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Positive-Type Photosensitive Polyimide Based on a Photobase Generator Containing Oxime-Urethane Groups as a Photosensitive Compound

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Abstract: The chemical structure of a semi-aromatic polyimide-I, which was prepared by the chemical imidization of cyclopentanetetracarboxylic dianhydride and 2,2-bis(4-aminophenyl)hexafluoropropane, was characterized by ^{13}C-NMR spectroscopy. The chemically imidized polyimide-I was used for the preparation of a photosensitive polyimide (PSPI) through the addition of benzophenone and benzophenone oxime hexamethylene diurethane (BOHD), a photobase generator containing oxime-urethane groups. The polyimide-I film containing benzophenone and BOHD was not soluble in 2.38 wt% tetrabutylammonium hydroxide solution in H_2O. However, it became soluble following irradiation with 310 nm UV light. A positive tone image with a resolution of 5 μm was obtained with this PSPI, having sensitivity (D_c) of 1.2 J/cm^2 and contrast (γ_p) of 1.08. Thus, a polyimide, which is not intrinsically photosensitive, can become photosensitive through the addition of a photobase generator containing oxime-urethane groups as a photosensitive compound.

Keywords: irradiation, photobase generator, positive photoresist, photosensitive polyimide, photosensitive compound.

Introduction

Polyimides have been widely used in microelectronics as protection and insulation layers, buffer coating materials, passivation layers, flexible printed circuit boards, and so on,[1] because of their high chemical and thermal stability, high mechanical strength, and excellent electrical properties. In particular, the application of photosensitive polyimides (PSPIs) in the microelectronic industry is increasingly important since they can be patterned by direct exposure and developed without the use of photoresist. PSPIs simplify the processing steps, and avoid the use of photoresist in the fabrication of various electronic devices.[2] In addition, PSPIs are expected to play an important role in the manufacturing of electro-optic devices such as optical memory matrices, wave-guide, and non-linear optical materials - where higher thermal stability, better processability, and good chemical resistance are required.[3]

On the other hand, amines are very important compounds for their use in the thermal cross-linking reagent of the epoxy resins in adhesives, paints, and coatings industry. Photobase generators produce an amine upon irradiation, and are being increasingly used in the development of new technologies. For example, they have been applied to chemically reversible fluorescent imaging materials,[4] photolithographic micropatterning of electroluminescent polymers,[5] and patterning of conductive polyaniline films,[6] as well as various types of photoresists.

Photobase generators have been applied also in the preparation of PSPIs. McKean *et al.*[7-9] reported a PSPI based on the photobase catalyzed imidation of poly(amic alkyl ester). Similarly, Frechét *et al.*[10] reported the photogenerated amine acts as a catalyst in the imidation of precursor polymers containing amic acid or amic ester groups. Mochizuki *et al.*[11] reported a PSPI based on polyisoimide using a photobase generator as an isomerization catalyst.

In previous studies, it was reported that the photolysis of the oxime-urethane derivatives led to the photochemical formation of amines.[12] This reaction was applied in the preparation of various types of photo-functional polymers.[4,13-16] In this paper, a new type of positive-type PSPI, based on a photobase generator containing oxime-urethane groups, is

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reported. A polyimide, which is not intrinsically photosensitive, can become photosensitive through the addition of a photobase generator containing oxime-urethane groups as a photosensitive compound.

Experimental

Materials and Instruments. 1,2,3,4-Cyclopentanetetracarboxylic dianhydride (CPDA), 2,2-bis(4-aminophenyl) hexafluoropropane (APHF), and tetra-*N*-butylammonium hydroxide (TBAH) 10 wt% aqueous solution were purchased from Tokyo Kasei Chemical Co. and used as received. Reagent grade dimethylformamide (DMF) and *N*-methylpyrrolidone (NMP) were used after drying over a molecular sieve Type 5A. Dialysis was performed using a cellulose dialysis sack (No. 250-7U) obtained from Sigma Chemical Co. Bis(benzophenone oxime)-*N,N'*-hexamethylenediurethane (BOHD) was prepared using the reported procedure.[12]

