Photosensitive Polyetherimide (Ultem) Based on Reaction Development Patterning (RDP)

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Photosensitive polyetherimide (PEI) consisting of non-photosensitive PEI (Ultem®) and photosensitive diazonaphthoquinone (DNQ) compounds gave positive-tone behavior by UV irradiation, followed by development in solution including ethanolamine. The SEM of the resultant images showed fine patterns with 10-15 µm film thickness. GPC and 'H-NMR measurements that can give information on the structure of dissolved components in the irradiated region were carried out in order to clarify the mechanism of pattern formation. The imaging of photosensitive PEI is based on reaction development patterning (RDP), where the amine causes main-chain scission directly related to the pattern formation in development step to form low molecular weight amidized products.

Keywords: positive photosensitive polymer, polyetherimide, diazonaphthoquinone, reaction development patterning (RDP)

1. Introduction

Photosensitive polymers have been widely applied in the fields such as paints, UV curing inks, information recording, microelectronics, and others. In particular, photoresists for microlithography have contributed significantly to the present-day semiconductor technology.[1] In recent years, a number of photosensitive polyimides (PI) have been developed for their syntheses and potential application in microfabrication because of their excellent heat resistance and good electrical insulation.[2] However, most of them have not been used for practical purposes due to their structural limitations and troublesome syntheses. On the other hand, a few works have been reported on the other photosensitive condensation polymers, for example, polycarbonates (PC) and polyarylates (PAR), although these versatile engineering thermoplastics have favorable balance of thermal, physical and chemical properties.

We recently proposed new type of photosensitive PI based on reaction development patterning (RDP), which is principally different from classical fine-pattern-forming technique.[3] In this principle, an amine used as reactive developer causes chemical main-chain degradation of PI in the irradiated area alone during development. In our latest works, photosensitive polymers composed of commercially available bisphenol A type PC [4] or PAR (U polymer®) [5] as matrix resins and DNQ compound actually exhibited 10-µm resolution by UV irradiation and the following reaction development with ethanolamine. This RDP technique has advantage that any pendant specific functional groups (such as COOH or OH) and photoactive groups are not required for emergence of photosensitivity of polymers except for C=O groups adjacent to heteroatoms in the main-chain of polymers, and thereby such condensation polymers with DNQ would be applied to positive photoresists.

This study details the successful patterning of commercial high-performance condensation polymer PEI (Ultem®, Scheme 1), which contain imide linkage in the main chain, for novel photopatternable materials on the basis of RDP by combining with DNQ. PEIs are of major commercial and industrial importance due to their outstanding thermal and oxidative stability and excellent mechanical strength.[6] As far as we know, there has been no example of application of Ultem® as photosensitive polymers.
2. Method

2.1. Materials

Poly(bisphenol A-co-4-nitrophthalic anhydride-co-1,3-phenylenediamine (Ultem®, Melt index 9) was purchased from Aldrich. 1,2-Naphthoquinonediazide-5-sulfonic acid p-cresol ester (PC-5®, Scheme 2) used in this study was obtained from Toyo Gosei Kogyo Co., Ltd. Other reagents were used as received.

2.2. Measurement

Molecular weights were measured by GPC equipped with UV detector (TOSOH, UV-8020) using polystyrene standards and its mobile phase was DMF containing LiBr (30 mmol/L) and phosphoric acid (60 mmol/L) at room temperature. 1H-NMR spectra were recorded on a 270MHz instrument (JEOL, EX-270) at 60°C using DMSO-d6 and DMSO-d6/D2O as solvents and tetramethylsilane as the internal standard. The glass transition temperature (Tg) of Ultem® was determined as the onset temperature by differential scanning calorimetry (DSC, Shimadzu DSC-60) at a heating rate of 10°C/min under nitrogen. Thermal gravimetric analyses (TGA) were carried out on a Shimadzu TGA-50 at a heating rate of 10 or 50°C/min under air or nitrogen. Film thickness was measured with a contact-type thickness analyzer (Nikon, DIGIMICRO MFC-101). Irradiation was conducted by UV exposure apparatus (ORC, JP-2000-EXC), and the dose was measured at i-line in the wavelength of 320-390 nm (ORC, UV-331 AP2). Scanning electron micrograph (SEM) was taken with a JEOL JSM-5500LV instrument.

