Pattern formation of polyimide

by using photosensitive polybenzoxazole as a top layer

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1. Introduction

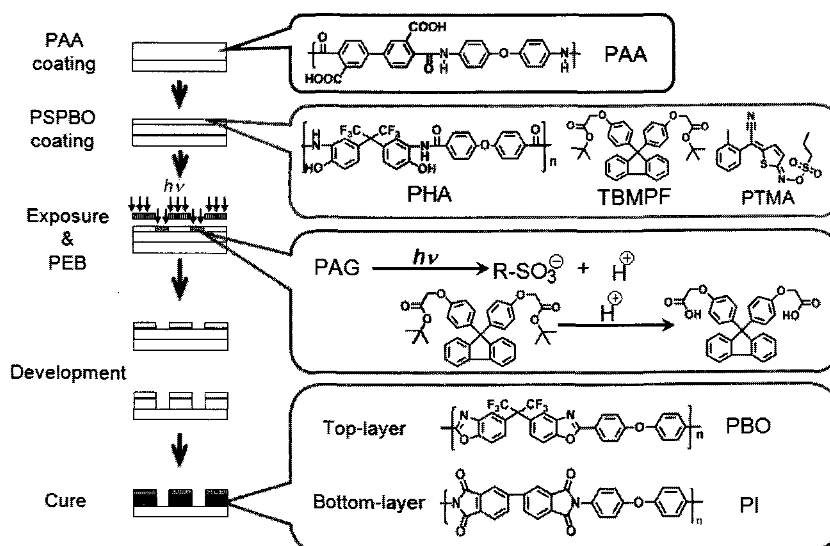
Protecting and insulating materials for microelectronics require essential properties such as high thermal stability, high mechanical property, insulating performance, and so on. Polyimides (PIs) and poly(benzoxazole)s (PBOs) are an important class of advanced materials and fulfill the above requirements, so photosensitive PIs (PSPIs) and PBOs (PSPBOs), which are formed by the addition of a photosensitizing agent to PIs and PBOs, have been widely used in microelectronics fields [1-12].

In general, PSPBOs are easily formulated from a precursor, poly(*o*-hydroxyamide) (PHA), and the photo-sensitizer, diazonaphthoquinone (DNQ) as a dissolution inhibitor [13-15]. Since the phenol group of PHA provides adequate solubility in an alkaline developer such as a 2.38 wt% tetramethylammonium hydroxide aqueous solution (TMAHaq), positive images are obtained at the exposed area. Furthermore, PSPBOs introducing a chemically amplified system normally show high sensitivity [16-19].

On the other hand, it is difficult to form TMAHaq-developable positive-type PSPIs based on a PI precursor, poly(amic acid)s (PAAs), because the dissolution rate of PAAs in a TMAHaq solution is too high to obtain proper dissolution contrast between exposed and unexposed areas due to the high acidity of the carboxylic acid in PAA. A few TMAHaq-developable positive-type PSPIs have been reported [20-22], where highly fluorinated or partially esterified PAAs are used to reduce the dissolution rate in TMAHaq. Recently, we have developed a chemically amplified positive-type PSPI which could be developed in a TMAHaq solution and showed good sensitivity [23]. This PSPI was directly formulated from a PAA-polymerized solution, a vinyl ether crosslinker, a thermobase generator and a photoacid generator (PAG). Although the formulation of this PSPI is facile, the physical properties are strongly affected by the residues of the crosslinker and the PAG. Additionally, these residues will cause

out-gassing from films and fretting metal lines. These are generally unavoidable phenomena of PSPIs, because PSPIs include several additional compounds other than PAAs. On the other hand, photoresists were previously used for the patterning of PIs, and then the resists were removed after an etching process.

Herein we use PSPBO as a photoresist for PAA patterning, which is unnecessary to remove after development, and report the successful development of a TMAHaq-developable, chemically amplified, positive-type patterning of PI using a novel two-layer system based on a pristine PAA thick bottom-layer and a PSPBO thin top-layer consisting of 9,9-bis[4-(*tert*-butoxycarbonylmethyloxy)phenyl]fluorene (TBMPF) [24] as a dissolution inhibitor, and (5-propylsulfonyloxyimino-5*H*-thiophene-2-ylidene)- (2-methylphenyl)acetonitrile (PTMA) as a PAG. The patterning process of this two-layer system is shown in Scheme 1.



