MICROTRANSFER MOLDING USING METALLIC STAMPS

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Abstract

This paper describes the fabrication of patterned polymeric microstructures by a transfer molding method. We use alkanethiolate-modified metallic molds that allow pattern transfer with 100 nm resolution. Rigid metallic molds avoid the typical pattern deformations observed when elastomeric molds are employed. The alkanethiolate layer changes the adherence properties of molds enabling an easy release, even for high adherent polymeric materials.

Resumen

El presente trabajo describe la fabricación de microestructuras poliméricas regulares mediante un método de moldeo de relieves superficiales. Utilizamos moldes metálicos modificados con monocapas autoensambladas de alcanotiolatos que permiten transferir patrones regulares con resolución por debajo de los 100nm. Los moldes metálicos rígidos permiten evitar las típicas deformaciones observadas cuando se utilizan moldes elastoméricos. La película de alcanotiolato cambia las propiedades de adherencia de los moldes posibilitando un fácil despegue, aún para materiales poliméricos altamente adherentes.

Introduction

The development of new technologies capable of generating polymeric micro- and nanostructures has had an extreme relevance in the last years. This fact is due to the great utility of this sort of systems in several technological applications such as microanalytical techniques, by using plastic microfluidic devices [1], and optical devices, considering the use of polymeric gratings in optoelectronic devices [2,3] and for alignment of liquid crystals [4].

The idea of designing new strategies, with potential applications in serial fabrication, is based on developing novel methods, which satisfy two main requirements: high-resolution and low-cost fabrication. Generally, the term “resolution” is referred to the lateral dimension of the smallest feature that can be generated by a determined method [5].

It has been shown that molding and replication of a master is one of the most powerful and inexpensive routes for the serial nano / microfabrication. This strategy have

been widely employed by many information-storage-related industries [6] for serial fabrication of diverse dispositives [7], such as compact discs (CDs), digital-versatile-disc (DVDs), holograms, optoelectronic devices, etc. The fabrication of a nano / micro-patterned master often requires sophisticated and expensive procedures, and the use of complex techniques such as electron-beam lithography [8] , X-ray lithography [9], ion sputtering [10], cluster beam fabrication [11], scanning probe-assisted lithography [12] and atom optics [13]. Currently, great efforts are made in order to fabricate metal- and semiconductor-made templates by a simpler and inexpensive way. Under this focus, it could be mentioned a recent work on polymer imprinting [14] using the well-known nanostructured alumina [15] as a template. The following fabrication step involves the mold fabrication that is used to obtain master replicas.

New fabrication methods for polymer-made micro- and nanostructured architectures have been extensively reported in the literature [16-19]. The most common procedures involve embossing, injection molding, imprinting, and soft lithographic techniques. The soft lithographic techniques include replica molding, microtransfer molding, microcontact printing, micromolding in capillaries, and solvent-assisted micromolding [5]. Most of these methods involve complex steps and highly specific instrumentation. Therefore, simpler alternative routes to obtain such architectures should be explored. In fact, it is desirable to develop methods that allow direct printing of the polymeric material onto the substrate without masks and intermediate steps. At present, other polymer molding techniques such as nanoimprinting lithography [20] (NIL) and step and flash imprint lithography [21] (SFIL) have shown very good performance in polymer molding, bringing new alternatives for serial fabrication. In these cases, the molds were fabricated by hard lithographic techniques on Si/SiO_2 (NIL) and quartz (SFIL) substrates. On the other hand, the microtransfer molding [5] (μTM) is a relatively simple method that allows direct pattern transfer to a polymeric material. However, the use of elastomeric molds, which allows versatility in the shape of the patterns to be transferred, i.e. non-planar substrates, could introduce deformations and distortions [22] and limitations in the architectures to be achieved [23]. In fact, the polymeric material used in μTM is poly(dimethylsiloxane) (PDMS). It has been pointed out that the elastomeric character of PDMS leads to some of the most serious problems of the method originated in adhesion and capillary forces that exert stress on the elastomeric features. These effects generate defects in the formed patterns and limit the architectures to be achieved. Therefore, at present the resolution limit of this technique is only 1 μm [5].

