nucleation at surfaces[17] and by Whitesides et al. in the patterned wetting of SAMs.[18]

In conclusion, we have demonstrated that the concept of nitroxide-mediated “living” free radical procedure can be extended to the surface-initiated polymerization of *tert*-butyl acrylate. These well-defined poly(*tert*-butyl acrylate) brushes can then be patterned using photolithographic techniques to yield novel patterned polymer brushes in which there are well-defined hydrophobic and hydrophilic domains. The surface properties of these domains are controllable and can be used to influence interactions of the surface with external agents.

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[14] Typical spinning solvent was propylene glycol monomethyl ether monoacetate.

[15] Resolution limits were defined by lithographic techniques.

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