

Development of a Chemically Amplified Photosensitive Polyimide Based on Poly(amic acid), a Dissolution Inhibitor and a Photo Acid Aenerator

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1. Introduction

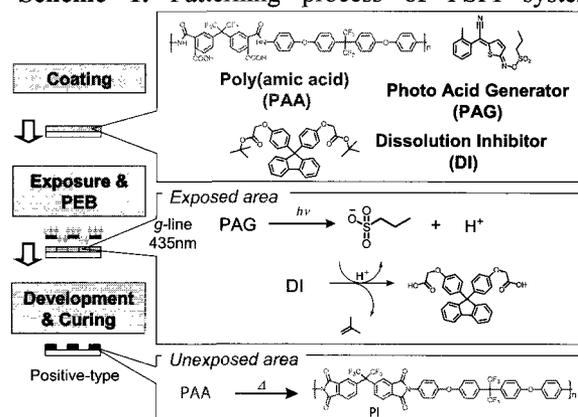
Photosensitive polyimides (PSPIs) are widely used as stress buffers and insulation layers of integrated circuit package in micro-electronics field, because they reduce the processing steps for the desired photolithographic pattern, furthermore, possessing excellent thermal stability, mechanical properties, and reasonably low dielectric constant. [1]

Most negative-type PSPIs, which are extensively employed in the semiconductor industry, are prepared from poly(amic acid)s (PAAs), where cross-linking sites are introduced to PAAs through ester [2, 3] or acid amine ion linkages. [4] On the other hand, positive-type PSPIs consisting of poly(hydroxyimide)s and diazonaphthoquinone (DNQ), [5] *o*-nitrobenzyl esters of PAAs, [6] or poly(isoimide)s and DNQ [7, 8] have been reported. In these cases, modified PAAs are used as a matrix because the dissolution rate of PAAs in a 2.38 wt% aqueous tetramethylammonium hydroxide solution (TMAHq.) is too high to obtain a sufficient dissolution contrast between unexposed and exposed areas. In fact, only a few TMAHq.-developable positive-type PSPIs using DNQ have been reported [9, 10], where highly fluorinated or partially esterified PAAs are used to reduce the dissolution rate in TMAHq. Conventional PSPIs based on DNQ, however, possess low sensitivity (>100 mJ/cm²) and a strong absorbance at 436 nm (*g*-line), and are difficult to use for thick patterns. To improve a photo-sensitivity of PSPIs, the introduction of chemically amplified system into PSPIs is effective, and an alkaline-developable, chemically amplified PSPI based on PAA is one of the most simple and suitable formulation methods.

In this paper, we report an alkaline-developable and chemically amplified PSPI based on PAA, 9,9-bis[4-(*tert*-butoxycarbonylmethoxy)-phenyl]fluorene (TBMFPF) as a dissolution inhibitor (DI), and (5-propylsulfonyloxyimino-5*H*-thiophene-2-ylidene)-(2-methylphenyl)-actonitrile (PTMA) as a

photo acid generator (PAG). The patterning process of this PSPI system is shown in Scheme 1. The PSPI resist solution is spin-coated on a silicon wafer and prebaked. Then, the film is exposed to *g*-line through a photo-mask to produce propanesulfonic acid from PAG. Upon post-exposure baking (PEB) treatment of the PSPI film, propanesulfonic acid deprotects the *tert*-butyl ester of TBMFPF and produces the

Scheme 1. Patterning process of PSPI system



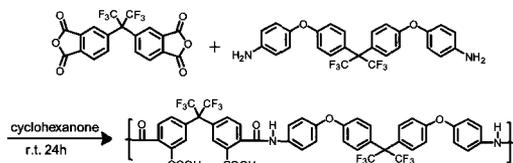
corresponding acid that promotes the dissolution rate of PAA in 2.38 wt% TMAHq. because of its high acidity. Therefore, the positive image is easily delineated.

