Oxygen Effect on Characteristics of a PGMA Resist

Poly(glycidyl methacrylate) (PGMA), used as an electron beam resist,[1,2] has also been used as a deep UV resist. It has previously been reported[2] that PGMA shows a negative-working characteristic to electron beam exposure and that crosslinking of PGMA polymers continues to some extent in a vacuum even after electron exposure is stopped (the so-called vacuum curing). PGMA can also crosslink by baking. On the other hand, it shows a positive working characteristic to deep UV light.

It was recently found that the characteristics of PGMA polymers are influenced by oxygen during deep UV irradiation or baking. This paper describes the effects of oxygen on the characteristics of a PGMA resist.

EXPERIMENTAL

The PGMA polymer used in this study was prepared and characterized as described in a previous paper.[2]

The characteristics of the PGMA resist under deep UV irradiation were evaluated in various atmospheres. The resist films were spin-coated on a Si wafer and prebaked at 200°C for 1 h in air. Through this process, the polymers became insoluble, probably because of crosslinking by ring opening in small parts of epoxy groups. The insoluble films were exposed to deep UV light. Exposure was carried out using a system with a 3-kW metal halide lamp made by the EYE Graphics Co., Ltd. of Japan. The exposed samples were developed by immersing them for 2 min in a 5:2 mixture of methylethylketone and ethanol. The sample were then rinsed for 2 min in methylisobutylketone and dried. The remaining film thicknesses were measured and plotted against exposure times.

The molecular weight distribution of the polymer was measured with a Waters Gel Permeation Chromatography Apparatus (Type GPC-244). Each sample dissolved in tetrahydrofuran was filtered through 0.5 μm pores. The weight average and number average molecular weights (M_w and M_n) and polydispersity (M_w/M_n) were calculated from the observed molecular weight distribution.

RESULTS AND DISCUSSION

The exposure characteristics of PGMA under various atmospheric conditions are shown in Figure 1. The initial film thickness is 0.7 μm in this figure.

The PGMA behaves as a positive working resist for deep UV exposure of less than 10 s. However, it exhibits a negative working characteristic when overexposed in atmospheres of nitrogen or air.

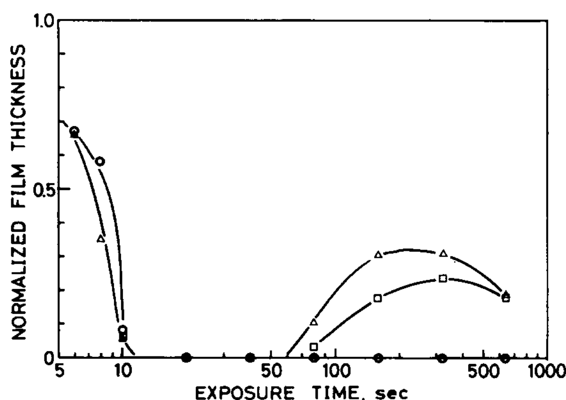

Fig. 1. Exposure characteristics of PGMA in various atmospheres. Film thickness: 0.7 μm. (△) In N_2, (□) in air, (○) in O_2.

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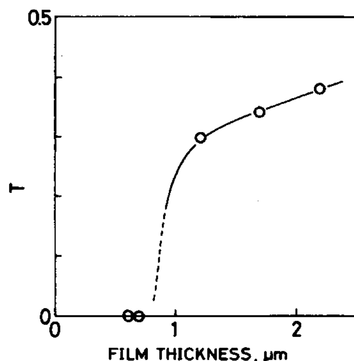

Fig. 2. Effect of film thickness on the negative working of PGMA. T is the normalized film thickness after 320-s deep UV irradiation, in an atmosphere with oxygen, and development.

This negative-working tendency is somewhat weaker in air than in nitrogen, and is not observed in oxygen.

Since PGMA includes the epoxy groups and the quaternary carbons, both crosslinking and scission of molecules are feasible. The scissions mainly function as a resist characteristic in relatively weak incident deep UV light. However, PGMA tends to crosslink when overexposed in air or nitrogen. The molecular weight decreases, but relatively complex crosslinked polymer are formed. It seems that the oxygen molecules quench the active species produced by deep UV irradiation and they are able to crosslink.