One module of a Rayonet photochemical reactor (The Southern New England UV Co., model 310), equipped with a 310 nm fluorescent lamp was placed horizontally and used for irradiation of the polymer films. The light intensity was 1.26 mW/cm^2 measured using a radiometer (Vilbmer Lourmat Co., model VLX-3W). Differential scanning calorimetry (DSC) measurements were carried out with a DuPont model 910 analyser under N_2 atmosphere at a heating rate of 10 °C/min. Thermal stability was examined on a TA instruments model 2050 at a heating rate of 10 °C/min under nitrogen atmosphere. The thickness of the polymer film was measured using an α-step surface profiler (Tenco Instruments Inc., model AS-500). Micropatterns were observed using an atomic force microscope (DI, model Nanospace SI-2).

Preparation of Polyimide-I. APHF (0.69 g, 1.9 mmol) and quinoline (14.3 mg, 0.026 mmol) were dissolved in NMP (3 mL) under an N_2 atmosphere. CPDA (0.42 g, 2.0 mmol) was added slowly to the APAF solution for 2 hrs. The mixture was heated for 6 hrs at 70-80 °C, and then the temperature of the mixture was raised slowly up to 202 °C during next 2 hrs. The mixture was heated for 8 hrs at 202 °C. The resulting polymer was isolated through precipitation into methanol and purified by reprecipitation from NMP into methanol. The polymer was dried at 60 °C, and then dissolved in the THF (8 mL). The polymer solution in THF was put into a cellulose dialysis tube, and dialyzed with distilled water for 3 days. The polyimide-I was obtained after freeze-drying of the dialyzed polymer solution (yield: 39%).

FTIR (KBr pellet, cm^{-1}): 2943 (C-H), 1786, 1722 (imide C=O), 1517, 1379, 1259, 1205, 1178.

UV Absorption Spectra. A 10 wt% polyimide-I solution containing the polyimide-I (0.05 g), benzophenone (2.5 mg), and BOHD (15 mg) in DMF (0.5 mL) was spin coated on a quartz plate for 60 sec at 1,500 rpm, and 60 sec at 3,000 rpm. The polyimide-I film on the quartz plate was dried overnight at 40 °C in a vacuum, and UV absorption spectral changes upon irradiation with a 310 nm UV light were observed.

Normalized Thickness. A 20 wt% polyimide-I solution containing polyimide-I (0.05 g), benzophenone (2.5 mg), and BOHD (15 mg) in NMP (0.34 mL) was spin coated on a silicon wafer for 10 sec at 2,000 rpm, and 10 sec at 4,000 rpm. Thickness of the polyimide-I film was 0.3 μm after drying. The film on silicon wafer was irradiated with 310 nm UV light, and dipped into 0.2 wt% TBAH in H_2O/ ethanol (1/10, v/v) solution for 10 min. The dipped film was then immersed in water, and subsequently dried at 40 °C for 4 hrs in a vacuum. The normalized thickness was determined from the following equation.

$$\text{Normalized thickness} = \frac{\text{Absorbance at 1726 cm}^{-1}\text{ after dipping}}{\text{Absorbance at 1726 cm}^{-1}\text{ after irradiation}}$$

Micro Patterning. A polyimide-I solution, which was prepared by dissolution of polyimide-I (0.05 g), benzophenone (2.5 mg), and BOHD (15 mg) in THF (1.0 mL), was spin coated on a silicon wafer for 10 sec at 400 rpm, and 20 sec at 1,200 rpm. After drying, the polyimide-I film on silicon wafer was covered with a photomask and irradiated with 310 nm UV light for 3.2 J/cm^2. The irradiated film was then dipped into a developing solvent (2.38 wt% TBAH in H_2O) for 6 min. The dipped film was immersed in water, and subsequently dried at 40 °C for 3 hrs in a vacuum. The micro pattern formed on the silicon wafer was observed using an atomic force microscope.

Results and Discussion

We used a semi-aromatic polyimide containing cycloaliphatic groups, since the color of fully aromatic polyimide interferes with the effective photochemical reaction of the added BOHD and benzophenone. Semi-aromatic polyimides are soluble in organic solvents and transparent in the visible region. However, the synthesis of high molecular weight polyimide cannot always be successful by the two-stage method because of the lower reactivity of cycloaliphatic tetracarboxylic acids compared with aromatic analogs. Therefore, one-step high-temperature synthesis in aprotic solvent was employed.

