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# Alkaline-developable and Positive-type Photosensitive Polyimide based on Fluorinated Poly(amic acid) from Diamine with High Hydrophobicity and Fluorinated Diazonaphtoquinone

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An alkaline-developable positive-type photosensitive polyimide (**PSPI**) based on fluorinated poly(amic acid) (**FPAA**) and fluorinated diazonaphtoquinone (**FDNQ**) as a photoactive compound has been successfully developed as a promising material for use in microelectronics. The **FPAA** was prepared from 4,4'-(hexafluoroisopropylidene)diphtahlic anhydride and aromatic diamines, 4,4'-oxydianiline (80 mol%), and 4,4'-oxybis(4-phenoxyaniline) (20 mol%). The **PSPI** consisting of **FPAA**, catechol (3 wt% to **FPAA**), and **FDNQ** (25 wt % to **FPAA**) showed a high sensitivity of 45 mJ/cm$^2$ and a high contrast of 10 when it was exposed to a 365 nm line (*i*-line), and developed with 2.38 wt % TMAHaq for 10 seconds at room temperature. A clear positive image of a 6-μm line and space pattern was printed on a film, which was exposed to 80 mJ/cm$^2$ of *i*-line by a contact printing mode. Thus, this system will be a good candidate for next generation **PSPIs**.

**Keywords: photosensitive polyimide, fluorinated poly(amic acid), fluorinated diazonaphtoquinone, alkaline-developable, positive-type, photoactive compound.**

## 1. Introduction

Polyimides (PIs) are some of the best super-engineering plastics and have been widely used in microelectronics, such as a stress buffer and insulation layers due to their excellent thermal, mechanical and reasonable dielectric properties. For use in these applications, micro-fabricating properties using photolithography techniques are required. There are two types of photolithographic processes. One is to make a PI pattern by etching through a photoresist pattern, which is known as the conventional method, and the other is to use photosensitive PIs (**PSPIs**). **PSPIs** simplify processing and avoid the use of photoresists in the microelectric industry [1-15]. **PSPIs** are divided into two types, i.e. the positive and negative types. Recently, much effort have been extended to develop positive-type **PSPIs** because of their several advantages compared to negative **PSPIs**, such as a high resolution due to low swelling during development and the use of an alkaline aqueous solution as a developer in place of organic

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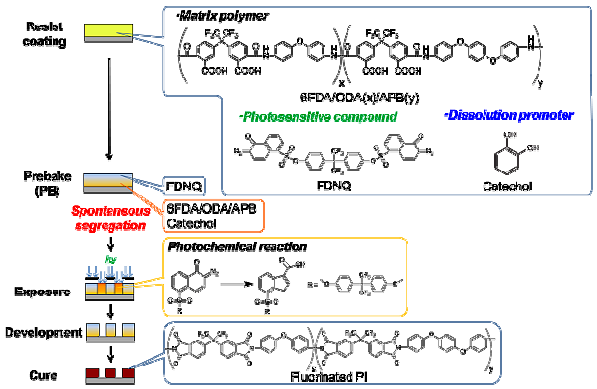
developers. Furthermore, they form a V-type pattern which is suitable for a wire-bonding process. However, the dissolution rate of precursory **PAAs** in a 2.38 wt% tetramethylammonium hydroxide solution (TMAHaq) used as the aqueous alkaline developer is too high to obtain a sufficient dissolution contrast between the unexposed and exposed areas due to the high acidity of the carboxylic acids in the **PAAs**. Therefore, only a few TMAHaq-developable positive-type **PSPIs** have been reported in which highly fluorinated or partially esterified **PAAs** are used to reduce the dissolution rate in the TMAHaq [16-19]. To decrease the dissolution rate of **PAAs** in the 2.38 wt% TMAHaq, more hydrophobic **PAAs** should be prepared from diamines and/or tetracarboxylic dianhydrides with a high hydrophobicity.

