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Polymer masks for structured surface and plasma etching

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ABSTRACT

Silica and silicon structures have been prepared at the sub-micrometer length-scale, using laterally phase-separated thin films of poly(styrene) (PS) and poly(lactic acid) (PLA) homopolymer blends. The selective removal of one polymer and the filling of the released space by silica precursor solution led, after calcination, to silica structures on silicon such as arrays of bowl-shape features or pillars, layers with through or non-through cylindrical holes, which has not been observed for some of them. The control of the morphology of the initial polymer film was a key point to achieve such type of structures. Particularly relevant was the use of solvent vapor annealing (vs thermal annealing) of the initial spin-coated films that favored and stabilized laterally phase-separated morphologies. Characteristic dimension of the domains were shown to be coupled with the thickness of the film, thinner films giving smaller domain sizes. Despite a relatively high incompatibility of the two polymers, a macro-phase separation was prevented in all the studied conditions. Sub-micrometric domains were formed, and for the thinner films, nanometric domains as small as 74 nm in size can be obtained. The silica structures formed by the infiltration of the polymer templates were used as hard masks for the cryogenic etching of underlying silicon. New structured surfaces, arrays of silicon pillars which can be plain or hollow at the upper part or arrays of cylindrical holes were formed. A selectivity as high as 21 was obtained using this type of mask for 1.5 μm deep holes having a typical diameter of 200 nm.

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1. Introduction

Homopolymers with different chemical compositions are generally incompatible, due to the low value of their entropy of mixing, in such way that their blends exhibit compositional heterogeneities in the solid state resulting from phase-separation process [1]. In the form of solid films, generally prepared from the deposition of a homogeneous solution of the blends in a common organic solvent (typically spin-coating), phase separation occurs during the evaporation of the solvent, as a consequence of the increase in the incompatible polymer interactions [2]. Meanwhile, the viscosity increases due to the solvent evaporation, freezing the phase-separation process into a more or less advanced stage and producing co- or discontinuous phase-separated morphologies. The confined geometry in the case of thin films (i.e. not more than few hundreds of nm thick) may render those phenomena even more complex due to the predominance of interfacial effects [3]. Surface-directed spinodale decomposition, resulting from the development of composition waves normal to interfaces, has been especially reported and modeled [4–7], creating layered phase-separated morphologies that can be trapped in the dried state in the case of rapid solvent evaporation. In some cases, the vertical stratification is only a transient state in the liquid film, evolving toward more complex patterns of micro-phases separated in the dried state when the interface between the stratified layers becomes unstable [8–10]. Dewetting phenomenon plays then a crucial role on the final morphology [11,12].

As a result of a subtle interplay between these simultaneous phenomena that occur during the solvent evaporation, it has been shown that the final dried morphology was very sensitive to various parameters such as the characteristics of the polymers (polymer/polymer interaction parameters, molecular weight, crystallinity), of the solvent (evaporation speed, polymer/solvent interaction parameters), of the substrate (surface energy), of the casting conditions [3] (film thickness). Consequently, a wide variety of thin-film morphologies have been reported upon the last two decades, including co-continuous or discontinuous laterally phase-separated morphologies as well as layered system, with compositional heterogeneities length-scale varying from few tens of nanometer to several microns [2,13–15]. On this subject, we

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direct the reader to a recent comprehensive review describing mesoscale structure formation in polymer films [16].

Such heterogeneous polymer thin films have been the subject of a lot of interest for their potential direct uses in organic photovoltaic devices and organic light emitting diodes [17–20], organic antireflective coatings [21–25], bioengineered surfaces for controlled cells growth. Interestingly, they can also serve as intermediate patterns for the preparation of inorganic nanostructures, with a myriad of potential applications such as active devices [26] or hard mask for lithographic process [27]. The transformation of such organic films into silica templates can be performed using sequential infiltration synthesis (SIS) if one polymer could be selectively infiltrated with inorganic gas-phase precursors by diffusion [27–29]. This has been done with poly(styrene) (PS) and poly(methyl methacrylate) (PMMA) blends, where gaseous trimethylaluminum (TMA) and water selectively diffuse into PMMA. Another method involves the formation of perforated films by selectively removing one polymer, filling the remaining space by liquid inorganic precursors and fabrication of inorganic replica by sol–gel reaction during thermal heating. Existing examples are, however, very limited and essentially based on PS and PMMA blends. For instance, ZnO islands, TiO_2 pillars and μdonuts were prepared using liquid depositions of inorganic precursors onto such perforated templates, followed by a thermal elimination of the polymer [30–32]. Masks for dry etching were also prepared using these perforated polymer templates, using a chromium [33] or a self-assembled monolayer (SAM) [34] deposition through the polymer film and a lift off of the polymer. All these inorganic structures with a characteristic scale between 100 and 1000 nm could be useful for applications where this characteristic scale is needed such as energy storage, optical devices [35] and macromolecules detecting [36].

