Nanoprocessing and Nanofabrication of a Structured Polymer Film by the Focused-Ion-Beam Technique

Ken-ichi Niihara,[†] Takeshi Kaneko,[†] Toshiaki Suzuki,[‡] Yasuhiko Sato,[‡] Hideo Nishioka,[‡] Yukihiro Nishikawa,[†] Toshio Nishi,[§] and Hiroshi Jinnai*,[†]

Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Kyoto 606-8585, Japan, JEOL Co. Ltd. 1−2 Musashino 3-chome Akishima Tokyo 196-8558, Japan, and Department of Organic and Polymeric Materials, School of Science and Engineering, Tokyo Institute of Technology, 2-12-1, Ohokayama, Meguro-ku, Tokyo 152-8552, Japan

Received August 5, 2004
Revised Manuscript Received November 11, 2004

I. Introduction. The focused-ion-beam (FIB) technique is a powerful tool for semiconductor-related processing and is routinely used for failure analysis, integrated circuit debugging and repair, etc. Thus, the use of a high-energy FIB for mask-less patterning is a well-established technique in microelectronics and microfabrication.[1] Micromilling in silicon is particularly useful in microelectric−mechanic systems, micro-opto-mechanic systems, microsensors, and actuators. Therefore, there is a large amount of literature concerns fundamental mechanisms of FIB milling of silicon.

Compared with the use of FIB in such "hard materials", e.g., metals and semiconductors, only a few investigations have dealt with milling and processing of "soft materials", e.g., polymers, cells, complex fluids, etc. This is probably due to the common belief that the soft materials, unlike hard materials, would not sustain a high-intensity ion beam and hence would easily be damaged. The local heating due to the focused ion beam may be a primary cause of the damage: The temperature rise under the ion beam, modeled by Melngailis,[2] was estimated to be ca. 115 °C for a typical polymer, polystyrene, under our experimental conditions, indicating that the polymer would locally melt instead of being milled. Therefore, the FIB milling of polymers at room temperature is not considered to be realistic. On the other hand, however, there exists the need for nanofabrication of polymers, e.g., flexible nanofabrication of polylactide to produce biocompatible nanomachines.

To our best knowledge, the FIB was first applied to a polymer-based solar cell consisting of soft polymer layers deposited on a hard glass substrate.[3] To investigate thickness and interfacial roughness of the layers, the FIB was utilized to prepare cross-sectional specimen of polymer-based solar cells for transmission electron microscopy (TEM) experiments. A conventional preparation technique such as ultramicrotomy was not capable of providing such cross-sectional specimen simply because glass (or diamond) knifes cannot cut the substrate. Likewise, Stark et al. milled resist and other polymers and also showed that polymer milling could be greatly enhanced by applying water vapor as a precursor gas.[4] A polymer (epoxy)/clay composite was recently subjected to the FIB in order to prepare thin sections for TEM.[5] In all cases, the polymers were supported or reinforced by the hard components, i.e., the glass substrate or clay, which are better thermal conductors than the polymers. Hence, as described earlier, the substrate underneath (or clay inside) the polymers probably acted like a "heat sink" so that the local heating due to the focused ion beam flowed through the substrate, which accordingly lower the temperature of the polymers even at room temperature. After all, there has not been a single example of patterning of soft materials consisting of pure polymer(s) alone. In the present study, we demonstrate that a block copolymer film (without any supporting materials) can be freely milled and processed by the FIB at cryogenic temperatures.

II. Experimental Section. A poly(styrene-*block*-isoprene) (SI) block copolymer was purchased from Polymer Source Inc., Canada. The number-averaged molecular weight and polydispersity are $M_n = 108000$, $M_w/M_n = 1.08$. The glass transition temperatures (T_g) of polystyrene and polyisoprene blocks are, respectively, +104 and about −50 °C. A volume fraction of polystyrene is 0.34. A specimen film (thickness: ca. 500 μm) was cast from 5 wt % benzene solution, which was subsequently stained by OsO_4 vapor for a day. The SI block copolymer film with 1.5 mm × 1.5 mm area was placed on a TEM grid with carbon paste glue. The carbon and then platinum were deposited on the grid by vacuum deposition in order to enhance charge and heat transfer.