2. Results and Discussion

2.1. Synthesis of PAA

As described in Introduction, a typical PAA has the high dissolution rate in a 2.38 wt% TMAHq. solution, and little dissolution inhibitors have not been reported. Thus, the synthesis of PAA with a suitable dissolution rate in a 2.38 wt% TMAHq. is important. The dissolution rate is determined by both of an amide acid content and hydrophobicity in a repeating unit. To satisfy both properties, the PAA is expected to obtain from dianhydrides and diamines with a trifluoromethyl group. Thus, we selected 6FDA and 6FAA as a dianhydride and a diamine, respectively. To control the molecular weight, polymerization was carried out under the stoichiometric imbalance $r = 0.879$ of two monomers 6FAPP/6FDA, giving the PAA with an

inherent viscosity of 0.12 dL/g in cyclohexanone (Scheme 2). The resulting PAA had a good dissolution rate in a 2.38 wt% TMAH aq. solution as expected.



Scheme 2. Synthesis of PAA.

2.2. Imidization of PAA

As the imidization of PAA during PEB treatment generally influences the dissolution rate of the resist, it was estimated by FT-IR spectroscopy. The PAA film was heated on a hotplate at designated temperatures at 80 °C for 2 min for the pre-bake and at each temperature (100~300 °C) for 10 min for PEB. A reference PI film was prepared by the following thermal treatment, such as at 250 °C for 0.5 h and 300 °C for 1 h in the air. Figure 1 shows that the imidization starts at 100 °C, and completes until 250 °C due to a relatively flexible PI chain. Furthermore, the thermal and mechanical properties of PI were determined by DMA (Figure 2). The DMA curves of PI film prepared by curing at 250 °C for 1 h are shown in Figure 2. The initial storage moduli (E') of PI is 1.5 GPa, and its loss moduli (E'') at the same temperature is 70 MPa. The T_g of PI, determined from the peak temperature of the E'' plots, is observed at 236 °C, and this relatively low T_g is attributed to the trifluoromethyl groups in the main chain.

2.3. Lithographic Evaluation

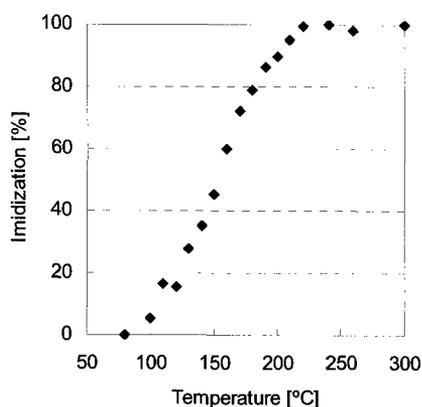


Figure 1. Degree of imidization by FT-IR

In a previous paper, we reported TBMPF which promotes the dissolution of poly(*o*-hydroxy amide) in a 2.38 wt% TMAH aq after deprotection of *tert*-butyl group by photogenerated acid. [14]

T h u s , t h e P S P I w a s

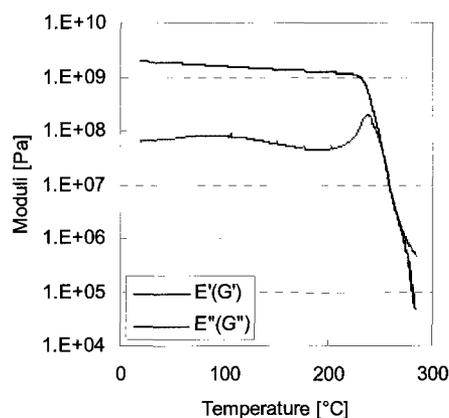


Figure 2. DMA curves of PI film.

formulated by mixing PAA solution with TBMPF as a DI and PTMA as a PAG, as shown in Scheme 1.

To obtain contrasting pattern profiles from exposed and unexposed areas, the effect of PEB temperature, PEB time, TBMPF content, PTMA content and exposure dose were investigated. The films were obtained by spin-casting the diluted polymerization solution of the PAA containing TBMPF (8.5 wt %) and PTMA (8.5 wt %) on a silicon wafer, and then pre-baking at 80 °C for 2 min in air. This photosensitive polymer film was irradiated with UV light at *g*-line using a filtered super-high-pressure mercury lamp, PEB at a set temperature, and developed with TMAH aq. / 5 wt% IPA at 25 °C. The dissolution rates were estimated by the change in film thickness before and after development.

