Positive Pattern Formation and its Mechanism from Ionic bonded Negative Photosensitive Polyimide

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We found positive pattern formation by ionic bonded photo-sensitive polyimide (PSPI). The PSPI is composed of poly(amic acid), photo-reactive tertiary amine (such as N,N-dimethylaminoethylacrylate), and photo-initiator. The PSPI basically has negative photo-sensitivity. However, we found that positive pattern formation from the PSPI when adding a post-exposure bake (PEB) about 120-140C. By adding PEB, imidization rate of unexposed area of PSPI is higher than that of exposed area. High imidization of unexposed area of PSPI makes hard to solubule to alkaline solution. The imidization rate difference attributes to glass transition temperature difference between exposed area and unexposed area.

Keywords: poly(amic acid), photosensitive amine, imidization control

1. Introduction

Polyimide coatings are applied to stress buffer of semiconductor devices and interlayer dielectrics of electronic devices because of its excellent heat resistance and solvent resistance [1]. Photo-sensitive polyimide coatings are promising to simplify the polyimide patterning process and to obtain fine pattern resolution with high accuracy. Especially, positive photo-sensitive polyimide becomes popular due to its alkaline developability, and fine pattern capability [2]. In order to add good patterning property, polymer design of posi-PSPI is limited.

On the contrary, we developed the negative ionic bonded PSPI which is composed of poly(amic acid) and photo-reactive amine (such as N,N-dimethylaminoethylacrylate) [3]. To obtain the negative photo-sensitive polyimide, we have some more room to select the polyimide back-bone. Initial photo-reaction of ionic bonded PSPI is not simple free radical photo-polymerization but photo-induced charge separation. [4].

In this article, we found image-reverse technique to obtain positive image pattern from ionic bonded negative tone photo-sensitive polyimide. In addition, we investigated a reaction mechanism.

2. Experimental

2.1 Synthesis of polyimide precursor solution

100mmol of 4,4'-diaminodiphenyl ether (20.3g, ODA, Wakayama-Kasei) is dissolved into 200mL of N-methyl-pyrrolidone (NMP, Mitsubishi Chemical) in 500ml of 4-neck flask with a stirrer, thermometer, and nitrogen inlet. 3,3',4,4'-benzophenone-tetra-carboxylic acid dianhydride (BTDA, 32.2g, Daicel) was added to the solution with 30mL of NMP. The solution was stirred at 40C for 3hrs. The solution was used as a polyimide precursor solution.

2.2 Photo sensitive polyimide precursor

1g of bis(4-dimethyl-amino)benzophenone (Tokyo Kasei), N-phenylglycine (Tokyo-Kasei) and 10g of dimethylaminoethyl(methacrylate) (Mitsubishi Gas Chemical) are added to the 100mL of poly(amic acid) solution prepared in 1.1. The solution is used as a photosensitive polyimide precursor solution.

2.3 Patterning

SCW-636 (Dainippon-Screen MFG) is used to make spin coating on 6inch wafer by its coater unit and to make soft baking on its hot plate unit. Soft

baking condition is 80C for 2min.

PLA-501 (Canon) is used as a UV light source. The dose is measured by an irradiation meter at 405nm (UVD-405, Ushio).

The exposed wafer was heat treated by hot plate of SCW-636 as a post exposure baking (PEB). Heating condition is 110C for 2min to 140C for 2min.

Development was done by immersing into the 2.38% tetra-methyl-ammonium solution (Mitsubishi-Gas Chemical) for 1 to 5 min at 23C.

2.4 FT-IR measurement

Horiba FT-720 was used to obtain FT-IR spectra. (Resolution: 8cm⁻¹, Accumulation: 16times)

2.5 Dynamic visco-elastic properties

DDV-4EA (Orientech) was used to obtain visco-elastic properties of photosensitive polyimide precursor film. (Heating Rate 2C/min from room temperature Frequency: 110Hz)

Fig. 1 Chemical structure of poly(amic acid)

3. Result and discussion

3.1 Image reverse technique

The PSPI is patterning following processes. 1. Coating, 2. Soft-baking, 3 Exposure, 4. Post exposure baking, 5. Development.

