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Inorganic Nanodots from Thin Films of Block Copolymers

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Received June 17, 2004

There has been considerable interest in fabricating submicrometer and nanometer-scale structures over the past decade.^{1–6} Numerous methods have appeared to generate nanostructures with regularly sized and spaced nanoscopic features. In particular, the self-assembly of two chemically different polymers covalently joined at one end into ordered nanoscale morphologies^{7–10} offers an attractive route to overcome the limitations of conventional lithographic techniques. Consequently, there has been tremendous interest in using block copolymers as a platform for nanostructured materials.^{11–17} Among various approaches, selective decoration of one of the constituent block copolymers with organic/inorganic moieties has been suggested as a promising route to nanofabrication.^{18–27} However, most of the works still have limitations in terms of the complexity of fabrication steps, synthesis of novel architectures, mass production with reasonable costs, and control of the morphology of the final structures.

Recently, Russell and co-workers have reported a rapid route by which the cylindrical nanodomains of an asymmetric poly(styrene-*co*-ethyleneoxide) block copolymer (PS-*b*-PEO) could be oriented normal to the surface.²⁸ It has also been shown that thin films of asymmetric PS-*b*-PEO could be used as scaffolds to define ordered arrays of nanoscopic reaction vessels wherein high-density arrays of silicon oxide nanostructures could be produced.²⁹ Highly ordered semiconductor nanostructures have attracted interest due to their potential applications in optical, optoelectronic, magnetic, and micro-mechanical devices. The most critical issue lies in controlling the size, spacing, and size distribution of the nanoscopic elements.^{30–37}

Here, a simple route is described to fabricate a nanopatterned array of inorganic oxide semiconductors using PS-*b*-PEO thin films as a scaffold. A schematic illustration of the process is shown in Figure 1. The surface of a PS-*b*-PEO film spin coated from benzene (Figure 1A) exhibits an array of hexagonally close packed cylindrical PEO domains with ~ 2 nm depressions in each of the PEO microdomains. By immersing the copolymer film in water, the PEO domains

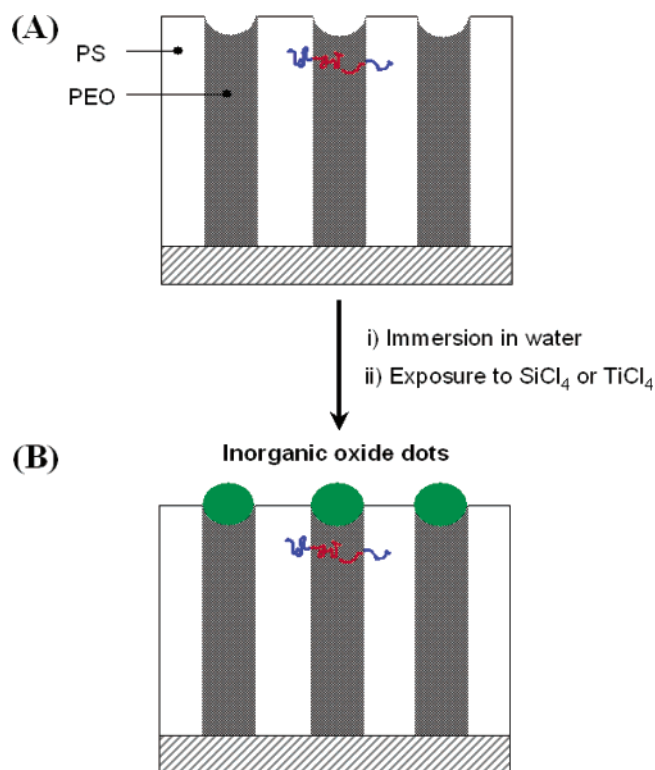


Figure 1. Schematic diagram to generate nanoscopic dot array of inorganic materials on PS-*b*-PEO thin film. The PS-*b*-PEO films spin coated from benzene solutions on Si wafer were immersed into water. Subsequently, the swollen copolymer film was exposed to the silicon tetrachloride (SiCl₄) or titanium tetrachloride (TiCl₄) precursor vapors.

swell, while the PS matrix remains unchanged. The swollen films were then exposed to precursor vapors of silicon tetrachloride (SiCl₄) or titanium tetrachloride (TiCl₄). Silica or titania dot arrays were produced on top of PEO domains through a binary reaction mechanism of these precursors with H₂O molecules as shown in Figure 1B.

