



## New positive-type photosensitive polyimide having sulfo groups

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### Abstract

A new positive-working photosensitive polyimide (PSPI) has been developed, which is based on polyimide bearing sulfo groups (PIS) and 1-{1,1-bis[4-(2-diazo-1-(2H)naphthalenone-5-sulfonyloxy)phenyl]ethyl}-4-{1-[4-(2-diazo-1(2H)naphthalenone-5-sulfonyloxy)phenyl]-methylene]benzene (S-DNQ) as a photosensitive compound. PIS was prepared by ring-opening polyaddition of 1,3-phenylenediamine-4-sulfonic acid (PDAS), 4,4'-oxydianiline (ODA), and 4,4'-hexafluoropropylidenebis(phthalic anhydride) (6FDA), followed by thermal cyclization in *m*-cresol. PIS containing 30 wt% of S-DNQ showed a sensitivity of 100 mJ cm<sup>-2</sup> and a contrast of 1.7, when it was exposed to 365 nm light followed by developing with 2.38 wt% aqueous tetramethylammonium hydroxide (TMAH) solution at room temperature. A fine positive image featuring 10 μm line and space patterns was observed on the film of the photoresist exposed to 200 mJ cm<sup>-2</sup> of UV-light at 365 nm by the contact mode. The positive image was successfully converted to the polyimide pattern by thermal treatment.

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**Keywords:** Photosensitive polyimide; Sulfo group; Tetramethylammonium hydroxide

### 1. Introduction

The continuous evolution toward portable and high-frequency microelectronic system places high demands on material properties, notably low dielectric constant ( $\epsilon$ ), low dissipation factor, low moisture uptake, and good thermal stability. Photopatternable insulating polymers with these properties are required for protective chip over coatings for mega-bit memories and logic components, and planarizing low  $\epsilon$  interlayer dielectrics in complex multi-layer electronic devices to achieve high switching speeds in thin-film multi-chip modules. Photosensitive polyimides (PSPIs) are attracting great attention as photosensitive and thermally stable polymers because of their high mechanical strength, thermal stability, and low dielectric constants [1].

Most of the standard resist materials used in semiconductor manufacturing are positive type resists based on novolac resins with diazonaphthoquinone (DNQ), in which DNQ acts as a dissolution inhibitor for aqueous base development of novolac resins. Therefore, positive-working PSPIs that can be developed with an aqueous base solution have been attracting great interest.

The most straightforward PSPI matrix is a poly(amic acid) (PAA) possessing hydrophilic carboxylic groups. Several groups have reported the preparation of PSPIs consisting of PAA and DNQ [2–4]. The dissolution rate of PAAs to 2.38 wt% aqueous tetramethylammonium hydroxide (TMAH) solution, however, is too high to get a sufficient dissolution contrast between unexposed and exposed areas. Thus, various designs of PSPIs have been reported so far such as poly(amic ester)s with cross-linking sites [5] or *o*-nitrobenzyl groups [6], poly(hydroxy imide) combined with DNQ [7] or cross-linking compounds [8].

It is of interest to develop a simpler PSPI precursor, in which an alkaline soluble group can be removed by thermal treatment after development. The cleavage of sulfo groups from aromatic rings easily occurs by heating [9]. Therefore, poly(imide)s (PIs) bearing sulfonic acids would be good candidates for alkaline developable PSPI precursors.

This paper describes the synthesis of a new positive working PSPI precursor based on PI having sulfo groups and 1-{1,1-bis[4-(2-diazo-1-(2H)naphthalenone-5-sulfonyloxy)phenyl]ethyl}-4-{1-[4-(2-diazo-1(2H)naphthalenone-5-sulfonyloxy)phenyl]methylene]benzene (S-DNQ) as a photosensitive compound.

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## 2. Experimental

### 2.1. Materials

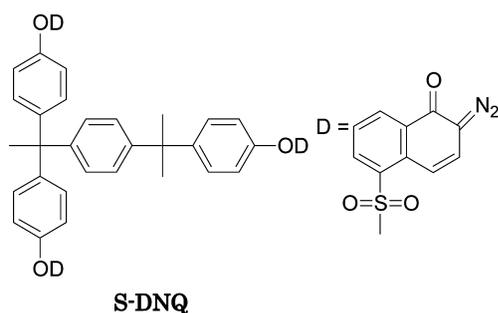
1,3-Phenylenediamine-4-sulfonicacid (PDAS) and 4,4'-hexafluoropropylidenebis(phthalic anhydride) (6FDA) were recrystallized from water and acetic anhydride, respectively. 1-Methyl-2-pyrrolidinone (NMP) was purified by vacuum distillation from calcium hydride and stored over 4A molecular sieves. Triethylamine (TEA), *m*-cresol, and 4,4'-oxydianiline (ODA) were purified by usual methods. S-DNQ was kindly donated by Shipley Japan and used without further purification (Scheme 1). Other reagents and solvents were used as received.

