Nanostructuring polymers by soft lithography templates realized via ion sputtering

This content has been downloaded from IOPscience. Please scroll down to see the full text.

2005 Nanotechnology 16 2714

(<http://iopscience.iop.org/0957-4484/16/11/041>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 155.69.4.4

This content was downloaded on 24/08/2015 at 23:00

Please note that [terms and conditions apply](#).

Nanostructuring polymers by soft lithography templates realized via ion sputtering

Elisa Mele¹, Francesca Di Benedetto¹, Roberto Cingolani¹,
Dario Pisignano¹, Andrea Toma², Francesco Buatier de Mongeot²,
Renato Buzio², Corrado Boragno², Giuseppe Firpo²,
Valentina Mussi² and Ugo Valbusa²

¹ National Nanotechnology Laboratory of INFN-CNR and Agilent Technologies joint lab,
Università di Lecce, via Arnesano, I-73100, Lecce, Italy

² Dipartimento di Fisica, Università di Genova, via Dodecaneso 33, I-16146, Genova, Italy

E-mail: elisa.mele@unile.it

Received 20 May 2005, in final form 4 August 2005

Published 6 October 2005

Online at stacks.iop.org/Nano/16/2714

Abstract

We demonstrate that a combination of ion sputtering and soft lithography is an alternative and effective way of nanostructuring soft matter. We create self-organized nanoscale structures on a glass template by irradiating the surface with a defocused, low energy Ar ion beam. Capillary force lithography is then used to transfer the pattern, exploiting the glass transition of polymeric layers. In particular, we demonstrate the pattern transfer of a periodic 150 nm ripple structure onto an organic compound. This new, unconventional combination is then a low-cost strategy that opens the way to a variety of applications in the field of organic-based devices.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Over the past decade, a number of lithographic techniques, such as electron and ion beams, x-rays, scanning probes [1], soft and imprinting lithographies [2–4], self-assembling [5], atom lithography [6], and micro-plasma discharges [7], have been developed as alternatives to photolithography for fabricating high quality micro- and nanostructures. In particular, soft lithographies embody the patterning methods (microcontact printing [5], replica molding [8], microtransfer molding [9], micromolding in capillaries [10], and solvent-assisted micromolding [11]), relying on the use of elastomeric replicas to transfer the pattern onto a substrate. The stamp, made of poly(dimethylsiloxane) (PDMS) or other compounds able to provide conformal contact, is used to replicate the geometry of a starting master, pouring the liquid prepolymer of the elastomer against the master surface, and curing it *in situ*. The elastic nature of the stamps allows one to produce faithful copies of the complex features of the master. The resolution achievable with the soft lithographic methods is

strongly dependent on the starting master, and thus it is limited by the availability of techniques to produce masters with nanometer resolution.

Recently, low-energy ion sputtering has been proposed as a simple and powerful method to produce nanostructures having feature sizes on the scale of some tens of nanometers at low cost, on large areas [12–16]. Depending on the experimental parameters, such as the surface temperature, sputtering time (ion dose) and ion incidence angle, it is possible to force the growth of a self-organized ripple structure. Besides its applicability to almost all materials, the microscopic mechanisms involved in the growth of the nanopatterns are different between metals or semiconductors and glasses. As a general rule, these structures result from the balance between the erosion induced by the ion collisions and the diffusion of surface atoms displaced after the ion impact. Bradley and Harper have proposed a linear equation describing such a surface height evolution, $h(r, t)$, with balance between erosion

and diffusion terms [17]:

$$\frac{\partial h}{\partial t} = v_x \frac{\partial^2 h}{\partial x^2} + v_y \frac{\partial^2 h}{\partial y^2} - B \nabla^2 \nabla^2 h, \quad (1)$$

where $v_{x,y}$ are the prefactors related to the curvature dependent erosion rate, and B accounts for the surface diffusion effects. However, in crystalline metals and semiconductors, a key role is played by the surface diffusion of the defects (adatoms, vacancies) created by the ions. The consequence is that the nanopattern geometry can be tailored by the surface symmetry and it can be strongly dependent on the temperature and on the ion flux. In glasses, viscosity diffusion and ion-induced diffusion represent the most important mechanisms for the recovery of the ion damage. This implies a longer time for the development of the nanopattern, whose direction depends on the ion beam projection on the surface [18, 19].