Scheme 1. Patterning process of two-layer system.

Firstly, the PAA solution is spin-coated on a silicon wafer and baked in the usual way. Then, the thin layer of PSPBO consisting of PHA, TBMPF and PTMA is formed onto the thick PAA film and dried by pre-baking. This film is exposed to UV light to generate propanesulfonic acid from PTMA. Upon post-exposure bake (PEB) treatment of the film, the acid deprotects the *tert*-butyl ester of TBMPF and gives the corresponding carboxylic acid. The exposed compartment of the PSPBO layer is developed with 2.38 wt% TMAHaq to provide a positive image. Subsequently, the PAA sublayer is developed under the patterns of PSPBO. As a result, a positive PAA image is obtained. These PSPBO-PAA patterns are converted to PBO-PI patterns by thermal cyclization. As a consequence, a pristine PAA pattern is obtained because there are no additives to PAA, so the problems of out-gassing and fretting metal lines due to PAG are solved. In addition, it is unnecessary to remove the PSPBO layer

as a thin top-layer after the formation of the PAA pattern due to its utility as a buffer coating material. TMAHaq-developed and positive-type patterns of PIs could be obtained from various PAAs by using this two-layer system.

2. Results and discussion

Based on our previous works [17, 24], *t*-BocBHF and TBMPF were chosen as dissolution inhibitors for PSPBO layer. First, the relationship between the decomposition percentages of dissolution inhibitor and the dissolution rates of PSPBO at each temperature were studied. Under optimization conditions in our previous works [17, 24], PSPBO films consisting of PHA (77 wt%), *t*-BocBHF (20 wt%) and PTMA (3 wt%) were exposed to 100 mJ/cm^2 of *i*-line and post-exposure baked at a set temperature for 5 min. Subsequently, these films were dissolved in DMSO-d_6 and the molar ratios of *t*-BocBHF and the corresponding phenol were calculated from the integration of the *tert*-butyl signal observed in ^1H NMR spectra. In a similar way, PSPBO films consisting of PHA (74 wt%), TBMPF (22 wt%) and PTMA (4 wt%) were exposed to 200 mJ/cm^2 of *i*-line and post-exposure baked at a set temperature for 2 min. The molar ratios of TBMPF and the corresponding carboxylic acid were also calculated from the integration of the methylene signal in ^1H NMR spectra. The decomposition percentages and the corresponding dissolution rates at each PEB temperature are summarized in Figure 1. They increase by increasing the PEB temperature. *t*-BocBHF and TBMPF almost decompose above a PEB temperature of 130 °C. However, the dissolution rate of the PSPBO using TBMPF is 2 or 3 times higher than that using *t*-BocBHF. It indicates that the corresponding carboxylic acid generated from TBMPF accelerates the dissolution rate of PHA film due to the higher acidity of the carboxylic acid than that of phenol. Therefore, TBMPF is a more suitable dissolution inhibitor than *t*-BocBHF.