Figures 2A and 2B show the phase contrast scanning force microscopy (SFM) images of ~ 140 nm thick PS-*b*-PEO on silicon (Si) wafer treated with SiCl₄ and TiCl₄, respectively, along with corresponding perspective views of the surface topography (Figures 2C and 2D, respectively), where dense, ordered arrays of uniformly sized silica and titania dot arrays

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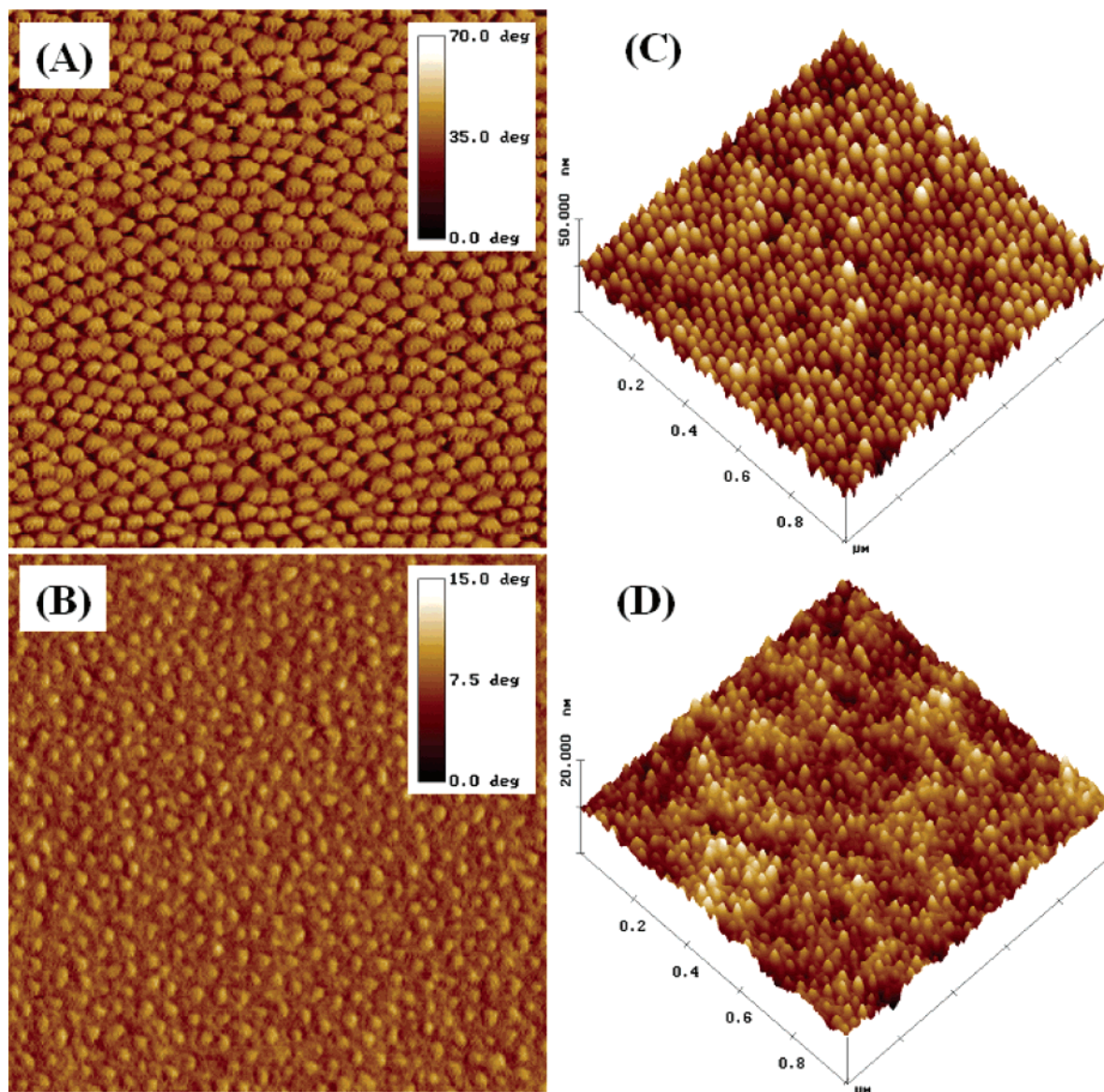