Scheme I shows a synthetic route for the preparation of polyimide-I. Chemical imidization of CPDA, an aliphatic cyclic anhydride, and APHF, a diamine containing fluorine groups, in the presence of quinoline as a imidization catalyst[17] led to the formation of polyimide-I. A slight excess of CPDA was used in this experiment in order to increase solubility of the polyimide by incorporating -COOH groups in the polymer end groups. The polyimide-I was obtained by double precipitation into methanol, and purified by dialysis to remove low molecular weight compounds. The polyimide-I

was soluble not only in aprotic solvents such as DMF, NMP, dimethyl acetamide, and dimethylsulfoxide, but also in organic solvents such as THF and acetone. The intrinsic viscosity measured in DMF was 0.27 g/dL.

Figure 1 demonstrates UV-VIS transmittance spectra of a polyimide-I film and its fully aromatic polyimide analog. Polyimide-I, a semi-aromatic polyimide is transparent above 300 nm (transmittance > 90%). However, its fully aromatic polyimide analog absorbs light up to 550 nm (transmittance < 90%) and has brown color.

Figures 2 and 3 show DSC and TGA curves of the chemically imidized polyimide-I, respectively. T_g was observed at 308 °C. The polyimide-I was stable up to 350 °C and 10% weight loss was observed at 490 °C. The char yield was 36 wt% at 700 °C. However, a mixture of polyimide-I, BOHD, and benzophenone (100 : 30 : 5 by wt ratio) became less stable due to the added compounds. The reaction conditions and physical properties of the polyimide-I are summarized at Table I.

The chemical structure of the polyimide-I was characterized by FTIR and ^{13}C-NMR spectroscopy. The presence of an absorption band around 3100~3600 cm^{-1} in the IR absorption spectrum of the polyimide-I indicates the presence of -COOH groups in the polymer chain. The chemically imidized polyimide-I was heated further at 300 °C for 6 hrs in order to observe whether further imidization reaction took place or not by thermal treatment. However, no change was observed in the IR absorption spectrum between before and after the thermal treatment, indicating that no chemical change was observed. The degree of imidization was about 81%, which was determined from the absorbance difference at 3400 cm^{-1} (υ_{OH}) between before and after imidization. The absorption band at 1517 cm^{-1} ($\upsilon_{C=C}$) was used as a reference band for the normalization of the absorption band at 3400 cm^{-1}.

Figure 4 shows ^{13}C-NMR spectrum of polyimide-I. It contains -$COOCH_3$ groups at the end of polymer chain as shown in Scheme I, since slight excess molar amount of CPDA was added, and the anhydride groups at the end of polymer chain reacted with methanol during precipitation.

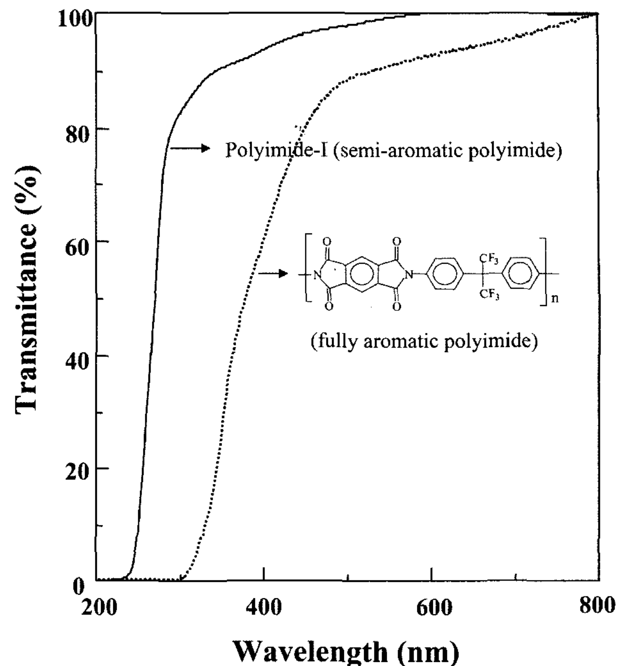


Figure 1. UV-VIS transmittance spectra of a polyimide-I film (film thickness = 0.16~0.18 μm) and its fully aromatic polyimide analog (0.15 ~ 0.19 μm).