Based on these considerations, we have reported the **PSPI** consisting of the fluorinated **PAA** (**FPAA**) obtained from 4,4'-(hexafluoroisopropylidene)diphtahlic anhydride (**6FDA**), 4,4'-oxydianiline (**ODA**), and a new fluorinated diazonaphthoquinone (**FDNQ**) as a photoactive compound prepared by the reaction of 1,2-naphthoquinone-2-diazo-5-sulfonyl chloride with 4,4'-(hexafluoroisopropylidene)diphenol [20]. In this system, the **FDNQ** is spontaneously segregated at the surface of the film during the prebaking step due to the high polarity difference between **FPAA** and **FDNQ**. Thus, the dissolution rate in the 2.38 wt% TMAHaq significantly decreases on the surface of the film. This PI patterning is simple, but still requires more than a 120 mJ/cm$^2$ dose and 2.38 wt% TMAHaq containing isopropyl alcohol (IPA). In addition, the development time was very short, only one second. Thus, a novel **PSPI** should be developed to remedy these problems, and be suitable for use in a practical process.

This article describes the development of an alkaline developable and positive-type **PSPI** consisting of the **FPAA** from **6FDA**, **ODA**, 1,4-bis(4-aminophenoxy)benzene (**APB**), and **FDNQ** in which **APB** with high hydrophobicity was introduced to reduce the solubility of **FPAA** in the alkaline developer. Scheme 1 shows the photolithographic process. The solution of **FPAAx** and **FDNQ** is spin-coated on a silicon wafer and prebaked. The **FDNQ** rich top layer is spontaneously formed. The film is then exposed to the *i*-line through a photomask to produce an indenecarboxylic acid by a photochemical reaction. The indenecarboxylic acid is extremely soluble in the alkaline aqueous developer. As a result, the dissolution rate of the exposed area to the 2.38 wt% TMAHaq increases and a positive image is formed. The new **PSPI** possesses several advantages over previous TMAHaq-developable and positive-type **PSPIs**, such as a higher sensitivity for the PI patterning and longer development time. Furthermore, the development is carried out with 2.38 wt% TMAHaq without using IPA.




Scheme 1**.** Patterning process of the resist based on **FPAAx** and **FDNQ**

## 2. Experimental

2-1. Marerials

*N*,*N*-Dimethylacetamide (DMAc) and tetrahydrofuran (THF) were purified by vacuum distillation. The commercially available monomers, 4,4'-oxydianiline (**ODA**), 1,4-bis(4-aminophenoxy)benzene (**APB**) and 4,4'-(hexafluoroisopropylidene)diphthalic anhydride (**6FDA**) were purchased from Tokyo Chemical Industry Co., Ltd. **6FDA** was purified by vacuum sublimation. The new fluorinated diazonaphthoquinone (**FDNQ**) was prepared from 1,2-naphthoquinone-2-diazo-5-sulfonyl chloride with 4,4'-(hexafluoroisopropylidene) diphenol according to our previous paper [19]. A 2.38 wt% TMAH aqueous solution was used as a standard developer. Other reagents and solvents were used as received.

2-2. Synthesis of **FPAA** from **6FDA**, **ODA** and **APB**

**6FDA** (0.444 g, 1.00 mmol) was added to a solution of **ODA** (0.168 g, 0.84 mmol) and **APB** (0.061 g, 0.21 mmol) in DMAc (3.81 mL). This solution was stirred at room temperature for 1 h. An inherent viscosity of the **FPAA** in DMAc was 0.32 dL $g^{-1}$ at a concentration of 0.5 g $dL^{-1}$ in DMAc at 30 °C.

2-3. Degree of imidization.

