Photosensitive polyimides without side chain: negative-tone reaction development patterning

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1. Introduction

Photosensitive polymers have been widely used in various industries, such as photoresists for patterning of integrated circuits (ICs), buffer coat layers for IC chips and interlayer dielectric films in electronics industry, and manufacturing of printing plates, color filters, optical waveguides. Different properties are required for such the applications of photosensitive polymers, and the most appropriate molecular designs should be adopted for each application. In electronics packaging (Jisso) like buffer coat layers and interlayer dielectrics, though requirement for resolution is not strict, high thermal, mechanical and insulating properties are required for photosensitive polymers because of permanent utilization of patterns without removing. Therefore, photosensitive polymers based on engineering plastics, known as high-performance polymers, have been studied, and especially, photosensitive polyimides have received extensive attentions because of their excellent properties. Conventional photosensitive polyimides have utilized derivatives of polyimide precursor, poly(amic acid), or functionalized polyimides as polymer components. However, preparation of these polymers often requires complicated and high-cost synthetic routes. In addition, high temperature post-curing is needed for imide ring formation when poly(amic acid) derivatives are used as the polymer components.

We have been developed a novel pattern-forming mechanism, reaction development patterning (RDP), for unfunctionalized engineering plastics containing carboxylic-acid-derivative linkages (-C(O)-X-, X = O, N-C(O), etc) in the main chain. RDP realizes positive-tone pattern formation from unfunctionalized polyimides, polycarbonates and polyarylates only by photo-irradiation onto the polymer films containing diazonaphthoquinone (DNQ) and the following development with amine-containing solution. RDP uses main chain scission by nucleophilic acyl substitution between the -C(O)-X- linkages and amines in developer as a key reaction for pattern formation. However, RDP has some drawbacks for practical applications such as necessity of large amount of DNQ (~30 wt% for polymer), low sensitivity (~1000 mJ/cm² at 10 μm thickness) and use of organic amines as a component of developer.

On the other hand, we have recently developed negative-tone RDP (NRDP), where photo-irradiation
to polyetherimide (PEI) films containing \( N \)-phenylmaleimide (PMI) in addition to DNQ and the following development with a solution containing aqueous tetramethylammonium hydroxide (TMAH) enable negative-tone pattern formation.\textsuperscript{17,18} In this paper, we report lithographic evaluation of NRDP-based photosensitive PEI and pattern-forming mechanism of NRDP. Reduction of the amount of DNQ and improvement of sensitivity by applying chemical amplification mechanism to NRDP are also reported.

2. Experimental

2.1 Materials

Commercially available polyetherimide (PEI) (Ultem\textsuperscript{®}) (Scheme 1) was kindly provided by Sabic Innovative Plastics. 1,2-Naphthoquinonediazide-5-sulfonic acid \( p \)-cresol ester (PC-5\textsuperscript{®}) as DNQ (Scheme 2) was purchased from Toyo Gosei Kogyo Co., Ltd. \( N \)-phenylmaleimide (PMI, Scheme 2) was purchased from Wako Pure Chemical Industries, Ltd. Other reagents and solvents were commercially available.

2.2 Pattern formation by NRDP

15~30wt\% of PEI was dissolved in \( N \)-methylpyrrolidone (NMP). The DNQ compound (PC-5\textsuperscript{®}) as a photosensitive agent (15~30wt\% for PEI) and PMI (1~20wt\%) were dissolved in the NMP solutions. The resulting photosensitive PEI solutions were degassed and spin-coated onto a shiny side of copper foil, and the photosensitive PEI films with 10~15 \( \mu \text{m} \) in thickness were obtained after prebaking at 90 \( ^\circ\text{C} \) for 10 min in a far-infrared oven. The films were irradiated with an ultra high-pressure mercury lamp without any filter at both i and g lines through a negative photomask in a contact technique. The exposed films were developed in a mixture of TMAH / \( \text{H}_2\text{O} / \text{NMP} / \text{alcohol} \) under ultrasonication or by dipping, and rinsed with pure water.