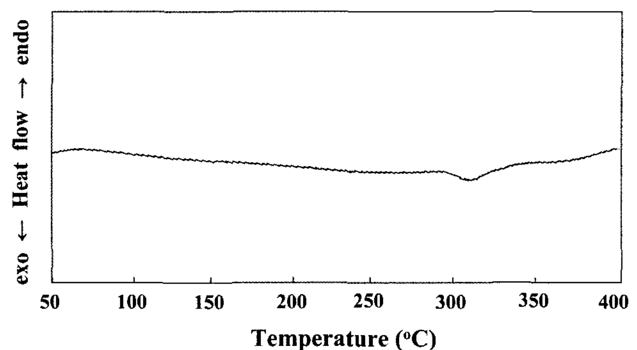


Figure 2. DSC curve of chemically imidized polyimide-I under N_2 atmosphere.

Scheme I

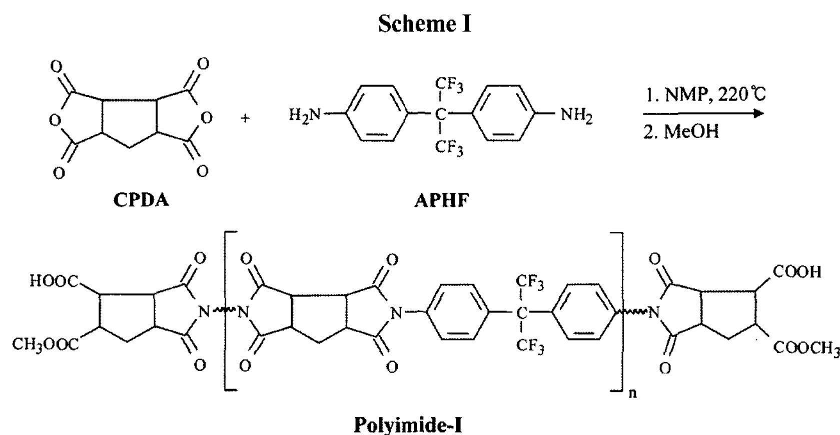


Table I. Preparation Conditions and Physical Properties of Polyimide

Polyimide	CPDA (mmol)	APHF (mmol)	NMP (mL)	Yield (%)	η_{inh}(g/dL)	M_n^a	M_w/M_n	T_g^b(°C)	T_{10}^c(°C)	Residue^d(%)
I	0.42 g (2.0)	0.69 g (1.9)	3	39	0.27	7200	1.24	308	491	36

^{a}Measured by GPC at flow rate of 1 mL/min in THF. ^{b}Measured by DSC at a heating rate of 5 °C /min under N_2.
^{c}The temperature of 10 % weight loss measured by TGA at a heating rate of 10 °C /min under N_2.
^{d}Weight residue at 700 °C measured by TGA at the same condition.

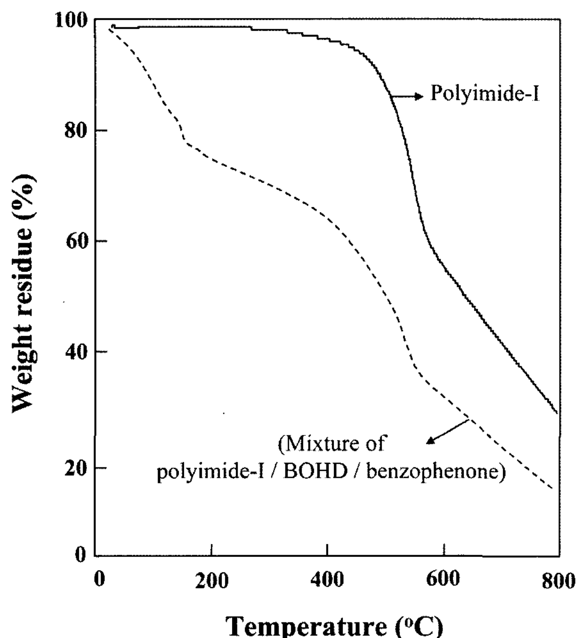


Figure 3. TGA curves of the chemically imidized polyimide-I (solid line) and that containing 30 wt% BOHD and 5 wt% benzophenone (broken line) under N_2 atmosphere.

