A Challenge to the Micro-phase Separation Limit of PS-\textit{b}-PMMA by Doping with Hydrophilic Materials


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We examined effects of doping with hydrophilic materials on micro-phase separation of polystyrene-\textit{block}-poly(methyl methacrylate) (PS-\textit{b}-PMMA). As the hydrophilic materials, three organic acid compounds; butane-1,2,3,4-tetracarboxylic acid (BTA), cyclobutane-1,2,3,4-tetracarboxylic acid (CBTC), and sulfonyl-4,4'-diphenol (SNDP) were utilized in this experiment. By adding them to the PS-\textit{b}-PMMA, it was found that they induced reducing phase-separation size. The doping of organic acid compounds into PS-\textit{b}-PMMA decreased the phase separation size, while increasing doping PMMA homopolymer increased it. The PS-\textit{b}-PMMA with low molecular weight PS 10.0 kg/mol-\textit{b}-PMMA 10.0 kg/mol was utilized to examine the effect for phase-separation limit. By doping with 5 wt\% of CBTC PS-\textit{b}-PMMA showed lamellar structure with 8.2 nm half pitch. We considered that the doping organic acid compounds were a promising path for overcoming the phase-separation limit in PS-\textit{b}-PMMA.

Keywords: directed self-assembly, DSA, lithography, PS-\textit{b}-PMMA, hydrophilic materials, lamellar

1. Introduction

Directed self-assembly (DSA) technology is one of the most promising candidates in next generation lithography (NGL) technologies [1-5]. DSA lithography using block copolymer (BCP) is attracting attention as a fine patterning method with lower cost of ownership in semiconductor device manufacturing. The DSA lithography has a potential to fabricate sub-10 nm half pitch patterns combined with conventional lithography or NGL technologies. In order to realize sub-10 nm half pitch patterning using the DSA lithography, a combination of BCPs with high $\chi$ (chi) parameter and suitable surface modification processes on substrate such as chemical or physical guide patterns is required [6].

Polystyrene-\textit{block}-poly(methyl methacrylate) (PS-\textit{b}-PMMA) is one of the most promising BCPs in the DSA lithography for practical semiconductor device manufacturing. However, it is difficult to form 12 nm half pitch patterns and beyond [7-9]. Some reports indicated that the BCP by doping with small molecules caused the modification of phase separation performance [10-12].

In this work, we report a challenge of the micro-phase separation limit of PS-\textit{b}-PMMA by doping with hydrophilic materials.

2. Experimental

As BCPs, PSMMMA-1 (PS (Mn=35.5 kg/mol) -\textit{b}- PMMA (Mn=12.2 kg/mol), Mw/Mn=1.04) for investigation of doping effect, and PSMMMA-2 (PS (Mn=10.0 kg/mol) -\textit{b}- PMMA (Mn=10.0 kg/mol), Mw/Mn=1.05) for examination of smaller phase separation size were prepared, respectively. As hydrophilic materials, three organic acid compounds; butane-1,2,3,4-tetracarboxylic acid (BTA), cyclobutane-1,2,3,4-tetracarboxylic acid (CBTC), and sulfonyl-4,4'-diphenol (SNDP) were used in this work. The chemical structures of the organic acid compounds are shown in Figure 1. As the reference material, PMMA homopolymer (Mn=6.4 kg/mol, Mw/Mn=1.06) was also prepared. Cyclohexanone solution of PSMMMA-1 or PSMMMA-2 with the organic acid compounds ranging from 2 to 8 wt\% was prepared. The solution was spin-coated on a silicon wafer to form thin films and
annealed at 230 °C for PSMMA-1 and 200 °C for PSMMA-2, respectively, for 3 min in the air.

The phase-separation structures of the thin films were observed using atomic force microscope (AFM) and X-ray reflectometry analysis (XRR).

The phase-separation size was determined by the peak value of fast Fourier transform (FFT) power spectrum of the AFM image.

3. Results and Discussion

3.1 Investigation of doping effect of organic acid compounds

To observe the doping effect of the organic acid compounds, we compared the phase separation structures of non-doped and doped PSMMA-1. Figure 2 (a) shows AFM image of the PSMMA-1. Dot shaped and elongated domains in PMMA phase were observed. Figure 2 (b) shows the relationship between the PMMA domain area and ratio of the domain area in the observed area. The domains larger than 2000 nm² were counted as cylindrical structure area.

