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Fabrication and Photodegradation Behavior of Photosensitive Polyimide LB Film

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Ultra thin film of polyamic acid having benzene and sulfonyloxyimide moieties was fabricated with a LB technique and then photosensitive polyimide LB film was obtained by the precursor method. Physical properties and photodegradation behavior of polyimide LB film were investigated by π -A isotherm, UV-Visible and FT-IR spectroscopic measurements. Especially, it has been found that the ultra thin LB film of polyimide is an effective positive type resist material for obtaining high lithographic resolution.

Keywords polyamic acid; polyimide LB film; photodegradation behavior; positive resist; resolution

INTRODUCTION

Photosensitive aromatic polyimides have attracted considerable interest in the fabrication of fine patterns for their good electrical, mechanical and thermal properties. In the previous work, we have reported that the preparation and photodegradation characteristic of photosensitive polyimide with sulfonyloxyimide units in the polymer main chain[1].

In this study, the LB film of polyamic acid tert amine salt

having benzene and sulfonyloxyimide moieties was fabricated and the precursor LB film was imidized chemically with elimination of tert amine salt. Especially, the superiorities of LB film in UV light exposure lithography are discussed.

EXPERIMENTAL

The synthesis of monomers was carried out according to the procedures previously reported[1]. Polyamic acid was prepared by the condensation polymerization of *N,N'*-dihydroxybenzenetetracarboxylic amic acid and 2,6-naphthalenedisulfonyl chloride. The structure of polyamic acid was shown in Figure 1.

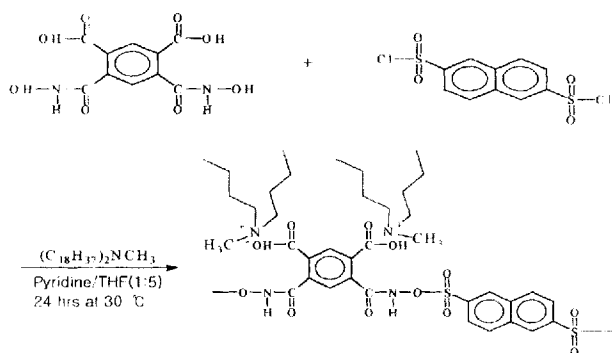


FIGURE 1. Polyamic acid structure

All monomers and polymer were identified through elemental analysis, HPLC, FT-IR and ^1H , ^{13}C -NMR. In a typical LB experiment, 300 μl benzene and DMAc (1:1) of polyamic acid was spread on deionized water and π -A isotherm was measured at a barrier speed of 5 cm^2/s at 25 $^\circ\text{C}$. The polyamic acid multilayers were obtained at a constant surface of 35 mN/m as Y-type deposition. Polyimide LB films were prepared by the chemical treatment of the precursor multilayers. Thermal properties and photodegradation characteristics of the LB film were investigated with TGA, DSC and UV-Visible. Following

exposure with 254 nm deep UV light, the wafer was developed in THF solvent. The positive tone image of polyimide was observed with a Nikon optical microscope.

RESULTS AND DISCUSSION

Figure 2 showed the π -A isotherm for the monolayer of polyamic acid. The polyamic acid is able to form a stable and condensed monolayer. A condensed to expanded phase transition at about 60 mN/m was observed. The limiting area estimated by extrapolating the steepest region of the condensed phase to zero pressure was about 38 $\text{\AA}^2/\text{molecule}$.

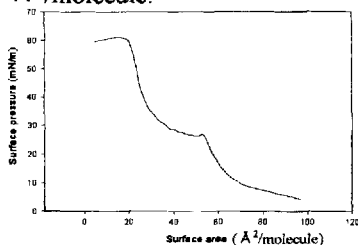


FIGURE 2. π -A isotherm of polyamic acid

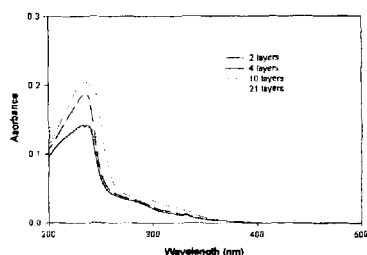


FIGURE 3. UV-Visible spectra of polyimide LB films

UV-Visible spectra of polyamic acid LB films with different number of layers were shown in Figure 3. The intensity of absorption maximum peak corresponding to the $\pi \rightarrow \pi^*$ transition of pyromellitic diimide increased with increasing number of layers, indicating that polyamic acid LB films well deposited with higher stroke numbers. The well-ordered LB film was imidized chemically by thermal elimination of tert amine salt. Figure 4 showed the UV-Visible changes of polyimide LB film on the quartz plate upon the irradiation of 254 nm deep UV light. When the polyimide LB film was irradiated with 254 nm deep UV light, the absorption band at 236 nm decreased with increasing exposure time, implying photocleavage of N-O bond or ring

opening of imide moiety.

Positive-tone image of polyimide LB film was shown in Figure 5. The fine patterns of isolated spaces with 2~6 μm width were obtained at a dose of 15 mJ/cm^2

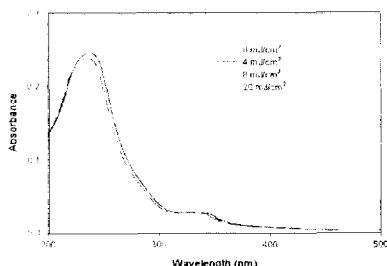


FIGURE 4. UV-Visible absorption spectral changes of polyimide LB film

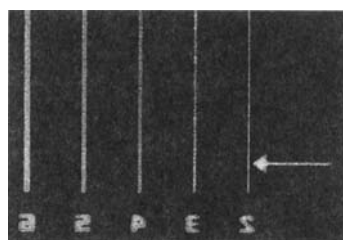


FIGURE 5. Positive-tone image of polyimide LB film

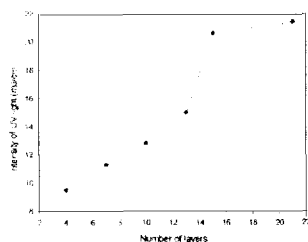


FIGURE6. Photosensitivity of polyimide LB films with different number of layers

The contrast of LB film was better than that of spin-cast film under same energy. The photosensitivity and resolution of polyimide LB film was higher than those of usual spin-cast film. Especially, the photosensitivity was increased with decrease in thickness of polyimide LB film as shown in Figure 6.

Acknowledgement

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1. S.Y. Oh, J.Y. Lee, S.Y. Cho, and C.M. Chung, *Polymer(Korea)*, **24**, 407 (2000).