The effect of coating film thickness on the negative working of PGMA was investigated in further detail. This effect is shown in Figure 2, where the insolubilized film thickness obtained by 320-s exposure in oxygen and development is plotted as a function of initial film thickness. Negative working is not detectable in a coating film thickness thinner than the boundary, around 1 μm, as shown in this figure. On the other hand, it appears in thicknesses above this boundary even in an oxygen atmosphere. This result indicates that the number of oxygen molecules supplied through the film is insufficient to prevent crosslinking in thicker films.

The effect of coating film thickness on the crosslinking of PGMA molecules in baking was also investigated. The polymer was coated on the Si wafer with thickness of 0.8 and about 100 μm. Each film was baked at 160°C or 180°C for 30 min. The films were then dissolved in tetrahydrofuran, and their molecular weight distribution were measured. The molecular weight distributions of these thin and thick films are shown in Figures 3 and 4, respectively. The molecular parameters of PGMA after baking are listed in Table I.

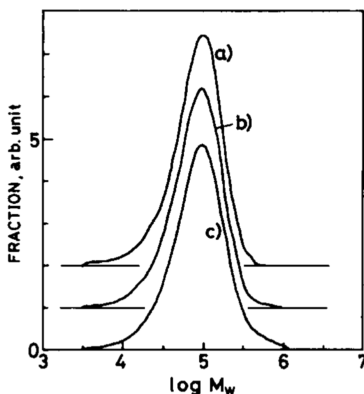

Fig. 3. Molecular weight distribution in a thin film after baking. Film thickness: 0.8 μm. (a) Nontreatment; (b) after baking at 160°C for 30 min; (c) after baking at 180°C for 30 min.

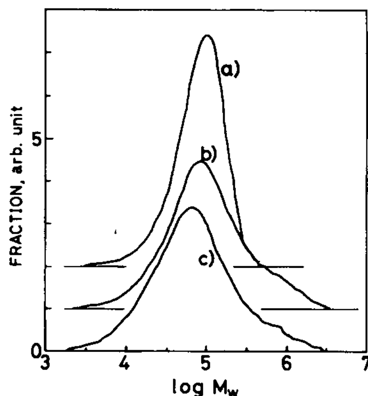

Fig. 4. Molecular weight distribution in a thick film after baking. Film thickness: 100 μm. (a) Nontreatment; (b) after baking at 160°C for 30 min; (c) after baking at 180°C for 30 min. Sample removed: 51 wt % of the insoluble part.

The change in molecular weight distribution caused by baking is very small for the thin film, as shown in Figure 3 and Table I.

In the thick film baked at 180°C for 30 min, gel was produced by crosslinking of the polymers. The gel portion amounted to 51 wt %. Only the soluble part was used to measure the molecular weight distribution. Consequently, both average molecular weight (M_w) and polydispersity (M_w/M_n) are larger than those marked by [a] in Table I. The changes in M_w and M_w/M_n caused by baking are large in the case of the thick film. The thin film did not produce gel after the same baking process. The molecular weight of the polymer increased very little even in the thick film after baking at 120°C.

These results also indicate the effect of oxygen. Active species with the ability to crosslink are produced by baking. These active species may be quenched by oxygen molecules from the surrounding atmosphere. As the supply of oxygen molecules through the film is insufficient in the thicker film, the probability of crosslinking in the thick film is greater than in the thin film. This oxygen effect may be the same as oxygen quenching in vacuum curing for electron beam exposure.

Further experiments on the active species are being carried out.

TABLE I
Molecular Parameters of PGMA after Baking

Thickness / Parameter / Treatment	0.8 μm		100 μm	
	M_w	M_w/M_n	M_w	M_w/M_n
Non	1.01×10^5	1.69	1.01×10^5	1.69
160°C, 30 min	1.07	1.81	2.28	3.74
180 °C, 30 min	1.28	2.07	1.65[a]	4.24[a]

[a] Sample removed: 51 wt % of the insoluble part.

CONCLUSIONS

PGMA shows a positive-working resist property under deep UV light. However, it shows a negative-working characteristic for over exposure. This negative-working tendency is prevented by oxygen molecules.

PGMA polymers can crosslink themselves through baking. However, this crosslinking is also influenced by oxygen molecules.

Thus, oxygen molecules quench active species with the ability to crosslink.

References

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