This result indicated that composition of the non-doped PSMMA-1 showed mixture of the dot-shaped and the elongated domains. We considered that the doping with the organic acid compounds induced change of the phase separation balance in the PSMMA-1 and that the effect could be observed as a change of domain size ratio.

Figure 2 (a) shows AFM image of the non-doped PSMMA-1. (a) Phase mode image, (b) Relationship between the PMMA domain area and ratio of the domain area. (on silicon wafer / annealed at 230°C for 3 min. / Thickness: 33 nm).

Figure 3 (a) shows AFM image of the PSMMA-1 doped with 4wt% SNDP. The relationship between the PMMA domain area and ratio of the domain area is shown in Figure 3 (b). In comparison with the non-doped PSMMA-1, the small size domain ratio was decreased.

Divided by domain size of 600 nm², the smaller domain-size ratio by doping with 4 wt% SNDP, showed 48%, while the non-doped PSMMA-1 showed 71%.

The effect of other organic acid compounds with various concentrations were examined using the same manner.
To clarify the volume effect, PMMA homopolymer doping samples were also prepared.

The relationship between concentration of additives and large domain size area ratio than 600 nm$^2$ is shown in Figure 4. The large domain size area ratios were increased in both concentration of the organic acid compounds and the PMMA homopolymer.

From the result it was considered that the organic acid compounds stayed in PMMA phase as well as the PMMA homopolymer.

Figure 5 shows relationship between concentration of additives and phase separation size. The phase-separation size of the PSMMA-1 doped with PMMA homopolymer increased with increasing the concentration of additives. On the other hand, the phase separation size of PSMMA-1 doped with the organic acid compounds was smaller than that of the non-doped PSMMA-1.

This result indicated that behavior of the organic acid compounds in the PMMA phase was different from that of the PMMA homopolymer.

3.2 Doping effects of organic acid compounds on micro- phase separation limit

We examined the effects of doping organic acid compounds on small molecular weight of PS-PMMA
(PSMMA-2) in this experiment.

Topographical analysis of the films was performed using the AFM measurements. Figures 6 (a) and (b) show topographical structures of non-doped and doped PSMMA-2 films after annealing, respectively. Steps in Figure 6 were obtained by scratching the BCP films before annealing. The doped film with 5 wt% CBTC showed holes on the surface.

On other hand, the non-doped PSMMA-2 film did not form any characteristic holes in any thicknesses of 20.4 nm, 21.8 nm, 22.7 nm, 26.4 nm and 29.4 nm. This result suggested that the organic acid compounds were supposed to promote the phase-separation, even in the case of the small molecular weight of PS-\textit{b}-PMMA.

The depths of the holes in Figure 6 (b) were measured to be 15.3 nm. The effects of the other organic acid compounds were examined using the same manner. The depths of the holes of the SNDP and the BTC doped PMMA-2 were 15.4 nm and 15.3 nm, respectively.

The internal structures of the horizontally oriented lamellar phase separation were analyzed using the XRR. Figure 7 shows the XRR spectrum of the 5 wt% CBTC doped PSMMA-2. The curve fitting was examined with lamellar layers number, density and thickness.

4 layered PS and PMMA model showed good agreement with the measurement curve. The thickness of each layer was calculated to be 3.7 nm, 8.4 nm, 8.0 nm, and 3.0 nm from the substrate surface. The density in 3.7 nm layer and 8.0 nm layer showed higher than the other layers. Generally, the density of the PMMA is larger than that of the PS [15].

From these results, the internal structure of the horizontally oriented lamellar phase separation was expected to be the schematic image shown in Figure 8. The hole depth expected from the XRR analytical results showed 15.2 nm. The hole depth from the AFM measurement showed similar value.
According to these data, it was concluded that the PSMMA-2 film doped with 5 wt% CBTC formed horizontal oriented lamellar structure of 16.4 nm full pitch (8.2 nm half pitch).

The non-doped PSMMA-2 with 20kg/mol molecular weight showed no phase-separation. The doping with the organic acid compounds could extend the micro-phase separation limit.

4. Conclusions

We examined the effects of doping with organic acid compounds on micro-phase separation limit of the PS-b-PMMA.

The doping of organic acid compounds into the PS-b-PMMA decreased the phase-separation size, while increasing the doping of PMMA homopolymer increased it.

We demonstrated lamellar structure of 8.2 nm half pitch by doping with organic acid into low molecular weight PS-b-PMMA, which shows no phase separation without doping.

We considered that organic acid doping was a promising path for reducing the phase separation limit in PS-b-PMMA. Our result showed that this approach was a good candidate for sub-10nm patterning.

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References