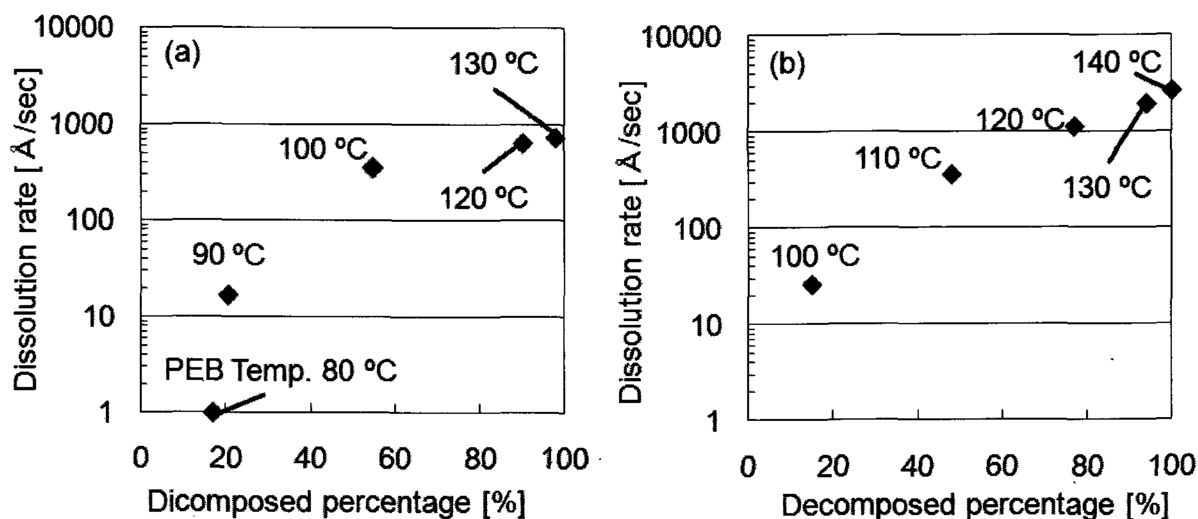


Fig. 1. The decomposed percentages of dissolution inhibitor and the corresponding dissolution rates at each PEB temperature: (a) *t*-BocBHF in PSPBO film (1.2 μm) constructed of PHA, *t*-BocBHF, and PTMA (77/20/3 w/w/w), (b) TBMPF in PSPBO film (1.6 μm) constructed of PHA, TBMPF, and PTMA (74/22/4 w/w/w).

To obtain contrasting pattern profiles from the exposed and unexposed areas, the effects of PEB temperature, PEB time, PSPBO layer thickness and exposure dose were investigated in detail. The 1.5-μm-thick PAA films were obtained by spin-casting from diluted polymerization solutions of PAA on a silicon wafer, and then pre-baked at 100 °C for 2 min in air. Subsequently, PSPBO thin film consisting of 74 wt% PHA, 22 wt% TBMPF, 4 wt% PTMA was prepared by spin-coating from their cyclohexanone solution on PAA film, and then pre-baked under the same condition while drying the PAA film. The thickness of the PSPBO layer was around 150 nm, measured by a surface profiler. These two-layer photosensitive films were irradiated with UV light at the *i*-line using a filtered super-high-pressure mercury lamp, baked after exposure at a set temperature, and developed with TMAHaq/5 wt% *i*PrOH at 25 °C. To improve compatibility between the developer and PHA containing a high hydrophobic hexafluoroisopropylidene unit, 5 wt% *i*PrOH was added to a 2.38 wt% TMAHaq solution. To clarify the difference in the dissolution behavior between the exposed and unexposed areas, the dissolution rates were estimated by the change in film thickness before and after development.

The PEB temperature is crucial for chemically amplified resist systems because the decomposition percentage of TBMPF and the following dissolution rate depend on the PEB

temperature. As shown in Figure 2, the dissolution rate at the exposed area is relatively low with PEB at 100~110 °C, because TBMPF in PSPBO layer is not fully decomposed at that PEB temperature. On the other hand, the large DC between the exposed and unexposed areas in 2.38 wt% TMAHaq/5 wt% *i*PrOH is obtained with PEB at 120~150 °C due to enough decomposition of TBMPF.

