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Large-Area Domain Alignment in Block Copolymer Thin Films Using Electric Fields

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Block copolymer thin films are currently of interest as model systems for research on the interfacial behavior of structured fluids, as well as for their potential application as self-assembled templates for nanolithographic patterning.[1] Successful pattern transfer from block copolymer thin films into various semiconductor substrates was recently demonstrated,[2] allowing the patterning of large area substrates with dense, periodic arrays of holes and troughs with features and spacings of several tens of nanometers in size. The microdomains in block copolymer thin films have also been used as nanoreactors for the synthesis of planar arrays of metal and semiconductor nanoparticles.[3−5] However, an obvious and serious limitation of these patterning techniques is the inability to control the positioning and orientation of the features. Monolayer films of asymmetric block copolymers, having cylindrical and spherical morphologies, typically have a polydomain character, with periodic ordering being maintained only over distances of several tens of lattice constants (i.e., distances of about 1 μm).[6,7] A greater range of lithographic applications might be possible if greater control over the orientation and position of the microdomains were possible.

The use of an in-plane electric field to uniformly orient the cylindrical microdomains of a P(S-*b*-MMA) diblock copolymer film was recently demonstrated.[8] Field-induced alignment in P(S-*b*-MMA) is believed to be a consequence of the difference in the static dielectric constants between the two constituent polymers and has been observed previously in the bulk.[9,10] To visualize the domain arrangements by transmission electron microscopy (TEM), it was necessary to carry out the experiments on an 80 nm thick silicon nitride membrane spanning a 50 μm square hole in a silicon wafer. The electrodes, fabricated by e-beam lithography, defined an area of approximately 5 μm,^{2} within which the field strength was a maximum and the cylinders were well aligned.

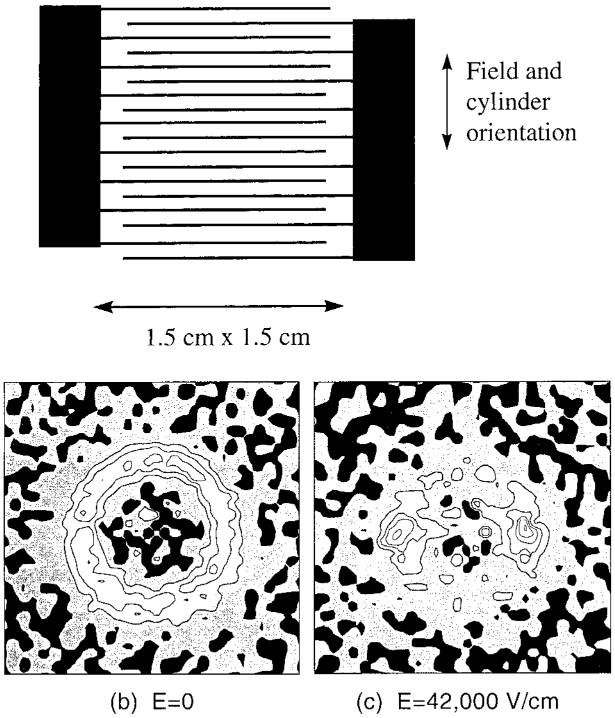

Figure 1. (a) Electrode geometry. The line width and separation are 3 and 12 μm, respectively. The lines were 1.5 cm long, and there were 1000 lines total, for an active area of 2.25 cm^2. (b), (c) Small angle neutron scattering data from films annealed on the electrodes, in zero electric field (b) and at a field strength of 42 kV/cm (c). The orientation of the electrodes relative to the scattering pattern in the experiment was as shown in the figures.

Here, the scale-up of this technique to produce alignment over an area of approximately 2 cm^2 is demonstrated. To create an in-plane electric field with the required strength of at least 30 000 V/cm over such a large area, without using prohibitively high voltages, a set of lithographically fabricated interdigitated electrodes deposited on an 0.5 mm thick quartz substrate was used. Since block copolymer films supported on thick substrates cannot be imaged by TEM, we have used small angle neutron scattering (SANS) from the copolymer films to characterize the degree of alignment.[11]

The electrode geometry is shown in Figure 1a. The active region of the electrodes measured 1.5 cm × 1.5 cm (2.25 cm^2). The individual lines were 3 μm wide, 1.5 cm long, and were separated by gaps of 12 μm. Five hundred lines projected from each of the two contact pads. The electrodes were fabricated using standard photolithographic techniques and consisted of 50 nm of gold deposited on top of a 5 nm thick chromium adhesion layer. A polished quartz substrate was used to minimize leakage currents through the substrate. A small number of localized shorts between opposite polarity lines occurred in some sets of electrodes, due to incomplete metal lift-off or other impurities on the surface, resulting in two-probe resistances of 100−1000 Ω between the contact pads (nonshorted electrodes had resistances greater than 10 MΩ). It should be noted that the presence of localized shorts between certain pairs of opposite polarity wires does not affect the field strength between pairs of nonshorted wires. Any wire

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that is not shorted (not carrying current) will be at the same voltage as the contact pad to which it is connected, over its entire length, ignoring leakage currents through the substrate (which can be shown to be insignificant). Therefore, most of the electrode area experiences the full electric field strength, even in the presence of some localized shorts.