Inspired from our previous works based on block copolymer [37], this paper aims at demonstrating that polymer blends can be used to prepare laterally phase-separated thin films, which can be transformed into polymer templates by selective removal of one phase and further transformed into inorganic replicas by infiltration of reactive compounds. Unlike block copolymers where a fine control of the morphology can be obtained at a nanometric scale, uncontrolled phase separation and micrometric scale of the compositional heterogeneities are generally observed in the case of the homopolymer blends. Using block copolymers is not without difficulty since their alignment in ordered patterns is not trivial and although a lot of progresses in the synthetic methods have been made, they are still rather expensive to synthesize, requiring intensive care to achieve the desired morphologies. Using polymer blends, which are much more simple and affordable compounds, is consequently worth considering if both the size and the localization of the domains could be controlled. While the latter subject has already been addressed using directed self-assembly [38–40], there is still today the need to examine new polymer systems which are not based on the conventional PS/PMMA blend to expand the variety of phase behavior.

In this work, we focused on poly(styrene) (PS)/poly(lactic acid) (PLA) blends, two polymers that can be easily and selectively removed. This choice was also guided by their similar silicon native oxide affinity and surface energy (42 and 36 (to 41) mJ m^{-2} for PS and PLA respectively) [41], which is a favorable parameter for laterally separated blends. The polymer templates were used to produce silicon oxide structured surfaces, which further served as masks for silicon etching using the plasma cryogenic etching process. The nature of mask was guided by the high selectivity of plasma etching between silicon and SiO_2. These silicon oxide structures as well as the etched silicon structures have been never observed in the literature and could be useful for devices where structuration at 100–1000 nm scale is needed [35,36].

2. Experimental

2.1. Materials

Poly(styrene) (PS) with a molecular weight of 60 kg mol^{-1} and poly(lactic acid) (PLA) with a molecular weight of 16 kg mol^{-1} were used. All the chemical products were purchased from Sigma-Aldrich and used without further purification.

2.2. Thin films preparation and porous masks preparation

Si(1 0 0) substrates of 10 mm × 10 mm were cleaned by sonication in dichloromethane, methanol and distilled water for 10 min each. Solutions of PS and PLA blends were prepared as follows: PS and PLA were weighted in order to get the adequate mass ratio (namely PS/PLA 70:30 called S70L30 and 30:70 called S30L70) and dissolved in 1,2-dichloroethane to obtain a concentration of polymer blend varying from 10 to 30 mg mL^{-1}. The solutions were stirred at least 2 h. Thin films were deposited by spin-coating on Si substrates at 2500 rpm for 30 s. The film thicknesses, ranging between 50 and 300 nm, were controlled by the concentration of the polymer solution. In order to obtain the desired morphologies, films were further exposed to tetrahydrofuran (THF) in a closed vessel of 150 mL containing 15 mL of solvent at 25 °C.

PLA was eliminated by depositing a drop of glacial acetic acid onto the film during 15 s and wiping it out through an N_2 flow. PS was eliminated by dipping into cyclohexane for 10 min and wiping it out through an N_2 flow.

2.3. Precursor solutions preparation

A silica precursor solution (0.33 M) with a molar proportion of 1:5.6:46:0.005 TEOS:H_2O:EtOH:HCl was prepared by mixing in this order 60 mL ethanol (EtOH), 1 mL deionized water, 1.25 mL HCl 0.1 M and 5 mL tetramethoxysilane (TEOS) and stirring at least for 16 h at room temperature. Silica precursor solutions with lower concentrations (namely 0.1 and 0.15 M) were prepared by mixing the previous solution and ethanol with the adequate volume ratio.

2.4. Impregnation of the porous polymer films by precursor solution: silica frames formation

The porous films were impregnated by spin-coating one drop of silica precursor solution at 2500 rpm for 30 s. This step was repeated two or three times with the 0.15 M TEOS solution when silica frame with a continuous silica top layer was wanted. The samples were then heated under air during 5 min at 450 °C to provoke precursor condensation, oxide formation and elimination of the polymer template to yield oxide frames formation. This procedure has already been detailed in one previous paper [37]. After cryogenic plasma etching, the remaining silica was cleared by dipping the samples into a solution 1:1 HF (30%):H_2O and rinsed with deionized water.

2.5. Silicon cryogenic etching

Cryogenic etching of the samples through the porous masks was achieved in an Alcatel 601E etching tool. Inductively coupled plasmas (ICP) are generated in the alumina tube of the source using an external copper ring antenna driven with a 13.56 MHz power supply which can be powered up to 2 kW. Gases, injected through a nozzle at the top of the source, are SF_6 and O_2, with respectively 600 and 20 sccm maximum flows. Pressure can be regulated with a throttle valve between 0.5 and 10 Pa. A diffusion chamber is located under the source, where the plasma can be homogenized. The wafers were loaded via a loadlock and were mechanically

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