Nano-Scale Patterning by Gold Self-Assembly on PS-PB-PS Triblock Copolymer Thin Film Templates

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PS-PB-PS 삼블럭 공중합체 박막형판에서의 금의 자기응집에 의한 Nano-Scale 패턴형성

ABSTRACT : This paper describes how the gold particles self assemble on the specific phase on the microphase separated block copolymer thin film and form a well ordered patterns. For this study, polystyrene-polybutadiene-polystyrene(PS-PB-PS) triblock copolymer(30wt % PS) thin films (~100nm) having a cylindrical morphology were cast from 0.1wt% toluene solution to be used as polymer thin film templates. The films having either vertical PS cylinders or in-plane PS cylinders in PB matrix from each different solvent evaporation condition were obtained. Cross-sectional transmission electron microscopy(TEM) was used to study the surface and bulk morphologies of block copolymer thin films. Small amount of gold particles was evaporated on a block copolymer thin film template to obtain a nano-scale pattern. When an as-cast thin film template was used, gold particles preferentially self assemble on the low surface tension PB phase and a relatively well ordered pattern in nano-scale was produced. However, after the formation of a low surface energy PB rich layer upon annealing, a gold self-assembled pattern was not observed.

요약 : 본 논문에서는 미세 상분리된 블럭 공중합체 박막의 특이상에서 금 입자들이 어떻게 자기응집 (self assemble) 되고 잘 배열된 패턴을 형성하는지를 살펴보았다. 본 연구에서는 원통형 모폴로지를 갖는 PS-PB-PS 삼블럭 공중합체(30wt% PS) 박막(~100nm)을 0.1wt% 톨루엔 용액으로부터 캐스팅하여 고분자 박막 형판(template)으로 사용하였다. 각각의 상이한 용매 증발조건으로부터 PB matrix내에 수평배열 PS cylinder와 수직 PS cylinder를 함께 갖는 막이 얻어졌다. 블럭 공중합체 박막의 표면 및 bulk 몰폴로지를 살펴보기 위하여 단면투과전자현미경(TEM)을 사용하였다. Nano-scale 패턴을 얻기 위하여는 소량의 금입자를 블럭 공중합체 박막상에 증발시켰다. 캐스팅된 상태 그 대로의 박막형판이 사용되어질때 금입자들은 표면 장력이 적은 PB상에 우선적으로 자기응집(self assemble)하여 비교적 잘 배열된 nano-scale의 패턴을 형성하였다. 그러나 열처리(annealing)에 의하 여 표면장력이 적은 PB-rich 층이 형성된 후에는 금입자의 자기응집에 의한 패턴은 관찰되지 않았다.

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I. Introduction

In normal polymer blends consisting of more than two immiscible homopolymers, a macroscopic phase separation commonly occurs. However, block copolymers such as diblock copolymers or triblock copolymers produce pretty well-ordered microstructures in meso-scale at equilibrium.[1-5] As a matter of thermodynamic equilibrium, the system should choose to assume the geometry that corresponds to its lowest free energy minimizing the contact area between incompatible chain segments. Usually, the block copolymers are microphase separated into spheres, cylinders and lamellae with long range order depending on the block composition at equilibrium and the ordered patterns are typically on the order of 10 nanometers. The microdomain size and the interdomain spacing are governed by the chain dimension.

In recent days, the long-range ordered microstructures of amorphous block copolymers have fascinated major research groups working on nanolithography. Many published results have shown the possibility of the usage of polymer thin film templates to produce the ordered patterns in a large area.[6-9] Extensive applications of the two dimensional ordered structures of block copolymers such as the fabrication of quantum dots,[10,11] the high density magnetic recording device[12] and the epitaxial growing DNA electrophoresis media[13] have motivated the researches on the nanolithographic application of block copolymer templates. They also have achieved some success in obtaining a well ordered nanoscale pattern on the semiconductor substrate using a body centered cubic(BCC) arrayed spherical morphology and an alternating lamellar morphology of block copolymers.