2.3 Pattern formation by chemically amplified NRDP

15~30wt\% of PEI was dissolved in \( N \)-methylpyrrolidone (NMP). The DNQ compound (PC-5\textsuperscript{®}, 5~10wt\% for PEI), PMI (1~5wt\%) and an acid amplifier (5~10wt\%) were dissolved in the NMP solutions. The resulting systems were degassed and spin-coated onto a shiny side of copper foil, and the photosensitive PEI films with 10~15 \( \mu \text{m} \) in thickness were obtained after prebaking at 90 \( ^\circ\text{C} \) for 10 min in a far-infrared oven. The films were irradiated with an ultra high-pressure mercury lamp through a
negative photomask in a contact technique, and then baked at 110 °C for 1~3 min. The exposed and post-baked films were developed in a mixture of TMAH / H₂O / NMP / methanol under ultrasonication at 50 °C, and rinsed with pure water.

3. Results and Discussion

3.1 Dissolution behavior

Effect of PMI on dissolution behavior of photosensitive PEI films based on NRDP was examined by measuring change in normalized film thickness during development with TMAH / H₂O / NMP / CH₃OH mixture with or without irradiation in the presence or absence of PMI (Figure 1). Though little difference in dissolution behavior between the exposed and unexposed areas was observed when no PMI was added to the system, the addition of 10~20wt% of PMI largely decreased dissolution rate of the exposed area. Relationship between exposure and dissolution behavior was also examined (Figure 2), and difference in dissolution rate between the exposed and unexposed areas was observed from exposure of 100 mJ/cm². These results suggest that negative-tone pattern based on NRDP can be formed with smaller exposure than that in positive-tone RDP (more than 1000 mJ/cm² at ~10 μm film thickness). ⁹

3.2 Lithographic evaluation

Line and space (L/S) pattern formation based on NRDP was then attempted. Photosensitive PEI varnish was easily prepared by dissolving PEI (Scheme 1), a photosensitive DNQ compound (Scheme 2) and PMI (Scheme 2) into NMP. The varnish was spin-coated onto copper foil and prebaked, and the resulting film was irradiated by UV through a photomask and developed with TMAH / H₂O / NMP / CH₃OH mixture. A scanning electronic
microscopy (SEM) photograph of the patterns formed from the film with 30wt% of DNQ and 20wt% of PMI is shown in Figure 3a. Clear negative-tone L/S patterns were successfully prepared.

Reduction of the additives from NRDP system was then examined. Negative-tone patterns were formed from the PEI film with 15wt% of DNQ and 10wt% of PMI (Figure 3b), but further decrease in the amount of DNQ resulted in unsuccessful pattern formation. On the other hand, application of NRDP to the film with 15wt% of DNQ and 1wt% of PMI and use of ethanol instead of methanol as a component of developer afforded negative-tone patterns with shorter development time despite no ultrasonic treatment during development (Figure 3c). Further optimization of development condition enabled use of developer without NMP, that is, a mixture of aqueous TMAH / alcohols (poly(ethylene glycol) (PEG400, M = 400) + ethanol) (Figure 4a). Sensitivity curve for this system was shown in Figure 4b, and the sensitivity \( E_{50} \), the exposure where 50% of the film remained, was found to be 31 mJ/cm\(^2\) for the film with 9.2 \( \mu \)m initial thickness. This value is much higher than those of conventional positive-tone RDP (~1000 mJ/cm\(^2\))\(^9\) and also higher than those of

![Figure 3](image_url)

**Figure 3** SEM images of NRDP-based photosensitive PEIs (~10 \( \mu \)m L/S patterns)

- DNQ (wt% for PEI): a) 30, b, c) 15
- PMI (wt% for PEI): a) 20, b) 10, c) 1
- Initial thickness (\( \mu \)m): a) 10.0, b) 11.7, c) 12.3
- Exposure: 100 mJ/cm\(^2\)
- Developer (TMAH / H\(_2\)O / NMP / CH\(_3\)OH (EtOH in c) (by weight)): a, c) 2 / 8 / 5 / 18, b) 2 / 5 / 5 / 18
- Development condition: a, b) 50 \(^\circ\)C / ultrasonication, c) 50 \(^\circ\)C / dipping
- Development time: a) 9 min 27 sec, b) 6 min 50 sec, c) 8 min
- Residual thickness at exposed areas after development (%): a) 95, b) 93, c) 60

![Figure 4](image_url)

**Figure 4** NRDP-based photosensitive PEI developed with aqueous TMAH / alcohols (DNQ: 15wt% for PEI, PMI: 1wt% for PEI, Development: TMAH / H\(_2\)O / PEG400 / EtOH = 2 / 8 / 5 / 12 (by weight), 50 \(^\circ\)C / dipping)

- L/S patterns (~10 \( \mu \)m) (Initial thickness: 11.1 \( \mu \)m, Exposure: 100 mJ/cm\(^2\), Development time: 8 min 20 sec. Residual thickness at exposed areas after development: 88%)
commercially available photosensitive polyimides.

