Surface Property Control for 193nm Immersion Resist

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The surface property of the resist film is critical for photoresist processing especially for immersion lithography. To control the interaction between resist film and water fluid, the polymer blend between the conventional acryl polymer and the fluorine-containing homo-polymer are examined. The polymer blend successfully modifies the film surface as verified by the dynamic contact angle measurement. The distribution of the blend polymer in the film gives an impact to the surface property. The surface can be also controlled by the use of blended polymer without any impact on the pattern profile at 193nm dry exposure. However, the optimization in resist formulation is necessary to achieve both the hydrophobic surface and imaging performance for a topcoat-less resist processing.

Keywords: immersion lithography, polymer blend, fluorine containing, contact angle

1. Introduction

193nm immersion lithography is a promising candidate for 65nm half-pitch and beyond. However, it requires solutions, in relation to water fluid, from the viewpoints of material development. It has been previously reported that there are some correlations between dynamic contact angles (sliding and receding angles) of water with watermark defects and scan speed of immersion exposure tool.^{1,2} We have also reported the correlation between the dynamic contact angles and the resist component elution.³ The surface property of the imaging stack is therefore critical in resolving the issues observed with immersion lithography. Currently, the topcoat application, which has flexibility in hydrophobicity control but would require an additional step in the lithography process, is aggressively investigated and is in the feasibility stage. In order to reduce the complexity of the immersion process infrastructure, resist will have to absorb this characteristic and reduce the use of topcoats. In this paper, we report an effective technique for altering the film property of resist for advantageous performance. As examined in the

topcoat applications, the hydrophobicity is controlled by the weight percentages of fluorine atom. Especially, using the fluorine-containing polymers, the polymer and resist film properties are examined with several blending approaches for dynamic contact angles and imaging performances.

2. Experiment

2.1 Materials

The monomer structures for the tested polymer samples are shown in Fig. 1. All three monomers, γ -butyrolactone-2-yl methacrylate (MA-GBL), 2-methyl-2-admantyl methacrylate (MA-MAd) and 3-hydroxy-1-adamantyl acrylate (A-HAd), are representative of a typical ArF resist formulation.

Fig. 1 Structure of composition monomer.

Table 1 Polymer composition.

Sample ID	Polymer composition (NMR composition)	Mw	Calculated F-content (wt%)
P-1	MA-GBL/MA-Mad/A-HAd (49/31/20)	10,000	0
P-2	MA-GBL/MA-Mad/A-HAd/ A-NB-HFA (45/27/15/10)	9,800	5.3
P-3	MA-GBL/MA-Mad/A-HAd/ A-NB-HFA (35/21/14/30)	11,400	14.0
P-4	MA-GBL/MA-MAd/A-NB-HFA (50/31/19)	11,600	9.7
P-5	Homo polymer of A-NB-HFA	3,300	33.0
P-6	Homo polymer of A-NB-HFA	5,000	33.0
P-7	Homo polymer of A-NB-HFA	8,200	33.0
P-8	Homo polymer of A-NB-HFA	19,400	33.0
P-9	Homo polymer of A-NB-HFA	39,700	33.0
P-10	Homo polymer of A-NB-HFA	61,800	33.0
P-11	Blended polymer of P-1 and P-7 (5wt%)	---	1.6
P-12	Blended polymer of P-1 and P-7 (10wt%)	---	3.0
P-13	Blended polymer of P-1 and P-7 (20wt%)	---	5.5
P-14	Blended polymer of P-1 and P-7 (50wt%)	---	11.0
P-15	Blended polymer of P-1 and P-5 (10wt%)	---	3.0
P-16	Blended polymer of P-1 and P-6 (10wt%)	---	3.0
P-17	Blended polymer of P-1 and P-8 (10wt%)	---	3.0
P-18	Blended polymer of P-1 and P-9 (10wt%)	---	3.0
P-19	Blended polymer of P-1 and P-10 (10wt%)	---	3.0

Table 2 Resist formulation.

Sample ID	Base polymer	PAG	Quencher
R-1	P-1	TPS-PFBS	TEA
R-2	P-12	TPS-PFBS	TEA
R-3	P-18	TPS-PFBS	TEA

There has been reports of ArF resist examples that incorporates a fluorine unit that contain the 6-[3,3,3-Trifluoro-2-hydroxy-2-(trifluoromethyl)propyl]bicyclo[2,2,1]hept-2-yl 2-acrylate (A-NB-HFA).⁴ The polymer compositions of the samples examined are listed in Table 1. The fluorine content (F-content) is calculated and described in the last column. Homo polymers of A-NB-HFA were used as the blend fluorine-containing polymer. The mixture ratio and the molecular weight (Mw) were varied for the homo-polymer. The resist formulations are shown in Table 2. Triphenylsulfonium perfluoro-1-butanesulfonate (TPS-PFBS) were used as photo acid generator in combination with triethyl amine (TEA) as quencher. The loading amount of TPS-PFBS and TEA were 4.0 and 0.4 weight percent respectively, as normalized to the polymer weight. All polymer and resist components were dissolved in propylene glycol mono-methyl ether 2-acetate and filtered prior to the film preparation.

2.2 Contact angle measurement

The contact angle measurement was performed under a dynamic condition to investigate the

inherent polymer surface property. First, the polymer films were prepared on silicon wafers by adjusting the spin speed with a Clean Track ACT-8 manufactured by Tokyo Electron Ltd. The film thickness was adjusted to 175 nm. The post-applied bake (PAB) was carried out at 125 °C for 60 seconds. Next, the static contact angle (CA), sliding angle (SA), and receding angle (RA) of the deionized water (DI-water) were measured. The equipment used was DROP MASTER 700TM Contact Angle Master manufactured by Kyowa Interface Science Co., Ltd. All measurements were taken for a single droplet of 50 micro liters.

