Microdomain orientation dependence on thickness in thin films of cylinder-forming PS-*b*-PMMA

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Abstract

The self-assembly of block-copolymer thin films in periodic nanostructures has received considerable attention during the last decade due to their potential applications in nanofabrication and nanolithography. We followed the morphologies developed in thin films of a cylinder-forming diblock copolymer polystyrene-*b*-poly(methylmethacrylate) ((PS-*b*-PMMA), PS 46.1 kg mol^{-1}, PMMA 21.0 kg mol^{-1}, lattice spacing $L_0 = 36$ nm), as a function of the film thickness (t), analyzing the effect of thickness commensurability on domain orientation in respect to the substrate. The study was circumscribed to the unexplored range of thickness below L_0. Two thickness windows with perpendicular orientation of the PMMA domains were identified: a well-known window at $t \sim L_0$ and a new window at $t \sim L_0/2$. A half-parallel cylinder morphology was observed for $t \sim \frac{3}{4}L_0$ with a progressive change in morphology $C_\perp \rightarrow C_\parallel \rightarrow C_\perp$ when thickness increases from $L_0/2$ to L_0. This experimental evidence provides new insights on the mechanism of block copolymers self-organization and indicates the possibility to tune the thickness of the nanostructured polymeric film below L_0, allowing the fabrication of ultrathin soft masks for advanced lithographic processes.

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

1. Introduction

In recent years the continuous shrinking of microelectronic devices faced the problem of a manufacturing solution to patterning feature sizes beyond the 22 nm node. The physical and economical limitations of conventional nanolithographic techniques forced researchers to look for alternative approaches to create structures with dimensions equal to or below 20 nm. Block copolymer lithography is an emerging nanolithographic process utilizing self-assembled nanoscale morphologies of block copolymers to fabricate uniform, densely spaced nanometer-scale features over wafer-scale areas [1, 2]. Self-organizing block copolymers are fully compatible with standard semiconductor technology and represent a low-cost and efficient instrument for the creation of nanostructures with critical dimensions below the current photolithographic resolution limits. Very recently the potential

of self-assembling patterning for the fabrication of transistors smaller than 22 nm was highlighted by Wong *et al* that employed diblock copolymers (DBC) for the fabrication of the industry's first functional devices and circuits that employ DBC patterning for sub-22 nm CMOS technologies on a full wafer scale [2].

In this respect DBC thin films forming cylindrical domains are particularly interesting, since the selective removal of the minor component transforms the material in a nanoporous film with a periodic array of hexagonally packed pores characterized by well-defined sizes and by spacing on the scale of tens of nanometers. In the last ten years these nanostructured materials were widely investigated for their potential application in advanced lithographic processes; in particular, they were suggested to be suitable as soft masks, i.e. as a sacrificial layer, for the transferring of the block copolymer pattern to the selected material by either etching the underlying substrate or depositing new material on top

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of it [3, 4]. As a requisite for their possible implementation in advanced lithographic processes, a complete control of the self-assembly process should be addressed in order to induce perpendicular orientation of the nanopores with respect to the substrate [5–9]. Despite a lot of work on the subject, the control of the orientation is not trivial, since DBC microdomains spontaneously self-assemble into the configuration that minimizes the total free energy of the system, which, in thin films, is additionally influenced by the film thickness (t) and by the interactions between the film and the substrate. The block with the lower interfacial tension (with the substrate) preferentially wets the substrate whereas the block with the lower surface energy tends to locate at the free surface. These energetic fields, exerted by the substrate and the free surface, are strong enough to induce the parallel orientation of nanodomains [10–13]. The strategies developed to induce perpendicular ordering of the nanodomains in respect of the substrate have been achieved by surface modification [14–22], strong electric field [23, 24] and solvent annealing [25, 26]. The most robust of these strategies is surface modification via a neutral or non-preferential wetting of the substrate, enabling A-*b*-B block copolymer to promote microdomain orientation perpendicular to the film surface by balanced interfacial interaction. Surface neutralization could be attained by using a random copolymer (A-*r*-B) anchored to the surface [14, 17].

