Positive-Working Alkaline Developable Photosensitive and Second-Order Nonlinear Optical Polyimide

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A polyamic acid having a nonlinear optical chromophore was prepared by the ring-opening polyaddition of pyromellitic dianhydride and bis(4-aminophenyl)ether, and *N,N*-[bis(*p*-aminophenyl)amino]azo-4'-nitrobenzene. The polymer containing 30 wt% of 2,3,4-tris(1-oxo-2-diazonaphthoquinone-5-sulfonyloxy)benzophenone (5-DNQ) functioned as an alkaline developable photosensitive resist, and then converted to polyimide by thermal treatment.

Second order optically nonlinear polymers have potential uses for second-harmonic generation (SHG) and for very high speed optical switching and modulations. For the practical applications, these polymers must satisfy the following requirements: a stability of the dipole orientation, an adequate optical nonlinearity, and a low optical loss.[1] Polyimides (PIs) are excellent candidates for electrooptical materials because of low dielectric constants and high Tg values, and are compatible with semiconductor processes. Recently, a general approach to the synthesis of second-order nonlinear optical (NLO) PI exhibiting high thermal stability has been developed. This method involves a polymerization between the diamine containing an NLO chromophore and a dianhydride monomer[2] or an introduction of NLO chromophore to poly(hydroxy-imide) *via* the Mitsunobu reaction.[3]

On the other hand, photosensitive polyimides (PSPI) are currently receiving considerable attention for their potential use in the fabrication of semiconductor devices and multichip modules, since they enable the number of process steps to be reduced by avoiding the use of classical photoresists.[4] Therefore, the synthesis of PSPIs with NLO property will be interesting in developing effective electrooptical devices. We now report the new positive working alkaline developable PSPI having second-order NLO property.

Positive resists based on a novolak resins with *o*-diazonaphthoquinone (DNQ) are standard materials utilized in semiconductor manufacturing, where DNQ acts as a dissolution inhibitor for aqueous base development of the novolak resin. Upon exposure to light, DNQ is converted to indenecarboxylic acid that increases the dissolution rate of the novolak matrix in the regions where exposure has occurred.[5]

NLO materials are assembled from organic dyes possessing large second-order nonlinear optical susceptibilities by incorporating them into polymer glasses and poling with electric field. Thus, NLO polyimides exhibit low optical transparencies in the UV-visible region.

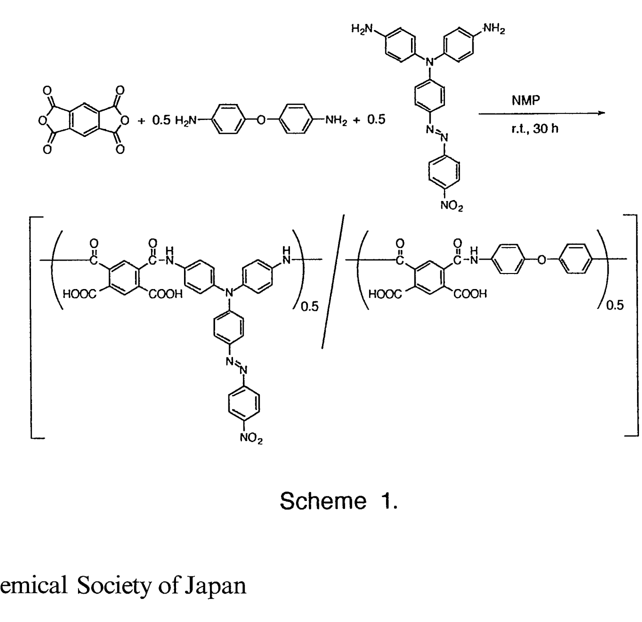
On the other hand, DNQs generally have an absorption maximum at approximately 350-400 nm. Therefore, it is important to design an NLO-PI which does not have strong absorptions in the region of 350-450 nm.

Quite recently, Verbiest and co-workers reported that the polyimide prepared from hexafluoroisopropylidene diphthalic anhydride and *N,N*-(bis(*p*-aminophenyl)amino)azo-4'-nitrobenzene (BAAN) having the well-known dye molecule Disperse Red I structure was a thermally stable polymer for second-order NLO applications.[2a,2b]

PSPI employed in this study was prepared in the form of a copolymer, utilizing another diamine component, so as to allow for better control of the dissolution rate. Conventional monomers for making polyimide, pyromellitic dianhydride (PMDA) and bis(4-aminophenyl) ether (BAPE) was used as the dianhydride and the co diamine, respectively for making this copolyimide.