In this work, we demonstrate that the combination of ion sputtering and soft lithography can be exploited for nanostructuring soft matter. We realized self-organized nanoscale structures on a glass template by irradiating the surface with a defocused, low energy Ar ion beam. Capillary force lithography is then used to transfer patterns exploiting the glass transition of polymeric layers. In particular, we demonstrate the pattern transfer of a periodic 150 nm ripple structure onto organic compounds.

2. Experimental details

The basic scheme of the CFL is summarized in figure 1. Glass masters were fabricated by ion sputtering. Glass was chosen because it is inert, rigid and can be heated up to high temperatures without any damage to the nanopattern. The sample is sonicated in acetone in order to eliminate organic contaminants and rinsed in pure water, then the substrate is inserted in a UHV chamber equipped with a defocused microwave ECR plasma source. The sample is ion bombarded at a temperature of 300 K with Ar ions having energy of 800 eV. The ion flux, measured by a Faraday cup, is about $400 \mu\text{A cm}^{-2}$. The angle of incidence is fixed at 35° with respect to the substrate normal. To prevent the charging of the sample, a W filament (Th coated) is positioned at the end of the source, thus ensuring efficient neutralization of the substrate. In these conditions, a rippled nanopattern is produced, with crests perpendicular to the ion beam projection on the sample (for a detailed morphological characterization by means of a scaling law approach see [20]). A PDMS replica (Sylgard 184, Dow Corning, Midland, MI), fabricated by the nanostructured templates by a standard replica molding procedure [2], was then placed in conformal contact onto a polymeric film cast on a substrate. In our experiments, 0.8×10^{-3} M chloroform solution of poly(methylmethacrylate) (PMMA) (Sigma-Aldrich, MO, average molecular weight of 120 k) was spin-coated at 1500 rpm onto a silicon substrate. When the polymer is heated at 170°C , a temperature value higher than T_g (120°C), capillary effects force the polymer melt into the void space of the features formed between the replica and the polymeric film. After the subsequent cooling to ambient temperature, the replica is peeled off, and the pattern remains on the target.

I. Contact between the elastomeric template and the thermoplastic film

II. Filling of the void spaces of the features formed between the replica and the polymeric film by capillary force during heating above T_g .

III. Template separation after cooling at room temperature

Figure 1. Schematic diagram of the capillary force lithography procedure by elastomeric template (features not in scale).

3. Results and discussion

Since the spatial periodicity as well as the depth of the troughs depends on the sputtering dose as shown in figure 2, the sputtering time was set at 100 min to obtain an average wavelength of about 200 nm. Under these conditions the morphology of the glass surface is dominated by a quasi-regular array of long channels, of depth of (11.2 ± 1.1) nm (RMS). The crest to valley height modulation lies in the broad range 30–60 nm, as can be appreciated in figure 3. This is due to the stochastic fluctuations related to the self-assembly process. The ripple wavelength, λ , can be calculated from the two-dimensional map of the height–height correlation function $G(i, j)$ as described in [21]. $G(i, j)$ is defined as

$$G(i, j) = \frac{1}{l^2} \sum_{m,n=1}^l h(i+m, j+n)h(i, j), \quad (2)$$

where $h(i, j)$ denotes the surface height at position (i, j) . The AFM image of the nanopatterned glass is reported in figure 3.

Among the different soft lithography approaches, we chose the soft molding (SM [22]) or capillary force lithography (CFL [23]), which joins the advantages of nanoimprint lithography (NIL) and replica-assisted techniques. In the

Figure 2. Ripple wavelength λ (a) and RMS surface roughness w (b) versus sputtering time t . The solid lines represent a linear fit according to the power law $\lambda = t^\gamma$ and $w = t^\beta$, with $\gamma = 0.95 \pm 0.05$ and $\beta = 1.02 \pm 0.20$ respectively.