Figure 2. (A) Phase contrast AFM image of silica dot arrays on PS-*b*-PEO film. (B) Phase contrast AFM image of titania dot arrays on PS-*b*-PEO film. (C) 3D view of the height contrast AFM image of silica dot arrays on PS-*b*-PEO film. (D) 3D view of the height contrast AFM image of titania dot arrays on PS-*b*-PEO film. The images are in $1\ \mu\text{m} \times 1\ \mu\text{m}$ scale.

on PS-*b*-PEO films are evident. The average diameters of the silica and titania dots were 24 and 22 nm, respectively, with average center-to-center distance ($d_{\text{C-C}}$) between adjacent dots of 40 nm in both cases. The z -ranges of the two phase contrast images indicate that the silica is harder than the titania. The silica and titania dots also protruded from the surface of the PS matrix by ~ 5 nm and ~ 2 nm in height, respectively, based on the SFM line scans.

X-ray photoelectron spectroscopy (XPS) was used to determine the chemical composition of the inorganic oxides. The characteristic peak of silicon ($\text{Si}_{2\text{p}}$) was observed at 102.8 eV and the peaks for titanium, $\text{Ti}_{2\text{p}1/2}$ and $\text{Ti}_{2\text{p}3/2}$, were observed at 468.0 and 462.3 eV, respectively, with the $\text{C}_{1\text{s}}$ peak position referenced at 285.0 eV.^{38–40} However, the grazing angle incidence X-ray diffraction pattern did not exhibit any noticeable peaks for the silica or titania containing PS-*b*-PEO film in the range of $20^\circ \sim 70^\circ$, presumably due

to either the lack of crystallinity or the small amount of the dots to be detected.

To investigate the distribution of the inorganic particles inside the PEO domain, X-ray reflectivity measurements were performed as a function of the scattering vector $Q_z (= 4\pi \sin \theta / \lambda)$, where θ is the incidence angle and λ is the wavelength. The X-ray reflectivity profiles of a PS-*b*-PEO film (~ 140 nm thick) on a Si wafer are shown in Figure 3A and 3B. The solid line represents the best fit to the data using the electron density profile shown in the inset. Kiessig fringes, characteristic of the total film thickness of the samples, are seen in both profiles. However, the amplitude of the oscillations is more pronounced for the film after reaction with SiCl_4 , as would be expected with the incorporation of the electron-dense silica in the PS-*b*-PEO film. The electron density profile for the pure PS-*b*-PEO film is uniform across the film as would be expected for a diblock