The synthesis of polyamic acid (PAA) was carried out by ring opening polyaddition of PMDA, BAPE, and BAAN in NMP at room temperature (Scheme 1). The PAA was isolated by pouring the reaction mixture into 50% aqueous methanol, collecting the precipitate and subsequent drying in vacuo. The polymer was produced in excellent yield with an inherent viscosity of 0.37 dl•g^{-1}. The PAA was identified as the corresponding polyamic acid by infrared spectroscopy. The IR spectrum exhibited carbonyl and amide carbonyl absorptions at 1710 and 1640 cm^{-1}, respectively, and N-H stretching band at 3430 cm^{-1}. The polymer was a reddish purple powder and its transparent film was obtained by casting the polymer from solution.

The UV-visible spectrum of a 1 μm thick film of the PAA (Figure 1) indicates that the film has a strong absorption centered at 500 nm due to the chromophore and is relatively transparent around 400 nm. Thus, we have chosen 5-DNQ as the photoractive DNQ compound which has a strong absorption in the range of 300-450 nm. The polymer was dissolved in 20 wt% in DMAc at room temperature, to which was added 5-DNQ (30 wt%). Films spin-cast on silicon wafers were prebaked at 80 °C for 10 min, exposed 1



Scheme 1.

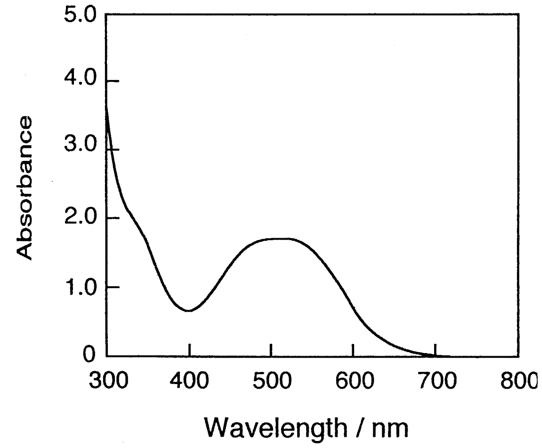


Figure 1. UV-visible spectrum of 1 μm thick film of PAA.

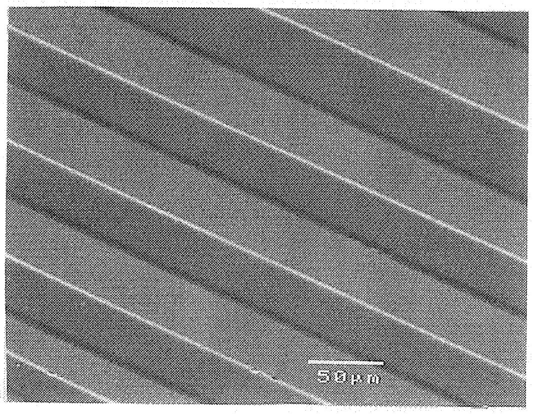


Figure 2. A scanning electoron micrograph of positive project-printed.

J•cm^{-2} to UV light, developed with 0.5% tetramethylammonium hydroxide (TMAH) aqueous solution, and rinsed with water/isopropyl alcohol (3:1, vol%). Figure 2 shows a scanning electron micrograph of positive image projection-printed. This resist is capable of resolving 10 μm features when a 4-μm thick film is used.

Figure 3 shows TGA curves of films after development (dashed line) and curing at 250 °C for 30 min (solid line). The dashed line exhibited a two-step weight loss. The first weight loss starts at around 120 °C, indicating cyclization and degradation of 5-DNQ begin at this temperature. The weight loss continues up to 250 °C, and the decomposition of polyimide occurs at temperature higher than 500 °C. On the other hand, the solid line shows no weight loss up to 300 °C. These results indicate that 5-DNQ as the photoractive compound can be effectively removed with a 300 °C post-development bake, and the NLO-PI has good thermal stability.

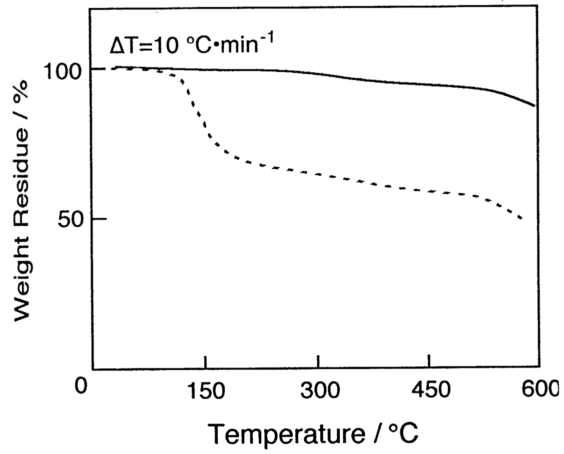


Figure 3. TGA curves of PAA films containing 5-DNQ after development (_ _ _ _) and curing at 250 °C for 30 min (______).

References and Notes

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