The polymer solution (**FPAA**) was diluted with DMAc to a concentration of 15 wt%. This solution was spin-coated on a silicon wafer, baked at 80 °C for 60 min in air. The film thickness was about 1.1–1.2 μm. Then, the films were baked on a hot-plate at each temperature (100–250 °C) for 5 min. A reference PI film was prepared by heating at 250 °C for 0.5 h and 350 °C for 1 h. Absorption intensities on a FTIR spectrum at 1376 $cm^{-1}$ ($A_{1376}$) attributed to the C–N stretching of an imide group and at 1500 $cm^{-1}$ ($A_{1500}$) attributed to C=C stretching of a phenyl group were measured, and the degrees of imidization were determined using the following equation;

$$\text{Imidization}(\%) = \frac{A_{1376}/A_{1500(samp)} - A_{1376}/A_{1500(init)}}{A_{1376}/A_{1500(imide)} - A_{1376}/A_{1500(init)}} \quad (1)$$

where subscripts between parentheses that followed $A_{1376}/A_{1500}$ in the equation indicate the states of the polymer films; for example, (samp) is the polymer sampled at each heating temperature (100–250 °C); (init) is initially prebaked **PAA** at 80 °C for 1 h and (imide) is the fully cured polymer at 250 °C for 0.5 h and 350 °C for 1 h in air.

2-4. Dissolution rate.

**FDNQ** was added into the mixture of **FPAA** solution in DMAc (the total solid content was 15 wt %). The resist films with 1.2 μm thickness were obtained by spin-coating from the solutions on silicon wafers. These films were pre-baked under each condition, then exposed to a filtered super-high pressure mercury lamp at 365 nm (*i*-line). The dissolution rate (Å/sec) of the film was determined from changes in the film thickness before and after the development with the 2.38 wt% TMAHaq followed by rinsing with water.

2-5. Photosensitivity.

The photosensitive polymer film with 1.2 μm thickness was prepared by dissolving 25 wt% of **FDNQ** in the **FPAA** solution in DMAc, followed by spin-coating on a silicon wafer and prebaking at 120 °C for 2 min, exposure to irradiation at a wavelength of *i*-line with changing an exposure dose, development with 2.38 wt% TMAHaq for 10 sec at room temperature, and rinsing with water. A characteristic photosensitive curve was obtained by plotting a normalized film thickness against the exposure dose (unit: $mJ/cm^2$).

2-6. Measurements

The infrared spectroscopy (IR) was carried out with a Horiba FT- 210 spectrophotometer. The $^1H$ and $^{13}C$ NMR spectra were obtained on a BRUKER DPX-300S spectrometer ($^1H$ at 300 MHz and $^{13}C$ at 75 MHz). Deuterated chloroform ($CDCl_3$) and dichloromethane ($CD_2Cl_2$) were used as solvents with tetramethylsilane as an internal standard. Elemental analyses were performed on a Yanaco MT-6 CHN CORDER with antipyrine as a standard sample. Viscosity measurements were carried out using an Ostwald viscometer at 30 °C in DMAc. The contact angles of water were measured by placing drops of distilled water on the prepared films using a microscope goniometer (Kyowa Interface Science CA-A) at 25 °C. The film thickness was measured with a Veeco Instrument Dektak3 surface profiler. Field emission scanning electron micrographs (FE-SEM) were taken using Hitachi S4500. Pt/Pd was sputtered on films before the SEM measurement.

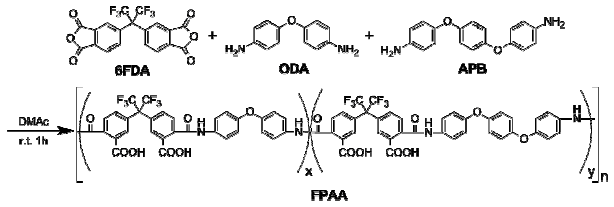
## 3. Results and Discussion

3-1. Lithographic Evaluation

The dissolution rate of **PAA** in 2.38 wt% TMAHaq may depend on the weight percent of the carboxylic acid in the repeating unit. Therefore, the use of a diamine with a high molecular weight would be effective to reduce the dissolution rate of **PAA**. Based on this reasoning, **APB** was selected as a diamine with a high molecular weight.