An FIB microscope (JEM-9039FIB, JEOL Ltd., Japan) was used for imaging and milling the block copolymer film. The FIB microscope works along with the same principle as the scanning electron microscopes (SEM) except for the fact that the charged particle beam used in the scanning ion microscope (SIM) is positively charged ions (typically Ga) rather than electrons. The Ga ions are accelerated at 30 kV and focused on the specimen with ca. 30 nm in diameters (in the milling process). Upon irradiation of Ga ions, local temperature elevation in the specimen takes place, causing the polymeric specimen to melt locally. To prevent such local melting, the polymer film (thickness: ca. 500 μm) in the sample chamber of the FIB microscope was cooled to a cryogenic temperature (−177 °C). A cryo specimen holder for TEM (model 626 Cryotransfer system, Gatan Inc.) was used. A "lift-out" technique,[6] often used for metals and semiconductors, was employed to prepare specimens for TEM observations in the following way. First, rectangular FIB trenches were cut on both sides of the area of interest. Prior to thinning the area (that will be a TEM section), the sample was tilted and then the bottom was cut free. The sample was tilted back to its original position and the specimen was thinned to the desired thickness ("polishing"). As shown later in Figure 1, three different thicknesses ranging from ca. 150 to 350 nm were elaborated in a single TEM section. The last step of the sectioning procedure was the cutting of both the right and left side of the polished ultrathin specimen to disconnect it from the bulk SI block copolymer sample. The specimens were heated back to ambient temperature and then transferred to Cu grids

* To whom correspondence should be addressed. E-mail: hjinnai@kit.ac.jp.
[†] Kyoto Institute of Technology.
[‡] JEOL Co. Ltd.
[§] Tokyo Institute of Technology.

10.1021/ma048380m CCC: $30.25
Published on Web 03/17/2005

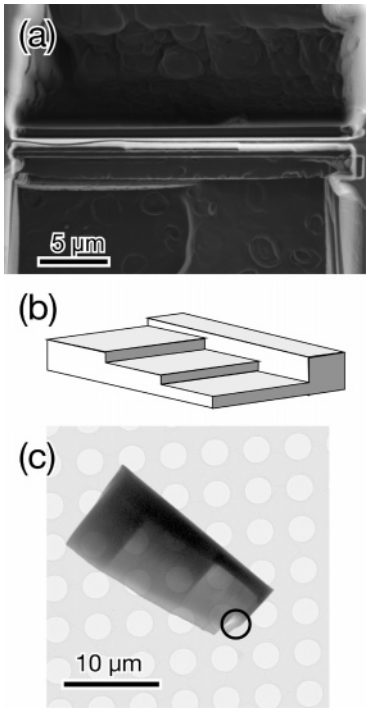

Figure 1. (a) In situ FIB SIM image during sample preparation, top view. (b) Schematic of "three-story" TEM section. (c) TEM micrograph of SI diblock copolymer section. Three different thicknesses in a single specimen can be seen.

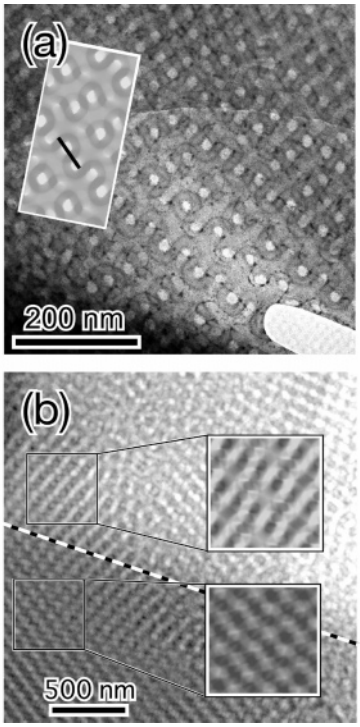

Figure 2. (a) High magnification TEM micrograph (×20000) of the three-story section shown by a circle in Figure 1c. A computer simulated TEM image based on ordered double Gyroid (G) structure was overlaid on TEM micrograph. Solid line in the figure represents $\sqrt{3}a/2$ (a is a lattice constant of G structure). $a \simeq 130$ nm. (b) A TEM micrograph of the three-story section of SI diblock copolymer prepared by FIB, in which two different regions with different thicknesses, i.e., 155 (top) to 270 nm (bottom), and their boundary (a broken line) are observed. Computer-generated projections simulated using the lattice constant and each thickness were shown as insets.

coated with a carbon substrate (Quantifoil R2/2, Quantifoil Micro Tools GmbH) by a micromanipulator. TEM observations were made on JEM-2200FS (JEOL Ltd., Japan) operated at 200 kV.