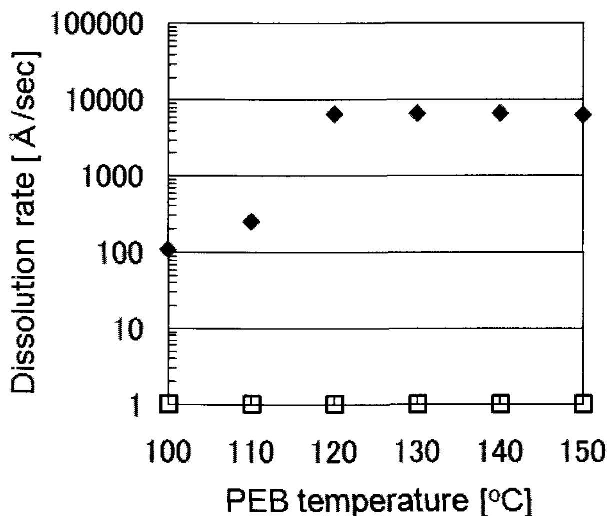


Fig. 2. Effect of PEB temperature on the dissolution rate for the two-layer resist system based on the PSPBO (150 nm)/PAA (1.5 μm) under exposed (♦) and unexposed area (□). The PSPBO was constructed of PHA, TBMPF, and PTMA (74/22/4 w/w/w). The pre-bake, the *i*-line exposure and PEB time were fixed to 100 °C for 2 min, 200 mJ/cm^2 and for 2 min, respectively.

The effect of PEB time on the dissolution rate of the film was investigated, as shown in Figure 3. The dependence of the dissolution rate on PEB time is almost not observed at a PEB temperature of 130 °C. The sulfonic acid generated from PTMA diffuses efficiently within a short PEB time because the PSPBO layer is very thin.

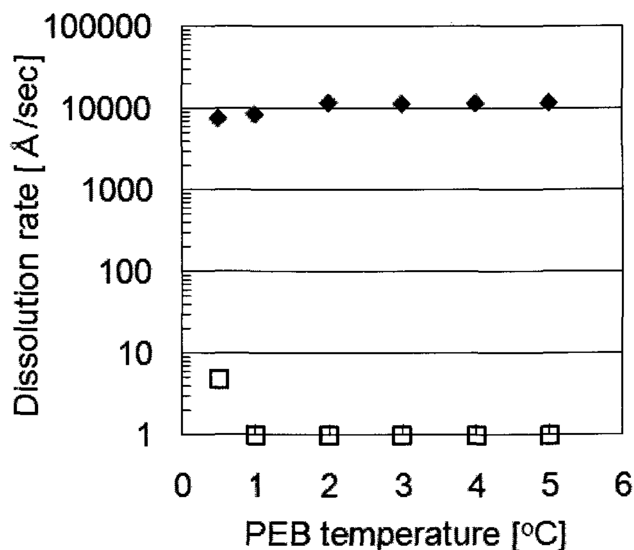


Fig. 3. Effect of PEB time on the dissolution rate for the two-layer resist system based on the PSPBO (150 nm)/PAA (1.5 μm) under exposed (♦) and unexposed area (□). The PSPBO was constructed of PHA, TBMPF, and PTMA (74/22/4 w/w/w). The pre-bake, the *i*-line exposure and PEB temperature were fixed to 100 °C for 2 min, 200 mJ/cm^2 and at 130 °C, respectively.

The effect of the PSPBO layer thickness on the dissolution rate is shown in Figure 4. Even in a 20-nm thickness of a PSPBO layer, a large DC is obtained. It is assumed that the developer could not penetrate into the PSPBO layer because of a short developing time (within 2 sec).

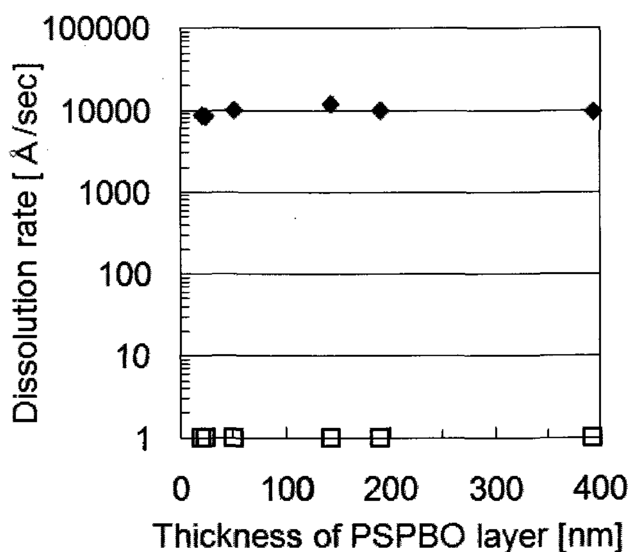


Fig. 4. Effect of PSPBO layer thickness on the dissolution rate for the two-layer resist system based on the PSPBO/PAA (1.5 μm) under exposed (♦) and unexposed area (□). The PSPBO was constructed of PHA, TBMPF, and PTMA (74/22/4 w/w/w). The pre-bake, the *i*-line exposure and PEB conditions were

fixed to 100 °C for 2 min, 200 mJ/cm^2 and at 130 °C for 2 min, respectively.

