Alkaline developable Positive type Photosensitive Polyimide Based on Fluorinated PAA, PAA, and Fluorinated diazonaphthoquinone

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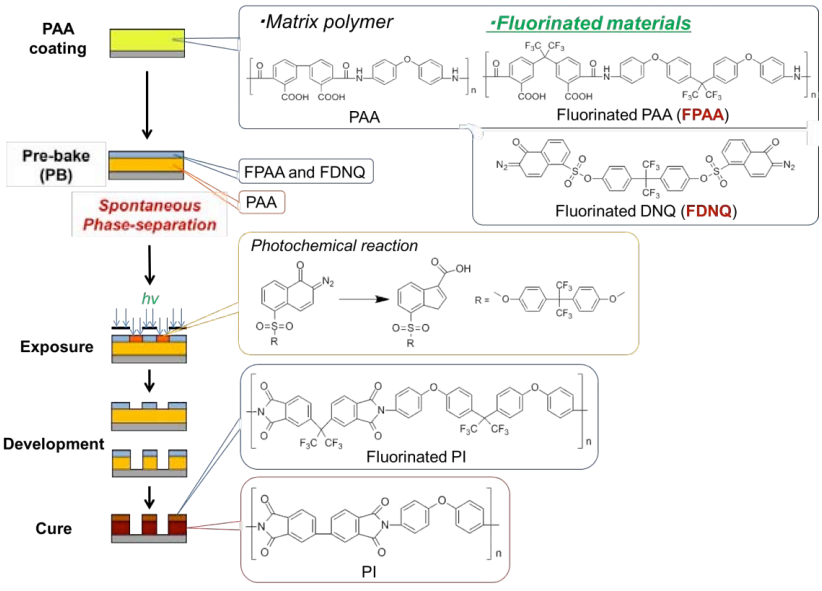
Introduction

Photosensitive PIs (PSPIs) have been widely applied as stress buffer and insulation layers due to their excellent thermal and reasonably dielectric properties.[1] Positive type PSPIs are suitable to avoid the swelling of negative type PSPIs. In addition, the environmentally-friendly fabrication and patterning process are required in microelectronics filed without exception. Thus, an alkaline aqueous solution is preferable as a developer in place of organic developers. PAAs possess hydrophilic carboxylic groups and show promise as PSPI precursors. However, the dissolution rate of PAAs in a 2.38 wt% aqueous tetramethylammonium hydroxide (TMAHaq) solution is too high to obtain a sufficient dissolution contrast between unexposed and exposed areas due to the high acidity of the carboxylic acids in PAAs.

Recently, we have developed a chemically amplified positive-type PSPI consisting of PAA, a vinyl ether cross-linker, a thermo-base generator and a photo-acid generator (PAG).[2] The formulation of this PSPI is facile, but the physical properties are strongly affected by the residues of the cross-linker and the PAG. Additionally, these residues will cause out-gassing from films and fretting metal lines. To remedy these problems, quite recently, we have reported a versatile method for positive-type patterning of PI based on a novel two-layer system consisting of a pristine PAA thick bottom-layer and a PSPBO thin top-layer consisting of 9,9-bis[4-(*tert*-butoxycarbonylmethyloxy)phenyl]fluorene as a dissolution inhibitor, and (5-propylsulfonyloxyimino-5*H*-thiophene-2-ylidene)-(2-methylphenyl)acetonitrile (PTMA) as a PAG.[3] This PI patterning is versatile, but still requires two steps to form two-layer. To provide a more efficient and versatile process, the new pattern formation of PI should be developed.

In this paper, we report a more straightforward pattern formation of PI by using a fluorinated PAA (FPAA), a PAA, and a fluorinated diazonaphthoquinone (FDNQ) as a photoactive compound. The solution of FPAA, PAA, and FDNQ is spin-coated on a silicon wafer and prebaked. The two phase-separated layers, a thin layer of FPAA containing FDNQ and a thick layer of PAA, is formed due to a large polarity difference of FPAA and PAA. Then, the film is exposed by the *i*-line through a photomask to produce an indenecarboxylic acid. The photoproduct, unlike its precursor, is extremely soluble in aqueous base by virtue of the photogenerated carboxylic acid functionality. The dissolution rate of the exposed area to TMAHaq increases and a positive image is formed (Scheme).



Scheme Patterning process of the resist based on FPAA, PAA, and

FDNQ-1.

Results and Discussion

Figure 1 shows the cross-sectional SEM image of the patterned **PAA** film (**PAA** (85 wt%), **FPAA** (15 wt%) and **FDNQ-1** (25 wt% to polymers)). PB condition was 130 ºC for 2 min. A clear phase separation is observed in which the polar **PAA** and the fluorinated components (**FPAA** and **FDNQ-1**) are located in the bottom and top layers, respectively, indicating that **FDNQ-1** with very high hydrophobic property efficiently promotes the phase separation.