The post exposure baking is applying in order to make stable for storing the exposed PSPI film. For the purpose the baking temperature is about 60-100C. The baking makes molecular movement to PSPI to obtain large free volume for the PSPI film.

In this study, we found that we obtain positive photo-image when applying the 120-140C baking after exposure. Those results are summarized in Table 1. It is very sensitive for post exposure baking temperature to obtain good pattern. Allowance of post exposure baking temperature is only 2 to 3 degree. As shown in table 1, Isoxazolone and oximeester are good photo-initiator in this study.

By applying the post exposure baking at 120-140C, imidization ratio at exposed area is about 30%. On the contrary, the imidization ratio at

unexposed area is about 40 to 50% from FT-IR measurement.

So dissolution rate to alkaline solution, such as tetramethyl ammonium solution, of exposed area is higher than that of unexposed area due to imidization difference.

In addition, thickness of exposed area is thicker than that of unexposed area. Actually, we suspected to change the refractive indices between exposed area and unexposed area. To make clear, we obtained the thickness unevenness by tracing method.

Table1 Summary of this study

Photoinitiator	Thickness after prebake	Thickness after PEB Unexposed	Thickness after PEB Exposed	Development time	Thickness after development
Isoxazolone	4.92um	3.95um	4.21um	120sec	3.42um
Dimethylamino(ethylbenzoate)	4.73um	3.79um	3.91um	210sec	2.09um
IG-369	4.88um	3.88um	4.01um	330sec	2.38um
2-mercaptobenzthiazole	4.43um	3.53um	3.71um	120sec	2.65um
Oximeester	4.89um	3.91um	4.14um	150sec	3.17um

Fig.2 Effect of PEB on development time

3.2 Visco-elastic property

In order to obtain glass transition temperature (T_g), we measure dynamic mechanical property (DMA) of PSPI films. We found 2C difference between exposed area and unexposed area. The exposed area shows higher T_g. From Nielsen's empirical equation [5], cross linking density is estimated as follows.

$$Mc = (Tg1 - Tg0) / 3.9 \times 10^4$$

Mc: Cross linking density

Tg1: T_g at cross linking region

Tg0: T_g at none cross linking region

The cross linking density is about 2×10^{-4} . This is quite small for chemically cross linking from the equation.

On the contrary, we studied that the

photo-reaction of ionic bonded PSPI is not photo-polymerization but weak interaction from photo-induced charge separation [4]. Interaction makes weak pseudo cross linking at exposed area. The weak interaction makes molecular motion slow at exposed area.

From those data, positive type pattern obtained by the difference of imidization between exposed area and unexposed area. The imidization difference is derived from the Tg difference.

3.3 Patterning mechanism

From those experimental results, we think that positive tone pattern obtaining by following mechanism. Exposed area has higher Tg and slower molecular motion due to its pseudo cross linking. When applying the post exposure bake, imidization of exposed area is slower than that of unexposed area due to its molecular motion speed difference. After post exposure baking, imidization ration of exposed area is smaller than that of unexposed area. Exposure area should have much carboxylic group due to lower imidization ratio. The exposed area shows higher dissolution rate to alkaline solution comparing to unexposed area.

As a result, exposed area is dissolved to alkaline solution. The unexposed area remains after immersing in alkaline solution.

In addition, there may have some effect by photo-charge separation. Imidization suppress at exposed area due to photo-charge separation.

Before cure After cure (350C for 1hr)
Fig.3 SEM photos obtained in this work

4. Conclusion

We observed positive patterning formation from originally negative ionic bonded photo-sensitive polyimide. The pattern forming mechanism is as follows.

1. Tg of exposed area is higher than that of unexposed area by weak interaction.
2. By applying post exposure baking, molecular motion of exposed area is slower than unexposed area. Imidization rate of exposed area is smaller than unexposed area.
3. When immersing in alkaline solution, dissolution rate of exposed area is higher than that of unexposed area. So we obtain positive pattern.
4. To make good pattern, it is important to keep post exposure baking temperature. The post exposure baking temperature is between Tg of unexposed area and Tg of exposed area. As we mentioned before, it is quite sensitive for temperature.

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