To produce a block copolymer thin film template having a well ordered microphase-separated structure, it is important to understand and control the morphological behavior of block copolymer in the thin film. One of the previous studies[14] on the cylindrical morphology of a block copolymer thin film showed that the polystyrene(PS) cylindrical domain orientation in the 30wt% PS content PS-polybutadiene(PB)-PS triblock copolymer thin film is changed as a function of solvent evaporation rate and annealing. Increasing the exposure to solvent via slower solvent evaporation rate and thermally enhanced polymer mobility in the absence of solvent evolve a less stable state of an as-cast block copolymer microstructure to an equilibrium state while changing the orientation of microdomains. Radizilowsky et al.[15] using cross-sectional transmission electron microscopy(TEM) observed the thickness effect on the microdomain orientation of PS cylinders in a PS-PB diblock copolymer. When the thickness of thin film was less than 30nm, the cylinders align preferentially themselves perpendicular to the free surface. Park et al.[6] studied the substrate effect on the microstructure of PS-polymethylmetacrylate(PMMA) block copolymer thin film having a lamellar morphology. They also obtained a well-ordered pattern on a semiconductor substrate using a hexagonally arrayed cylindrical structure of PS-PB block copolymer templates.

This paper describes initial results of gold self-assembly on the block copolymer templates as a function of a solvent evaporation rate and an an-

nealing condition with considering thermodynamics and kinetic effects associated with microphase separation at the surface of block copolymer thin films. This research explores experimentally how the metal particles self assemble on the block copolymer thin film and how the surface structure of polymer thin film templates effect on the formation of a well ordered patterns. The thin films having either vertical PS cylinders or in-plane PS cylinders in PB matrix from each different solvent evaporation condition are used as polymer templates. TEM was used to study the surface and the bulk morphologies of the block copolymer thin films. A relatively well-ordered nano-scale pattern was obtained using a simple gold evaporation tech-

nique on the PS-PB-PS triblock copolymer thin films. The fact that gold particles preferentially self assemble on the low surface tension and soft polymer domains makes it possible to get a novel pattern in nano-scale on the thin film templates.

II. Experimental Procedure

The thin-films of a PS-PB-PS triblock copolymer were cast from 0.1wt% toluene solution. Characterization by Gel permeation Chromatography(GPC) and proton NMR determined that this polymer was 30% by weight polystyrene with M_w =100,000 and contained small amounts($\leq$5%) PS/PB diblock and PS homopolymer. ~50μl of so-
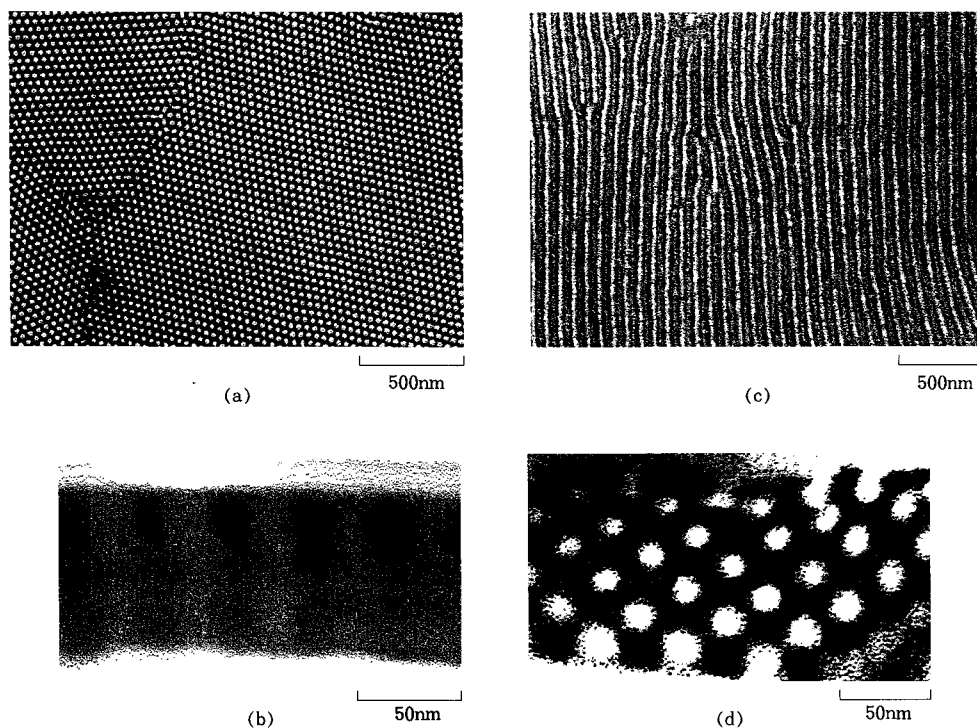