An asymmetric diblock copolymer of perdeuterated polystyrene and poly(methyl methacrylate), denoted P(dS-*b*-MMA), was synthesized anionically. Residual homopolymer styrene was removed by Soxhlet extraction with cyclohexane. The molecular weight, determined by size exclusion chromatography, was $M_w =$ 57 800, with $M_w/M_n = 1.08$. The styrene content was determined to be 70% by NMR. Bulk samples were annealed in a vacuum for 72 h at 170 °C, microtomed, and examined in a JEOL 100CX transmission electron microscope, operated at 100 kV, without the use of any stains. The bulk morphology was found to be cylindrical, with a center-to-center cylinder spacing (nearest neighbor separation) of approximately 53 nm.

Films of the block copolymer were cast directly onto the electrodes, by spin coating from dilute (1−2 w/v %) solutions in toluene at spinning speeds of 500−2000 rpm. The resulting films were essentially conformal to the substrate and electrodes, with no significant nonuniformity resulting from flow of the solution over the pattern edges during spinning. Films of the block copolymer were also spin coated onto 5 cm polished silicon substrates, for use in neutron reflectivity measurements. Analysis of the reflectivity data for an annealed sample showed wetting of the substrate by a PMMA layer and wetting of the free surface by dPS, with layers of PMMA cylinders between lying parallel to the substrate. The periodicity of the layers in the direction normal to the substrate was approximately 37 nm.

Films (200 nm thick) were deposited on two sets of electrodes and were annealed simultaneously at 200 °C for 24 h under a nitrogen atmosphere. One sample was annealed with no applied electric field, while the other sample was annealed with a field of strength of (50 V)/(12 μm) = 42 kV/cm, well above the values found necessary for good alignment of P(S-*b*-MMA) block copolymers in previous studies.[8] The voltage was applied before heating the sample above T_g, while the polymer was still in the disordered state resulting from spin casting. The samples were then slowly cooled to room temperature after annealing. Small angle neutron scattering (SANS) measurements were performed on the NG7 beam line at the National Institute of Standards and Technology, at room temperature and with no electric field present. The neutron beam was incident normal to the substrates. The neutron wavelength was $\lambda = 0.5$ nm, with a wavelength spread $\Delta\lambda/\lambda$ of 22%. The sample-to-detector distance was 12 m, and the data acquisition time for the results presented here (Figure 1b,c) was 1 h.

Figure 1b,c shows the data for these two films, after background subtraction. The orientation of the scattering pattern relative to the electrodes in the experiment was the same as shown in the figure. The difference in the scattering patterns is dramatic. The sample annealed in zero field gives an isotropic ring, characteristic of a film with locally correlated but globally random cylinder orientation, while the sample annealed in the field gives two well-defined spots. The angular position of the spots is consistent with the cylinders being oriented parallel to the electric field direction (the vertical direction in both figures, normal to the wires). The intensity at the maxima of the anisotropic pattern is approximately 50% higher than the peak intensity of the isotropic ring, consistent with reorganization of the sample and the redistribution of the scattering intensity.

However, the integrated intensity of the entire scattering pattern from the aligned sample is approximately 35% less than that of the isotropic ring. In addition, there is a change in the position of the scattering maximum, from $Q = 0.16$ nm^{-1} in the unaligned sample to $Q = 0.14$ nm^{-1} in the aligned sample, corresponding to spacings of 39 and 45 nm respectively ($Q = (4\pi/\lambda)$ $\sin\,\theta$ is the momentum transfer where 2θ is the scattering angle). If the observed anisotropy resulted simply from field-induced alignment of a hexagonal close-packed cylindrical array, with no other changes, then one would expect that the integrated scattering intensity would remain the same (or possibly increase due to longer range coherence in the sample) and that the peak position would remain the same as well.

It is not possible to explain these observations definitively at this point; however, we note that the spacing calculated from the anisotropic scattering maxima, L = 45 nm, agrees well with the spacing between the planes in a hexagonally packed array with a nearest neighbor distance of 53 nm ($\sqrt{3/2} \times 53$ nm = 46 nm). If correct, this would imply that the planes are oriented normal to the substrate. On the other hand, the spacings inferred from reflectivity and SANS experiments on unaligned samples are 37 and 39 nm, respectively, nearly equal to each other, and inconsistent with any allowed peak positions for a hexagonally packed cylinder array with a nearest neighbor spacing of 53 nm, for either parallel or perpendicular orientation of the (110) planes. This indicates that the morphology of an unaligned sample is not hexagonally close-packed cylinders and that, under the electric field, the hexagonally close-packed geometry is favored.

While the above discussion is speculative, these details do not affect the main result of this work, which is the clear observation of field-induced orientation in a large-area thin film of asymmetric block copolymer. When combined with appropriate pattern transfer techniques, aligned films of this type may be used to template uniform arrays of lines or wires into solid substrates, with useful potential applications such as the fabrication of X-ray diffraction gratings with ~30 nm periodicities. The use of neutron scattering to characterize the degree of alignment opens up the possibility of real-time studies of the alignment process in thin films on thick substrates, which may help to elucidate the alignment mechanism and the role of the substrate in inhibiting or promoting ordering and alignment.

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