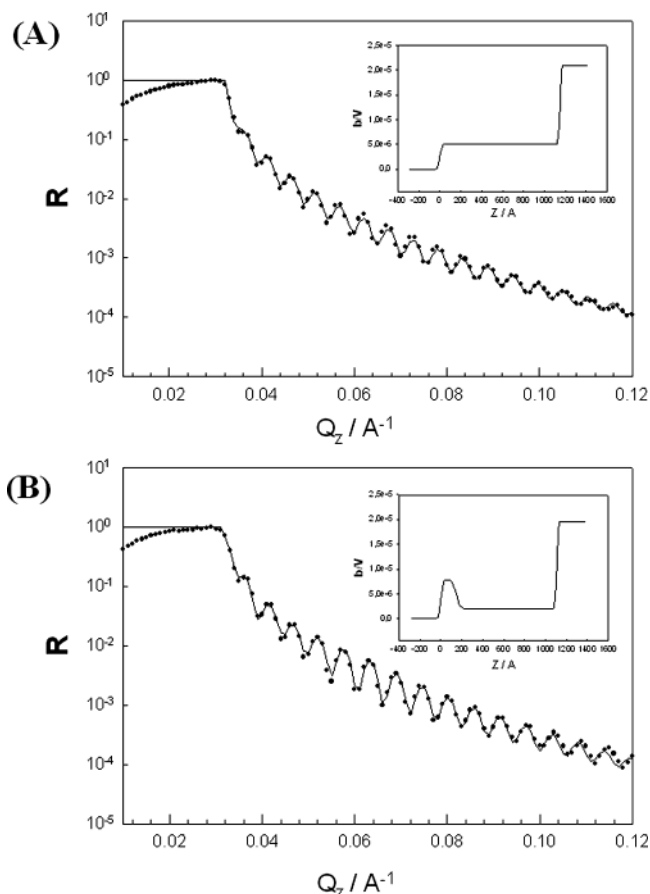


Figure 3. (A) X-ray reflectivity profile of a PS-*b*-PEO thin film with 140 nm thickness. (B) X-ray reflectivity profile of an identical PS-*b*-PEO thin film reacted with SiCl₄. Insets in the figures are the calculated scattering length density profiles.

copolymer film where the cylindrical microdomains were oriented normal to the surface. After reaction with SiCl₄ a higher electron density is seen at the surface, indicating that the generation of silica has occurred predominantly at the surface of the film and not in the center of the film. Consequently, the reaction is exclusively restricted to the PEO microdomain and the penetration of the SiCl₄ into the film is retarded by the silica formed at the top of the cylinders.

The optical properties of PS-*b*-PEO films containing titania dot arrays were examined by fluorescence spectroscopy. The photoluminescence (PL) spectra from the titania arrays with $d_{C-C} \sim 40$ nm on PS-*b*-PEO film (Figure 2B or 2D) under different excitation wavelengths are shown in Figure 4. In the emission spectra, using excitation at 413 and 473 nm, peaks were observed at ~ 566 nm and ~ 623 nm, respectively.^{26a,41–43} With an increase of excitation wavelength, the PL spectra show a red shift that can be attributed to a strong correspondence between excitation energy and the vibronic structure of the emission spectra.

In summary, a general route to fabricate highly dense nanoscopic dot arrays of inorganic oxides or semiconductors was presented using thin film block copolymer templates. Silica and titania could be grown selectively on the PEO domain of asymmetric PS-*b*-PEO film by exposure to

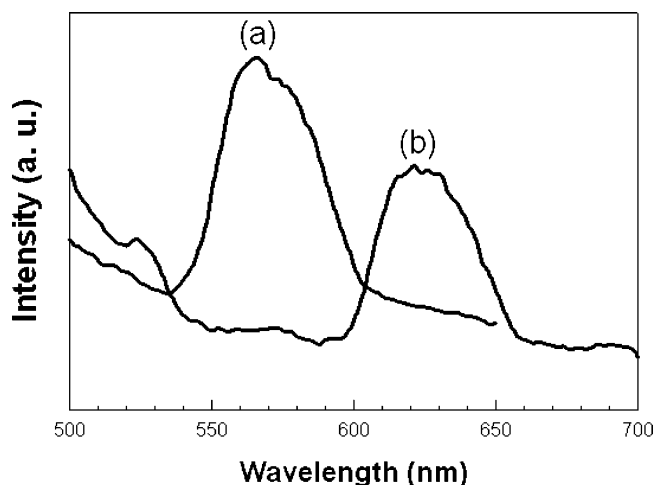


Figure 4. Photoluminescence spectra from a PS-*b*-PEO thin film containing titania dot array obtained at different excitation wavelength: (a) 413 nm; (b) 473 nm.