**FPAAs** were prepared from **6FDA**, **ODA**, and **APB** by changing the molar ratio of **ODA** and

**APB** (Scheme 2). The inherent viscosities of these **FPAAs** in DMAc were controlled around 0.3 $dLg^{-1}$ at a concentration of 0.5 $gdL^{-1}$ at 30 °C.




Scheme 2**.** Synthesis of **FPAA**

To understand the dissolution behavior of the resulting **FPAAs** in the 2.38 wt% TMAHaq, a **FPAA** solution in DMAc was spin-coated on a silicon wafer and prebaked at 120 °C for 2 min. The film with a 1.0 μm thickness was developed with the 2.38 wt% TMAHaq at room temperature. The results are summarized in Table 1.

Table 1 Dissolution rate of **FPAA**

| Polymer | Dissolution rate [Å /sec] |
|---|---|
| FPAA-0 (ODA:APB=100:0)* | 14000 |
| FPAA-0 (FDNQ) | 5500 |
| FPAA-1 (ODA:APB=90:10)* | 12000 |
| FPAA-1 (FDNQ) | 2600 |
| FPAA-2 (ODA:APB=80:20)* | 8000 |
| FPAA-2 (FDNQ) | 1200 |
| FPAA-3 (ODA:APB=70:30)* | 6000 |
| FPAA-3 (FDNQ) | swelling |

*mole ratio

Although the **FPAA** shows a very high dissolution rate around 14,000 Å/sec, the dissolution rate of **FPAA-x** decreases with the increasing molar ratios of **APB/ODA**, and that of **FPAA-3** drops to 6,000 Å/sec. These dissolution behaviors of the resulting **FPAA-x** clearly support our speculation. The effect of the **FDNQ** loading (25 wt%) on the dissolution rate of the film was then studied (Table 1). The dissolution rate of the films containing **FDNQ** was effectively decreased and that of **FPAA-2** reduced to 1,200 Å/sec. On the other hand, a swelling behavior was observed in **FPAA-3** probably due to the high hydrophobicity of **APB**.

Based on these findings, the effects of the **APB** contents, prebake (PB) temperature, **FDNQ** loading, and amounts of catechol as a dissolution promoter were investigated to obtain contrasting pattern profiles from the exposed and unexposed areas.

The films were obtained by spin-casting diluted polymerization solutions of **FPAA** containing **FDNQ** on a silicon wafer, and then prebaking at a set temperature for 2 min in air. These photosensitive polymer films were irradiated with UV light at 365 nm (*i*-line) using a filtered super high pressure mercury lamp, and developed with 2.38 wt% TMAHaq at 25 °C.

First, the effect of the **APB** contents on the dissolution rate of the film was investigated (Fig. 1) in which each film was prebaked at 120 °C for 2 min, and exposed to 80 $mJ/cm^2$. The dissolution rate of the unexposed area abruptly decreases by the increasing **APB** contents, and becomes almost zero in 20 mol% of **APB** to **ODA**, while the exposed area is rapidly dissolved in the developer. The dissolution contrast (**DC**) between the exposed and unexposed areas in the 2.38 wt % TMAHaq reached 10,000 times. Moreover, the development time could be extended to 10 sec by the introduction of hydrophobic **APB** in the **FPAA**. Thus, the **FPAA-2** solution was formulated for the following lithographic evaluation.

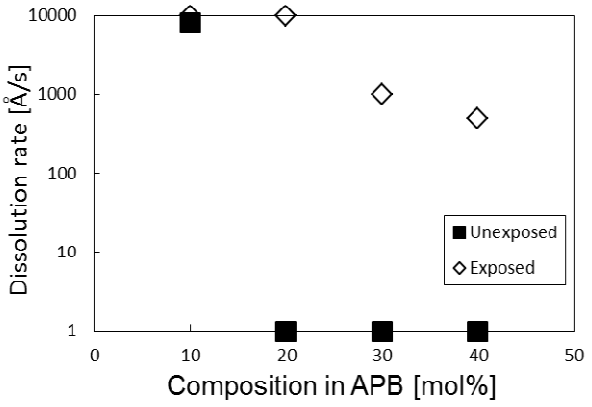



Fig.1 Effect of **APB** contents on the dissolution rate of the exposed and unexposed films (**FPAA** and **FDNQ** (25 wt% to **FPAA**)). The *i*-line exposure dose, PB temperature and PB time were

fixed to 80 mJ/cm$^2$, 120 °C and 2 min, respectively.