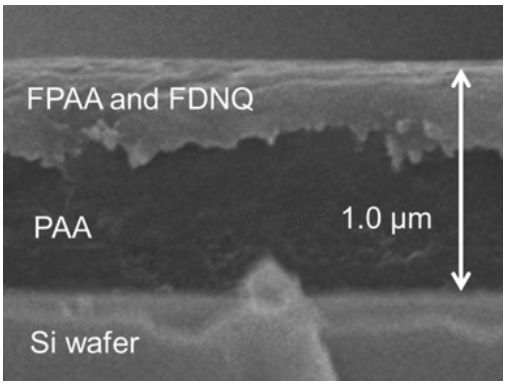


Figure 1 shows the cross-sectional SEM image

Based on these preliminary optimization studies involving the PB temperature and time and the composition of **PAA**, **FPAA**, and **FDNQ-1**, the **PSPI** containing **PAA**(85 wt%), **FPAA** (15 wt%), and **FDNQ-1** (25 wt% to polymers) was formulated. The photosensitive curve of the resist films with a 1.2-μm thickness is shown in Figure 2. The **PSPI** has an excellent sensitivity of 60 mJ/cm^2 and a good contrast of 3.3 with *i*-line exposure.

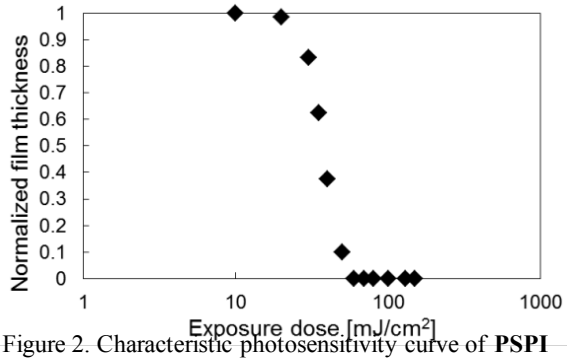


Figure 2. Characteristic photosensitivity curve of **PSPI**

The SEM image of the contact-printed pattern was obtained using the **PSPI** film (Figure 2). The **PSPI** consisting of **PAA**(85 wt%), **FPAA** (15 wt%), and **FDNQ-1** (25 wt% to polymers) was pre-baked at 130 ºC for 2 min, exposed to 100 mJ/cm^2 of the *i*-line, and developed with 0.238 wt% TMAHaq for 5 sec. Consequently, a clear positive pattern was successfully obtained with a 6-μm feature on a 1.0-μm thick film.

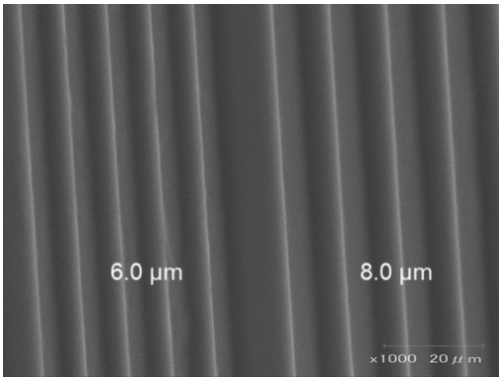


Figure 3**.** SEM image of patterned **PAA**

Conclusions

A new photoactive compound, **FDNQ-1** that acts as a dissolution inhibitor for aqueous base development of **FPAA**, has been developed. **FDNQ-1** has been successfully used to develop an alkaline-developable and positive-type **PSPI** based on **FPAA** and **PAA**. This resist solution was spin-coated on a silicon wafer and prebaked, spontaneously forming the two phase-separated layers after PB treatment, that is, a top thin layer of **FPAA** containing **FDNQ-1** and a bottom thick layer of **PAA** with PB treatment. The exposed compartment of the thin layer of **FPAA** containing **FDNQ-1** was developed with 0.238 wt% TMAHaq to provide a positive image. Subsequently, the **PAA** layer was developed under the pattern of the top layer. As a result, a positive **PAA** image is obtained. The **PSPI** exhibited an excellent sensitivity of 60 mJ/cm^2 and a good contrast of 3.3 with *i*-line exposure, and delineated a fine positive pattern of 6 μm. This positive type **PSPI** resist system can be one of the candidates for the next generation microchip fabrication process which provides a facile formulation of **PSPI**.

References

1. Fukukawa, K.; Ueda, M. *Polym. J.* 40, 281-296 (2008).2. Ogura T, Higashihara T, Ueda M. *J. Polym. Sci. Part-A, Polym. Chem.,* 47, 3362-9 (2009).3. Ogura T, Higashihara T, Ueda M. *Eur. Polym. J.,* **46**, 1576 – 1581 (2010).