Nanostructure Fabrication by Self-assembly of Block Copolymer on 3-D DLC Structure

Hiroyuki Mino, Reo Kometani, Shin-ichi Warisawa, Sunao Ishihara
Graduate School of Engineering, The University of Tokyo
7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8685 Japan

The block-copolymer self-assembly has a good potential to form nano-scale periodic patterns in large area at low cost. Currently, block-copolymer self-assembly processes are examined only on 2-D flat plane substrates. If the block copolymer nanostructures can be formed onto 3-D structure, those nanoscale patterns would extend their applications to 3-D wiring for electric circuits and 3-D nanomechanical devices. In this paper, we demonstrate a nanoscale pattern formation on a 3D substrate by a modefied self-assembly process of poly (styrene-block-metyl methacrylate) (PS-b-PMMA) block copolymer.

As the substrate for 3-D self-assembly experiments, a slope surface on Si substrate was prepared by using focused-ion-beam chemical vapor deposition (FIB-CVD). Using the FIB system (SMI3050: SII NanoTechnology Inc.), Ga^+ FIB was irradiated under a *phenanthrene* gas atmosphere and a slope structure made of a diamond-like carbon (DLC) was formed.

In case of the process for the block-copolymer self-assembly on a regular flat substrate, copolymer-toluene solution is normally spin-coated. However, the spin-coat can not be applied to the slope surface. Therefore we applied the "dip-coat process" for the block-copolymer coating. The Si substrate with DLC slope structure was dipped into copolymer-toluene solution and pulled-up from the solution. The film thickness of the copolymer was controlled by changing pull-up velocity. From the thickness control characteristics as shown in Fig. 1, we examined an appropriate copolymer coating thickness on the slope surface.

Firstly, we coated PS-r-PMMA random copolymer onto DLC slope structure for surface affinity control. Then, PS-b-PMMA was dip-coated onto DLC slope structure with a pull-up velocity of 4 mm/s and annealed at 210 degree in 5 minutes. The self-assembled patterns were formed sparsely on the DLC slope surface as shown in Fig. 2. Then, to achieve uniformly periodic patterns of the self-assembled PS-b-PMMA, we tried to adopt Au instead of PS-r-PMMA. As an experimental result, regularly dense nano-scale patterns were formed not only on the flat (Fig. 3-d) but also on the slope (Figs. 3-a and b) surfaces. Moreover, PS-b-PMMA was successfully self-assembled uniformly on the boundary between the slope and flat (Figure 3-c). It is considered that the difference of the pattern formation characteristics between in Fig. 2 and in Fig. 3 is due to the difference of the surface free energy between DLC and Au. Because surface energy of DLC was smaller than that of Au, copolymer was not coated well on DLC.

These results suggest that surface treatment with materials of large surface energy is effective to form regularly dense nanoscale patterns on 3-D DLC structure, where "dip-coat process" can be applicable to control the coating film thickness.
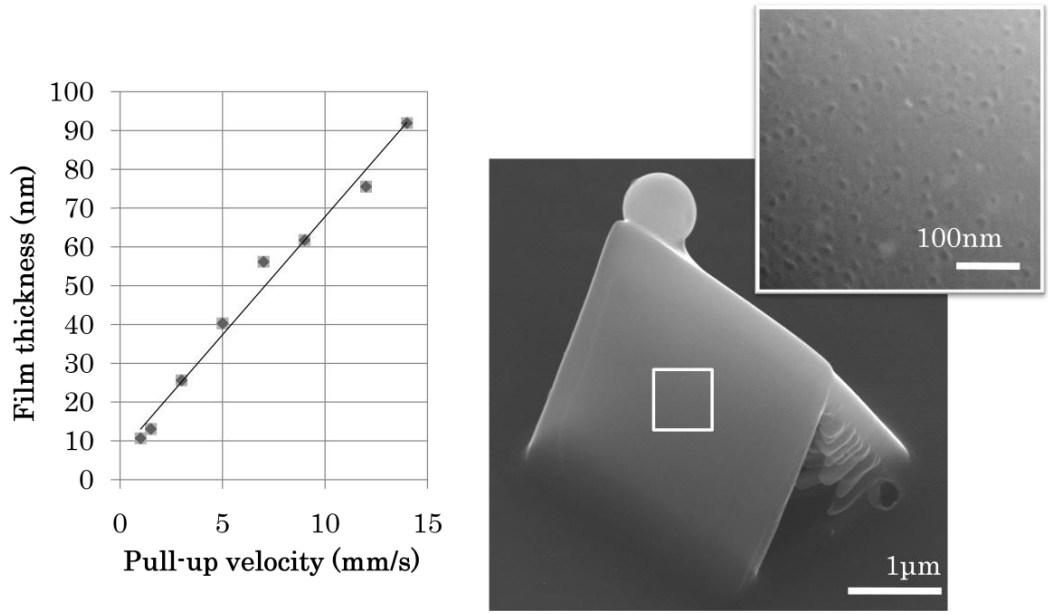
Figure1. Relationship between the copolymer film thickness and pull-up velocity in the dip-coat process.

Figure 2. SEM image of the PS-b-PMMA patterns formed on the DLC slope pre-treated with PS-r-PMMA.
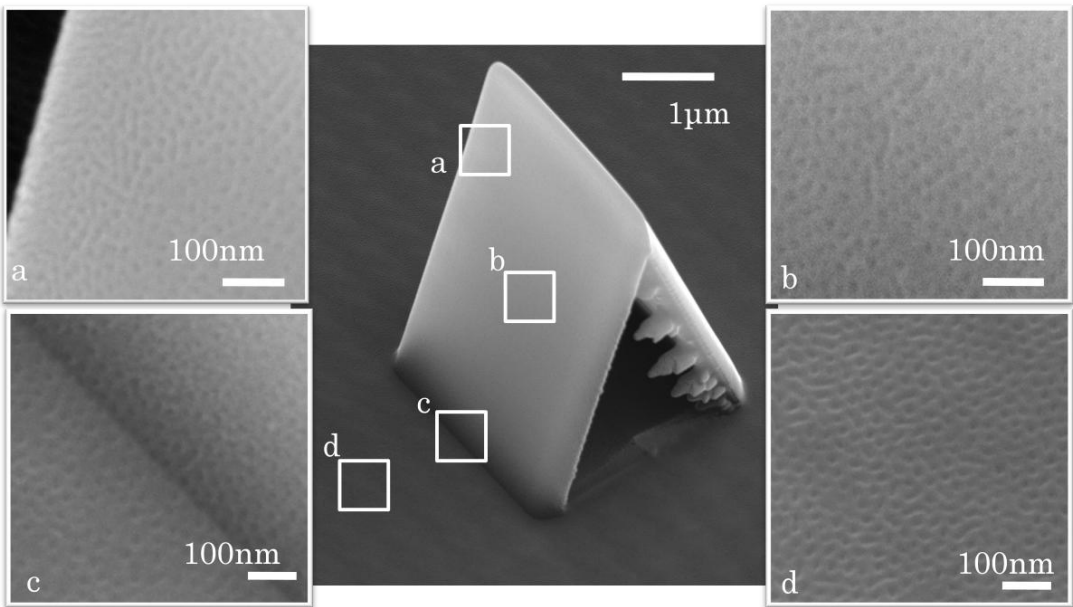

Figure 3. The SEM images of the PS-b-PMMA patterns on the DLC slope pre-treated with Au.