Fig. 1. Osmium stained TEM images of the as-cast PS-PB-PS block copolymer thin films; (a) a plan-view of a vertical cylindrical morphology; (b) a cross-sectional view of (a); (c) a plan-view of an in-plane cylindrical morphology; (d) a cross-sectional view of (c).

lution was deposited on a NaCl single-crystal sub-strate contained in a small evaporation dish. The solvent evaporation rate could be controlled by adding toluene drops to the dish around, but not on the substrate, and by partially covering the dish. Two qualitatively different solvent evaporation rates were used in this study. An intermediate evaporation rate to obtain vertical PS cylinders in PB matrix in the thin film was generated by covering the dish leaving only a small hole on the cover for solvent vapor to escape. Under these conditions, the casting process occurred over approximately 3 hours. A very slow evaporation condition for the in-plane cylindrical structure was achieved by covering the top of the dish. Evaporation was complete after approximately 3 days.

After solvent evaporation, each thin film was cut into small squares on its salt substrate using a razor blade, floated from the substrate in water and collected on a copper TEM grid. Some specimens were subjected to a post-cast annealing treatment at 140℃, higher than $T_g(\sim100℃)$ of polystyrene, for 18 hours under a vacuum of 10^{-6} torr after being mounted on a Cu TEM grid. Both the as-cast and the annealed thin sections on the grids were stained by exposure for 20 minutes to OsO_4 vapor. In all micrographs presented here the PB stained phase appears dark and the PS phase appears light. The cross-sectional TEM specimens of various PS-PB-PS films were prepared by a sequence of steps. After observing a thin film morphology in plan view, a thin carbon layer was evaporated on both sides of the stained film on its TEM grid, embedded in epoxy and subsequently cured at room temperature. Cross-sectional specimens were cut using a Reichert-Jung Cryo-

Ultramicrotome with the specimen at -110℃, below the T_g of PB($\sim$-90℃). Microtomed sections were collected on holey carbon TEM grids.

Some of the as-cast and the annealed thin films were decorated with a small amount of gold ($\sim$0.01g) without staining. Approximately 4nm of gold was evaporated on the polymer films under 10^{-6} torr vacuum using Denton Vacuum DV-502 evaporator. A discontinuous layer of fine gold particles, $\sim$3-5nm diameter, was produced. Some of these gold decorated films were subsequently annealed at 120℃ for two hours under vacuum. TEM was done using a Philips CM30 Super Twin TEM and a Philips CM20 FEG TEM/STEM.