### 2.2. Synthesis of polyimide bearing sulfo groups (PIS)

To a solution of PDAS (0.338 g, 1.8 mmol), TEA (0.30 ml, 2.2 mmol), and *m*-cresol (3.8 ml) were added with stirring ODA (0.040 g, 0.2 mmol) and 6FDA (0.888 g, 2 mmol) at room temperature under nitrogen atmosphere. The mixture was stirred at 80 °C for 4 h, then 180 °C for 1.5 h. The resulting viscous solution was diluted with *m*-cresol (5 ml) and poured into a mixed solvent of 2 M aqueous hydrogen chloride solution/2-propanol (1/1 in volume ratio, 100 ml). The precipitate was collected and dried in vacuo at 80 °C for 6 h. The yield was 95%. IR (film):  $\nu$  3000–3500 (OH), 1785 (C=O), 1732 (C=O), 1600 (Ar), 1365 (CF<sub>3</sub>), 1253 (–O–), 1023 (O–S–O), 683 cm<sup>-1</sup> (S–O). Anal. calcd for C<sub>25.6</sub>H<sub>10.4</sub>O<sub>6.8</sub>N<sub>2</sub>F<sub>6</sub>S<sub>0.9</sub>: C, 51.5; H, 1.76; N, 4.77. Found: C, 50.8; H, 2.62; N, 4.77.

### 2.3. Synthesis of reference polyimide (RPI) from *m*-phenylenediamine, 6FDA, and ODA

A mixture of *m*-phenylenediamine (0.194 g, 1.8 mmol), ODA (0.040 g, 0.2 mmol), and 6FDA (0.888 g, 2 mmol) in *m*-cresol (3.8 ml) was stirred at 80 °C for 4 h, then 180 °C for 1.5 h under nitrogen. The resulting viscous solution was diluted with *m*-cresol (5 ml) and poured into 2-propanol (100 ml). The precipitate was collected and dried in vacuo at 80 °C for 6 h. The yield was 96%. IR (film):  $\nu$  1785 (C=O), 1736 (C=O), 1604 (Ar), 1357 (CF<sub>3</sub>), 1257 cm<sup>-1</sup> (–O–).



Scheme 1.

### 2.4. Dissolution rate

PIS was dissolved in NMP at a concentration of 20 wt%, to which was added S-DNQ (30 wt% of the total solid). Films spin-cast on silicon wafers were pre-baked at 100 °C for 10 min, and then exposed to a filtered super-high pressure mercury lamp. Exposed films were developed with 2.38 wt% aqueous TMAH solution at 25 °C. The changes in the film thickness against the exposure energy were measured with a Dektak<sup>3</sup> surface profiler (Veeco Instrument Inc.).

### 2.5. Photosensitivity

A 1.3 μm-thick polymer film on a silicon wafer was exposed to radiation at a wavelength of 365 nm through the filtered super high-pressure mercury lamp, developed with 2.38 wt% aqueous TMAH solution at 25 °C, and rinsed with water. A characteristic curve was obtained by a normalized film thickness against exposure energy. Image-wise exposure through a mask was carried out in a contact-printing mode.