Among the commercially available block copolymers, polystyrene-*block*-poly(methylmethacrylate) (PS-*b*-PMMA) is a good material of choice because the cylindrical PMMA domains can be selectively removed using UV + acetic acid rinse, leaving porous PS films that can be used as a soft mask for nanolithographic processes. The PMMA block is known to wet the silicon oxide/polymer interface due to its lower interface tension, while PS exhibits an affinity for the free surface. As a result of the substrate preferential wetting, an underlying monolayer of copolymer (known as the wetting layer, W) with PMMA blocks strongly adhering to the substrate is generated and does not lead to useful lithographic structures. Mansky *et al* [14] showed that a random copolymer with a styrene fraction equal to 0.58 creates a surface with no preferential affinity for either PS-*b*-PMMA component. Following this approach, for asymmetric PS-*b*-PMMA it is widely reported that microdomains are oriented normal to the substrate in a limited film thickness window located in the vicinity of L_0 (L_0 = lattice spacing) [6, 7, 26–32], due to commensurability between the film thickness and L_0. However, as far as we know, not much work has been devoted to study the morphologies developed in the sub-L_0 range of thicknesses, which could give interesting results, taking into account the possibility of obtaining perpendicular oriented films with higher aspect ratios (D/t, where D = diameter of the pores). Apart from the scientific interest in the full understanding of the DBC self-assembling processes, the possibility to obtain nanoporous polymeric films of different thicknesses, starting from the same block copolymer, could be important for the implementation of lithographic protocols based on deposition or etching processes through the polymeric mask. The purpose of this paper is the study of the morphologies developed in the unexplored range of thicknesses located bellow L_0, in order to have a complete scenario of the potentiality of this formulation as a mask for nanolithography.

2. Experimental procedure

2.1. Substrate preparation

Silicon pieces (1×1 cm^2) were cut from 200 mm diameter Si(100) wafers on top of which a 16 nm thick SiO$_2$ film was thermally grown. Cleaning with fresh piranha solution (1/3 v/v mixture of 30% H$_2$O$_2$ and 98% H$_2$SO$_4$) at 80 °C for 60 min was performed to eliminate any residual organic trace and to afford a highly hydroxyl-terminated silicon surface (and a consequently higher concentration of anchoring points for random copolymer cleavage). The pieces were then rinsed in water, cleaned with isopropanol for 15 min in an ultrasonic bath and finally dried under vigorous N$_2$ flow.

2.2. Thin film deposition

The random copolymer was a commercial one with a styrene fraction of 0.58, M_n = 11 400, PDI = 1.64 (Polymer Source Inc.), terminated on one end with a moiety containing a hydroxyl (OH) group. The OH-end group is used to graft the copolymer to the silicon oxide layer through a dehydration reaction. PS-*r*-PMMA was anchored by annealing the spin-coated films under vacuum for 48 h at 170 °C, i.e. well above the glass transition temperature of both PS and PMMA, to allow chain ends to diffuse and react with the substrate. The thermal annealing was conducted under vacuum (8×10^{-3} mbar). The unattached copolymer chains were finally removed by rinsing in toluene for 5 min at room temperature. The thickness of the resulting layer was about 4 nm and was independent of the thickness of the initial film.

Commercial asymmetric PS-*b*-PMMA, with total molecular weight M_n = 67 100 and PDI = 1.09, was purchased from Polymer Source Inc. and used without further purification. The volume fraction of PMMA block was 0.29. This block copolymer self-assembled in hexagonal arrangements of ≈18 nm diameter cylindrical PMMA domains (center-to-center spacing or natural domain period $L_0 \approx 36$ nm) in a matrix of PS. Thin films were obtained by spin-coating toluene solutions of the cited block copolymer onto previously neutralized Si wafers. By varying the spinning speed and solution concentration, samples with different film thicknesses were obtained. To promote self-assembly of the diblock copolymer the films were heated at 190 °C for 1 h under vacuum ($p = 8 \times 10^{-3}$ mbar). The relative high annealing temperature was selected in order to promote the formation of large grains, which is very desirable in terms of template generation [33]. We should mention that equilibrated morphologies were obtained after 1 h at 190 °C since longer times did not produce any changes in the developed morphologies, agreeing with previous works reported in the literature [6, 34]. The high temperature process allows us to dramatically reduce the annealing time [6], providing an industrially appealing approach for the technological implementation of block copolymer-based lithographic protocols.
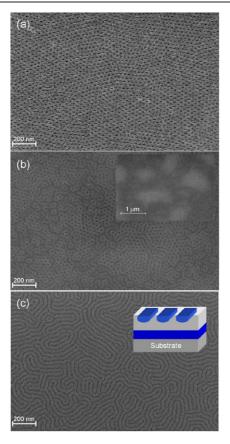
Figure 1. FESEM morphologies of $\approx$36 nm thick PS-*b*-PMMA films self-assembled on a random layer annealed at (a) $p = 8 \times 10^{-3}$ mbar, (b) $p = 2 \times 10^{-1}$ mbar and (c) $p = 1 \times 10^3$ mbar.