In order to overcome the above-mentioned problems there are other alternatives, such as ultrathin [24] and "hardened" PDMS stamps [25] or even composite stamps [26]. In addition a modified microtransfer molding (MμTM) method [27] employing a metal covered mold has also been developed allowing the formation of a continuous patterned film of a polymeric material with considerable resolution (25 nm). However, in this case molding is restricted to low adherent polymeric materials because the transferred patterns could be damaged during the release of the gold-made mold. Therefore, this method is inapplicable for molding a wide number of polymeric materials with intermediate and high adherence properties.

In this work, we present a new route that eliminates the distortions introduced by the elastomeric molds in the conventional μTM, and that eliminates the restrictions of the MμTM concerning the adhesive properties of the polymeric material. Our procedure differs from the conventional μTM in the use of a metallic mold, and from the MμTM in the use of a self-assembled alkanethiolate monolayer covering the metallic mold [28]. The alkanethiolate layer modifying the metallic-made mold enables a complete release of the mold from the polymeric film producing defect-free patterns irrespective of the adhesive properties of the polymer, thus eliminating the severe restrictions present in the MμTM. The versatility of our method is demonstrated by the fabrication of glass-supported gratings of polymer materials with very different adhesive and mechanical properties [29,30], with architecture similar to those fabricated by laser ablation [31].

Experimental

The copper mold was prepared by copper electrodeposition on a dodecanethiol-covered copper grid (the template). The copper electrodeposition was performed in a conventional three-electrode electrochemical cell. The temperature and current densities used were 25°C and 20 mA cm^{-2}. The composition of the plating bath was: 0.6 M $CuSO_4$. $5H_2O$+0.5M H_2SO_4+0.025mM thiourea. All chemicals were of analytical grade. High-impact polystyrene (14.5% w/w) and polystyrene (12.5% w/w) solutions were prepared by dissolving the polymer pellets in toluene. Atomic force microscopy (AFM) images of the metallic master, metallic molds and polymer replicas were taken using a Nanoscope III microscope (Digital Instruments, Santa Barbara CA) operating in contact mode with Si_3N_4 nanotips.

Results and Discussion

The method to obtain the polymer-made-grating involve few and very simple steps as shown in Figure 1. A copper-made mold, fabricated from an alkanethiol-modified copper master by copper electrodeposition [32], was immersed during one hour in a 5mM dodecanethiol solution containing toluene as solvent [33] in order to cover the surface with a dodecanethiol monolayer. The dodecanethiol-modified mold is placed about 30 minutes in pure toluene to remove physisorbed molecules forming multilayers. Then, the liquid polymer is poured on the glass support (Figure 1c), and immediately the thiol-modified copper mold is pressed on the glass supported liquid polymer film (Figure 1d), controlling the applied pressure by using a micrometer screw.

The use of metallic molds, in contrast to PDMS molds, allows applying high pressures without introducing significant deformations. Once the polymer is cured, the thiol-modified mold is easily released from the polymeric film (Figure 1e). In our method the release procedure requires only a minimum mechanical effort producing no damages to the polymer-made grating or to the copper-made mold. The low adherence properties of methyl-terminated self-assembled monolayers have been previously exploited for micropatterning conducting polymers on gold surfaces [34].

