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Pattern Transfer Using Alkanethiolate-Protected Templates: A New Approach in Polymeric Materials Nanofabrication

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ABSTRACT

A new approach for the nanofabrication of polymeric structures based on the use of methyl-terminated thiolate self-assembled monolayers as anti-adherent molecular coatings is presented. These monolayers modify the surface characteristics of a rigid template by enhancing the detachment of the polymeric material poured and polymerized onto the template. The advantages of this approach are extremely high vertical and lateral resolution, easy procedure for building the anti-adherent layer and the capability of using rigid instead of elastomeric templates.

The development of new techniques to generate micropatterned structures had an increasing interest in the past decade as a consequence of their potential applications in several technological fields such as microelectromechanical systems (MEMS)[1,2] and the microelectronic industry.[3] This represents a constant challenge in order to design more specific routes to obtain nanostructures in such a way to optimize the fabrication procedure.

Patterned polymeric materials have shown great utility in microanalytical applications such as plastic microfluidic devices[4] and in optical dispositives, such as single-mode polymeric waveguides.[5] In particular, gratings having micron and submicron periodicity have important applications in optoelectronic devices[6,7] and for alignment of liquid crystals.[8]

Fabrication methods of polymer-made micro- and nanostructured architectures have been extensively reported in the literature in the last years.[4,9,10] The most common procedures are embossing, injection molding, imprinting, laser ablation, and soft lithographic techniques. The soft lithographic techniques include replica molding, microcontact printing, micromolding in capillaries and solvent-assisted micromolding.[9] These procedures are novel nanofabrication methods, considering the term nanofabrication as techniques capable of generating structures with at least one lateral dimension between 1 and 100 nm.[10]

Most of the methods for obtaining polymeric microstructures involve complex steps requiring highly specific instrumentation, i.e., laser ablation, being suitable alternative routes to obtain such microstructures.

In the last years several groups have begun to explore the use of self-assembled monolayers (SAMs) in micro- and nanofabrication. Generally, SAMs were patterned by stamping or contact printing[10] and then used as thin resists to transfer micropatterns onto thin metal films, either by selective chemical etching[11] or by selective deposition.[12]

In these cases the capability of thiol monolayers to protect the metal substrate against chemical agents was exploited. Recently, a procedure for obtaining polymeric microstructures using patterned self-assembled monolayers on SiO_2/Si surfaces has been reported.[13] In some cases the ability to alter the tail group of SAMs has been exploited in order to bind selectively Pd catalyst and to promote patterned electroless deposition.[14]

In this work we used methyl-terminated alkanethiols as anti-adherent coatings in order to promote an enhanced detachment of the polymeric material from a metallic template. It is well-known that alkanethiolate monolayers are easily self-assembled onto metal substrates, modifying in a drastic manner several surface characteristics such as wear, wettability, adherence, corrosion protection, etc. The idea of using a protective anti-adherent film on the template is not novel; this procedure has been employed in compact disks (CDs) manufacturing using an aluminum layer, and recently, Teflon-like ultrathin films have been developed for use in hot embossing.[15] However, the idea of using a methyl-terminated thiolate self-assembled monolayer is attractive due to the effectiveness, simplicity, and low cost of the molecular self-assembly procedure,[16] avoiding very complex procedures used in other techniques involving high-vacuum requirements.[15]

Our approach aims to show methyl-terminated thiol self-assembled monolayers as novel anti-adherent molecular

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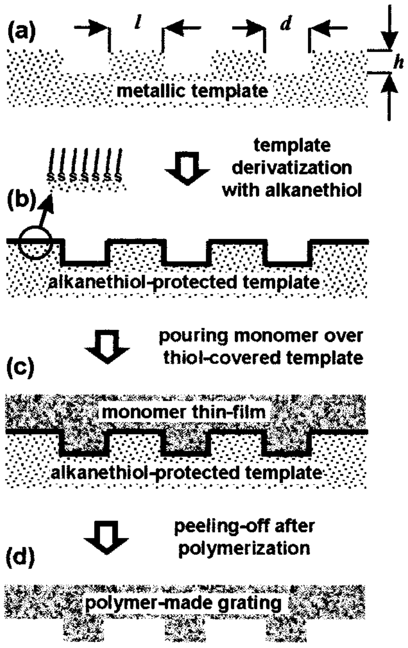