2.3 TOF-SIMS analyses

TOF-SIMS (Time of Flight Secondary Ion Mass Spectrometry) analysis was performed for depth profile analysis of the blended polymer film. The fragment intensity was monitored with a TFS-2000 manufactured by Physical Electronic.

2.4 Resist imaging

Resist imaging was preformed with a dry exposure. The resist film was prepared on substrates coated with anti-reflective coating. The PAB and film thickness target were the same as in

the polymer film analysis. The exposure tool used was a 193nm scanner of NSR-S302 manufactured by Nikon Corporation. The illumination condition was 0.60 numerical aperture in combination with 2/3 annular illumination. The post exposure bake was applied at 115 °C for 60 seconds. The development was done with a 0.26 N tetramethylammonium hydroxide aqueous at 23 °C for 30 seconds.

2.5 Surface roughness analysis

Surface roughness was analyzed with an atomic force microscopy (AFM) with a DIGITAL INSTRUMENTS Nanoscope IV. The measurement was done for a 1 μm by 1 μm region.

3. Results and Discussions

3.1 Film surface modification by polymer blend

Contact angle measurements were taken for the polymer samples of the blended polymer samples P-11, P-12, P-13 and P-14 in comparison to the polymer of P-1 and the fluorine-incorporated polymers of P-2 and P-3. The homo-polymer, P-7, was blended for this data collection. The RA results are shown in Fig. 2. The blended polymer sample presented higher RA in terms of F-content than that of the fluorine-incorporated polymers. It is also observed that the relatively low loading can achieve high RA and modify the surface property of the polymer film. TOF-SIMS analysis was done on the film layer to investigate the effect as a function of the film depth as shown in Fig. 3. The data plot of (a), (b), and (c) represent the samples of the fluorine-incorporated polymer (P-4), the blended polymer (P-12), and the conventional polymer (P-1) respectively. The normalized intensity of fluorine was monitored.

Fig. 2 Polymer F-content (wt%) and RA.

The data plots of P-1, which does not contain any F atoms, indicated low S/N ratio. The distribution of fluorine was uniform with P-4 in the depth direction. P-12 was the only sample with a distinct distribution. This indicates the localization of fluorine at the film surface for the blended polymer, in contrast to the uniform distribution for the fluorine-incorporated polymer. This explains the high RA of the blended polymer sample despite the calculated poor F-content.

Fig. 3 TOF-SIMS analysis: P-4, (b) P-12, and (c) P-1.

We changed the Mw of the homo-polymer for further investigation. The blend ratio was fixed at 10 wt% mixed into P-1. Homo-polymers samples P-5 through -10 were used and blended with P1 to formulate samples P-12 and P-15 through -19. The contact angle measurements were carried out for both SA and RA and are shown in Fig. 4. The changes in the SA and RA are not as pronounced, however, the curves interestingly display the Mw dependency of the blending homo-polymers. The blend is ineffective for SA and RA change with the low Mw homo-polymers. It also shows saturation behaviors for SA and RA with increasing Mw. The hydrophobic characteristic is not only defined by the calculated F-content but the distribution in the polymer film.

Fig. 4 Homo-polymer Mw and contact angle.

3.2 Resist evaluation

The addition of the fluorine material is advantageous for altering the surface property to have a hydrophobic surface. We formulated a 193nm resist comprised of the blended polymer of P-12, namely R-2, and compared the dynamic contact angles and pattern profiles. The baseline resist R-1, which is formulated with the conventional polymer of P-1, indicated SA of 23 degrees and RA of 54 degrees. R-2, on the other hand showed SA of 21 degrees and RA of 67 degrees. The contact angle trend observed with the polymer samples were similarly observed with the resist formulation. Figure 5 shows the pattern profile comparison of samples R-1 and R-2. The SEM pictures shows pattern profile 130 nm lines and spaces. No significant difference was seen between the two profiles. Thus, the blending method of using the fluorine-containing homo-polymer can attain the resist film property modification without any imaging impact on pattern profile.

Fig. 5 Resist pattern profiles of (a) R-1 and (b) R-2 (130 nm lines and spaces).

3.3 Surface roughness measurement

The investigation has been further continued for the film property by utilizing AFM for an aggressive blending case. The underlying issue that needed to be considered was the concern for a phase-separation in resist film when multiple polymers with various glass transition temperatures were blended. Table 3 shows the AFM images for resists R-1 and R-3. As visually shown, the resist surface of R-3 indicated quite rough compared with the relative smooth surface of R-1. The root cause of the roughness difference was not directly identified to our possible concern of phase-separation at this moment. However, we will need to pay careful attention when adopting the blending method as not to impact the total resist performance. At the same time, the formulation optimization is necessary to compensate the hydrophobic resist surfaces and good resist performance for immersion lithography.

Table 3 AFM image of polymer surfaces.

Sample	R-1	R-3
Image (Z-range 20nm)
Rms (nm)	0.29	5.42

4. Conclusions

The blend method was examined for the conventional 193nm resist polymer and the fluorine-containing homo-polymer of A-NB-HFA, to target for topcoat-less resist process with immersion lithography. The blend realized the surface modification of the polymer film, where the distribution of the blending polymer directly influenced. The blending method when used with the resist formulation can effectively control the dynamic contact angles of resist film without any pattern profile impact. However, careful attention is necessary for the optimization of resist formulation.

References

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