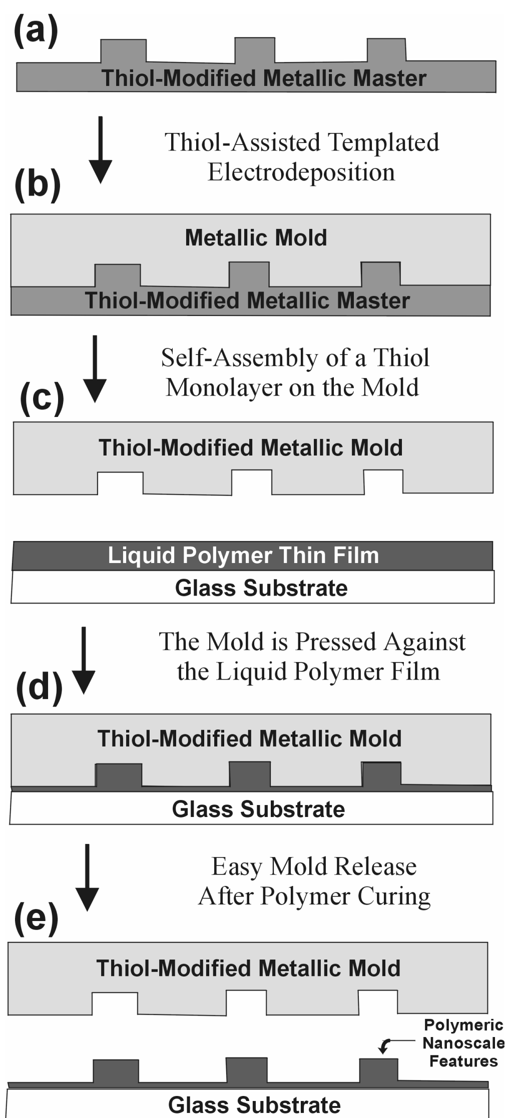

Figure 1. *Schematic illustration of the complete procedure for fabrication of polymeric nanostructures by the nanotransfer molding method.*
a) *Thiol-modified metallic master,* ***b)*** *Mold fabrication by thiol-assisted templated electrodeposition, followed by mold modification by thiol adsorption,* ***c)*** *polymer film on the glass substrate,* ***d)*** *The thiol-modified mold is pressed on the liquid polymer film supported on the glass substrate* ***e)*** *after casting, high impact polystyrene, or polymerization, poly(isobutylcyanoacrylate), the mold is easily released from the polymer-made film. The polymer face in contact with the mold is a replica of the template.*

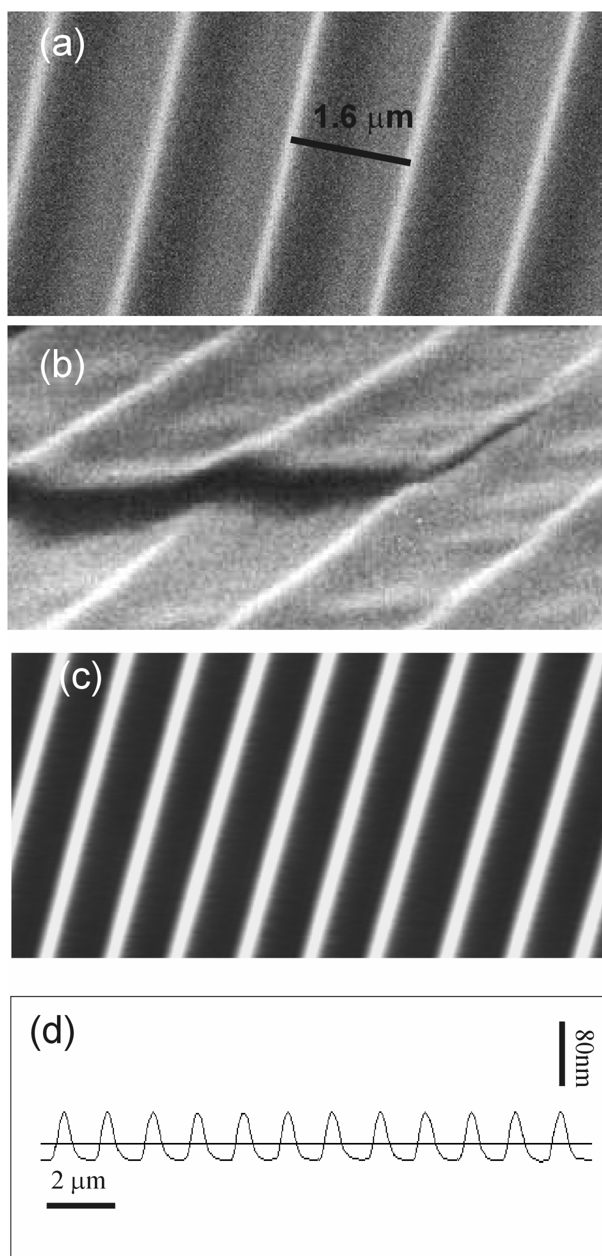

Figure 2. ***(a)*** *SEM image of the Cu-made master showing the track dimensions. The bar indicates 1.6 μm.* ***(b)*** *fractured Cu master showing the track shape.* ***(c)*** *20 x 20 μm^2 top view AFM images of the copper-made master.* ***(d)*** *Cross-section showing the typical dimension of track (l), channel (w) and depth (d): d = 80 nm, l = 590 nm, w = 980 nm.*

The first step of our method consists on the fabrication of the metallic mold from a metallic master. Combined scanning electron microscopy (SEM) and atomic force microscopy (AFM) imaging were employed to characterize the master structure used in our replication procedure. SEM data show that the master structure consists of rounded tracks (Figure 2a) 590 nm in width separated by 980 nm wide channels (Figure 2b). On

the other hand, AFM images and cross-sections reveal that the channels depth is 80 nm (Figure 2c,d). Note that the lateral dimension of tracks and channels from the AFM images agree with those derived from the SEM images due to the high lateral size/depth ratio of our structures that minimizes the tip-sample convolution. The typical root mean square roughness (rms) value measured at row top and channel bottom is 3 nm.

