Electrically Anisotropic Thin Films Consisting of Polymeric and Metallic Nanolayers from Self-Assembled Lamellae of Diblock Copolymers

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We demonstrated the fabrication of electrically anisotropic thin films of alternating polymeric layers and metallic layers in nanometer thickness by utilizing self-assembled nanodomains of symmetric diblock copolymers. Nanometer-thick metal layers macroscopically parallel to the film plane were synthesized by electroless Ag deposition on Au nanoparticles selectively in one of the blocks. Every Ag/Au layer was completely separated by nanometer-thick polymer layers in the direction perpendicular to the film plane. Therefore, the conductivity of the film was highly anisotropic, differing by at least 8 orders of magnitude in directions parallel and perpendicular to the film plane, even though the in-plane conductivity (2.8×10^{-6} S/cm) was in the range of semiconductors. If self-assembled nanodomains of diblock copolymers were not employed, a serial layer-by-layer process for each layer would be required to fabricate such an electrically anisotropic thin film.

Introduction

Recently, there has been intensive research conducted on thin films of diblock copolymers, two different polymers covalently connected, because of their potential applications in nanotechnology by utilizing their self-assembled nanostructures.[1−3] Diblock copolymers phase-separate to form periodic structures on the tens of nanometers length scale. The size and morphology of nanometer-sized domains can be easily controlled by the molecular weight and composition of the copolymers. In addition, the functionality of nanodomains for a particular application can be tailored by selection of the chemical type of each block.[4,5]

An example of utilization of the self-assembling nature of diblock copolymers is the fabrication of a multilayered structure of periodic repeats of nanometer-sized layers, which can be useful for electronic and photonic applications such as flip-chip interconnections and photonic band-gap materials.[6,7] In thin films of symmetric diblock copolymers, each block self-assembles into one of the alternating lamellar layers in the nanometer scale. Moreover, due to the preferential interaction of one of the blocks with the

substrate or the air interface, multilayers of the lamellae macroscopically parallel to the substrate can be generated in the thin film.[8−13]

As an effective method to functionalize one of the blocks for electronically, optically, or magnetically active nanodomains, nanoparticles of metals, semiconductors, or oxides can be incorporated selectively or synthesized in situ in nanodomains of diblock copolymers.[14−22] Recently, we also demonstrated the synthesis of Au nanoparticles selectively in the lamellar domains of diblock copolymers in thin films to fabricate a multilayered nanostructure of alternating pure polymeric lamellae and Au-nanoparticle-containing lamellae.[23,24]

In this article, we report the fabrication of electrically anisotropic multilayers of alternating polymeric layers

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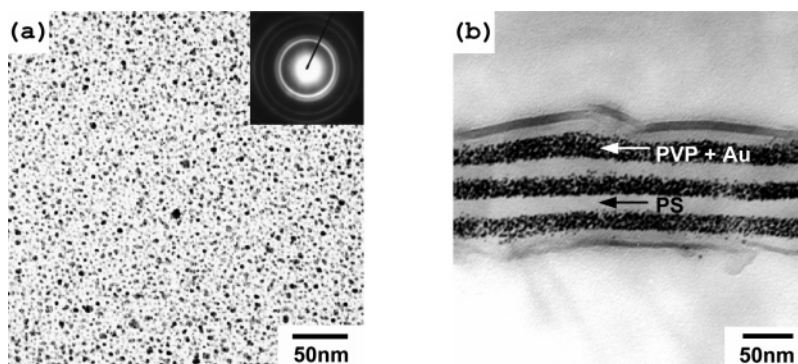(24) Sohn, B. H.; Seo, B. W.; Yoo, S. I. *J. Mater. Chem.* **2002**, *12*, 1730.

Figure 1. TEM images of PS−PVP thin films with Au nanoparticles in the PVP lamellae after a single cycle of the synthesis of Au nanoparticles: (a) in plane view; (b) in cross-sectional view. The inset in part a is a selected-area electron diffraction pattern of Au nanoparticles in the film.

and metallic layers in nanometer thickness, macroscopically parallel to the substrate, by utilizing self-assembled nanodomains of symmetric diblock copolymers without a layer-by-layer process. Nanometer-thick metal layers were synthesized by electroless Ag deposition on Au nanoparticles selectively in one of the blocks. The conductivity was highly anisotropic, differing by at least 8 orders of magnitude in directions parallel and perpendicular to the film plane.