III. Results and Discussion

A demixed surface microstructures are observed in the as-cast thin films. Fig. 1(a) shows a plain view image of the morphology resulting from $\sim$3 hour evaporation time. This displays high contrast of PS cylinders with their axes perpendicular to the film plane in a highly-ordered hexagonal array. The cross-sectional view from a film $\sim$ 95nm thick confirms that the PS phase is present as vertical PS cylinders extending to the free surface(Fig. 1(b)) in contrast to observations that a lower surface energy PB layer forms there. An in-plane cylindrical morphology is resulted from the much slower solvent evaporation rate(Fig. 1 (c)). This displays lower contrast than the vertical cylinder structure and indicates a different morphology that might at first be interpreted as alternating PS/PB lamellae. The cross-sectional view confirms, however, that the morphology remains one of PS cylinders with a hexagonal array

in a continuous PB matrix(Fig. 1(d)). The cylinder axis now lies in the film plane rather than perpendicular to it. There should be the formation of a top PB-rich surface layer, however, it was too thin to be identified in the TEM image in this study. A simple geometric model from G. Kim et al.[14] showing that a in-plane cylindrical microstructure is more stable than a vertical cylindrical structure was introduced.

In much the same fashion that various microstructures can be formed in the bulk region of the different films depending on the solvent evaporation rates and annealing treatment, so too is there a range of possible microstructure found at the film surfaces. Green et al.[16] using X-ray photoelectron spectroscopy(XPS) observed a mixed surface layer resulting from that the PS fraction in PS-PMMA symmetric diblock copolymers can deviate from unity allowing some surface enrichment by the slightly higher surface energy PMMA phase under relatively fast solvent evaporation conditions. In the study of solution-cast PS-PB diblock thin films, Torturo et al.[17] using TEM found that the composition, molecular weight, solvent evaporation rate, type of solvent, and polymer architecture affect the surface and bulk morphology. They show that the surface layer from a kinetically constrained condition is a mixture of two components or a demixed layer consisting of isolated domains.

When as-cast thin films are used as templates, well-ordered patterns are produced, as shown in Fig. 2. Evaporated gold particles preferentially self assemble to the PB regions of the thin film surface presumably in response to surface energetic considerations there and produce a well ordered pattern. Fig. 2(a) and 2(b) show unstained plan-

(a)   200nm
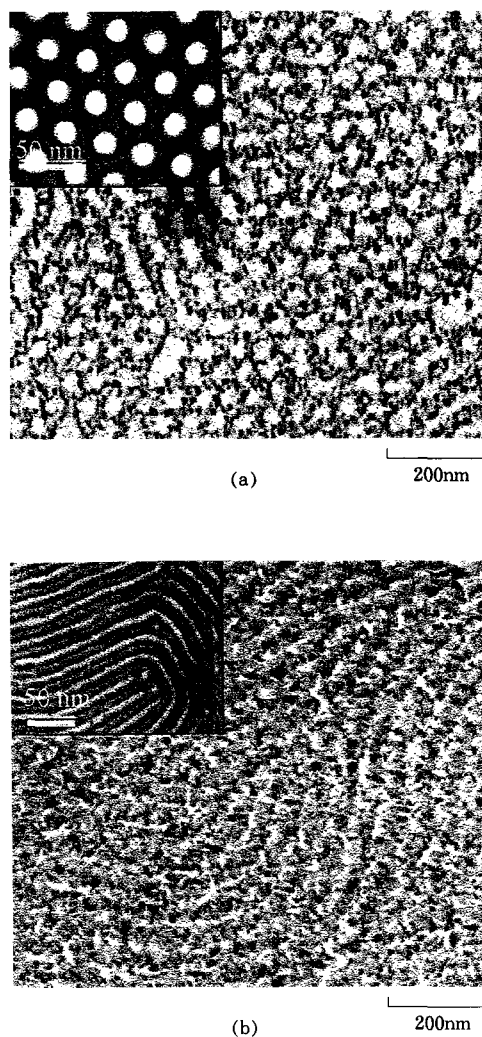

(b)   200nm

Fig. 2. Unstained TEM Images of PS-PB-PS block copolymer thin films after gold decoration with inset stained as-cast images; (a) a plan-view of a gold decorated thin film having a vertical cylindrical morphology; (b) a plan-view of a gold decorated thin film having an in-plane cylindrical morphology.

view images of the specimens produced under intermediate and slow solvent evaporation conditions, respectively, then coated with a thin layer of evaporated gold particles and annealed for two

hours at 120℃. Annealing the as cast films after gold deposition enhances the self-diffusion of gold particles into PB matrix and produces a relatively well-ordered pattern. The observed contrast is due to the self assembled gold particles on PB continuous domains. High surface energy of metal (~100-1,000 dyne/cm) makes the metal coating diffuse into the lower surface energy and soft polymer matrix (~30-60 dyne/cm) rather than into the glassy phase at the surface. The procedure of gold self-assembly at the thin film surface is introduced as a diagram in Fig. 3.