Figure 1. Schematic illustration of the procedure for grating fabrication. (a) Metallic template has dimensions $h = 80$ nm, $l = 980$ nm, $d = 590$ nm. (b) Template is derivatized with a dodecanethiolate self-assembled monolayer: (c) Monomer is poured on the dodecanethiolate-covered template. (d) After polymerization the polymer-made grating is easily peeled-off from the template.

coatings to be used in micro- and nanofabrication of polymeric materials. Although this method is similar to the replica molding method (REM), it differs from that in the characteristics of the template. In the REM method the template is made of a polymeric material, and in the method presented in this work the template is made of metal. The polymeric material used in REM is poly(dimethylsiloxane) (PDMS) and it has been pointed out that the elastomeric character of PDMS leads to some of the most serious problems of the method due to adhesion and capillary forces exerting stress on the elastomeric features, generating defects in the formed patterns.[9] This fact limits the achievable architectures in accordance with the ratio $0.2 < l/h < 2$, as was remarked in the literature.[17] Great differences exist between the templates considering the high mechanical stability of the copper-made template. The alkanethiolate layer protecting the copper-made template enables a complete peel-off of the polymeric material from the mold, producing defect-free patterns. It may be noted that this characteristic is independent of the adhesive properties of the polymeric material. To show this particular feature, we nanofabricated a grating, with an architecture similar to those fabricated by laser ablation,[18] using poly(isobutylcyanoacrylate). This polymeric material is characterized by its high adhesive properties and is commonly used as a superglue to bond metals, elastomers, and plastics. However, the most remarkable advantage of our method is the high vertical resolution. In fact, by using this procedure, we are able to replicate characteristic surface features of a Au(111) single crystal as small as 40 and 1 nm in lateral and vertical size, respectively.

The method for fabricating the polymer-made grating involves few and very simple steps. A copper-made template (Figure 1a), fabricated as described elsewhere,[19] was immersed for 1 h in a 5 mM dodecanethiol solution containing toluene as solvent (Figure 1b) in order to derivatize the surface with a dodecanethiol monolayer. Toluene was chosen as solvent since this type of solution produces high-quality dodecanethiolate self-assembled monolayers on copper substrates, as was previously reported in the literature.[20] After the surface is derivatized, the mold is placed for about 30 min in pure toluene to remove the physisorbed alkanethiol molecules forming multilayers. Then a drop of liquid prepolymer is poured on the thiolate-modified template (Figure 1c). Once cured, the polymeric material is easily peeled off the derivatized template. It may be noted that the peeling-off is a procedure that in our method requires only a minimum mechanical effort, producing no damages to the polymer-made grating or even the copper-made template. In fact, polymer adherence on methyl-terminated SAMs has been found to be extremely poor[21] and this property has been used for micropatterning conducting polymers using hydrophobic and hydrophilic patterned monolayers.

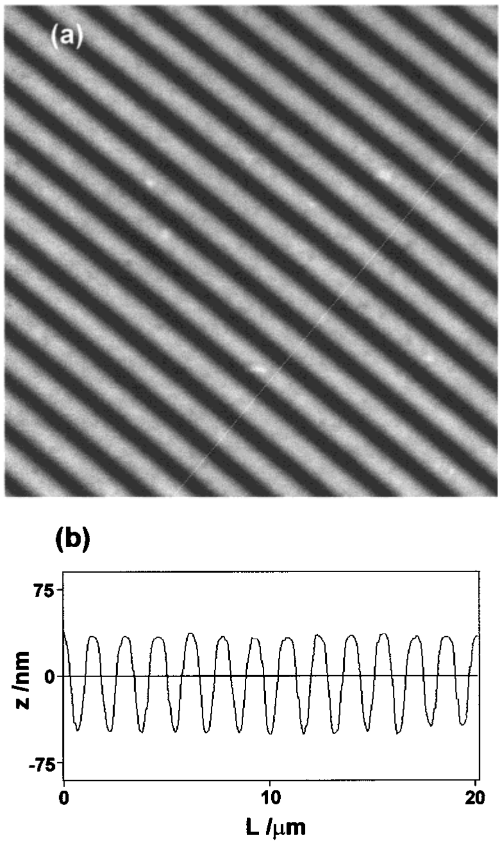

Figure 2. (a) 20×20 μm^2 AFM image of the copper-made template. (b) Cross-sectional analysis corresponding to the copper-made template.

