Examination of Pattern-forming Conditions in Negative-tone Reaction Development Patterning

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Keywords: Polyetherimide (PEI) / Photoresist / Diazonaphthoquinone (DNQ) /
Negative-tone Reaction Development Patterning (NRDP)

1. Introduction

The resolution of photoresists needed for producing printed wiring board and surface mount technology is not very high (10-100 μ m), but the resist films require good mechanical and thermal properties because of permanent remaining of the films in the manufactures. Thus, polyimides, or polyamic acids as their precursors, have been usually used as polymers for such purposes [1]. However, functional groups for affording photosensitivity must be introduced into the polymers in view of development step, and the introduction of such functional groups brings about some problems such as increased difficulty in the synthesis of photosensitive polyimides (PSPIs) and decreased physical and mechanical properties of PSPIs. When the polyamic acids were used, the problems like deformation of the patterns during thermal imidization often occur.

We have reported a novel pattern-forming process, reaction development patterning (RDP), for engineering plastics [2,3]. One of the largest differences between RDP and the previously established processes is that chemical reaction between developer and the polymers in development process is the main factor for pattern formation in RDP. One of the characteristics of RDP is that, in principle, every polymer can be used as photosensitive polymer if the polymer has functional group being able to receive nucleophilic acyl substitution from a nucleophile in the developer and the products of the reaction have solubility into some solvent.

We examined application of RDP for commercially available engineering plastics having carboxylic-acid-derivative linkages in the main chain such as polyetherimide (PEI) [4], polyarylate (PAr) [5], and polycarbonate (PC) [6]. In consequence, these novel photosensitive engineering plastics showed clear and sharp positive-tone line/space (L/S) patterns at $\sim 10\ \mu$ m resolution.

Recently, we found that PEI films containing photosensitive agent (diazonaphthoquinone (DNQ) compound), and *N*-phenylmaleimide (PMI) showed negative-tone behavior when the films were exposed to UV light from high pressure mercury lamp and then developed with tetramethylammonium hydroxide (TMAH) / NMP / H₂O / MeOH mixture [7]. The negative-tone pattern formation was found to be achieved based on reaction of OH⁻ in the developer with imide groups in PEI, and thus, we named this novel pattern forming mechanism as negative-tone RDP (NRDP). NRDP is realized only by adding PMI into conventional RDP system, and sensitivity of NRDP (less than 100mJ/cm² at 10 μ m thickness) is largely improved compared to that of RDP (about 1000mJ/cm²). Availability of the developer containing industrially-used aqueous TMAH solution is also an advantage of NRDP.

Although NRDP is a useful method for preparing photosensitive polyimides, reduction of the additives in the films will be advantageous toward practical application of NRDP. In this paper, we report a novel NRDP which does not require the addition of PMI. Relationship between

exposure dose and thickness of the DNQ-containing films with or without PMI, effect of the content of DNQ in the films on dissolution rate of the films, and pattern formation based on NRDP without PMI were examined. Pattern-forming mechanism was also discussed.

2. Experimental

2.1. Materials

PEI (Ultem[®], Scheme 1) was kindly supplied from Sabic Innovative Plastics Japan. The number- and weight-average molecular weights (M_n and M_w) of PEI were 21,000 and 34,000-35,000, respectively. 1,2-Naphthoquinonediazide-5-sulfonic acid *p*-cresol ester (PC-5[®]) (Scheme 2) was purchased from Toyo Gosei Kogyo Co., Ltd. Other reagents and solvents were commercially available.

Scheme 1

Scheme 2

2.2. Measurement

Molecular weight was determined using GPC (TOSOH TSKgel GMH_{HR}-M column, eluting rate 1.0 mL/min) equipped with UV detector (TOSOH, UV-8020) at room temperature using polystyrene standards and its mobile phase was DMF containing LiBr (30 mmol/L) and phosphoric acid (60 mmol/L). ¹H-NMR spectra were recorded on a JEOL JNM-270 spectrometer (270 MHz) at room temperature using DMSO-*d*₆ as a solvent and tetramethylsilane as an internal standard. Film thickness was measured with a contact-type thickness analyzer (Nikon, DIGIMICRO MFC-101). Irradiation was conducted by a UV exposure apparatus (ORC, JP-2000-EXC), and exposure dose was measured in the wavelength of 320-390nm (ORC, UV-331AP2). Scanning electron micrographs (SEMs) were taken with a JEOL JSM-6390LV instrument.