A continuous PB-rich layer (~10nm thickness) is formed at the free surface after thermal annealing, as shown in Fig. 4. Fig. 4(a) is a plan-view image of the post-cast annealed film showing a mixed morphology where vertical cylindrical regions and in-plane cylindrical regions are co-exist-
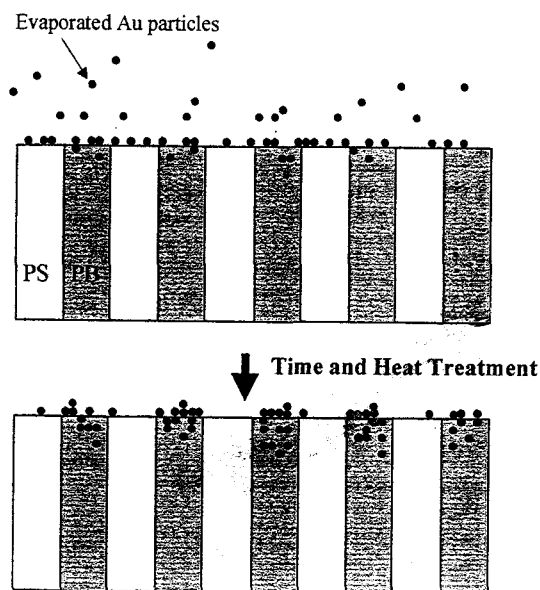
Evaporated Au particles

Fig. 3. A schematic diagram showing the gold self-assembly on the soft PB phase at the surface of the block copolymer thin film.

ed. However, the block copolymer still keeps hexagonally packed vertical PS cylinders in PB matrix presumably. Fig. 4(b) is a crosssectional view of the annealed specimen showing a continuous layer of dark contrast at the free surface. The image samples a film region with vertical PS cylinders avoiding areas with the mixed transition morpholgy. The lower surface tension PB block preferentially locates itself at the free surface and tends to form a surface layer to reduce the total surface energy of the block oppolymer.

When long exposure to high polymer mobility is provided, lower surface-energy constituent PB-rich surface layer is formed in the triblock copolymer thin film. This observation is consistent with both theory and experiment indicating that, at equilibrium, the lower surface energy blocks preferentially distribute at the free surface to reduce the total surface energy. Hashimoto and Hasegawa[18,19] used TEM with microtomed cross-sections of bulk specimens and showed that a surface layer of polyisoprene was formed in PS-PI diblock with a bulk lamellar morphology after solvent casting. Similar observations were made in the study of block copolymer surface structure under conditions of long annealing. Using electron microscopy and atomic force microscopy, Schwark et al.[20] observed a PB surface layer formed at the surface in 56wt% PS PS-PB diblock copolymer cast and vacuum annealed. In most previous TEM studies of surface structure of block copolymers, however, a single component layer at the surface was observed in diblock copolymers and the low surface energy layer has been usually confirmed by a dark contrast diene layer due to the deep staining by a heavy element. Less quantitative

TEM work has been done to figure out the surface microstructure, especially for the triblock copolymer systems. In case of triblock copolymer having diene center block, the departure from the formation of a single diene component layer would be expected, because of the different architecture and dynamics from diblock systems. A previous cross-sectional and analytical TEM study of the PS-PB-PS triblock copolymer thin film shows that the surface layer even after annealing is a PB-rich layer partially mixed with PS components, not a PB single component layer.[21]