Experimental Section

Polystyrene−poly(4-vinyl pyridine) (PS−PVP) diblock copolymers were purchased from Polymer Source, Inc. The number-average molecular weights of PS and PVP were 21 400 and 20 700 g/mol, respectively. The polydispersity index was 1.13.

Silicon wafers were cleaned in a piranha solution (70/30 v/v of concentrated H_2SO_4 and 30% H_2O_2) at 90 °C for 20 min, thoroughly rinsed with deionized water several times, and then blown dry with nitrogen. Fresh mica substrates were prepared by cleaving a piece of mica. After cleaning or cleaving, substrates were immediately used for the spin coating of copolymers.

PS−PVP thin films were spin-coated onto clean silicon wafers or freshly cleaved mica from a *N,N*-dimethylformamide (DMF) solution. Various film thicknesses were obtained by adjusting the spinning speed and solution concentration (3.0−5.0 wt %). The copolymer films were annealed at 180 °C in a vacuum oven for 36 h or longer.

After the annealing of a PS−PVP thin film on the substrate, the film was immersed into 1 wt % ethanol solutions of $HAuCl_4$, a precursor of Au nanoparticles, for ~30 min and then thoroughly rinsed with deionized water several times. For an equilibrium loading of the precursor, a dipping period of the film in the solution was selected when the film weight was not increased further by a quartz crystal microbalance.[24] The thin film loaded with $HAuCl_4$ was again dipped into 1.0 wt % $NaBH_4$ aqueous solutions for <30 s to reduce the precursors to Au nanoparticles. The same cycle of loading of precursors and reducing to Au nanoparticles was repeated twice.

For electroless deposition of Ag into the Au-nanoparticle-containing PVP domain, the loading of Ag ions and reducing to Ag in the film were separately performed, instead of adopting a single bath of Ag ions and reductants, which is commercially available as a silver enhancer.[25] After two cycles of the synthesis of Au nanoparticles, the film was dipped into 3.0 wt % $AgNO_3$ aqueous solutions for 30 min and then into 1.0 wt % $NaBH_4$ aqueous solutions. Then, the film was rinsed with deionized water several times and was completely dried in a vacuum oven. The same cycle of Ag deposition was repeated three times.

For plane-view transmission electron microscopy (TEM), the film was floated off from the mica substrates onto deionized water and collected on TEM grids. Cross-sectional TEM samples were prepared as described in the previous reports.[23,24] From the thin film embedded in epoxy with a carbon coating on both sides of the film after removing the substrate, thin sections (~70 nm

thick) were obtained using a Reichert ultra-microtome with a diamond knife. TEM was performed on a JEOL 1200EX instrument at 120 kV.

Out-of-plane conductivity, perpendicular to the film plane, was measured in the parallel-plate geometry. A highly doped silicon wafer (resistivity <0.01 Ω·cm) was adapted as a substrate. Gold electrodes (2.0 mm in diameter) were evaporated on top of the film fabricated on the conductive substrate to produce the parallel-plate structure. In-plane conductivity, parallel to the film, was also evaluated by the van der Pauw method, using a Keithley 2410 sourcemeter. A gold wire was attached with conductive silver-epoxy paste at each corner of the rectangular samples (~2.0 mm × ~2.5 mm). To aid the gold wires in contacting all layers in the film, a tiny portion of each corner of the film was removed before applying the conductive paste.

