Analysis on Radical Photo- and Thermal-Polymerization of Negative-Tone Acrylic Resist for High Resolution

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The effect of the post exposure bake (PEB) on the high resolution of dry film resist for semiconductor packaging was investigated using Hitachi Chemical’s dry film resist. The effective PEB was found to be the baking within 30 min after exposure at a temperature of 40–60 °C for 1–5 min. The longer holding time after PEB lowered the conversion of the upper layer of the resist. The oxygen passed through PET film was thought to deactivate the polymerization terminal radical during the holding time. The margin for the process was expanded by using PVA layer of low oxygen transmission rate. It was also found that the polymerization terminal radical reacted with the unreacted monomer during PEB process.

Keyword: photo resists, post exposure bake, photo radical polymerization

1. Introduction

The high resolution techniques of lithography has been required for miniaturization of electronic devices, and numerous studies of related new process and materials have been reported. Photolithography for resolution patterning is susceptible to exposure profile, and several studies focused on an optical transparency, reflection from substrates and diffusion of the initiating species. For example, contrast enhancement layer (CEL) process was developed with an available contrast enhancement material on top of a resist [1-2]. Multiple reflection from substance was suppressed by antireflection film [3-4]. Post exposure bake (PEB) process could reduce pattern walls defect under exposure and also promote acid generation, followed by cationic reaction of the photoresist such as chemical amplification type resist [5-8].

Negative-tone acrylic dry film resist (acrylic dry film resist) is photopolymer of which system is radical chain polymerization. At a temperature close to the glass transition temperature, polymerization rate becomes lower, and finally, it terminates even if unreacted monomers remain [9-10]. In this case, enough crosslinking density is not able to be obtained. Especially the bottom layer of the resist has lower conversion and lower crosslinking density because of “UV shielding effect” by the absorbance of the resist itself. Therefore, it is difficult to obtain high resolution patterns with high adhesion.

In this study, we focused on promotion effect of radical polymerization for dry film resist [9-10] by applying PEB process. PEB process is used for chemically amplified resist in order to promote diffusion of acid. Generally, PEB is not necessary for radical polymerization system because the reaction proceeds at room temperature. In addition, it is difficult to control PEB condition in radical polymerization system because of the short life time of initiating radical species. Few studies have focused on dry film resist for high resolution by using PEB process. In this research, we studied the factors to improve resolution of acrylic dry film
resist by PEB process.

2. Experimental
2.1. Materials
Negative-tone photosensitive dry film resist RD-1225 (Hitachi Chemical) was used. Photosensitive layer contained (meth)acrylic polymers and methacrylate monomers, photo radical initiators, adhesion improvers, and dye compound.

2.2. Lithographic evaluation
Glass epoxy multilayer material MCL-E-679F (Hitachi Chemical) was used as the substrate. Substrates were cleaned in 3.0 wt% NaOH aqueous solution for 60 s and in 1 vol% HCl aqueous solution for 30 s. The dry film resist was laminated on the substrate which was preheated in 80 ⁰C oven for 10 min, by the laminator HLM-3000 (Hitachi Chemical). The laminator roll temperature was 110 ⁰C. The roll speed was 1.5 m/min. The roll pressure was 0.4 MPa. The laminated dry film resist was exposed with direct UV laser exposure machine DE-1UH (Via Mechanics). After exposure, the dry film resist was baked on the hot plate, and developed with 1.0 wt% Na₂CO₃ aqueous solution using the alkali developing machine (Murata Kiko). Obtained patterns were observed by the SEM VE-8000 (Keyence). Resolutions of patterns were determined as the finest line without leaning, meandering, and crack. Errors of edge line patterns were ignored.

2.3. Conversion
FTIR spectra were recorded by the DIGLAB FTX3000MX FTIR spectrometer (32 times scanning, at spectral resolution of 2 cm⁻¹). The conversions of the cured films were measured by a diamond attenuated total reflection (ATR). The acrylate double bond conversion was calculated by monitoring the peak area at 1635 cm⁻¹.

2.4. PVA layer
The PVA layer contains 68 wt% polyvinyl alcohol (PVA-205, Kuraray), and 32 wt% polyvinylpyrrolidone K 30 (PVP K 30, Tokyo Chemical Industry). After water was weighed in a 200 mL three-necked flask, PVA-205 and PVP K 30 were added. The flask was stirred at 90 ⁰C for 3 h. The flask was cooled to RT, then water and methanol were added. After filtration, the mixture was spin-coated on the laminated dry film resist. The layered product of the PVA layer, the dry film resist and the substrate was obtained after baking on 95 ⁰C hot plate for 10 min. The PVA layer could be removed by water washing for 8 s.

2.5. Glass transition temperature
Glass transition temperature (Tg) of dry film resist was measured by X-DSC 7000 (Hitachi High-Tech Science). Temperature condition was from -50 to 150 ⁰C. The rate of temperature rise was 5 ⁰C /min. And surrounding condition was N₂ 50 mL/min.

2.6. Polymerization chain length
For analysis of polymerization monomer chain length, the modeled dry film resist was used. The modeled dry film resist contains (meth)acrylic polymers without any aromatic groups, 2-phenoxyethyl methacrylate (FA-310M, Hitachi Chemical), photo radical initiators, adhesion improvers, and dye compound. Cured dry film resists were dissolved in THF at a concentration of 5 mg/mL, and the weight-average molecular weight of polymerized FA-310M and the polydispersity index were measured by HLC-8320GPC (Tosoh). The measurement wavelength was 270 nm, and eluting solution was THF.

