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To Patterned Binary Polymer Brushes via Capillary Force Lithography and Surface-Initiated Polymerization

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Large-scale and high-throughput surface patterning is of fundamental importance not only to the semiconductor industry but also to other areas of modern technology, such as microelectromechanical systems (MEMS), biochips, biosensors, cell-growth regulation, micro/nanofluidic systems, and photonic crystal materials.[1] Specifically, patterned polymer-grafted layers, known as “brushes”, have drawn significant attention because of the diversity of chemical structures suitable for brush formation and the physical/mechanical robustness of the grafted films. Various patterning techniques have been reported for use in fabricating patterned polymer brushes. These include microcontact printing,[2] UV/electron-beam lithography,[3] scanning-probe lithography,[4] and imprint lithography.[5] In general, a single brush pattern has been created on a substrate surface leaving areas covered with the grafted polymer chains (brushes) adjacent to uncovered regions. A next generation of the patterned surfaces involves synthesis of binary polymer brushes. Here, the grafted layer possesses discrete areas to which dissimilar macromolecules are tethered. To the best of our knowledge, only two procedures to obtain the binary brushes have been developed to date. The procedures involve initial formation of a homogeneous polymer brush that is exposed to irradiation to create a pattern at the second stage. Hawker et al.[6] reported on synthesis of patterned, covalently tethered polymer brushes employing a combination of surface-initiated polymerization (SIP) and 248 nm photolithography. The lithographic technique was used to create a binary pattern by first locally irradiating a surface onto which a poly(*tert*-butyl acrylate) brush had been grafted by SIP. This was followed by hydrolysis to poly(acrylic acid) of the surface regions exposed to the radiation. Zhou et al.[7] fabricated a binary brush via two-step SIP. A homogeneous polymer brush was first grafted to a silicon substrate. The brush was then etched with UV radiation to create exposed sites for the subsequent attachment of the initiator onto which a second polymer was grafted.

Here, we report yet another original and effective method for generating patterned binary polymer brushes. This method is unique in that it is not based on any irradiation technique. The binary grafted layers are obtained via a combination of capillary force lithography (CFL)[8] and SIP. The method is based on an interesting phenomenon found in our laboratory. It was found that when an ultrathin polystyrene (PS) pattern was deposited (from solution or melt), over a layer of polymerization initiator already anchored to a surface, the pattern can withstand subsequent polymerization conditions and stay intact during brush synthesis provided that no solvent for polystyrene is involved. Thus, no monomer and catalyst are delivered to the initiator located on the PS-protected areas. In other words, the deposited PS mask will not permit grafting of a polymer brush in the regions underneath it, or between it and the surface. However, we also found that this desirable outcome was only obtained when the polystyrene polymer had a sufficiently high molecular weight (>100 000 g/mol) to survive throughout the grafting. PS with a relatively low molecular weight (3000, 8500, and 33 000 g/mol) was removed from the surface in the course of polymerization, and the anticipated patterned brush was not obtained.

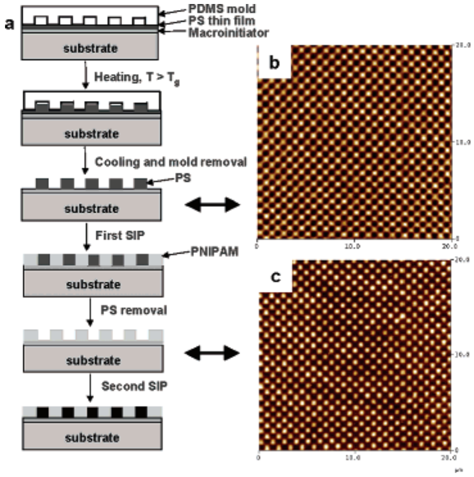

Figure 1. (a) Schematic diagram of patterned surfaces created by CFL and SIP. (b) AFM topography image of a PS pattern created on top of EPB/BPA macroinitiator surfaces (20 × 20 μm, AFM RMS roughness 7 nm). (c) AFM image of PNIPAM brush pattern created by CFL and SIP (20 × 20 μm, AFM RMS roughness 6 nm).

An overall schematic of the fabrication of patterned brushes via the combination of CFL and SIP is shown in Figure 1a. For the initial surface modification, a thin layer of an epoxidized polymer was deposited on the surface of a silicon wafer. Next, a macroinitiator, of atom transfer radical polymerization (ATRP), was synthesized on the substrate surface by the reaction between epoxy groups of the polymer and the carboxy functionality of a halogen-containing carboxylic acid. After the synthesis of the macroinitiator was completed, an ultrathin PS film was deposited (by spin coating from solution) to cover the primary initiating layer. To conduct CFL, a PDMS mold was placed over the PS film and the complete assembly was annealed in an oven. Next, the assembly was removed from the oven and allowed to cool to room temperature before the PDMS mold was peeled off the surface. CFL resulted in generation of patterned PS structures due to selective dewetting of the PS ultrathin film. Consequently, part of the macroinitiator layer becomes exposed and available for brush synthesis, whereas the other part remains covered with PS and thereby protected from the grafting of polymer chains. Surface-initiated ATRP was then conducted, and the first polymer brush was anchored to the uncovered fractions of the surface. After the grafting was complete, the PS mask was removed and a second brush was synthesized on the areas previously protected. This succession of procedures led to the generation of a binary patterned polymer brush.