Based on studies involving PEB temperature and time, a resist film consisting of a 1.5-μm-thick PAA bottom-layer and a 150-nm-thick PSPBO top-layer consisting of PHA (74 wt%), TBMPF (22 wt%), and PTMA (4 wt%) was formulated. The photosensitivity curve of resist films is shown in Figure 5. This resist film shows high sensitivity (D_0) of 35 mJ/cm^2 and good contrast (γ_0) of 10.3.

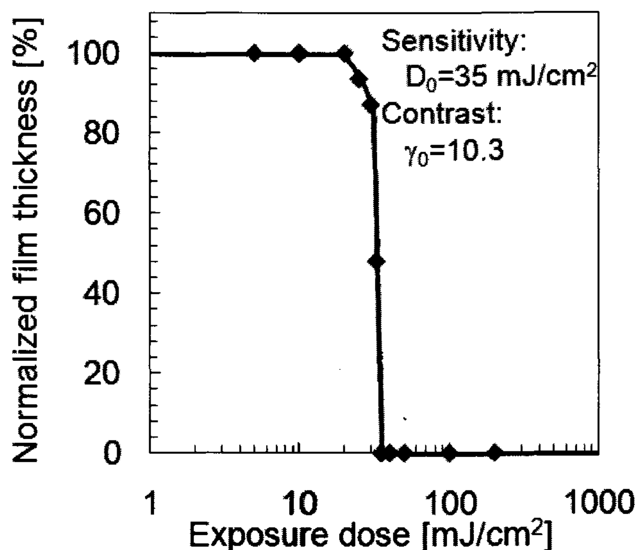


Fig. 5. Characteristic photosensitive curve for two-layer resist system based on the PSPBO (150 nm)/PAA (1.5 μm). The pre-bake and PEB conditions were fixed to 100 °C for 2 min and at 130 °C for 2 min, respectively.

Figure 6a shows the SEM image of a patterned film obtained with a system described as follows: the resist layer was exposed to 100 mJ/cm^2 of *i*-line, post-baked at 130 °C for 2 min, and developed with 2.38wt% TMAHaq/5wt% *i*PrOH at 25 °C for 2 sec. A clear and positive pattern with a 4-μm feature could be observed when using a 2.0-μm-thick film, in which the thickness of the PSPBO layer was 200 nm. The printed pattern was cured to the PBO/PI film by heating at an elevated temperature up to 250 °C for 30 min and then 350 °C for 30 min under nitrogen (Figure 6b). The formation of the PBO/PI film was confirmed by IR spectrum. The film thickness was changed to 1.5 μm and the PBO/PI pattern shrank slightly because of a cyclodehydration reaction. Figure 7 shows cross-section views of the non-cured and the cured two-layer film. A boundary line between the PAA and PSPBO layers is clearly observed, which indicates that the PSPBO layer is not miscible with the PAA layer (Figure 7a). After the curing process, the resulting PI pattern is covered with the PBO top-layer and the merged layer is

observed between both layers (Figure 7b). The peeling-off phenomenon between the PBO and PI layers is not observed, which indicates this two-layer pattern is integrated together by thermal curing process.