CFL the key element of soft lithography, namely the use of an elastomeric replica, is combined with the working principle of NIL, i.e. the molding of a polymer melt. The conventional NIL consists of the compression molding of thermoplastic polymers. A hard mold with an engraved pattern is mechanically pressed into a thin film of a thermoplastic polymer, which becomes a viscous liquid, upon heating above the glass transition temperature (T_g). This determines the subsequent adaptation of the polymer to the mold pattern. To date, 10 nm diameter and 40 nm period holes have been fabricated in polymeric films by NIL [24]. Nevertheless, NIL presents a series of limitations, such as the difficult mold release, and the requirement of a very high pressure, typically on the order of 10^6 Pa [24], to transfer the pattern. Moreover, the imprint quality is limited by the material transport, inherent to this technique, especially in the case of a negative stamp: the pattern transfer can be unsatisfactory and bubble-like defects can be observed, possibly due to a lack of conformal contact of the mold [25]. These limitations can be overcome by the use of a PDMS stamp. In fact, PDMS is chemically inert; consequently, it does not adhere irreversibly to the surface of the substrate, and its elastic characteristic allows the replica to spontaneously wet the surface, thus providing a conformal contact with the substrate, without any external force, over a large area.

The penetration of the polymer into the recessed features of the PDMS mold is driven by capillarity and favoured by a low polymer viscosity. In fact, the time t taken for the filling process depends on the viscosity of the polymer melt, η , according to equation [26]:

$$t = \frac{2\eta z^2}{\gamma R \cos \Theta}, \quad (3)$$

where z is the feature size, γ the fluid–air surface tension, R the hydraulic radius of the capillary, and Θ the contact angle between the liquid and the surface of the capillary. Moreover, above the glass transition temperature, the viscosity of many

Figure 3. AFM image ($5 \times 5 \mu\text{m}^2$) of a sputter rippled glass and corresponding cross section along the ripple wavevector. The sputtering parameters were $E_{\text{ion}} = 800$ eV, $j_{\text{ion}} = 400 \mu\text{A cm}^{-2}$, $\vartheta_{\text{ion}} = 35^\circ$, $t = 100$ min. The arrow indicates the projection of the ion beam. The inset reports the corresponding $G(i, j)$ (area $2 \times 2 \mu\text{m}^2$).

polymers varies with the temperature [27]:

$$\eta(T) = \eta_0 \exp\left(\frac{DT_0}{T - T_0}\right), \quad (4)$$

where D is referred to as the strength parameter and T_0 is the temperature for which equation (4) shows a divergence in the polymer structural relaxation time and, consequently, in the viscosity. Therefore, a suitable temperature increment determines a dramatic decrease of the polymer viscosity, favoring the filling of the pattern. A few minutes are therefore enough for the pattern transfer. In figure 4, the AFM image of the polymeric pattern is displayed, showing a nanostructured polymer surface with a crest to valley height modulation in the range of 15–45 nm, depending on the corresponding region of the master (i.e. with a loss of about 15 nm in the height profile). In particular, the achieved height of the imprinted features is strongly dependent on the imprinting time, and it can be increased by increasing the heating time during the CFL, which favors the complete capillarity filling of the void spaces of the PDMS template by the fluid polymer, thus accomplishing a faithful aspect ratio.

Finally, we have varied the morphology of the glass template in order to test the ability of the polymer to fill the profiles of the nanopattern under the action of capillary forces. Down-scaling the pattern to smaller pitches of the order 60 nm and to RMS depths of about 1.3 nm is easily achieved on glass substrates by reducing the irradiation dose to about 15 min. Even smaller pitches of about 30 nm can be achieved by selecting different substrates such as LiF and even

Figure 4. AFM two-dimensional view ($5 \times 5 \mu\text{m}^2$) of a nanostructured polymer and corresponding cross section. The inset shows the height–height correlation function $G(i, j)$ (area $2 \times 2 \mu\text{m}^2$).

smaller periodicities of about 10 nm are achieved on metal substrates [12–14]. In this case, since the RMS height of the features is correspondingly decreased, we expect an easy transfer of the pattern to the polymer surface by action of the capillary forces.