We also pursued potential of fabricating polymers by the FIB. An ultrathin section, prepared with a cryomicrotome (Ultracut UCT, Leica Microsystems inc.), was subjected to the FIB milling at −177 °C. Prior to the milling, carbon was deposited on the polymer films to enhance charge and heat transfer. The letters "KIT" were milled in the polymer ultrathin section, which was then observed by JEM-2010 (JEOL Ltd., Japan) operated at 200 kV.

III. Results and Discussion. Figure 1a shows the SIM secondary electron mode image after the polishing process (top view). Upper and lower rectangular hole were milled by the FIB, while white horizontal line represents polished specimen. At the cryotemperature, the SI diblock copolymer, a purely polymeric specimen without any kind of support such as Si substrate, was easily milled just like the metals and semiconductor materials. In the polishing process, the specimen was polished so that it became stairlike shaped by intentionally changing thicknesses. The thinnest, intermediate and thickest parts (from left to right in Figure 1a) correspond to thicknesses of ca. 155, 270, and 350 nm, respectively. The former two thicknesses were evaluated from the cross-sectional image of three-dimensional data obtained from transmission electron microtomography (TEMT)[7−9] (not shown here), while the thickness of the thickest part was estimated from the SIM image (Figure 1a). After polishing was performed, both sides of the specimen were cut and detached from the bulk, which was then transferred on the TEM grid and subjected to the TEM observation as shown in Figure 1c. The three steps in the SI thin section can be seen as three different gray levels. Obviously, darker region of the specimen corresponds to thicker region of the sample. This feature exactly agreed with the schematic presented in Figure 1b. Note that the ultrathin sections with such complicated shapes can never been obtained by the conventional microtoming procedure. It should be also emphasized that, in contrast to ultrathin sections obtained by ultramicrotome, the FIB-prepared section had a very flat surface; it is free from asperity due to glass (or diamond) knives. In what follows, a novel morphological characterization of the complex nanostructure of the SI copolymer with this FIB-prepared "three-story" TEM section will be presented.

Figure 2a is an enlarged TEM micrograph of the thinnest portion of the FIB-prepared section of the SI copolymer marked by a circle in Figure 1c. A highly periodic pattern of the microphase-separated structure can be seen, demonstrating that the FIB milling process and the accompanying heating did not destroy the existing microphase-separated structure. The inset with white frame in Figure 2a is a computer-simulated projection[10,11] characteristic of the ordered double Gyroid (G) structure ((211) plane).[12,13] The characteristic pattern showed excellent agreement with the micrphase-separated structure of SI copolymer, indicating that the complex morphology was the G morphology. Note, however, the identification of complex nanostructure by TEM is often inconclusive, since different models appear identical along several projection axes.[10] Therefore, it would still be unwise to conclude that the nanostructure of SI copolymer is the G structure at this stage. Provided that the morphology was G, a lattice

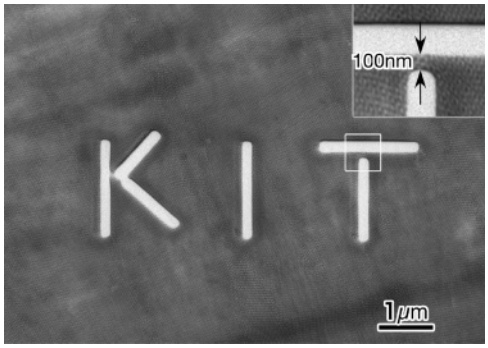

Figure 3. Example of nanofabrication. The letters "KIT" were written on the ultrathin section prepared by ultramicrotome. Length and width of each line are, respectively, ca. 2 μm and ca. 200 nm. Insets show an enlarged view of rectangular parts where microphase-separated domains can be seen.

constant a is estimated to be ca. 130 nm through a relation that a solid line in the inset of Figure 2a corresponds to $\sqrt{3}a/2$.