Results and Discussion

When a PS−PVP thin film was spin-coated and annealed above the glass transition temperatures of both blocks on silicon wafers or mica substrates, multilayered lamellae macroscopically parallel to the substrate were induced with an asymmetric wetting configuration, that is, the PVP block at the substrate interface and the PS block at the air interface, due to the lower surface energy of the PS block and the preferential interaction of the PVP block with the polar substrate.[1,12,23] Au nanoparticles were synthesized selectively into the PVP lamellae, resulting in alternating polymer layers and Au-nanoparticle layers.[23,24] $HAuCl_4$, a precursor of Au nanoparticles, was coordinated to a pyridine unit of the PVP block by protonation. Then, the selectively loaded precursors were reduced to Au nanoparticles within the PVP layers.[23,24]

Figure 1a shows a plane-view TEM image of the film containing Au nanoparticles, which is a through-view image from the top to the bottom of the film after removing the mica substrate. In the image, Au nanoparticles of 3.0 nm in average diameter were synthesized and distributed homogeneously in the direction parallel to the film plane. The selected-area electron diffraction pattern (the inset of Figure 1a) confirmed the cubic crystalline structure of Au.

The internal nanostructure of alternating polymer layers and Au-nanoparticle layers was clearly visualized in a cross-sectional TEM image of PS−PVP thin films after Au-nanoparticle synthesis (Figure 1b). Light gray carbon layers appeared on both sides of the film. The film apparently consisted of four layers of the PS block and three layers of the Au-nanoparticle-containing PVP block with the nanometer-scale thickness. Since the top PS layer actually corresponded to a half-thick lamella and the bottom Au-nanoparticle-containing PVP lamella was missing in the image due to incomplete detachment of the film from the substrate, the film shown in the cross-

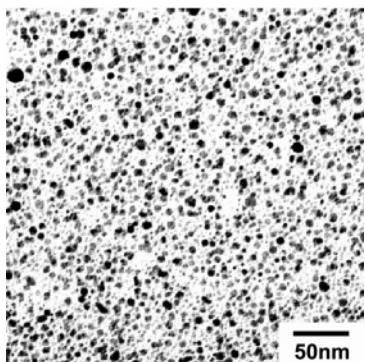(25) Park, S. J.; Taton, T. A.; Mirkin, C. A. *Science* **2002**, *295*, 1503.

Figure 2. Plane-view TEM image of PS−PVP thin films with Au nanoparticles after two cycles of the synthesis of Au nanoparticles.

Figure 3. Plane-view TEM image of PS−PVP thin films after Ag deposition on Au nanoparticles. The inset is a selected-area electron diffraction pattern of deposited Ag and Au nanoparticles in the film.

sectional image had originally 3.5 lamellae of the PS block and 3.5 lamellae of the Au-nanoparticle-containing PVP block. A detailed discussion on the number of lamellar layers in the thin film was given in the previous report.[23]

From the TEM images in plane and cross-sectional views, Au nanoparticles were localized and homogeneously distributed in the PVP layers so that Au-nanoparticle layers were continuous in the direction parallel to the film plane but were entirely separated by nanometer-thick PS layers in the direction perpendicular to the film plane. Therefore, highly anisotropic properties of the film can be expected. However, the conductivities of the film in both parallel and perpendicular directions were <1.0 × 10^{-14} S/cm, which was the limit of our measurement.

Although Au nanoparticles in the cross-sectional TEM image appeared dense (Figure 1b) because of the projection of all nanoparticles in an ∼70-nm-thick microtomed slice, Au nanoparticles in the PVP lamellae were not in contact with each other, as shown in the plane-view TEM image (Figure 1a). Thus, an in-plane conductivity could not be high without the percolation of Au nanoparticles. Also, a very low out-of-plane conductivity was expected due to the electrically insulating PS layers. Therefore, the film did not show electrical anisotropy.

To induce contact of Au nanoparticles by increasing their volume fraction in the PVP layer, we repeated the synthesis cycle of Au nanoparticles with the same PS−PVP thin film. We were able to load more precursors by repeating the synthesis cycle, presumably due to the regeneration of coordination sites for $HAuCl_4$ in the PVP block.[16,24] After two cycles of the synthesis, for example, the average diameter of Au nanoparticles increased to 6.0 nm, as shown in Figure 2. After each synthesis, however, the amount of $HAuCl_4$ loaded was decreased, and it reached saturation after five cycles of the synthesis.[24] The maximum volume fraction of Au nanoparticles in the film after five cycles of the synthesis was ∼15%.[24] Therefore, percolation of Au nanoparticles in the PVP lamellae could not be achieved simply by repeating the synthesis.

