블록 공중합체 박막내부에 기억 소자용 자성 금속 함침

최대근, 권기영, 정종률*, 정희태, 신성철*, 양승만
한국과학기술원 생명화학공학과
한국과학기술원 물리학과*

Magentic metal inclusion for memory devices in the block copolymer thin films

Dae-Geun Choi, Ki-Young Kwon, Jong-Ryul Jeong, Hee-Tae Jung, Sung-Chul Shin, Seung-Man Yang
Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology
Department of Physics, Korea Advanced Institute of Science and Technology

INTRODUCTION

Diblock copolymers consist of two chemically distinct polymer segments covalently bonded together, and microphase separate into ordered periodic arrays of spheres, cylinders or lamellae depending on the volume fraction of the component [1]. Indeed, the size and type of ordering can be controlled by changing the molecular weight, chemical structure, molecular architecture, and composition of block copolymers. This results in morphologies typically with domains of periodicity L_0 in the 10–100nm range [2].

Recently, thin films of block copolymers have considerable attention because of their potentials as templates for nanolithography to prepare nanoscopic magnetic and electronic media [3-5]. A variety of new patterning technologies (E-beam lithography, aluminum anodic etching, block copolymer self-assembly) have emerged, which attempts to create nanoscale structures over large areas at low cost. In these methods, self-assembly of diblock copolymers has advantages in the size control and low cost compared with other methods.

Park et al. have successively prepared thin films of nanoscopic patterns by using ozone etching and RIE (reactive ion etching), and transferred pattern into the silicon wafer [3,6]. T.P. Russell et al. have produced terabit nano-arrays in thin film by using surface neutral method and selective UV etching [4,7,8]. For thicker films, external electric fields have been used to prepare surface perpendicular nanowires [4,5]. Also, block copolymer nanostructuers with selectively bound metallic compounds can be used for nanoscopic pattern [9,10].

In this work, we prepared ordered patterns in thin films of PS-b-PMMA by using selective etching. Magnetic metals for memory device application, such as, Co, Fe, Cr, and their alloys, were impregnated as isolated state in these patterns.

EXPERIMENT

Polystyrene-block-methyl methacrylate ((PS-b-PMMA), (Mn = 82.5 Kg/mol, with a 1.12 polydispersity) was purchased from Polymer Source, Inc. and was used as received. The volume fraction of PMMA was 13.6 %. The block copolymer was mixed with toluene at a 1 %(w/w) concentration. Thin film of P(S-b-MMA) was prepared by spin coating from 1 %(w/w) toluene solution at 3000rpm and 60s onto the silicon oxide wafer. Film thickness was measured by using X-ray reflection and SEM. The specimens were annealed under vacuum at 160 ^{O}C, which was above the glass transition temperature of PS-b-PMMA blocks, for 30 hr. The morphology was quenched by liquid nitrogen. These films were photoirradiated with UV (254nm) for 30min, thoroughly rinsed with glacial acetic acid, washed with deionized water, and dried under nitrogen. The porous structure was obtained from the oriented polymeric template by UV photoirradiation of the thin polymeric film. This treatment induces the crosslinking of PS continuous phase and the degradation of the PMMA spheres that can be removed by subsequent solvent treatment [11]. UV irradiation crosslinked the PS matrix and degraded the PMMA spheres. Samples were then rinsed with acetic acid and deionized water to remove the degradation products. To image the copolymer film's internal microstructure with a scanning electron microscope, the free surface wetting layer was removed by reactive ion etching. The etching process was performed under a CF_4 flow, at a pressure of 20 mTorr, and power density of 80W. A dc self-bias of approximately 100 V. Metal layer of CoCrPt was evaporated onto this nanoporous template to cover of the template and fill the pores in the matrix

The SEM images were obtained with Philips-XL20SFEG. SEM work was performed with an incident electron beam energy between 1 and 2 KV and by collecting secondary electrons. The SEM images were typically obtained at a magnification of 100,000.

