Synthesis and Directed Self-Assembly of Modified PS-*b*-PMMA for Sub-10 nm Nanolithography

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The directed self-assembly (DSA) of block copolymers has attracted a great deal of interest due to its potential applications in sub-10 nm lithography. The conventional organic-organic DSA materials such as poly[styrene-*block*-(methyl methacrylate)] (PS-*b*-PMMA) have been extensively studied, however, the low etch contrast between two blocks and the difficulty to reduce L_0 (ca. 28 nm) limit its application. In this study, we designed and synthesized the novel DSA materials based on PS-*b*-PMMA. Through the modifying of acrylics part, segment–segment interaction parameter (χ) can be significantly increased, which leads to rapid self-assembly and high etch contrast. These block copolymers show the potential as DSA material with high intrinsic resolution for sub-10 nm and beyond nodes.

Keywords: Copolymer lithography, DSA materials, Sub-10 nm, Rapid self-assembly

1. Introduction

As we all know, photolithography has been the workhorse of the industry, which is crucial in the manufacture of smaller devices with excellent storage capacity. Following the Moore's Law, people now look for the next-generation lithography due to the resolution limit of 193 nm multi patterning technology. Directed Self-Assembly (DSA) lithography has attracted more and more attention due to its high potential resolution and extremely low cost when it is compared with EUVL [1-5].

Block copolymer DSA has improved disadvantages over the past few years, with the help of grapho- and chemo-epitaxy block copolymers are able to generate long-range order of nanostructures [6-8]. The traditional DSA materials have relatively low etch contrast between two blocks and the resolution limitation, such as PS-*b*-PMMA, the resolution is up to nearly 28 nm [9-11].

In this study, we synthesized a series of novel and rapid self-assembly block copolymers, which based on modifying of traditional DSA materials by anionic polymerization [12]. Also we synthesized different brush polymers to modify the surface of silicon wafers as neutral layers for the following DSA process [13,14]. In order to realize sub-10 nm

patterning capabilities, we precisely controlled the ratio of each component to reach max resolution.

All resulted materials show extremely high resolution up to 17.7 nm (full-pitch) separated lamella morphology and 14.7 nm (full-pitch) hexagonal morphology by SAXS (Small angle X-ray scattering) measurement, TEM (Transmission electron microscopy) and FESEM (Field-emission scanning electron microscope) indicating potential application as sub-10 nm full pitch DSA materials.

2. Experimental

2.1. Synthesis of block copolymers and characterization

We synthesized a series of modified PS-*b*-PMMA block copolymers following the standard process. After the polymerization the polymer was purified by dissolution and precipitation, following with the nuclear magnetic resonance (NMR) and gel permeation chromatography (GPC) measurement.

^1H -NMR spectra were acquired on a 400 MHz AVANCE III instrument using CDCl_3 as solvent and TMS as internal standard. From the ^1H -NMR spectra we can identify the characteristic peak of each component.

GPC measurements including molecular weight and PDI (polydispersity index) were carried out on

Shimadzu Prominence LC-20A, using two Shimadzu KF columns operating at 30 °C and Prominence SPD-20A UV-VIS and the refractive index detectors. The narrowly distributed polystyrene samples were used as calibration standards. All the block copolymers show a narrow distribution up to 1.13 during this synthesis process.

SAXS measurements were performed on a Nanostar SAXS (Bruker AXS GmbH, Germany), with pinhole collimation for point focus geometry. The X-ray source is a copper sealed target operating at 50 kV and 600 μ A, fitted with cross-coupled Göbel mirrors, resulting in a Cu K α radiation wavelength of 1.54 Å.

TEM images were taken with a FEI Tecnai G2 20 TWIN electron microscope equipped with a FEI BM-eagle CCD camera, operated at an acceleration voltage of 200 kV.

FESEM images were taken with Zeiss Ultra 55 at 3 kV accelerating voltage by In-lens detector.

By controlling the amount of the initiator and the ratio of monomers, we can precisely alter the pitch dimension and morphology. For the hexagonally packed cylindrical morphology (Hex): L_0 is the center-to-center spacing and for the lamellar morphology (Lam): L_0 is the domain spacing (full-pitch).

2.2. Annealing process of material

The novel modified PS-*b*-PMMA block copolymers were dissolved in toluene, and coating on the substrate, which were annealed at 100 °C for 5 min (or even less) in N₂ protection. The modification of this material remarkably reduced the annealing time when compared with traditional PS-*b*-PMMA. This demonstrates a potential prospect for this DSA material in the industry application.

3. Results and discussion

3.1. SAXS profiles

The scattering patterns were analyzed using the Bragg equation ($q=4\pi\sin(\theta/2)/\lambda$), and the scattering profiles illustrated the higher-order Bragg peaks with $q:q^*$ ratios at integer multiples of the first-order peak (q^*), characteristics to lamella or hexagonal morphologies (Fig. 1). The d-spacing was determined from the position of q^* .

3.2. TEM image of bulk novel DSA materials

The TEM image can further illustrate the morphology of these novel DSA materials. As can be seen from the picture, the lamella morphology

Fig. 1. Bulk morphologies at room temperature, after thermal annealing of typical lamella structure and hexagonal structure of sample one (a) and sample two (b) respectively, which were defined by SAXS measurement.

can be obtained after a short time annealing at a relatively low temperature. The clear light and dark lines represent two different components in the block copolymer respectively. When the scale bar is 100 nm, nearly five repeated units in this scale, which is consistent with the SAXS result. The full-pitch of this material in Fig. 2a is 21.4 nm (SAXS) and 18.6 nm (TEM). In Fig. 2b, the calculated full-pitch of this DSA material is 17.7 nm (SAXS) and 15.8 nm (TEM). Also the long range order of this material is clearly in Fig. 2. In the following work, we can selectively etch one component to get the sub-10 nm straight line, and then transfer the pattern into the silicon wafer or any other substrate for its litho application.

Fig. 2. TEM images of this rapid assembly material after the thermal annealing at 100 °C for 5 min. The regular stripes show that the lamella morphology forming in long range order. (a) 18.6 nm full-pitch, (b) 15.8 nm full-pitch.

3.3. SEM images

The film of novel DSA material is spin-coated on Si substrate from 1 wt% solution and post 60 s RIE with flow rates of 2 sccm CF_4 at 75 mTorr for 45 s after thermal annealing. Figure 3 presents scanning electron microscopy (SEM) images of a self-assembled structure with a 17.5 nm full-pitch. The different solvents result in the transition of orientation between parallel and perpendicular cylindrical morphologies.

4. Conclusion

In this work, we first synthesized a series of

Fig. 3. FESEM images of the novel DSA materials after thermal annealing. Different solvents of the block copolymer lead to the change of morphology of this material. (a) Parallel cylindrical morphology, (b) Perpendicular cylindrical morphology.

novel and rapid self-assembly block copolymers, which based on modifying of traditional DSA materials PS-*b*-PMMA. The structure of materials and the morphology of the self-assembly sample were measured with ^1H -NMR, GPC, SAXS and TEM. All these shows the reasonable structure and excellent performance.

By precisely controlling the ratio of each component we got different domain spacing and morphology. Also these novel materials easy to self-assembly in relatively low temperature and extremely short time. Finally, we managed to obtain the sub-10 nm patterning by using this high resolution DSA material.

Acknowledgement

Funding for this research was provided by the “1000 Talent plan” in China. The authors also acknowledge experimental support from State Key Laboratory of Molecular Engineering of Polymers in Fudan University.

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