The PB temperature is crucial in this system to obtain a high dissolution contrast between the exposed and unexposed areas because the PB temperature directly affects the phase separation behavior. Thus, the effect of the PB temperature was investigated and the results are summarized in Fig. 2. The dissolution rate in the unexposed area decreases with the increasing PB temperature. Very high dissolution contrasts were obtained at 120 °C for 2 min, indicating that the phase separation was efficiently promoted within a short PB time at 120 °C.

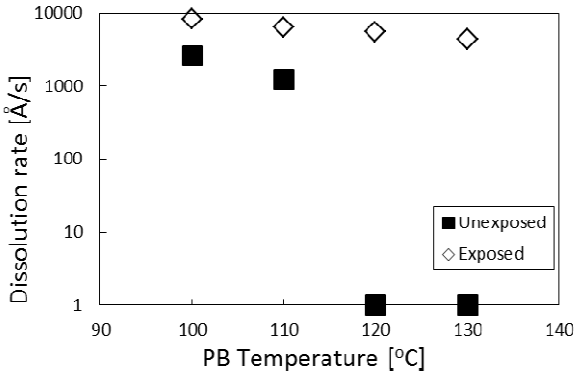



Fig. 2 Effect of PB temperature on the dissolution rate of the exposed and unexposed films (**FPAA-2** and **FDNQ** (25 wt% to **FPAA-2**)). The *i*-line exposure dose and PB time were fixed to 80 mJ/cm$^2$ and 2 min, respectively.

To clarify this behavior, the contact angles of water to the film consisting of **FPAA-2** and **FDNQ** (25 wt%) was measured at each temperature for 2 min. Fig. 3 shows the changes in their contact angles which gradually increase with the increasing PB temperatures, indicating that the phase segregation of **FDNQ** is effectively promoted during the PB treatment.

Since the highest dissolution contrast was obtained after the PB treatment for 2 min, the following lithographic evaluation was conducted based on the PB condition at 120 °C for 2 min. In a similar way, the effect of the **FDNQ** loading on the dissolution rate was investigated with the **FPAA-2**. The 25 wt% **FDNQ** loading for the amount of **FPAA-2** is required to obtain a large dissolution contrast between the exposed and unexposed areas (Fig. 4).

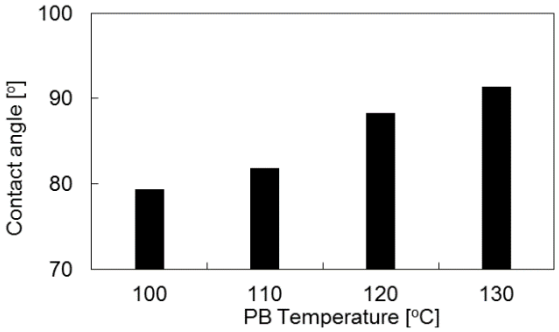



Fig. 3 Contact angles of the films after PB. The films consisting of **FPAA-2** and **FDNQ** (25 wt% to **FPAA**) were used. The PB time was fixed at 2 min.