Figure 2b shows an enlarged micrograph of the FIB section corresponding to the thinnest and the intermediate thickness. The broken line in the figure represents the boundary between these two regions. Taking the thickness and the lattice constant evaluated in Figure 2a into consideration, projected images were again generated based on the G structure and are compared in the figure as insets. In the simulation, thickness is varied according to the TEMT results while the other structural parameters, e.g. the spherical coordinates for the normal vector of the section surface, were kept constant. It was found that they seamlessly fit to the microphase-separated morphologies of SI copolymer, implying that the two regions are in the same grain: The appearance of the TEM image was simply due to the thickness variation. More importantly, the single model, with G morphology, explained all three different textures at different directions and thicknesses, demonstrating that the morphology of the SI copolymer is undoubtedly the G structure. Thus, with such three-story section, morphological characterization of the complex structures will become far more accurate and easy than before.[11]

Another great advantage of the FIB method is its capability of "nanofabrication" of materials. To the best of our knowledge, nanofabrication in polymeric materials has been carried out *for the first time* in the present paper as shown below. The ultrathin section prepared by conventional ultramicrotome was placed on the TEM copper grid with substrate made of poly(vinylformal) (PVF), and the word "KIT" was milled by the FIB at a cryogenic temperature (see Figure 3). The width of the lines of the letters is ca. 200 nm. As demonstrated in the inset of Figure 3, the sides of each line appeared to be smooth. The smoothness of the edge demonstrated that the surface damage due to the focused ion beam was small if the side of the beam was used for milling (the ion beam was irradiated from the top). McCaffrey et al.[14] studied the surface damage due to the ion beam on a silicon surface by examining amorphization of the silica. They observed a damaged layer of thickness ca. 20 nm. Similar surface damage in our technique may exist and should be studied in the future.

In addition, we milled the SI copolymer ultrathin film, leaving the PVF substrate untouched, by carefully choosing the milling depth. The channel made by the FIB milling in this way had walls with G-type nanopatterns. This kind of "asymmetric" container could provide a novel nanospace with periodic polymeric patterns, which would act as physical boundaries in the casting of block copolymer self-assembling processes inside such channel. We hope that the cryogenic FIB technique would find broad interest in the scientific community and initiate new reserch directions in the nanofabrication of polymer films.

Acknowledgment. The authors are grateful to NEDO for supporting this study through a Japanese National Project, "Nano Structure Polymer Project", by the Ministry of Economy, Trade, and Industry.

References and Notes

(1) Yongqi, F.; Kok, N.; Bryan, A.; Hung, N. P.; Shing, O. N. *Rev. Sci. Instrum.* **2001**, *72*, 2756.
(2) Melngailis, J. *J. Vac. Sci. Technol.* **1987**, *B5*, 469.
(3) Loos, J.; van Duren, J. K. J.; Morrissey, F.; Janssen, R. A. *J. Polymer* **2002**, *43*, 7493.
(4) Stark, T. J.; Shedd, G. M.; Vitarelli, J.; Griffis, D. P.; Russell, P. E. *J. Vac. Sci. Technol.* **1995**, *B13*, 2565.
(5) Miyagawa, H.; Chiou, W. A.; Daniel, I. M. http://www.nuance.northwestern.edu/epic/results.asp.
(6) Overwijl, M. H. F.; van den Heuvel, F. C.; Bulle-Lieuwma, C. W. T. *J. Vac. Sci. Technol.* **1993**, *B11*, 2021.
(7) Frank, J. *Electron Tomography*; Plenum: New York, 1992.
(8) Jinnai, H.; Nishikawa, Y.; Spontak, R. J.; Smith, S. D.; Agard, D. A.; Hashimoto, T. *Phys. Rev. Lett.* **2000**, *84*, 518.
(9) Jinnai, H.; Ikehara, T.; Nishi, T. *Adv. Polym. Sci.* **2004**, *170*, 115.
(10) Hasegawa, H.; Nishikawa, Y.; Koizumi, S.; Hashimoto, T.; Hyde, S. T. In *Advanced Materials '93*; Aoki, H., et al., Eds.; Elsevier Science B. V.: Amsterdam, 1993; Vol. II/A.
(11) Nishikawa, Y.; Kawada, H.; Hasegawa, H.; Hashimoto, T. *Acta Polym.* **1993**, *44*, 192.
(12) Thomas, E. L.; Anderson, D. M.; Henkee, C. S.; Hoffman, D. *Nature* **1988**, *334*, 598.
(13) Hajduk, D. A.; Harper, P. E.; Gruner, S. M.; Honeker, C. C.; Kim, G.; Thomas, E. L.; Fetters, L. J. *Macromolecules* **1994**, *27*, 4063.
(14) McCaffrey, J. P.; Phaneuf, M. W.; Madsen, L. D. *Ultramicroscopy* **2001**, *87*, 97.

MA048380M