4. Conclusion

Summarizing, we have demonstrated that the combination of ion-sputtering and soft lithography can be an alternative and cheap way for nanostructuring soft matter. The self-organized nanoscale structures are created on a glass template by irradiating the surface with a defocused, low energy Ar ion beam. The use of capillary force lithography (CFL) allows us to transfer the pattern using the glass transition phenomenology of the polymeric layer. Specifically, we have demonstrated the transfer of a periodic pattern consisting in a ripple structure

with a periodicity of 200 nm. These nanostructures have a wide interest in view of their applications to both photonic patterned devices and organic nanoelectronics.

References

- [1] Ross C B, Sun L and Crooks R M 1993 *Langmuir* **9** 632
- [2] Xia Y and Whitesides G M 1998 *Angew. Chem. Int. Edn Engl.* **37** 550
- [3] Chou S Y, Krauss P R and Renstrom P J 1995 *Appl. Phys. Lett.* **67** 3114
- [4] Chou S Y, Krauss P R and Renstrom P J 1996 *Science* **272** 85
- [5] Kumar A and Whitesides G M 1993 *Appl. Phys. Lett.* **63** 2002
- [6] Mutzel M, Tandler S, Haubrich D, Meschede D, Peithmann K, Flaspohler M and Buse K 2002 *Phys. Rev. Lett.* **88** 083601
- [7] Chai J, Li B and Kwok D Y 2005 *Appl. Phys. Lett.* **86** 034107
- [8] Xia Y, Kim E, Zhao X-M, Rogers J A, Prentiss M and Whitesides G M 1996 *Science* **273** 347
- [9] Zhao X-M, Xia Y and Whitesides G M 1996 *Adv. Mater.* **8** 837
- [10] Kim E, Xia Y and Whitesides G M 1995 *Nature* **376** 581
- [11] Kim E, Xia Y, Zhao X-M and Whitesides G M 1997 *Adv. Mater.* **9** 651
- [12] Rusponi S, Costantini G, Buatier de Mongeot F, Boragno C and Valbusa U 1999 *Appl. Phys. Lett.* **75** 3318
- [13] Sekiba D, Bertero S, Buzio R, Buatier de Mongeot F, Boragno C and Valbusa U 2002 *Appl. Phys. Lett.* **81** 2632
- [14] Sekiba D, Moroni R, Gonella G, Buatier de Mongeot F, Boragno C, Mattera L and Valbusa U 2004 *Appl. Phys. Lett.* **84** 762
- [15] Chason E, Mayer T M, Kellerman B K, McIlroy D T and Howard A J 1994 *Phys. Rev. Lett.* **72** 3040
- [16] Carter G and Vishnyakov V 1996 *Phys. Rev. B* **54** 17647
- [17] Bradley R M and Harper J M 1988 *J. Vac. Sci. Technol. A* **6** 2390
- [18] Flamm D, Frost F and Hirsch D 2001 *Appl. Surf. Sci.* **179** 95
- [19] Umbach C, Headrick R L and Chang K C 2001 *Phys. Rev. Lett.* **87** 246104
- [20] Toma A, Buatier de Mongeot F, Buzio R, Firpo G, Bhattacharyya S R, Boragno C and Valbusa U 2005 *Nucl. Instrum. Methods B* **230** 551
- [21] Koponen I, Hautala M and Sievanen O P 1997 *Phys. Rev. Lett.* **78** 2612
- [22] Pisignano D, Persano L, Cingolani R, Gigli G, Barbudri F, Farinola G M and Naso F 2004 *Appl. Phys. Lett.* **84** 1365
- [23] Suh K Y and Lee H H 2002 *Adv. Funct. Mater.* **12** 405
- [24] Chou S Y, Krauss P R, Zhang W, Guo L and Zhuang L 1997 *J. Vac. Sci. Technol. B* **15** 2897
- [25] Scheer H-C, Schulz H, Hoffmann T and Sotomayor Torres C M 1998 *J. Vac. Sci. Technol. B* **16** 3917
- [26] Mayers D 1999 *Surface, Interface, and Colloids* (New York: Wiley-VCH) pp 97–118
- [27] Vogel H 1921 *Phys. Z.* **22** 645
- Fulcher G S 1925 *J. Am. Ceram. Soc.* **8** 339
- Tamman G and Hesse W 1926 *Z. Anorg. Allg. Chem.* **156** 245