The capability of our method for generating polymeric architectures was monitored by imaging with atomic force microscopy (AFM) the channeled copper-made mold (Figure 2a) and the polymer-made grating (Figure 3a) obtained after carrying out the whole procedure. One of the advantages of using AFM is the capability of verifying the way that channels were reproduced; i.e., scanning probe techniques give reliable information on the z coordinate. Note that our

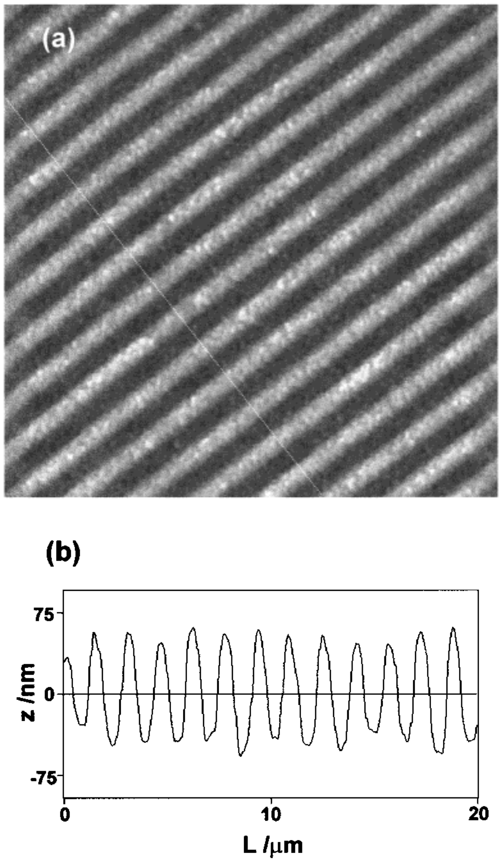

Figure 3. (a) 20 × 20 μm^2 AFM image of the obtained polymeric grating. (b) Cross-sectional analysis corresponding to the polymer-made grating.

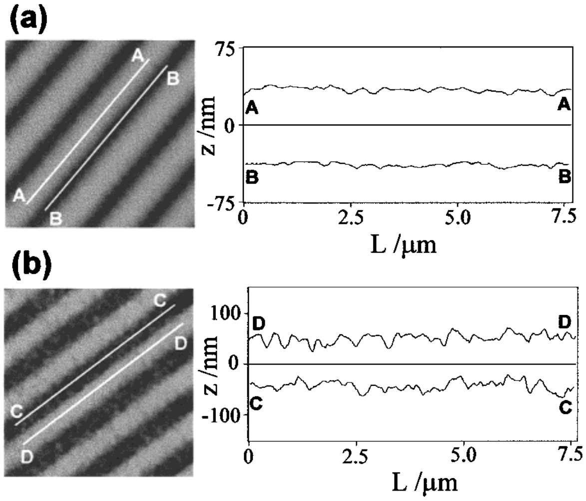

Figure 4. Detailed cross-sectional analysis of AFM images (8 × 8 μm^2) showing the morphology along the tracks in the patterned template (a) and the obtained polymeric grating (b).

