PL-01

Facile Synthesis of Photosensitive Polyimide and Poly(Benzoxazole) and Low-Temperature Cyclization of Poly(amic acid) and Poly(*o*-hydroxy amide)

Ken-ichi Fukukawa, Yuji Shibasaki, Mitsuru Ueda

Department of Organic & Polymeric Materials, Graduate School of Science & Engineering, Tokyo Institute of Technology, 2-12-1-H120, O-okayama, Meguro-ku, Tokyo 152-8552, Japan

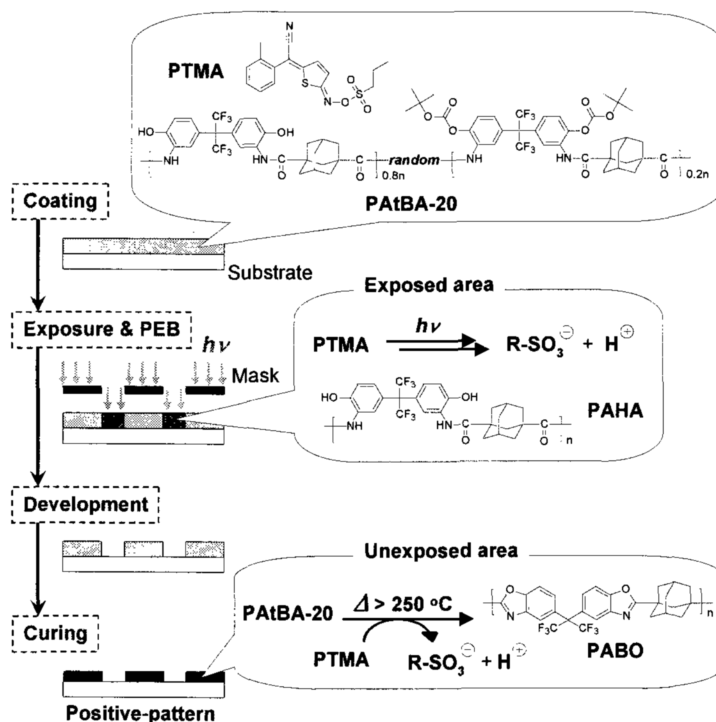
Photosensitive poly(imide)s (PSPIs) and poly(benzoxazole)s (PSPBOs) are widely used as protection and insulation layers for very large scale integration circuits and multichip modules for computers owing to their high thermal stability and excellent mechanical properties. The fabrication of electronic devices is simplified using these PSPIs and PSPBOs. Otherwise, an additional photoresist is required for patterning of those films, involving additional complicated process steps. Formulation of PSPIs and PSPBOs is also needed several steps. Thus, it is important to develop a straightforward route for the formation of these resists. Furthermore, high temperature treatment is required for cyclization of these precursors, poly(amic acid)s and poly(o-hydroxy amide)s. This process is hardly applicable to the conventional electric applications containing at least one or more thermally unstable organic components. Development of novel catalysts enabling low temperature solid-phase cyclization of these precursors is required.

The first topic is development of a negative-type photosensitive polyimide (PSPI) based on poly(amic acid) (PAA) and a photo-base generator (PBG). Furthermore, low-temperature thermal imidization of the negative image in this PSPI system is also described.

PAA-**2**, the polyimide precursor, was prepared from oxydianiline (ODA) and 4,4'-biphthalic dianhydride (BPDA) in *N,N*-dimethylformamide (DMAc), and used directly for lithographic evaluations. Since a photogenerated base, dimethyl piperidine (DMP), was effective for imidization of PAA-**2** to the corresponding PI-**2** at temperatures up to 200°C, the dissolution behavior of this system was studied in relation to PBG content, bake-temperature dependence, and composition of the aqueous alkaline developer. The PSPI using 85 wt% PAA-**2** and 15 wt% synthesized PBG showed a sensitivity of 220 mJ/cm^2 and contrast of 11.7 when exposed to 365-nm light (i-line) and developed with an aqueous alkaline developer (aqueous tetramethylammonium hydroxide and iso-propanol, TMAHaq/iPrOH). A clear negative image with 8-μm features was produced by contact-printing and converted into the PI-**2** pattern upon heating at 200°C, confirming the results obtained by SEM imaging and IR spectroscopy.

The second topic is development of positive-type photosensitive polybenzoxazole (PSPBO) based on partially *tert*-butoxycarbonyl (*t*Boc) protected poly(semi-alicyclic *o*-hydroxy amide) (PAtBA) and a photo-acid generator, (5-propylsulfonyloxyimino-5*H*-thiophene-2-ylidene)-(2-methylphenyl)acetonitrile (PTMA). PAtBA was prepared from poly(semi-alicyclic *o*-hydroxy amide) (PAHA) and di-*tert*-butyl dicarbonate in the presence of catalytic diethylmethyl amine in cyclohexanone, and used directly for lithographic evaluation. The *t*Boc protection to PAHA and thermal behavior of PAtBA were characterized by thermogravimetric analysis (TG), ^{1}H NMR, UV-vis, and FTIR spectrometry. As a result of photolithographic evaluation, the PSPBO precursor, PAtBA-20 containing 10 wt % PTMA, showed a sensitivity of 35 mJ/cm^2 and a contrast of 12.8, when it was exposed to a 365 nm light (*i*-line), post-baked at 110 °C for 5 min, and developed with a 2.38 wt % aqueous tetramethylammonium hydroxide solution (TMAHaq) at 25 °C. A fine positive image of 7.8 μm line-and-space pattern was printed in a film which was exposed to 50 mJ/cm^2 of *i*-line by contact-printing mode, and fully converted into the corresponding polybenzoxazole (PABO) pattern upon heating at 250 °C, confirmed by SEM and FTIR spectroscopy. Thus, PTMA is effective as a thermo-acid generator for low-temperature cyclization of PAtBA into the PABO as well to meet practical requirement in the industry (Scheme 1).

Scheme 1. Patterning process and subsequent low-temperature cyclization using positive-type PSPBO based on partially protected PAtBA and PTMA.



閉環速度を低下させるために入れるアルカリ(塩基)は
高温ではほとんど気化・分解する。(上田)注)