2.3. Characterization

Film thicknesses (prior to annealing) were measured with an M-2000U (J A Wollam Co. Inc.) spectroscopic ellipsometer using a xenon laser lamp at a 70° incident angle. The calibration and accuracy of the spectroscopic ellipsometer was cross-checked by x-ray reflectivity measurements performed on a set of selected samples. The film thicknesses reported in the following sections refer to the DBC film and do not include the underlying 4 nm thick brush layer. The morphology of the polymeric films after thermal treatment was characterized by scanning electron microscopy (Zeiss Supra 40 SEM with a field emission source) operated at an accelerating voltage of 15 kV.

3. Results and discussion

During surface pretreatment the random copolymers are chemically attached to the substrate through their terminal OH groups. This chemical reaction is very slow and requires relatively high temperature (170 °C) and very long annealing times in order to obtain the required grafting density [15]. Due to these severe conditions, the thermal treatment should be performed under vacuum. The presence of O_2 would cause oxidation of the random copolymer layer and the consequent annihilation of their neutral nature. Once the random copolymer layer is oxidized it preferentially attracts the PMMA block as the SiO_2 layer does, leading to the

formation of an undesirable lamellar wetting layer. It is worth mentioning that, in contrast with the indications reported by Guarini *et al* [6], only under $p = 8 \times 10^{-3}$ mbar, not less, perfect perpendicular orientation of hexagonally packed cylindrical domains (figure 1(a)) was obtained for films matching the natural domain period $L_0 = 36$ nm, reproducing the results previously cited in the literature for the same DBC [6, 7, 25–31]. When the annealing of the random layer was done under $p = 2 \times 10^{-1}$ mbar, film instabilities appeared, leading sometimes to terrace formation (for clarity see the low-magnification image on top) with mostly disordered morphology. Finally, when the annealing of the random layer was performed under atmospheric conditions, $p = 1 \times 10^3$ mbar, a complete parallel-oriented morphology was developed induced by the formation of a PMMA wetting layer (see the schematic representation in the inset of figure 1(c)). The observed trend suggests that, when operating at $p = 2 \times 10^{-1}$ mbar, the residual O_2 pressure in the furnace was enough to partially oxidize the random layer and consequently the slight preference of the pretreated substrate for PMMA block was sufficient to corrupt the perpendicular orientation of the domains at least at film thicknesses in the vicinity of L_0. A detailed investigation of the limited thermo-oxidative stability of thin polymeric films is beyond the scope of the present paper; nevertheless the present results may even call into question some of the conclusions reached by other groups in the literature, though the comparison is difficult to assess since data about the operating pressure during DBC thermal treatment are usually missing in many of the works reported in the literature. Further experiments are currently running to clarify this point.

PS-*b*-PMMA films of different thicknesses were self-assembled in order to follow the evolution of morphologies with thickness. Figure 2 shows FESEM images of the morphologies obtained. Perfect perpendicular orientation was obtained when the film thickness matched L_0 or half of it ($L_0/2$), corresponding respectively to $\approx$36 and 18 nm thick films. Perfect parallel orientation was developed at a film thickness close to $\frac{3}{4}L_0$.

In perpendicular-oriented films, after selective removal of the PMMA cylinders by UV degradation and rinsing in acetic acid, the resulting nanoporous PS film showed an average pore diameter close to 18 nm, independent of the thickness of the film (L_0 and $L_0/2$).

Looking at the evolution, as the thickness was gradually increased from 18 to 36 nm, a progressive change in morphology $C_\perp \rightarrow C_\parallel \rightarrow C_\perp$ ($C_\perp$ = perpendicular-oriented cylinders, $C_\parallel$ = parallel-oriented cylinders) was observed, with mixed morphologies developed in between.