precursor vapors. Thus, a nanoscopically patterned surface, consisting of an array of hexagonally close packed inorganic materials in an organic matrix, was generated. Such nano-patterned dot arrays can have wide applications in the field of sensory and optical devices.^{44,45} This investigation presents a novel route based on block copolymer templated nanofabrication and the methodology provides a facile approach to inorganic nanostructures with tunable size, lateral spacing, and diverse composition.

Experimental Section. An asymmetric diblock copolymer of PS and PEO, denoted PS-*b*-PEO, having a molecular weight of 25 300 g/mol (25 K) with PEO volume fractions of 0.25 (Polymer Sources Inc.) was used in this study. Benzene solutions of the copolymers were spin coated onto Si wafers, and the thickness of the films was controlled by the spinning speed and solution concentration. Film thickness was measured with a Rudolph Research AutoEL-II ellipsometer using a helium–neon laser ($\lambda = 632.8$ nm) at a 70° incidence angle.

Silicon tetrachloride (SiCl₄) and titanium tetrachloride (TiCl₄) were purchased from Aldrich and used as received without further purification. Silica was grown in the PS-*b*-PEO film by reacting SiCl₄ at reduced pressure. The PS-*b*-PEO films on Si wafer were swollen with water for 30 min prior to the reaction. SiCl₄ was cooled to -46 °C and its vapor was transferred to the reaction vessel containing a Si substrate covered with the copolymer films. The reaction was performed for 1 min at 25 °C, 70 mm Hg. Titania was grown by exposing the water-swelled PS-*b*-PEO film to TiCl₄ vapor in a closed vessel for 3 min at 25 °C under nitrogen atmosphere.

AFM images were obtained in both height and phase contrast modes using a Digital Instruments Dimension 3000 scanning force microscope in the tapping mode. Etched silicon tips on a cantilever (Nanoprobe) with spring constants ranging between 40.0 and 66.0 N/m (as specified by the manufacturer) were used.

X-ray reflectivity measurements were performed on the $\times 22B$ beam line at the National Synchrotron Light Source,

Brookhaven National Laboratory, with an 11 keV monochromatic beam. The incident and scattered beams were collimated so as to achieve a direct beam with a fwhm (full width at half-maximum) of 0.04° . Measurements were made under strictly specular conditions and corrected by subtracting the longitudinal specular background that was found to be almost negligible (3 orders of magnitude lower). The reflected intensity was normalized by the measured incident intensity to obtain reflectivity. The data were corrected for background scattering and invariance of the illuminated area at very low angles of incidence (below $\cong 0.125^\circ$, depending on sample size). The profiles are reported as a function of Q_z , the component perpendicular to the interface of the scattering vector of the incident photons ($4\pi \sin \theta/\lambda$), where λ is the X-ray wavelength and θ is half the angle between incoming and outgoing beams. The data were fitted using Parratt32 software (version 1.5).

Photoluminescence spectra were recorded on a Perkin-Elmer LS 50B luminescence spectrometer using a xenon discharge lamp for excitation. The emission spectra were collected at two different excitation wavelengths of 413 and 473 nm.

Acknowledgment. This work was funded by the Department of Energy, Basic Energy Sciences under contract DE-FG02-96ER45612, National Science Foundation under partnership in Nanotechnology (CTR-9871782), NSF sponsored Material Research Science and Engineering Center at the University of Massachusetts at Amherst.

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NL049063W