RESULT AND DISCUSSION

A 35 nm thin film was produced by spin coating a 1% solution at 3000rpm. Fig 1 shows 35nm thin film of P(S-b-MMA) prepared on bare silicon wafer. The surface of this sample was clean, flat in the large area, and any nanopattern was not shown because the holes are submerged below the surface and cannot be imaged. However, after we used CF_4 reactive ion etching (RIE) to image the pattern beneath the surface, which expose the underlying nanopattern, we could see well-ordered holes (hexagonally ordered holes) as shown Fig 2a. The diameter of holes is about 18nm, and center to center distance is about 38nm. The aspect ratio is about 1. The size of hole could be changed from

13 to 20 nm by varying etching condition. Fig 2b shows 10nm layer of CoCrPt metal alloy deposited onto nanoporous polymer template pattern. The size and ordering is replica of polymer template as shown fig 2b. In this step, the washing treatment was applied to remove the residue of metal onto the surface to prepare isolated metal dots. In Fig 3a shows AFM image of CoCrPt metal alloy deposited onto polymer template. The image of AFM is similar to that of SEM (Fig 2b). Fig 3b shows cross-sectional SEM image of Fig 3a.

SUMMARY

In summary, we successfully synthesized well ordered holes with P(S-MMA) polymer template. In addition, we impregnated magnetic metal into polymer template. By RIE and ion milling, we successfully transferred this pattern into silicon wafer substrate. Also, we anticipate this skill can be applied so many application such as DNA chip, storage memory device, and advanced nano-lithography, and so on.

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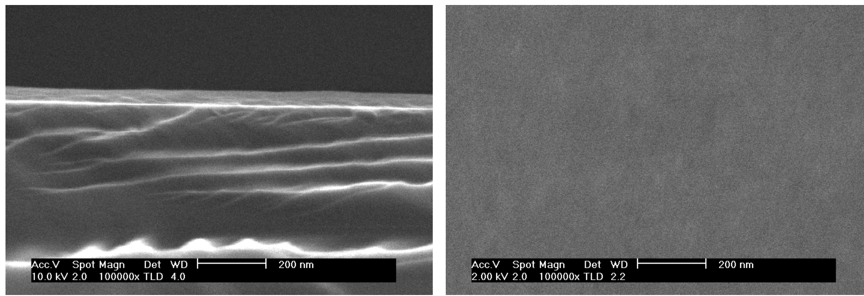

Figure 1. SEM image of PS-PMMA thin film

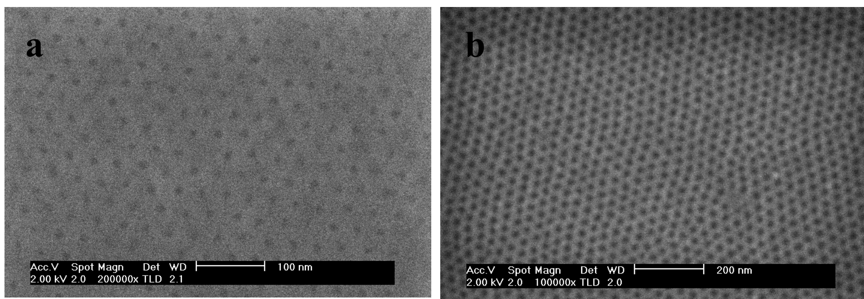

Figure 2. (a) SEM image of PS-PMMA thin film after RIE. (b) SEM image of CoCrPt matal layer of 10nm.

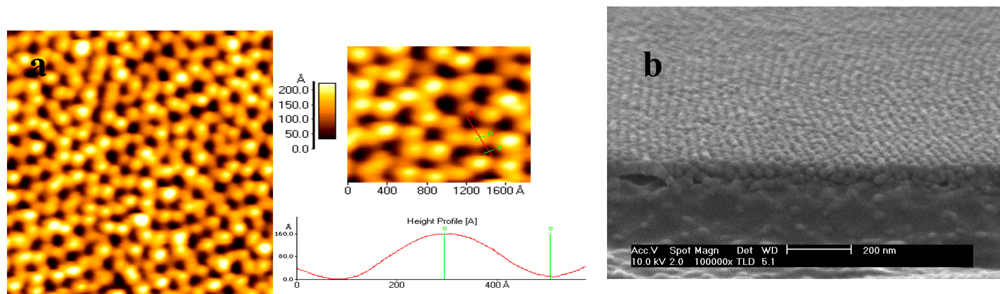

Figure 3. (a) AFM image of CoCrPt metal layer (b) SEM image of CoCrPt metal layer.