2.3. Model Reaction

The reaction of PEI (Ultem®) with various amines in N-methylpyrrolidone (NMP) was conducted at room temperature. The solution containing each amine and 10 wt% of PEI in NMP was stirred at [amine] / [imide] ratio of 1 with continuous analysis by GPC.

2.4. Photo-patterning Processes

Photosensitive PEI was simply formulated by dissolution of Ultem® in NMP, followed by the addition of PC-5® as photosensitive agent (30 wt% of polymer). The obtained clean varnish was spun onto a shiny side of copper foil, and then prebaked at 90°C for 10 minutes. After UV irradiation (> ~360 nm) in contact technique, the PEI films were developed with a mixture of ethanolamine/NMP/H2O (4/1/1 by wt.) at 40-45°C under ultrasonication.

3. Results and Discussion

3.1. Model Studies

In the reaction development patterning (RDP) system, amine-containing developer composed of ethanolamine, NMP and H2O was employed. The reaction between PEI (Ultem®, Mw 20,400; Mn 42,600; Mw/Mn 2.1; Tg 217°C; Td 518°C; Td 526°C) and ethanolamine was studied as a model reaction in order to make clear the mechanism of RDP.

Changes in the molecular weight of PEI were monitored by GPC in the reaction of PEI with the nucleophilic primary amine in NMP. Figure 1 shows the dependence of molecular weight of PEI on the reaction time at [amine] / [imide] ratio of 1. As the reaction proceeded, the molecular weight of PEI gradually decreased, and after 4 hours lowered to ~4,000 g/mol (oligomers). This suggests that PEI might be readily decomposed in the presence of ethanolamine.

In-situ 1H-NMR experiments were carried out to clarify the structure of the model reaction products having low molecular weight. Figure 2(a)
shows $^1$H-NMR spectrum of original PEI (Ultem®). Although PEI was partially soluble in deuterated DMSO, the solution became homogeneous after the addition of ethanolamine at [amine] / [imide] ratio of 1: (a) and (b) in DMSO-$d_6$ and (c) in DMSO-$d_6$/D$_2$O.

3.2. Lithographic Properties of Photosensitive PEI

The relationship between exposure dose through a photographic step tablet® (Kodak) and normalized film thickness was shown in Figure 3. The sensitivity (E$_o$) was estimated from the dose required to dissolve the irradiated area of photosensitive PEI film in developer completely. Value E$_o$ of the PEI system was determined to be approximately 2,000 mJ/cm$^2$ when about 10-$\mu$m thick film was employed. Decrease in film thickness in unirradiated area of the PEI film was little observed. Figure 4 shows the relationships between time immersed in developer and normalized film thickness of both the irradiated (dose of 2,000 mJ/cm$^2$) and unirradiated photosensitive PEI films. The dissolution of the unirradiated film in the developer scarcely progressed at the time of the complete dissolution of the irradiated one, and the margin for development time is relatively wide. The indencarboxylic acid derivative generated from DNQ by UV exposure was proved to be effective dissolution accelerator in irradiated area.

Figure 5 shows the representative line/space (L/S) patterns of photosensitive PEI. The PEI film was developed with ethanolamine-containing developer for 13 minutes. Clear and fine L/S patterns of the PEI system at 10-, 15- and 20-$\mu$m dimension were observed without any peeling off, swelling and deformation. Optimization of the UV exposure and development conditions will enable the formation of patterns with higher resolution. Figure 6 exhibits GPC trace of the irradiated and developed photosensitive PEI system. The molecular weight of PEI in the irradiated area
diminished significantly as compared with the original one. This result suggests that Ultem® is dissolved as depolymerized products and implies that the main-chain of Ultem® is cleaved during development.

The effect of the structure of amines on the dissolution of the irradiated photosensitive PEI film was examined by using developers containing various amines (Figure 7). The ~10-µm thick films, spin-coated from NMP solution and baked at 90°C for 10 minutes, were dipped in the developers consisting of amines, NMP, and H2O (1/1/1 by wt.) by ultrasonic treatment at ~40°C (dose of 2,000 mJ/cm²). The thickness of the remaining film was plotted as a function of the immersion time. High nucleophilic hydroxylamine (pK_a 6.0) and hydrazine (pK_a 8.0) gave extremely fast dissolution rates compared with ethanolamine (pK_a 9.5). The photosensitive PEI film also rapidly dissolved with ethylenediamine (pK_a 7.1, 9.9) of difunctional amine, whereas the dissolution of the film hardly proceeded in dilute ethanolamine-containing solution (ethanolamine/NMP/H2O 1/1/1 by wt.) within 15 minutes.