The PEB temperature is crucial in the chemically amplified resist system because the diffusion of photosensitive acid in the films is an important key factor. First, the effect of the PEB temperature on the dissolution rate was investigated and the results are shown in Figure 3. When the PEB temperature was lower than

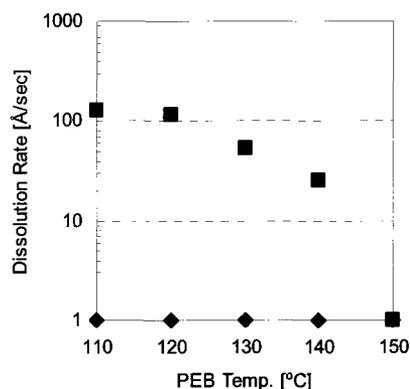


Figure 3. Effect of PEB temperature on the dissolution rate of the exposed (■) and unexposed (◆) 1.0 μm films (PAA / TBMPF / PTMA : 84 / 8 / 8 wt%). The *g*-line exposure and PEB time were fixed to be 200 mJ/cm^2 and 2 min, respectively.

100 $^{\circ}\text{C}$, the resist films were removed from silicon wafers during development. The dissolution rate of the exposed area decreases with increasing the PEB temperature, and becomes insoluble in a 2.38 wt% TMAH aq. with 5 wt% IPA. This behavior can be explained by imidization of PAA as described above. On the other hand, the film of unexposed area does not dissolve at all in the temperature range of 110 to 150 $^{\circ}\text{C}$. The highest dissolution contrast (DC) is obtained at 110 $^{\circ}\text{C}$, where the PEB time and exposure dose are 2 min and 200 mJ/cm^2 , respectively.

Next, the effect of PEB time is summarized in Figure 4. The PEB time is changed from 0 to 120 sec where the PEB temperature and exposure dose are fixed to be 110 $^{\circ}\text{C}$ and 200 mJ/cm^2 , respectively. The DC reaches around 100 times for 60 sec.

Then, the effect of TBMPF content on the dissolution rate of the film was investigated under the same conditions. Increasing TBMPF content affords the lower dissolution rate of the unexposed area (Figure 5). The dissolution rate becomes nearly zero under 8 wt% TBMPF loading to PAA. Finally, the effect of PTMA content on the dissolution rate of the film was studied (Figure 6). The dissolution rate of the exposed area increases with increasing PTMA loading and the DC reaches around 100 times in the presence of 8 wt% PTMA.

Based on these preliminary optimization studies, the PSPI consisting of PAA (84 wt %), TBMPF (8 wt %) and PTMA (8 wt %) was formulated. The photosensitivity curve of a film 1.0 μm

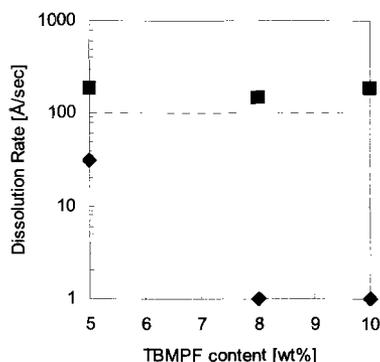


Figure 4. Effect of PEB time on the dissolution rate of the exposed (■) and unexposed (◆) 1.0 μm films (PAA / TBMPF / PTMA : 84 / 8 / 8 wt%). The *g*-line exposure

and PEB temperature were fixed to be 200 mJ/cm^2 and to be 110 $^{\circ}\text{C}$, respectively.

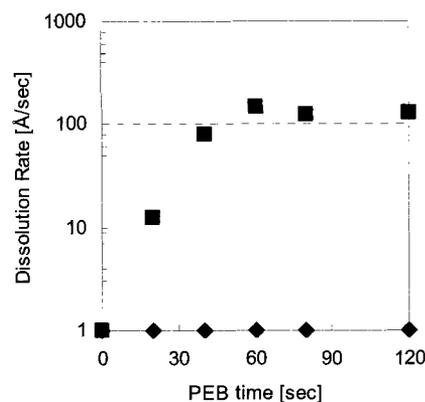


Figure 5. Effect of TBMPF content on the dissolution rate of the exposed (■) and unexposed (◆) 1.0 μm films. The *g*-line exposure and PEB were fixed at 200 mJ/cm^2 and at 110 $^{\circ}\text{C}$ for 2 min, respectively.