3. Results and Discussion
3.1. Influence of PEB time
Figure 1 shows the relationship between the PEB time and the resolutions of the dry film resist (RD-1225) obtained under the condition of 80 mJ/cm² at 60 ⁰C. As shown, the effect of PEB was obvious and the highest resolution was obtained when the PEB time was 1 min. As PEB time became longer, the effect for resolution was decreased.

Figure 2 shows the SEM images of patterns obtained varying PEB time. The amount of residues between patterns increased with increasing PEB time, suggesting that the thermal radical reaction penetrated to the unexposed area.
3.2. Influence of PEB temperature

Figure 3 shows the relationship between PEB temperature and the resolutions of the resist obtained by the exposure dose of 80 mJ/cm² for 1 min. As shown, PEB in range of 40–60 °C was effective for high resolution.

Figure 4 shows the SEM images of patterns varying PEB temperature. The amount of residues between patterns increased with increasing PEB temperature.

3.3. Influence of holding time before PEB

Figure 5 shows the relationship between holding time before PEB and the resolutions of the resist obtained by the condition of 80 mJ/cm² at 60 °C for 1 min. As shown, PEB of holding time of 30 min or less was found to be effective for high resolution. The highest resolution was obtained when the holding time was 1 min.

Figure 6 shows the SEM images of pattern varying holding time before PEB. The amount of residues between patterns increased at around 15 min. As holding time became longer, patterns tended to lean and meander.

Figure 7 shows the relationship between holding time and conversion. As shown, the level of the conversion at the bottom layer kept high even at 60 min after PEB. On the contrary, the conversion of the top layer decreased about 20% after PEB. Although the bottom of the resist contacts the substrate, the
top of the resist contacts PET during holding time. So, the oxygen inhibition may play an important role to explain these phenomena.

![Figure 6. SEM images of patterns with L/S = 5/5 μm varying PEB time before PEB](image)

| Without PEB | 1 min | 15 min | 45 min |
|-------------|-------|--------|--------|
| ![SEM images](image) | ![SEM images](image) | ![SEM images](image) | ![SEM images](image) |

Figure 6. SEM images of patterns with L/S = 5/5 μm varying PEB time before PEB

Figure 7. Relationship between holding time and conversion of top and/or bottom layer of the cured dry film resist

3.4. Influence of oxygen

To check the effect of oxygen inhibition, the effect of PVA layer as an overcoat was examined. PVA was known to have lower oxygen transmission rate than PET. So, as shown in Figure 8, the effect of 8 μm thick PVA overcoat was compared with that of 16 μm thick PET film.

![Figure 8. Cross section of sample with overcoat](image)

Figure 8. Cross section of sample with overcoat

![Figure 9. Relationship between holding time and conversion of top layer of cured dry film resist](image)

![Figure 10. SEM images of L/S = 6/6 μm resist pattern](image)

Figure 9. Relationship between holding time and conversion of top layer of cured dry film resist

Figure 10. SEM images of L/S = 6/6 μm resist pattern
3.5. Analysis of cured dry film resist after PEB

Table 1 shows the value of Tg and conversion of the resist obtained under various conditions. As shown, the Tg of the resist cured with PEB was ca. 39 °C, which is 4 to 5 °C higher than that without PEB, and the conversion was ca. 20% higher than that without PEB. So, it was confirmed that PEB has an effect to increase Tg as well as conversion.

Table 1. Tg and conversion of the resist obtained under various cure condition

| Exposure (mJ/cm²) | PEB Tg (°C) | Conversion (%) | Top | Bottom |
|-------------------|-------------|---------------|-----|--------|
| 0(Unexposed)      | -           | -28.7         | 0   | 0      |
| 80                | ×           | 34.9          | 66  | 64     |
| 80                | ○           | 39.3          | 84  | 77     |
| 120               | ×           | 35.1          | 66  | 68     |

3.6. Polymerization chain length after PEB

Figure 11 shows the weight-average molecular weight and polydispersity index (Mw/Mn) of cured model film obtained under various PEB conditions. As shown, the polymerization chain was extended by PEB, but the polydispersity index was not changed by PEB. Therefore, in PEB process, it is speculated that each polymerization terminal radicals mainly react with unreacted monomers.

The speculated mechanism of the high resolution with PEB was illustrated in Figure 12. In the system without PEB, the high exposure broadens the pattern width because of the redundant reaction by the reflected and scattered light, and the low exposure causes leaning or meandering of patterns due to the decrease of the resistance against developer. The reason of effectiveness of PEB may be the ideal curing profile obtained by combining moderate exposure dose with PEB.

4. Conclusion

The influence of PEB on the resolution of (meth)acrylic dry film resist was studied, and followings were concluded.

The oxygen inhibition was found to be a key factor to expand the process margin of holding time before PEB. Comparing with PET, the over-coating of PVA on the resist was more effective for higher resolution patterning. PEB was found to extend polymerization chain, suggesting that each polymerization terminal radicals mainly react with unreacted monomers. The reason of effectiveness of PEB may be the ideal curing profile obtained by combining moderate exposure dose together with PEB.

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