To generate a continuous metallic phase in each PVP domain, electroless Ag deposition was carried out after the synthesis of Au nanoparticles, which worked as an effective catalyst for Ag deposition.[25] The film containing Au nanoparticles shown in Figure 2 was employed for Ag deposition. Figure 3 shows a plane-view TEM image of the film after Ag deposition. Spherical nanoparticles were no longer discernible. Irregularly shaped lumps of ∼20.0 nm in diameter clumped together into a continuous form with some bright empty spaces.

The overlapped selected-area electron diffraction pattern of Ag and Au is also shown in the inset of Figure 3. Thus, the metallic phases of deposited Ag on Au nano-
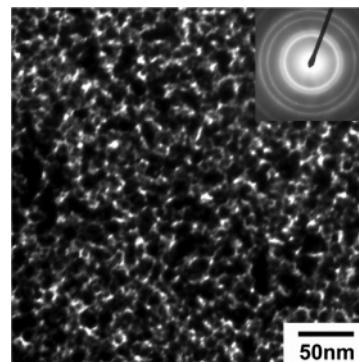
particles in the PVP lamella apparently contacted each other and were continuous in the direction parallel to the film plane. Without Au nanoparticles in the film, Ag was not deposited in the PVP layers, indicating that Au nanoparticles were necessary for electroless Ag deposition.

In the cross-sectional TEM image of the film after Ag deposition (Figure 4), a multilayered nanostructure of alternating polymeric PS layers and metallic Ag/Au layers was clearly discernible. Ag deposition was localized exactly in the Au-nanoparticle-containing PVP layers. The film apparently consisted of five PS layers and four Ag/Au layers. However, there were actually 4.5 lamellae of each layer in the film before the cross-sectional TEM sample was prepared, as explained earlier with Figure 1b. After Ag deposition, the thickness of the PVP layers increased to ∼20.0 nm but that of the PS layers decreased to ∼12.0 nm. Since the deposition was carried out at room temperature, shrinkage of the PS layer was less possible due to glassy PS blocks. Presumably, Ag would overgrow to PS layers during the deposition, resulting in apparently thin PS layers in the TEM image. However, each metal layer was evidently separated by each PS layer in the direction perpendicular to the film plane but was continuous in the direction parallel to the film plane. Also, the multilayered nanostructure of alternating polymeric layers and metallic layers was manifestly extended to a large area, longer than 1.4 μm in the direction parallel to the substrate in the image of Figure 4. This multilayered thin film was fabricated basically by utilization of the self-assembling nature of diblock copolymers without a layer-by-layer process.

The in-plane conductivity of the multilayered thin film shown in Figure 4 was 2.8 × 10^{-6} S/cm on average, whereas its out-of-plane conductivity was <1.0 × 10^{-14} S/cm. Thus, the film consisting of alternating PS layers and Ag/Au layers exhibited highly anisotropic electrical conductivities, differing by at least 8 orders of magnitude in directions parallel and perpendicular to the film plane.