Upon annealing, when a PB-rich surface layer is formed, the self-assembled gold patterns are not produced, as shown in Fig. 4(c). Fig. 4(c) is an unstained plan view image of the post-cast annealed thin film, then coated with a thin layer of evaporated gold and annealed for two hours at 120℃. Evaporated gold particles preferentially stay at the PB rich surface of a polymer thin film template presumably and produce a gold surface layer, as shown in Fig. 4(d). This may be because the partially mixed PS component in the surface layer are randomly distributed at the surface and would restrict the gold self assembly. In addition, there may be a penetration into the PB matrix in the bulk from the surface upon annealing, however, a relatively thick gold layer formed at the PB-
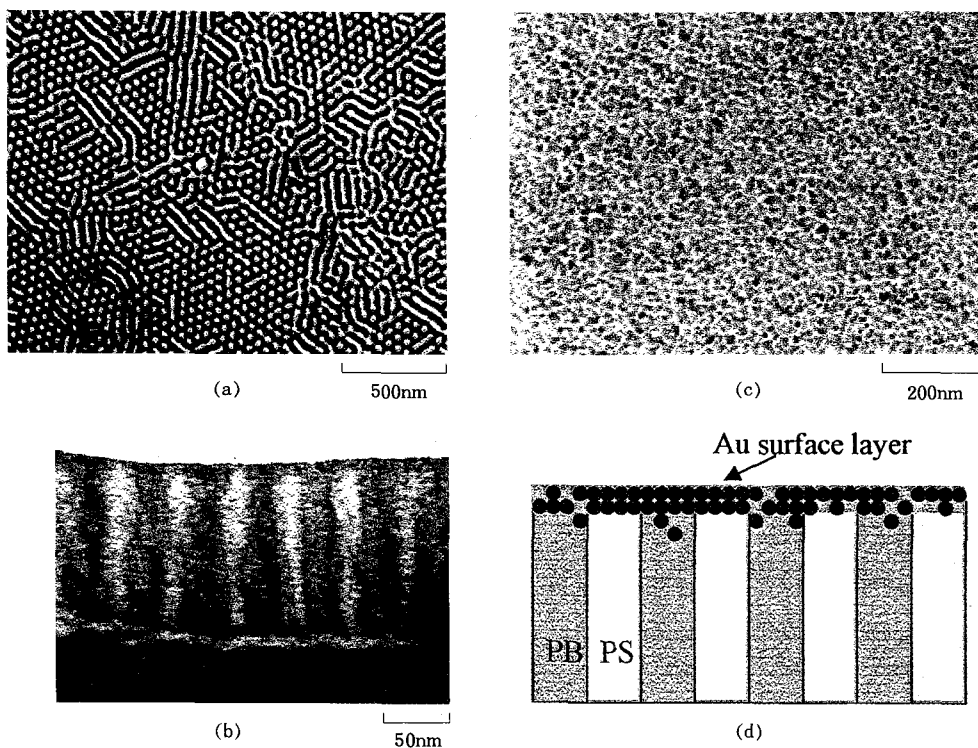

Fig. 4. (a) a stained plan-view image of the annealed cylindrical structure; (b) a cross-sectional image of (a) showing the formation of a PB-rich surface layer upon annealing; (c) an unstained plan-view image of a gold coated annealed thin film; (d) a schematic diagram of the formation of a gold surface layer on the post-cast annealed thin film.

rich surface also does not reveal the contrast in TEM.

IV. Summary

The stable PB-rich surface layer was observed in the films subjected to post-cast annealing. Metastable surface microstructure with surface domains of either PB or PS can be generated in the thin as-cast films from a relatively fast solvent evaporation condition and the surface domain patterns appear to largely mimic the bulk pattern below. This demixed surface structure allows evaporated gold particles to self assemble into the PB matrix. The high surface tension of gold makes gold preferentially align in clusters on the PB surface matrix. After the formation of a well-developed PB-rich surface layer upon annealing, a well ordered pattern is not produced.

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