2.3. Preparation and pattern formation of polyetherimide films containing a photosensitive agent.

17.5 wt% of PEI was dissolved in NMP. The DNQ compound PC-5[®] as a photosensitive agent (10-30 wt% for PEI) was dissolved in the NMP solution. The resulting photosensitive PEI solution was degassed and spin-coated onto a shiny side of copper foil, and the photosensitive PEI film with ~10μm in thickness was obtained after prebaking at 90°C for 10 min in a far-infrared oven. The film was irradiated with an ultrahigh-pressure mercury lamp without any filter (100mJ/cm²) at both the i line and g line through a negative photomask in a contact technique. The exposed film was developed in a mixture of TMAH/NMP/H₂O/MeOH at 50°C under ultrasonication, and rinsed with pure water.

3. Results and Discussion

3.1. Lithographic evaluation

To clarify effects of PMI and exposure dose on dissolution behavior of the photosensitive PEI films based on NRDP, thickness of the films after irradiation with various exposure doses and development with TMAH/NMP/H₂O/MeOH mixture was measured in the presence or absence of PMI (Figure 1). The thickness of the films without PMI decreased with increasing the exposure doses, probably because acid-base reaction between carboxylic acid generated from DNQ by UV irradiation and TMAH in the developer gave a salt and the salt accelerated

Figure 1. Relationship between exposure dose and film thickness after development. The films containing PC-5[®] (20wt% for PEI) were developed with TMAH/NMP/H₂O/MeOH (2/5/5/18 by weight) until complete dissolution of unexposed area.

Figure 2. Effect of the amount of PC-5® on dissolution rate of PEI films. The films were developed with TMAH/NMP/H₂O/MeOH (2/5/5/18 by weight) until complete dissolution.

Figure 3. SEM image of NRDP-based photosensitive PEI containing PC-5® (20wt% for PEI). Exposure dose: 100mJ/cm². Development: TMAH/NMP/H₂O/MeOH (2/5/5/18 by weight) at 50°C under ultrasonication for 3 min 58 s.

permeation of the hydrophilic developer into the films [2,3]. However, when the exposure dose was 100mJ/cm², the thickness of the film without PMI remained more than 70% after development. This result suggests that negative-tone patterns can be formed in the absence of PMI when exposure dose onto films is around 100mJ/cm².

Figure 2 shows effect of the amount of the photosensitive agent (PC-5®) on dissolution rate of the irradiated and unirradiated films. Little dissolution contrast was observed when 10wt% of PC-5® for PEI was added. On the other hand, higher loadings of PC-5® resulted in larger dissolution contrasts between the irradiated and unirradiated films. The largest difference in dissolution rates was achieved when 20wt% of PC-5® was added to the film.

Therefore, a photosensitive PEI film containing 20wt% of PC-5® for PEI with 10µm thickness was formulated, and irradiated at 100mJ/cm² through a negative photomask. Figure 3 shows a

scanning electron micrograph image of the obtained line-and-space patterns of the film after development. The clear negative pattern with 20µm resolution was observed without any peeling off, swelling and deformation.

3.2. Pattern-forming mechanism

To clarify pattern-forming mechanism, the developer after development process was measured by GPC and little difference in molecular weight was observed between PEI and the polymer dissolved in the developer. ¹H-NMR spectrum of PEI after reaction with the developer was also measured (Figure 4), and the peaks assigned to amide protons appeared. These results suggest that PEI is converted to poly(amic acid) by nucleophilic attack of ⁻OH in the developer (Scheme 3) and dissolved into the alkaline developer in the development process. At exposed areas, the ⁻OH anions were consumed not only by the reaction with imide rings (Scheme 3) but also by the reaction with indenecarboxylic acid generated from PC-5®, and this consumption by the indenecarboxylic acid would become the origin for the preferential dissolution of the unexposed areas. When the exposure dose becomes larger and the amount of the generated indenecarboxylic acid was too much, permeation of the developer into the exposed areas would be promoted by increase in hydrophilicity derived from the formation of the salt (tetramethylammonium carboxylate) (Figure 1).

Figure 4. ¹H-NMR spectrum of PEI after reaction with the developer (DMSO-*d*₆, r.t.)

Scheme 3 Ring-opening reaction of imide linkage by the nucleophilic attack of hydroxyl anion

Acknowledgements

This study was supported by Industrial Technology Research Grant Program in 2007 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

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