When film thickness was lower than $L_0/2$, the developed morphologies consisted of islands with perpendicularly oriented domains dispersed in a continuous featureless matrix, as reported in figure 2(a). As the film is so thin, upon annealing it redistributed itself to bring certain areas into commensurability with $L_0/2$ (where perpendicular morphology is developed). The concentration of these islands grew proportionally with thickness till covering all the substrate with perpendicular-oriented cylinders when film
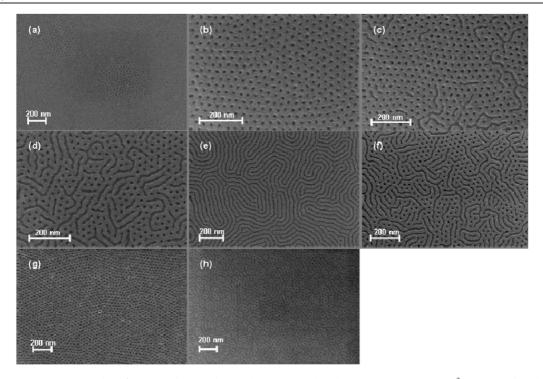
Figure 2. FESEM morphologies of PS-*b*-PMMA films self-assembled on a random layer annealed at 8×10^{-3} mbar as a function of film thickness: (a) 16 nm, (b) 18 nm, (c) 22 nm, (d) 25 nm, (e) 28 nm, (f) 31 nm, (g) 36 nm and (h) 40 nm.

thickness matched $L_0/2$. A minimum in free energy promoted the vertical orientation of domains at this film thickness. Above $L_0/2$, a small increment ($\Delta t < 4$ nm) in the film thickness was enough to destroy the perfect arrangement of perpendicular domains with the appearance of a few parallel oriented domains. Their concentration grew proportionally with thickness till complete coverage with parallel oriented domains was reached, at film thickness near $\frac{3}{4}L_0$ (figure 2(e)). Neutrality of the substrate ensures us that, in this case, the development of this parallel morphology was not promoted by the presence of a preferential lamellar wetting layer. Instead, a parallel cylindrical wetting layer was developed as illustrated in figure 3.

Theoretical simulations done by Wang *et al* [35] and Huinink *et al* [36] demonstrated that energetically neutral surfaces exhibit a slight preference for the shorter block (PMMA block in our film). This preference is attributed to *a purely entropic effect*, i.e. the enrichment of chain ends (shorter block segments are, on average, closer to a chain end) near a hard flat surface. As a result, parallel-oriented cylinders are developed at certain thicknesses since this configuration has stronger segregation of PMMA segments near neutral surfaces than perpendicular cylinders. Simulations of Wang *et al* [35] showed that, before the thickness reached L_0, a $C_\parallel^{1/2}-C_\parallel^{1/2}$ morphology is developed ($C_\parallel^{1/2}$ = half parallel cylinders). Our results suggest the presence of half-parallel cylinder morphology in thin films of PS-*b*-PMMA supported on a neutral surface, when film thickness is about $\frac{3}{4}L_0$. Half-cylinder morphology was also found experimentally by Kim *et al* [12] and Wang *et al* [8] for preferential surfaces.

The preservation of the parallel orientation when the film thickness is incremented beyond $\frac{3}{4}L_0$ causes stretching of the
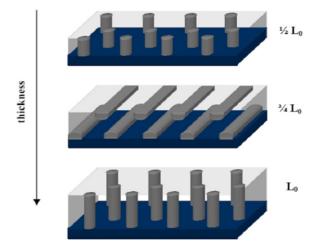

Figure 3. Schematic representation of the evolution of morphologies with thickness under neutral conditions.

polymer chains with the subsequent increase in free energy by entropic contributions. This extra tension was released by adopting again perpendicular-oriented morphology since this arrangement maximizes the conformational entropy of the chain by allowing L_0 to express laterally. Consequently DBC restores the normal orientation of domains with a progressive enrichment with vertically oriented cylinders, as could be seen in figure 2(g). Once the film reached L_0, complete coverage with perpendicular domains is obtained. Above L_0, the appearance of small islands with disordered morphology start to become important till they filled the entire sample when the thickness approximates 40 nm.

4. Conclusions

We investigated the evolution of the morphology of PS-*b*-PMMA as a function of the film thickness when annealed at 190 °C for 1 h in vacuum (8×10^{-3} mbar). Two thickness windows with perpendicular orientation of the PMMA domains have been identified: a well-known window at $t \sim L_0$ and a new window at $t \sim L_0/2$. A half-parallel cylinder morphology has been observed for $t \sim \frac{3}{4}L_0$ with a progressive change in morphology $C_\perp \rightarrow C_\parallel \rightarrow C_\perp$ when thickness increases from $L_0/2$ to L_0. These experimental results provide a new insight into the phenomenology of phase separation of block copolymer thin films.

Acknowledgments

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