As expected from the master geometry, AFM images of the Cu-made mold exhibit 900 nm wide tracks separated by 600 nm wide and 80 nm deep channels (Figure 3a). The root mean square roughness increases 2 nm with respect to that observed for the Cu master at both rows and channels as a consequence of the electrodeposition process.

AFM images of the high impact polystyrene (HIPS)-made (Figure 3b) and poly(isobutylcyanoacrylate)-made (Figure 3c) gratings after carrying out the whole procedure described in Figure 1a reveal that the master structure has been replicated. A slight increase in the rms value with respect to that measured on the Cu mold was also observed for the polymeric materials. Cross-section analysis (Figure 4a-c) shows that both the track size and channel depth of the metallic master (Figure 2c) were reproduced in the polymeric grating. From these results it can be concluded that this method allows the fabrication of ordered gratings irrespective of the adhesive and mechanical properties of the polymers. In fact, HIPS and poly(isobutylcyanoacrylate) are polymeric materials with completely different surface and bulk properties.

HIPS is a polymer less rigid than poly(isobutyl-cyanoacrylate) considering the chemical modification introduced in the polymerization process in order to modify its mechanical properties [30]. Otherwise, both polymers markedly differ on their surface properties considering the highly adhesive character of poly(isobutylcyanoacrylate) in contrast to HIPS.

The importance of the surface chemical modification introduced by the alkanethiol layer is clearly revealed by performing control experiments where the polymer deposition was directly made onto a bare Cu mold. In these cases polymer films cannot be released from the Cu mold. Recently interactions at polymer/alkanethiol interfaces have been studied by an adaptation of the superlayer test [35]. It has been found that the work of adhesion between a mixed COOH/CH_3-terminated self-assembled monolayer on gold and a polymer layer decreases as the fraction of methyl groups in the mixed monolayer increases, thus revealing the crucial role of hydrophobic groups in reducing metal/polymer interactions.

The sidewall structure is a key element in microlithography, especially in microelectronics. We have used a Cu mold with sharp steps (Figure 5a) in order to verify the capability of the metallic molds to transfer surface-relief structures with well-defined geometries. The SEM image of the PS grating (Figure 5b) after carrying out the whole procedure described in Figure 1 reveal also sharp steps with well defined angles.

In conclusion, we have developed a modification of the μTM method by using alkanethiolate-modified metallic molds instead the conventional elastomeric molds. The use of the alkanethiolate layer enables an easy release of the metallic mold irrespective of the adherent properties of the polymers, thus avoiding the restrictions found in the high resolution MμTM method. Our modified method has potential applications in serial fabrication of polymeric microstructures.