### 2.6. Measurements

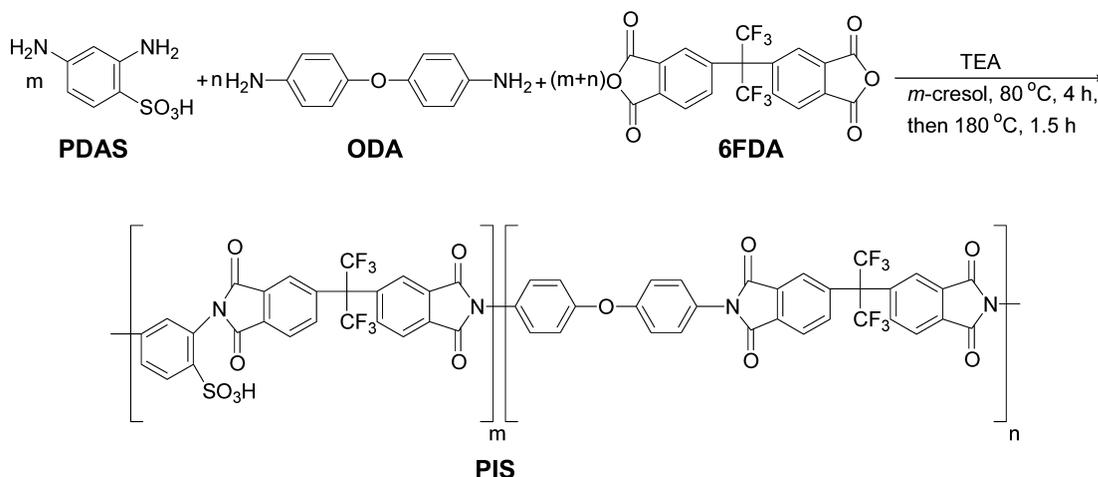
The infrared spectra were recorded on a Horiba FT-210 spectrophotometer. UV–Vis spectra were obtained on a Jasco V-650 spectrophotometer. Thermal analyses were performed on a Seiko thermal analyzer at a heating rate of 10 °C min<sup>-1</sup> for thermogravimetry (TG). Number- and weight-average molecular weights ( $M_n$  and  $M_w$ ) were determined by gel permeation chromatography (GPC), calibrated with standard polystyrenes, on a Tosoh HLC-8120 GPC system equipped with polystyrene gel columns (TSK GELS, GMH<sub>HR</sub>-M and GMH<sub>HR</sub>-L), at 40 °C in DMF (containing 0.01 M of lithium bromide, the flow rate: 1.0 ml min<sup>-1</sup>). The film thickness was measured by a Dektak<sup>3</sup> surface profiler (Veeco Instrument Inc.).

## 3. Results and discussion

### 3.1. Synthesis of PIS

It is important to design a matrix polymer to make a new PSPI system, because PSPI precursors must possess good solubility and transparency in UV region, as well as good film properties. A diamine monomer having sulfo groups PDAS was chosen due to its availability. PIS employed in this study was prepared in the form of a copolymer, using ODA as a co-monomer, so as to dilute the content of sulfo-imide moieties and allow for better control of the dissolution rate.

In addition, PIs generally exhibit low optical transparency to UV light and have a yellow color due to charge transfer complexation. This coloration limits the



Scheme 2.

formation of thick film patterns [10]. Therefore, less colored PIs were prepared by modifying the molecular structure through introduction of fluoroalkyl groups, separating chromophoric groups and reducing the electronic interaction between color-causing center [11]. In particular, introducing a fluoroalkyl unit into the polymer main chain is considered to be a very versatile technique to improve both the transparency and the solubility of the resulting PI. Thus, 6FDA was selected as a tetracarboxylic dianhydrides. Table 1 summarizes the results of the polymerization. The polymerization proceeded in a homogeneous state by one-step procedure through ring-opening polyaddition and subsequent thermal cyclodehydration in *m*-cresol, in which TEA was added to make salts with sulfo groups, preventing the salt-formation of amines with sulfo groups (Scheme 2). Although PIS obtained from PDAS and 6FDA showed a high  $M_n$  of 17,000, its film was brittle (run 1). Incorporation of ODA as a co-monomer into PIS gave tough and flexible polymer films with reasonably high  $M_n$ s (run 2 and 3). As a matrix polymer for PSPI, PIS obtained from 6FDA, PDAS (0.9 equiv.), and ODA (0.1 equiv.) was chosen because of its high solubility in TMAH solution. The obtained PIS was a white solid, and soluble in NMP, DMF, dimethylsulfoxide, acetone, and tetrahydrofuran.

A reference polyimide (RPI) was prepared from *m*-phenylenediamine, 6FDA, and ODA in *m*-cresol by the

Table 1  
Synthesis of PIS

Run	Monomer feed PDAS:ODA	Yield (%) <sup>a</sup>	$M_n^b$	$M_w/M_n^b$
1	10:0	85	17,000	1.5
2	9:1	95	17,000	1.6
3	8:2	97	22,000	1.5

<sup>a</sup> Isolated yield after precipitated in a mixed solvent of 2 M aqueous hydrogen chloride solution/2-propanol (1:1 in volume ratio).