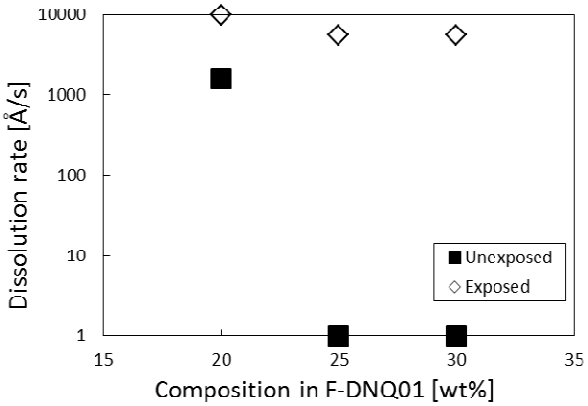



Fig. 4 The effect of **FDNQ** contents on the dissolution rate of the exposed and unexposed films. The *i*-line exposure dose and PB condition were fixed to 80 mJ/cm$^2$, 120 °C for 2 min, respectively.

The dissolution rates of the exposed area are also expected to decrease with the increasing PB temperature due to the imidization of the **PAAs**. Thus, the degree of imidization (DI) in the **FPAA-2** was determined by IR spectroscopy. The DIs were obtained using eq. (1) and the results are summarized in Table II. The DIs after the PB treatment up to 130 °C are less than 3 %, indicating that a large dissolution contrast between the exposed and unexposed areas results from the phase separation.

Table 2 Degree of Imidization for **FPAA-2** after Prebaking

| Prebaking Condition | Temp. °C | 80 | 100 | 110 | 120 | 130 | 350 |
|---|---|---|---|---|---|---|---|
| | Time min | 60 | 2 | 2 | 2 | 2 | 60 |
| Degree of imidization (%) | FPAA | 0 | 0 | 0.8 | 1.72 | 2.71 | 100 |

During the course of our investigation, we found that a very thin film remained on a silicon wafer after development. This may be attributed to the strong hydrogen bond interaction between the **PAAs** and hydroxyl groups of the silicon wafers. 3,4-Dihydroxyphenylalanine (DOPA) is a well-known adhesive for various substrates in which catechols enhance the interfacial adhesion of materials [21-22]. Thus, catechol would interact with the hydroxyl groups of the silicon wafers, reducing the hydrogen bond between the **PAAs** and silicon wafers.

To remove this thin film, catechol was added to the **PSPI** solution. The **PSPI** film was completely removed by the addition of 3 wt% catechol to **FPAA-2** after development with 2.38 wt% TMAHaq.

Based on these preliminary optimization studies, the **PSPI** containing **FPAA-2**, **FDNQ** (25 wt% to **FPAA-2**) and catechol (3 wt% to **FPAA-2**) was formulated. The photosensitive curve of the resist films with a 1.2 μm thickness is shown in Fig. 5. The **PSPI** had an excellent sensitivity of 45 mJ/cm$^2$ and a good contrast of 10 with *i*-line exposure.

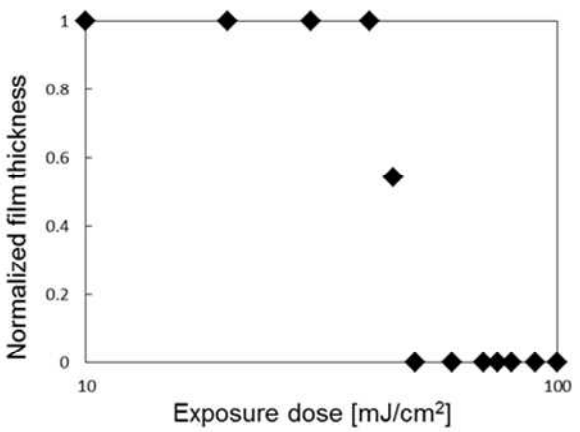



Fig. 5 Characteristic photosensitive curve of **PSPI** (**FPAA-2** and **FDNQ** (25 wt% to **FPAA-2**)) in the 1.8-μm-thick film. The PB condition was fixed to 120 ºC for 2 min, respectively.

The SEM image of the contact-printed pattern was obtained using the **PSPI** film (Fig. 6). The **PSPI** consisting of **FPAA-2**, and **FDNQ** (25 wt%), and catechol (3wt%) was prebaked at 120 °C for 2 min, exposed to 80 mJ/cm$^2$ of the *i*-line, and developed with 2.38 wt% TMAHaq for 10 sec. Consequently, a clear positive pattern was successfully obtained with a 6 μm feature on a 1.2 μm thick film.