The ability of these amines to depolymerize PEI was also evaluated by model reaction at [amine] / [imide] ratio of 1 in NMP. Figure 8 indicated that degradation of PEI proceeded readily in the reaction with inorganic amines (including water) such as hydroxylamine and hydrazine. When anhydrous ethylenediamine was used, the gelation of the PEI solution took place immediately after the addition of the diamine.

Figure 3. Sensitivity curve for photosensitive PEI.

Figure 4. Dissolution curves of photosensitive PEI films in both the irradiated (○) and unirradiated (●) area.

Figure 5. SEM of L/S patterns for photosensitive PEI developed with ethanolamine-containing solution.

Figure 6. GPC profiles of original Ultem® (solid line) and of the irradiated photosensitive PEI after development (dashed line).

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Figure 9 shows the L/S patterns of photosensitive PEI at 50-µm dimension developed with hydrazine-containing solution (hydrazine monohydrate/NMP/H2O 1/1/1 by wt.). Although
Figure 7. Dissolution curves of photosensitive PEI film in various amine-containing developers (amine/NMP/H₂O 1/1/1 by wt.) at 40°C under ultrasonication: dose, 2,000 mJ/cm²; ethanolamine (○); ethylenediamine (□); hydroxylamine (△); hydrazine (◇).

Figure 8. GPC profiles of PEI after the reaction with various amines in NMP for 1 hour at [amine] / [imide] ratio of 1.

Figure 9. SEM of L/S patterns for photosensitive PEI developed with hydrazine-containing solution.

3.3. Pattern Forming Mechanism Based on RDP

The detailed mechanism for RDP as a result of the degradation of the photosensitive PEI system is schematically illustrated in Figure 10. The pattern formation in this RDP is based on a difference in the affinity for the developer between the exposed and unexposed regions. In the exposed area, DNQ eliminates nitrogen to yield alkaline-soluble carboxylic acid derivative by Wolff rearrangement in the presence of water. At the interface between the exposed area of the film and the developer, the acid-base reaction between the resulting acid and ethanolamine in the developer affords an ammonium salt, which is considered to result in the accelerated permeation of the developer into the exposed polymer matrix. The permeated amine induces ring-opening by its nucleophilic attack to imide moieties, and the depolymerization of the imide-containing polymer readily takes place by the successive attack of the excess amine to give low molecular weight amidized products. The opening of the rigid imide rings also accelerates the dissolution of the film in the amine-containing developer.

On the other hand, unreacted, hydrophobic PC-5® reduces the diffusion of the amine into the unexposed part, and gives the film increased insolubility in the developer. Thus, photosensitive DNQ acts as both accelerator in the exposed area and inhibitor in the unexposed area.

3.4. Thermal Properties

Figure 11(a) shows TGA curve of the photosensitive PEI film as function of heating time. The temperature was quickly raised to 250°C at the heating rate at 50°C/min and held constant for 30 minutes in air. The 18wt% weight loss of the film at the heating up to 250°C was caused by degradation of DNQ. After the initial heating step, no weight loss was observed.

Figure 11(b) represents TGA curves of original PEI pellet (Ultem®) without PC-5® (solid line) and
the photosensitive PEI film after baking at 250°C for 30 min (dashed line) at the heating rate at 10°C/min in nitrogen. Though the decomposition onset temperature of the reanalyzed sample was appreciably low compared to the original PEI, no weight loss up to around 300°C was observed. These results indicate that the photosensitive PEI might exhibit good resistance to solder heat at 260°C for 10 seconds by postbaking at 250°C in a short time although PC-5® as photosensitive agents can not be thoroughly removed. However, thermally treated positive images at a temperature over $T_g$ (217°C) of Ultem® could be deformed.

4. Conclusion

PEI (Ultem®)/DNQ combination shows good positive photosensitivity by reactive development with ethanolamine after UV exposure. PEI without any specific functional groups as well as PIs, PCs, and PArS is found to be applied to positive photoresists. GPC analysis indicated that the molecular weight of the solubilized parts largely decreased as compared with original PEI, and $^1$H-NMR experiments also suggested the formation of amide compounds. The pattern forming mechanism was based on RDP, in which polymer main-chain scission occurred by the amine-induced degradation during development.

References