<sup>b</sup> Estimated by GPC (PSt, DMF).

same procedure, to compare the IR spectrum of desulfonated PIS. The structure of the polymer was identified as the corresponding PIS by IR spectroscopy and elemental analysis. The IR spectrum showed two characteristic absorptions at 1780 and 1730  $\text{cm}^{-1}$  due to imide carbonyl groups and sulfonic acid absorptions at 1023 and 683  $\text{cm}^{-1}$ . Elemental analysis also supported the formation of the expected PIS. PIS was readily converted to the corresponding PI by thermal treatment. The traces of TG for PIS and for the corresponding PI are shown in Fig. 1. A weight loss was observed at 250–350 °C for PIS. In this range, the weight loss of 11% is in good agreement with the value (12%) calculated from the elimination of sulfo groups. The IR spectrum of thermally treated polymer at 350 °C for 2 h is shown in Fig. 2, in which characteristic sulfo absorptions at 3000–3500, 1023, and 683  $\text{cm}^{-1}$  had completely disappeared. The resulting IR spectrum is identical to that of the reference polymer RPI. The above findings indicate that PIS was converted to the corresponding PI by thermal treatment (Scheme 3).

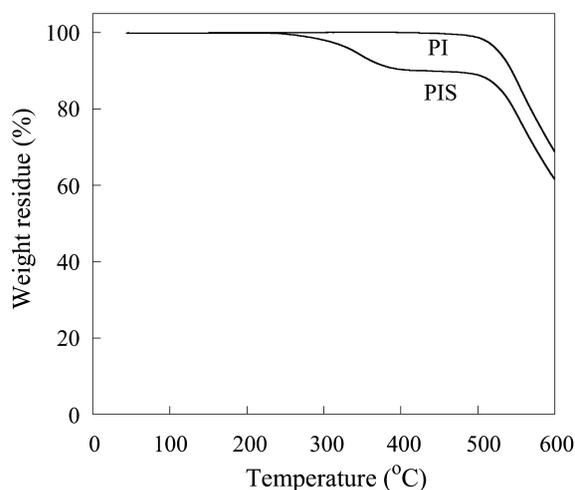


Fig. 1. TG curves of PI and PIS under nitrogen.

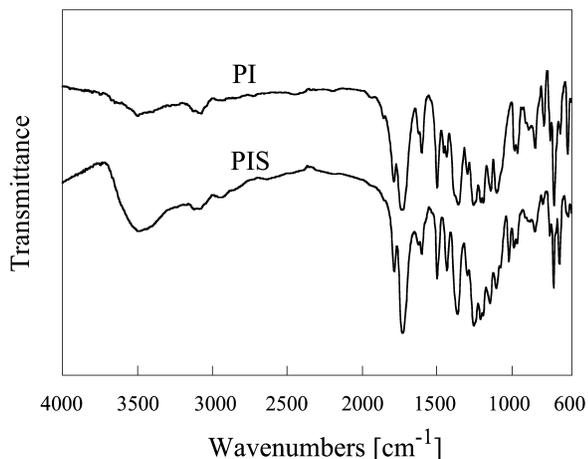


Fig. 2. IR spectra of PI and PIS.