3.3 Pattern-forming mechanism

In order to reveal pattern-forming mechanism, a PEI film containing 30wt% of DNQ and 20wt% of PMI was irradiated through a photomask and developed with TMAH / H2O / NMP / CH3OH solution (2 / 5 / 5 / 18 (by weight)), and molecular weight of the component dissolved into the developer was measured. As a result, no decrease in molecular weight after development was observed, and this indicates that pattern-forming mechanism in NRDP is different from that in conventional positive-tone RDP, where molecular weight of polymers decreases as a result of main chain scission during development process.10,13,15 Reaction of PEI with solution of TMAH / H2O / NMP / CH3OH in a flask was also carried out. Although the mixture was heterogeneous at first, the system became homogenous after 30-min stirring at 50 °C. After the reaction for 2 h at 50 °C, the polymer was isolated and characterized by GPC and 1H-NMR spectrum. In GPC measurement, just as the experiment using PEI film, little decrease in molecular weight was observed. 1H-NMR spectrum of the isolated polymer after HCl treatment showed peaks assigned to amide and carboxylic acid protons. These results suggest that PEI was dissolved into developer as a form of poly(amic acid), generated by nucleophilic attack of hydroxyl anion (OH-) of TMAH to imide groups in PEI (Scheme 3).

Role of PMI for pattern formation in NRDP was also examined. UV-irradiated PEI film containing 20wt% of PMI was dissolved into DMSO-d6 and 1H-NMR spectrum of the solution was measured. As a result, a small peak assigned to dimer of PMI, considered to be generated by photo-dimerization of PMI (Scheme 4), was observed. We also synthesized the dimer not by photo-dimerization but by organic synthetic method, and found that this dimer was hardly soluble in almost all organic solvents. This low solubility would be the reason why the peak of dimer was small in the 1H-NMR spectrum, and also the reason for the reduced dissolution rate of the irradiated areas in NRDP. Further examinations for elucidation of detailed pattern forming mechanism are in progress.

3.4 Chemically amplified NRDP

Application of chemical amplification to NRDP was examined by adding a small quantity of DNQ and acid amplifier instead of a large quantity of DNQ in usual NRDP. The acid amplifiers are protected
low-molecular-weight acid molecules. A small amount of acid generated from DNQ by irradiation is expected to act as a catalyst for deprotection of the acid amplifier at post-exposure baking after irradiation and this catalytic deprotection will increase the amount of acid only at the exposed areas. Thus, chemically amplified NRDP is expected to reduce the amount of photosensitive agent required and to achieve higher sensitivity than that obtained with conventional NRDP.

Pattern formation based on chemically amplified NRDP was investigated by adding acid amplifiers in addition to DNQ and PMI into PEI films, irradiating UV, post-exposure baking for chemical amplification, and then developing with TMAH-containing developers. Carboxylate and sulfonate esters were used as acid amplifiers, and chemically amplified NRDP system containing 2TB (Scheme 5) was found to show good L/S patterns with less amount of DNQ (10wt%) and higher sensitivity ($E_{50}$ of 12 mJ/cm$^2$ for the film with 10.7 μm initial thickness) than those of NRDP (Figure 5).

4. Conclusion

Negative-tone pattern formation based on NRDP from films of commercially available PEI containing DNQ and PMI was accomplished with 10 μm resolution. Addition of PMI was found to retard dissolution of photo-irradiated areas. Much higher sensitivity than conventional positive-tone RDP and development with TMAH-containing solution were achieved by NRDP. The patterns in NRDP were prepared by preferential formation of poly(amic acid) at unexposed areas, and photo-dimerization of PMI would decrease dissolution rate at exposed areas. Application of chemical amplification mechanism to NRDP was also found to be effective for improving sensitivity while reducing the amount of DNQ.

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**References**