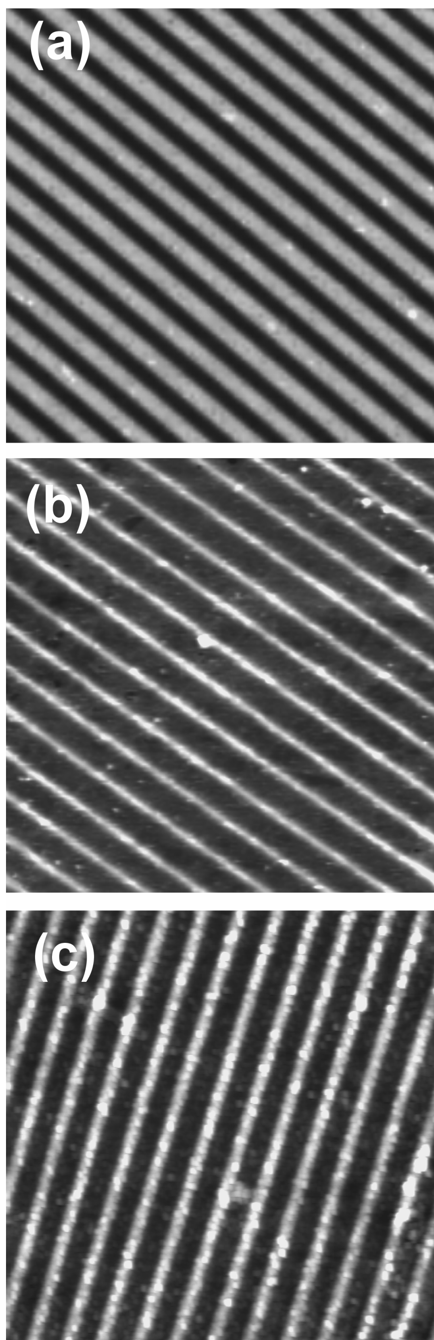

Figure 3. *20 x 20 μm² top view AFM images* ***(a)*** *copper made mold,* ***(b)*** *high-impact-polysteyrene-made replica,* ***(c)*** *poly(isobutylcyanoacrylate)-made replica.*

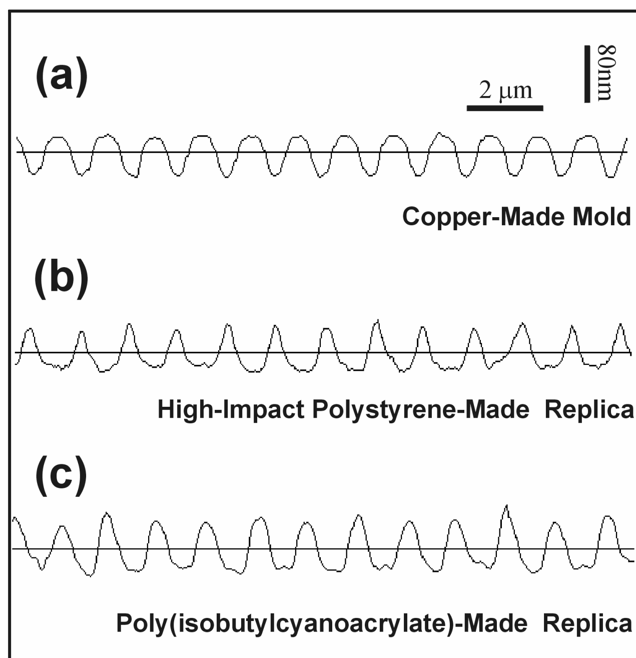

Figure 4. *Cross-sectional analysis corresponding to:* ***(a)*** *copper-made mold, dimensions: d = 80 nm, l = 980 nm, w = 590 nm.* ***(b)*** *high impact polystyrene-made replica, dimensions: d = 80 nm, l = 590 nm, w = 980 nm.****(c)*** *poly(isobutylcyanoacrylate)-made replica, dimensions: d = 80 nm, l = 590 nm, w = 980 nm.*

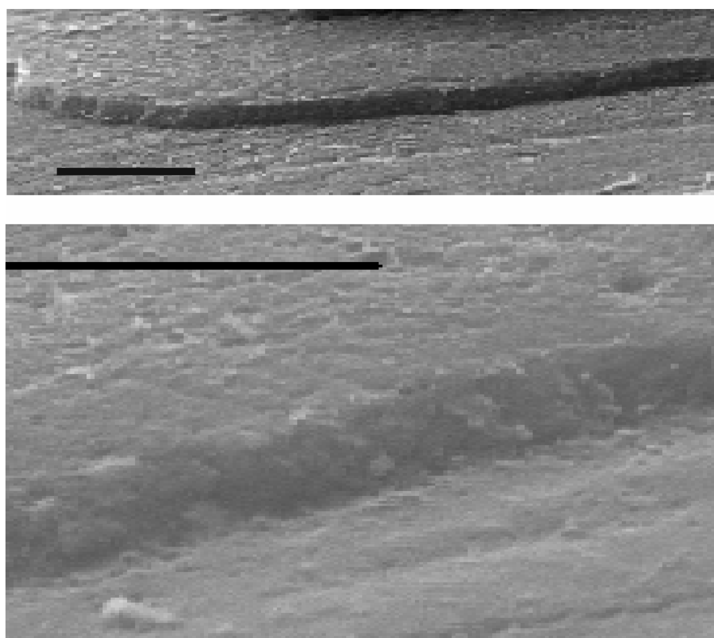

Figure 5*: (a) SEM image of a copper-made template with sharp steps (upper panel). (b) SEM image showing the PS grating after µTM (lower panel).*

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