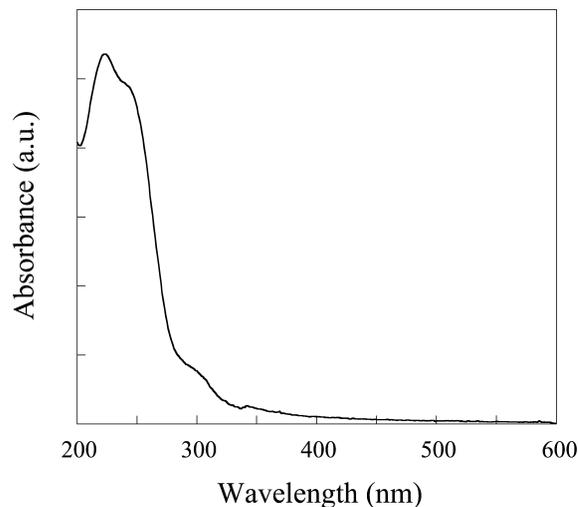


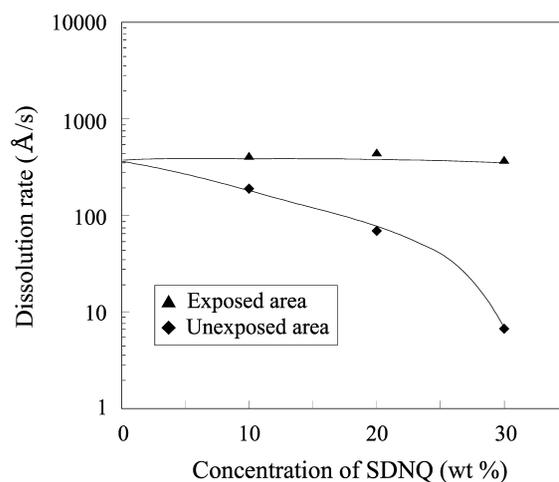
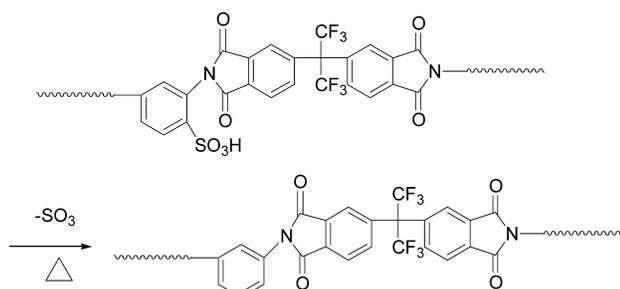
Fig. 3. UV-Vis spectrum of PIS.

### 3.2. Lithographic evaluation

The transmission UV-Vis spectrum of the PIS film (1.1  $\mu\text{m}$  thickness) is shown in Fig. 3. The film was almost transparent above 300 nm. This means S-DNQ, which has a strong absorption at 350–420 nm, can be used as a photosensitive compound. S-DNQ is photochemically transformed to indenecarboxylic acid derivative.

To clarify the difference of dissolution behavior between the exposed and unexposed areas, the effect of S-DNQ loading on the dissolution rate in the developer (2.38 wt% aqueous TMAH solution) was studied, and the results are shown in Fig. 4. The films spin-cast on silicone wafers were prebaked at 100  $^{\circ}\text{C}$  for 10 min, and then exposed to a filtered super-high pressure mercury lamp (365 nm, 200  $\text{mJ cm}^{-2}$ ). The dissolution rate was estimated by measuring the film thickness after development. The solubility of exposed areas remained constants even if increasing S-DNQ contents. On the other hand, the dissolution rate of the unexposed areas decreased with increasing S-DNQ contents. The difference of the dissolution rates between the exposed and unexposed areas was 50 times at the 30 wt% S-DNQ loading.

A photosensitive polymer consisting of PIS and 30 wt% S-DNQ in NMP was formulated. The sensitivity curve for a 1.1  $\mu\text{m}$ -thick film shown in Fig. 5 was consistent with dissolution behavior studied above, indicating that the

Fig. 4. Influence of S-DNQ loading on the dissolution rate using 2.38 wt% aqueous TMAH solution as a developer. Exposure dose: 200  $\text{mJ cm}^{-2}$ .

Scheme 3.

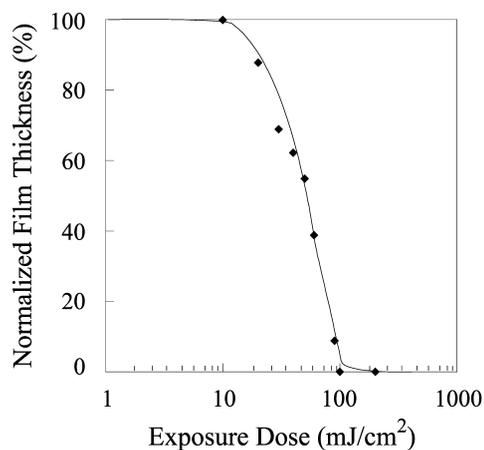


Fig. 5. Exposure characteristic curve for PIS containing 30 wt% of S-DNQ.