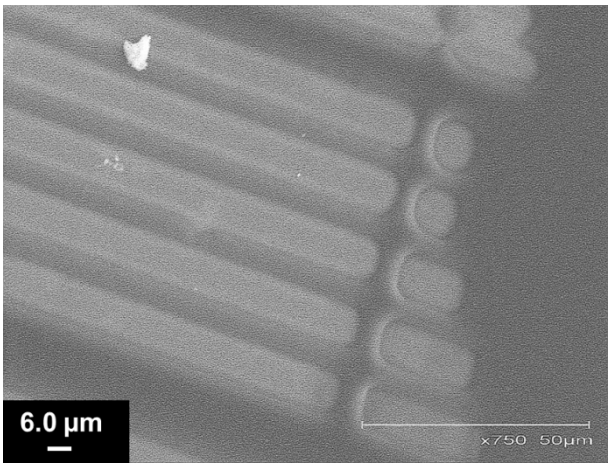



Fig. 6 SEM image of patterned **FPAA-2** in a 1.2-μm-thick film (**FPAA-2** and **FDNQ** (25 wt% to **FPAA2**)). The *i*-line exposure dose and PB condition were fixed to 80 mJ/cm$^2$ and 120 ºC for 2 min, respectively (3.0 kV x 1.30 k).

The printed **FPAA** pattern was cured to obtain the PI pattern by heating at elevated temperatures up to 250 °C for 30 min and then at 350 °C for 1 h under nitrogen (Fig. 7). The film thickness decreased from 1.2 to 1.0 μm due to a cyclodehydration and decomposition of **FDNQ**. However, no damage to the formed patterns was observed. The IR spectrum after curing indicated that the **PAA** films were successfully converted to the PI films.

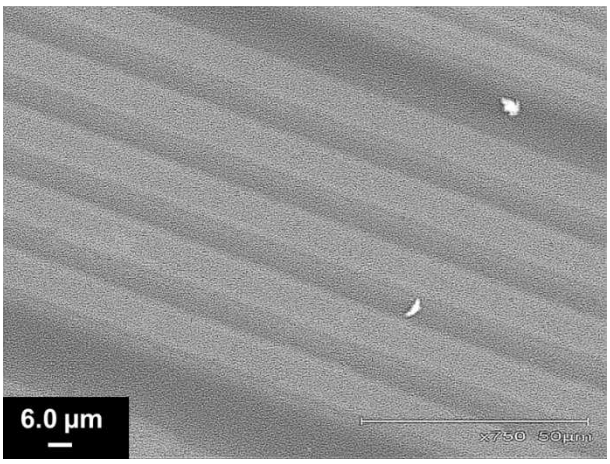


Fig. 7 SEM image of the positive-patterned PI film by thermal curing at 250 ºC for 30 min and then 350 ºC for 1 h under nitrogen (3.0 kV x 1.30 k).

## 4. Conclusion

**FPAAs** with an appropriate dissolution rate in 2.38 wt% TMAHaq were prepared by the polymerizations of **6FDA**, **ODA**, and **APB**. An alkaline developable and positive-type **PSPI** based on **FPAA-2**, **FDNQ** and catechol was successfully developed. The resist solution was spin-coated on a silicon wafer and prebaked, spontaneously forming the **FDNQ** rich surface on the film, that is, a top **FDNQ** rich layer and a bottom **FDNQ** less layer of **FPAA-2** with PB treatment. The exposed compartment of the thin top layer of **FPAA-2** with rich **FDNQ** was developed with 2.38 wt% TMAHaq, producing a positive pattern. Subsequently, the **FPAA-2** bottom layer containing less **FDNQ** was developed under the pattern of the top layer. The **PSPI** exhibited an excellent sensitivity of 45 mJ/cm$^2$ and a good contrast of 10 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 processes which can provide a facile formulation of **PSPI**.

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