The layer of macroinitiator on the wafer surface was synthesized by the method recently developed in our laboratory and published elsewhere.[9] In brief, an ultrathin (3 nm) layer of epoxidized

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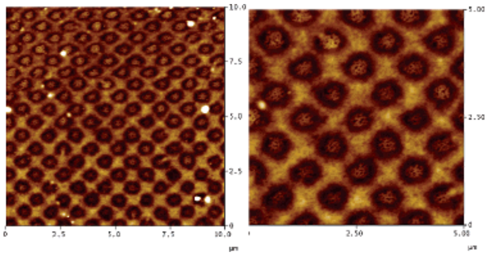

Figure 2. AFM topography image of binary polymer patterned brushes of poly(PEGMeMA) and PNIPAM. Left, 10 × 10 μm, right, 5 × 5 μm, AFM RMS roughness ∼ 4 nm.

polybutadiene (EPB) was deposited on the silicon substrate by dip coating from methyl ethyl ketone solution. The film was annealed for 15 min at 110 °C under vacuum to chemically attach the EPB chains to the surface. Only a fraction of the EPB epoxy groups reacted with the substrate. The epoxy units located in the "loops/tails" sections of the attached macromolecules were not connected to the surface and served as reactive sites for the subsequent synthesis of the macroinitiator. Specifically, the initiator was obtained by attachment of 2-bromo-2-methylpropionic acid (BPA) via the reaction between carboxylic and epoxy functionalities. The reaction produced tethered α-bromoester groups capable of initiating SIP by the ATRP mechanism.

Having obtained a layer of the macroinitiator, a 15 nm thin PS film was deposited on the wafer surface by spin coating from toluene solution. AFM demonstrated (image not shown) that the substrate was completely covered with an extremely smooth PS film (AFM roughness 0.2 nm). Next a PDMS mold was utilized to selectively dewet the ultrathin PS film employing CFL. The lithography was conducted at 130 °C for 20 min. Figure 1b shows that a PS pattern replicating the PDMS mold was successfully generated on the surface. The cross-section profile of the patterned surface revealed that the PS-patterned structures possessed an average height of 30−40 nm (approximately twice as high as the original thickness of the spin-coated PS film). SIP of *N*-isopropylacrylamide (NIPAM) from the patterned PS surfaces was carried out in a drybox at room temperature for 24 h (PNIPAM is of particular interest because the polymer exhibits a lower critical solution temperature (LCST) in water near the temperature of the human body[4]). After the polymerization was completed, the PS mask was removed by rinsing the sample with MEK. An AFM image of the patterned PNIPAM brushes obtained is presented in Figure 1c. The imaging demonstrated that polystyrene is, indeed, an effective resist for SIP of NIPAM. The polymerization was initiated only from regions of the surface that were not covered with the PS mask. The AFM section analysis revealed that the height of the PNIPAM patterned brushes (in a dry state) was about 20 nm.

In Figure 1c, the darker region corresponds with the areas on the surface covered with the active EPB/BPA macroinitiator, which was protected by the PS mask during the grafting of NIPAM. These surface regions are still capable of initiating polymerization. Grafting of poly(ethylene glycol) methyl ether methacrylate (PEGMeMA)—a polymer capable of preventing nonspecific binding of proteins[10]—was carried out in order to obtain a second component of the binary patterned brush. An AFM topography image of the fabricated binary patterned poly(PEGMeMA)/PNIPAM layer is presented in Figure 2. The matrix consists of poly(PEGMeMA) brushes (thickness ∼ 30 nm, AFM section analysis), and the islands are PNIPAM chains. (Since no preventative measures were taken to arrest formation of PNIPAM-*b*-poly(PEGMeMA) block copolymer, formation of the block copolymer chains during the second stage of the grafting can be anticipated. However, since it has been shown that the typical ATRP of NIPAM is not a "living"/controlled process,[11] the number of the copolymer macromolecules grafted is expected to be small.)

In conclusion, we have demonstrated a novel approach to synthesize binary patterned polymer brushes through the combination of CFL and SIP. The approach is based on the employment of a PS mask to prevent grafting on the fraction of a surface protected by the polymer pattern. The major limitation of the method is that the first SIP must be conducted in an environment that does not dissolve the mask that is introducing the pattern. Since there is no specific restriction for the second SIP, virtually any polymer/copolymer obtainable by the ATRP method could be anchored to the surface at this stage of the process. Therefore, a variety of interesting combinations of binary patterned polymer brushes could be achieved by the approach reported above. The size of the features fabricated can be as small as 100 nm, as evidenced by publications on the CFL technique.[8] This unique method does not utilize irradiation and includes just one step for the introduction of the SIP initiator on the surface. Finally, the method described here may be applied to various substrates since it has been demonstrated that the layer of macroinitiator can be successfully deposited on various organic polymeric and inorganic surfaces.[12]

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Supporting Information Available: Experimental procedures and additional AFM images and height profiles. This material is available free of charge via the Internet at http://pubs.acs.org.

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