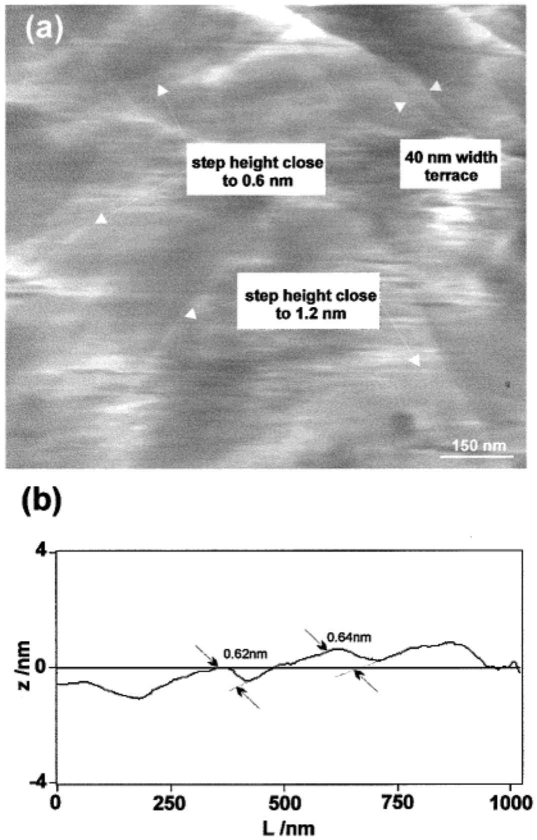

Figure 5. (a) AFM image of the inner face of the polymeric film detached after curing on a dodecanethiolate-modified Au(111) single-crystal surface. (b) Typical cross-section showing the step-terrace morphology, transferred from the substrate, to the inner face of the polymeric film.

AFM instrument (Digital Instrument, Santa Barbara, CA) was calibrated in the *z* direction using monoatomic height steps present on a Au(111) single-crystal surface.[22] Cross-section analysis (Figures 2b and 3b) shows the accurate form in which the periodicity and microchannels depth were reproduced in the polymeric grating.

The morphology of the employed materials plays a key role in the pattern transfer process because roughness and/or nodule or grain sizes could introduce severe restrictions to reproduce nanometer scale features. AFM images at a high resolution of the Cu mold and the polymer grating are shown in Figure 4. The AFM images reveal that the Cu mold is formed by small grains with an average size $d \approx 50$ nm (Figure 4a), whereas the polymer grating consists of nodules with $d \approx 100$ nm (Figure 4b). Accordingly, the root-mean-square roughness is slightly higher for the polymer grating than that of the Cu mold. Therefore, the architecture of the polymer grating differs slightly from that expected from the Cu mold. However, no significant distortion is introduced in the pattern transfer process despite differences in the material structure, i.e., grain and nodule size difference. Another important point regards the influence of the template granular structure to induce a nodular polymer structure. To clarify this point, we have used a dodecanethiolate-modified Au(111) single-crystal surface as template. After detachment, AFM imaging of nanometer-sized domains of the polymeric material that has been in contact with the thiol-modified Au(111) surface exhibits the typical triangular terraces (Figure 5a). Some of them are as small as 40 nm in width and they are separated by steps with a height equivalent to 2 or 4 Au atoms (Figure 5b). Only a few isolated polymer nodules randomly distributed on the polymeric sample were observed, probably nucleated at defective sites of the thiolate-modified single-crystal surface. The fact that at nondefective regions we are able to reproduce characteristic features of the Au(111) single-crystal surface with a lateral size ≈40 nm and vertical size ≈1 nm, is a promising result when compared to other pattern transfer methods. Note, however, that in our method the template quality plays a key role in achieving high resolution; i.e., polycrystalline templates (granular) or the presence of defective sites in the thiol monolayers limit the capability to fabricate in the nanometer range. Finally, another advantage of this method is that by using a suitable mold, this procedure enables the repeated production of a desired polymeric nanostructure, considering that the alkanethiol layer remains on the mold just like at the starting point.

In conclusion, in this work we have presented a new method using alkanethiolate self-assembled monolayers as high-performance anti-adherent molecular coatings. This method has potential applications in serial nanofabrication of polymeric materials. The high lateral and vertical resolution obtained from our procedure opens the chance to reach new fabrication routes involving nanometer resolution. Besides, despite the similarities of this procedure with the REM method, the capability of using rigid molds brings an alternative method and the possibility of generating polymeric nanostructures with no limitations on the architecture.

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