An extremely low conductivity perpendicular to the film plane was mainly due to dielectric PS layers between Ag/Au layers. However, the in-plane conductivity of the film, which resulted from the electrical conduction through the parallel Ag/Au layers, was in the range of semiconductors. As shown in Figure 5, a linear Arrhenius plot of temperature-dependent conductivities parallel to the film plane, the conductivity decreased with decreasing temperature, implying that conduction in the Ag/Au layer originated from activated hopping of electrons.[26−28] The electrostatic activation energy for charge transport in the Ag/Au layer was ∼0.01 eV, evaluated from the slope of the Arrhenius plot. This activation energy was smaller than
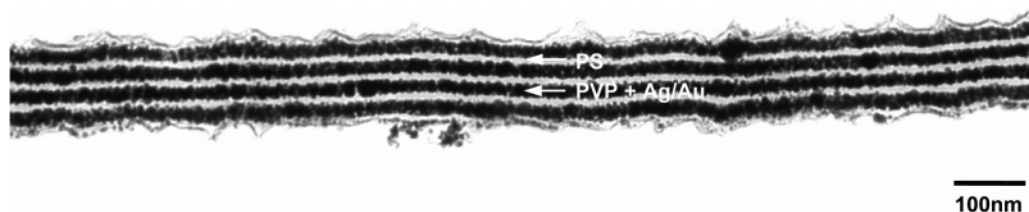
Figure 4. Cross-sectional TEM image of PS−PVP thin films after Ag deposition on Au nanoparticles.
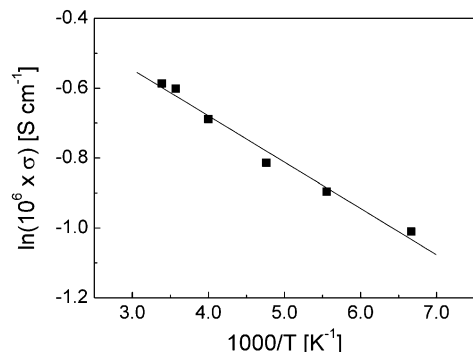

Figure 5. Logarithmic plot of the temperature dependence of the in-plane conductivity of PS−PVP thin films after Ag deposition on Au nanoparticles.

Figure 6. Cross-sectional TEM image after annealing of the PS−PVP thin films containing Ag/Au layers at 300 °C for 1 h.

that of assemblies of alkanethiol-protected Au nanoparticles.[26−28] Since the synthesis of the Ag/Au layer was carried out inside the PVP domain, polymeric barriers within the Ag/Au layer could be responsible for nonmetallic conduction parallel to the film plane.

For the purpose of enhancing the in-plane conductivity, the film of the multilayered nanostructure was annealed because all of the synthesis procedures were performed at room temperature. Temperatures higher than one-third of the melting temperatures of metals are typically selected as annealing temperatures to improve their crystallinity.[29] Thus, annealing of the film was carried out at 300 °C, although the melting temperatures of nanometer-sized Ag and Au could be lower than those in bulk.[30] After annealing, the in-plane conductivity of the film was dramatically increased to 0.28 S/cm on average. However, the multilayered nanostructure of alternating PS layers and Ag/Au layers was completely destroyed, as shown in the cross-sectional TEM image of Figure 6. The annealing temperature, far above the glass transition temperatures of PS and PVP, was too high to keep Ag and Au in the PV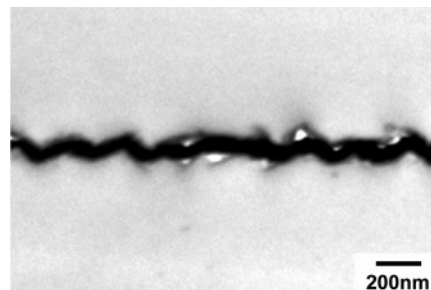P domain with the PS barrier. After annealing, the diblock copolymers, particularly the PS blocks, could not be entirely covered by the Ag/Au phase so that some of them could exist separately from the metallic phase, although it was difficult to discern the separated phase in the TEM image. After annealing, it was not easy to obtain a consistent value of the out-of-plane conductivity because the surface of the film became irregular, resulting in large variations of the film thickness. However, its order of magnitude was similar to that of the in-plane conductivity, indicating loss of the electrical anisotropy of the film.

Conclusions

By utilization of self-assembled nanodomains in thin films of symmetric PS−PVP diblock copolymers, we fabricated electrically anisotropic multilayers of alternating polymer layers and metal layers, which were macroscopically parallel to the substrate. Metal layers of nanometer thickness were synthesized by electroless Ag deposition on Au nanoparticles selectively in the PVP lamellae. Every Ag/Au layer was completely separated by PS layers in the direction perpendicular to the film plane. Thus, the conductivity was highly anisotropic, differing by at least 8 orders of magnitude in directions parallel and perpendicular to the film plane. The self-assembling nature of diblock copolymers enabled us to synthesize a highly anisotropic thin film consisting of polymeric and metallic nanolayers without a serial layer-by-layer process.

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