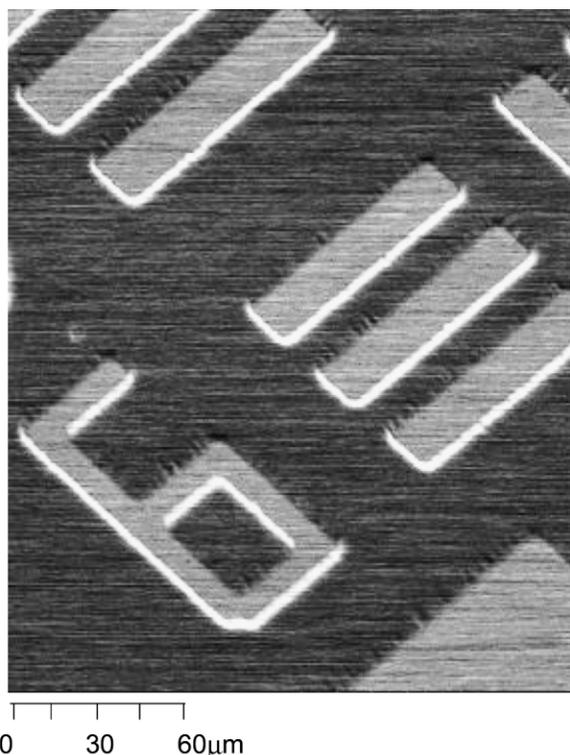


Fig. 6. SEM micrograph of positive image obtained from the resist consisting of PIS and S-DNQ.

sensitivity ( $D^{\circ}$ ) and contrast ( $\gamma^{\circ}$ ) were  $100 \text{ mJ cm}^{-2}$  and 1.7, respectively.

Fig. 6 presents a scanning electron micrograph (SEM) of the contact-printed image after exposure of  $200 \text{ mJ cm}^{-2}$  light, followed by development with 2.38 wt% aqueous TMAH solution. Clear positive patterns with  $10 \mu\text{m}$  resolution were obtained. Furthermore, this positive image in the PIS film was converted to a positive image of PI film by high-temperature treatment ( $350 \text{ }^{\circ}\text{C}$ , 2 h,  $\text{N}_2$ ) without any deformation (Fig. 7).

#### 4. Conclusion

A polyimide with sulfo groups (PIS) with a high molecular weight was prepared by ring-opening polyaddition of 6FDA with PDAS and ODA, and subsequent thermal cyclodehydration. PIS containing 30 wt% S-DNQ functioned as positive-type photosensitive polymer, and its sensitivity and contrast were  $100 \text{ mJ cm}^{-2}$  and 1.7 with 365 nm light, respectively. The positive image of PIS film after development was converted to the corresponding PI image by thermal treatment. This direct resist formulation method using PIS as a PI precursor is very simple and

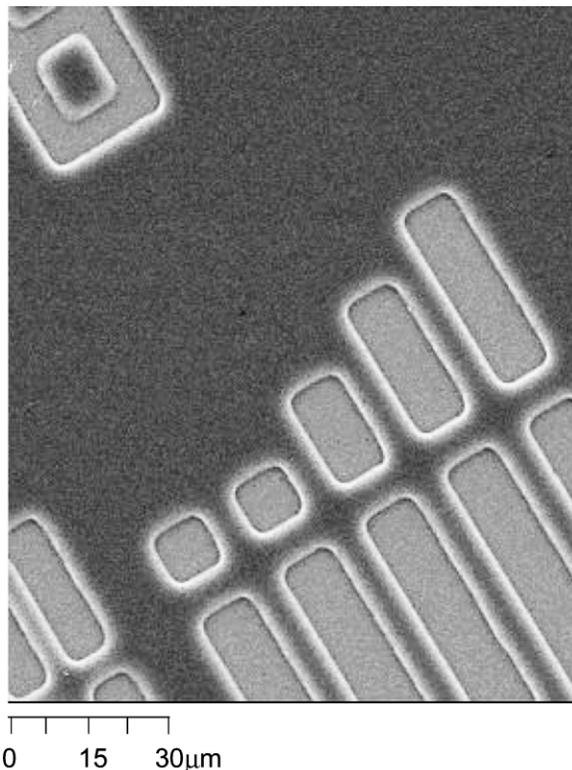


Fig. 7. SEM micrograph after curing at  $350 \text{ }^{\circ}\text{C}$  for 2 h under  $\text{N}_2$ .

advantageous in comparison with the reported multi-step procedure for PSPIs.

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