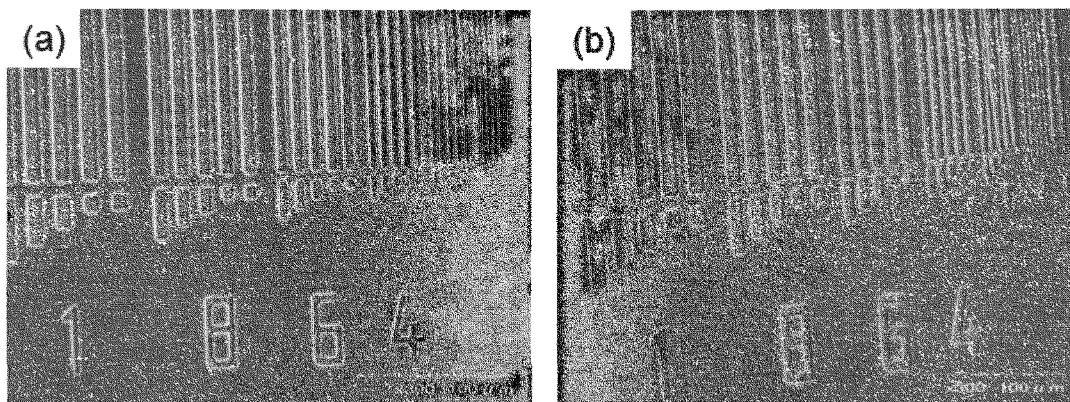


Fig. 6. SEM images of positive-patterns: (a) a 2.0 μm-thick two-layer film based on the PSPBO (200 nm)/PAA (1.8 μm). The PSPBO was constructed of PHA, TBMPF, and PTMA (74/22/4 w/w/w). The pre-bake, the *i*-line exposure and PEB conditions were fixed to 100 °C for 2 min, 200 mJ/cm^2 and at 130 °C for 2 min, respectively, (b) a 1.4 μm-thick PI/PBO film cured at 250 °C for 30 min and then 350 °C for 30 min under nitrogen.

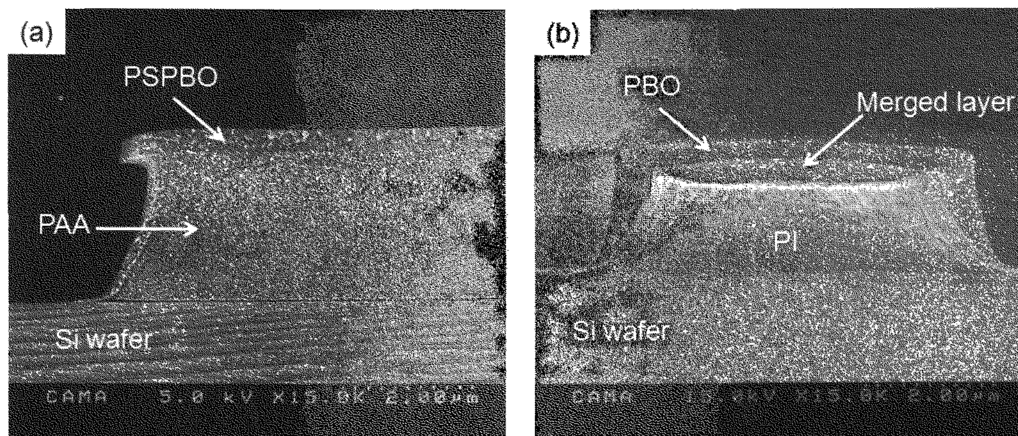


Fig. 7. Cross-section views of the two-layer film observed by SEM: (a) PSPBO/PAA film, (b) PBO/PI film after the curing process at 250 °C for 30 min and then 350 °C for 30 min under nitrogen.

4. Conclusion

A novel PI patterning system consisting of PAA and PSPBO bi-layers has been developed. The acid-catalyzed deprotection of TBMPF as a dissolution inhibitor for PSPBO immediately occurred in the presence of acid in the PEB process and a high dissolution rate was achieved. Positive-type and alkaline-developable PI patterns were easily formed by spin-casting the PSPBO consisting of PHA,

TBMPF, and PTMA on PAA film. The new resist system showed high sensitivity and contrast of 35 mJ/cm^2 and 10.3, respectively with *i*-line exposure. Furthermore, the clear positive image after development was converted to a patterned PBO/PI film. The new pattern formation of PI provides a more efficient and versatile process compared to that using conventional PSPIs that requires a large amount of a photosensitizing agent or matrix polymers having complex structures.

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