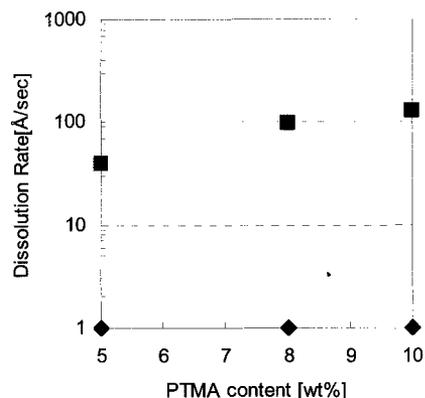


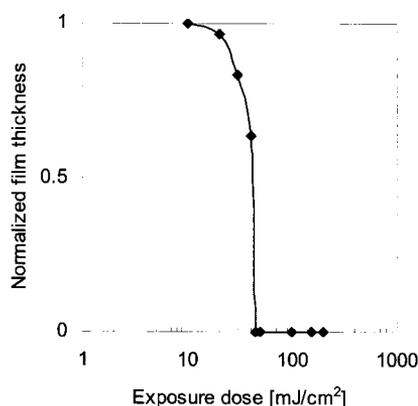
Figure 6. Effect of PTMA content on the dissolution rate of the exposed (■) and unexposed (◆) 1.0 μm films. The *g*-line exposure and PEB were fixed at 200 mJ/cm^2 and at 110 $^{\circ}\text{C}$ for 2 min, respectively.

thick is shown in Figure 7 (PEB treatment was conducted at 110 $^{\circ}\text{C}$ for 2 min and developed with a 2.38 wt% TMAH aq. / 5 wt% IPA). This resist system realized excellent photosensitivity (D_0) of 45 mJ/cm^2 and contrast (γ_0) of 12 with *g*-line exposure. This PSPI has an excellent sensitivity and a high contrast. The high sensitivity is attributed to the chemically amplified resist system.

Figure 7. Characteristic photosensitivity curve of PSPI (PAA / TBMPF / PTMA : 84 / 8 / 8 wt%) in 1 μm film. The PEB temperature, PEB time, and development time were fixed at 110 $^{\circ}\text{C}$, for 2 min, and for 30 sec, respectively.

2.4. Image Formation

Figure 8 shows a SEM image of the line and space patterning of 1.4 μm thick film obtained by a



contact-printing mode. The clear positive-type pattern film with 4 μm resolution is observed (Figure 8). This patterned film is successfully converted to the corresponding PI pattern by curing at 250 $^{\circ}\text{C}$ for 1 h in the air as shown in Figure 9. After thermal curing, the thickness of PAA film was reduced from 1.2 μm to 1.0 μm due to cyclization involving the elimination of H_2O , removal residual solvent, and the decomposition of unconverted additives such as TBMPF and PTMA.

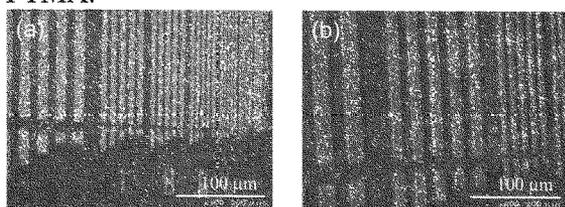


Figure 8. SEM images of positive pattern; (a) a 1.4- μm film thickness of PAA (PAA / TBMPF / PTMA : 84 / 8 / 8 wt%). The g -line exposure and PEB were fixed at 200 mJ/cm^2 , and at 110 $^{\circ}\text{C}$ for 2 min, respectively. (b) a 1.0- μm film thickness of PI cured at 250 $^{\circ}\text{C}$ for 0.5 h in air.

3. Conclusions

A positive-type chemically amplified PSPI based on the PAA, TBMPF as a dissolution inhibitor, and

PTMA as a photo acid generator has been developed. The photosensitivity and contrast of 1.2 μm thick resist film consisting of PAA (84 wt %), TBMPF (8 wt %), and PTMA (8 wt %) were 45 mJ/cm^2 and 12, respectively. This PSPI produced a clear positive-tone image with 4- μm features, and this pattern was converted subsequently into the corresponding PI upon heating at 250 $^{\circ}\text{C}$. This three-component PSPI system will be applied to a PAA which has moderate dissolution rate in a 2.38 wt% TMAH aq.

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