The δ value of the carbon at the ester -CH_3 groups (**d**) at the end of the polymer chain appeared at 51.1 ppm and that at the ester C=O groups (**m**) appeared at 178.1 ppm.

The ^{13}C-NMR spectrum of the polyimide-I shows that four kinds of carbonyl carbons at 174.8 (imide C=O, **k**), 177.4 (amide C=O, **l**), 178.1 (ester C=O, **m**), and 178.3 (carboxylic acid C=O, **n**) ppm, respectively. This result indicates that chemically imidized polyimide-I contains amide and -COOH groups in the polymer chain as shown in Scheme II.

Figure 5 shows UV absorption spectral changes of the polyimide-I film containing 5 wt% benzophenone and 30 wt% of BOHD upon irradiation with 310 nm UV light. The UV absorption spectrum of the polyimide-I film without BOHD and benzophenone was not affected by irradiation with a 310 nm UV light. However, in the presence of benzopheone and BOHD, the absorption band of the polyimide-I film around 250 nm, decreased upon irradiation, whilst that of approximately 330 nm increased. The absorption band around 250 nm comes from the aromatic groups of polyimide-I and BOHD. This result indicates that benzophenone photosensitized photodecomposition reaction of BOHD in the polymer film took place, since BOHD is more photosensitive than polyimide-I.

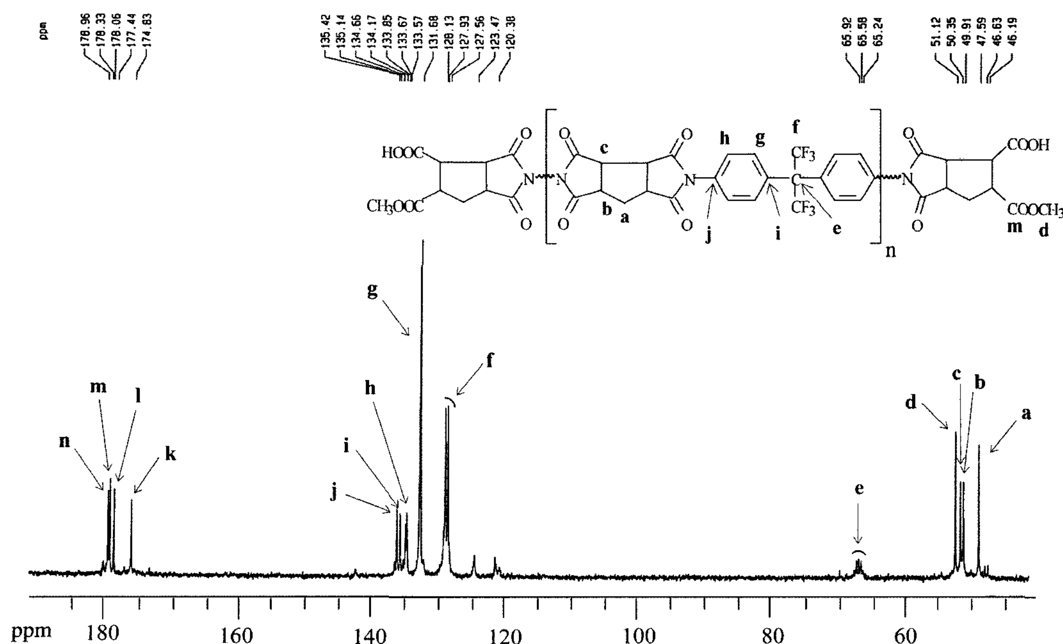


Figure 4. ^{13}C-NMR spectrum of polyimide-I in acetone-d_6.

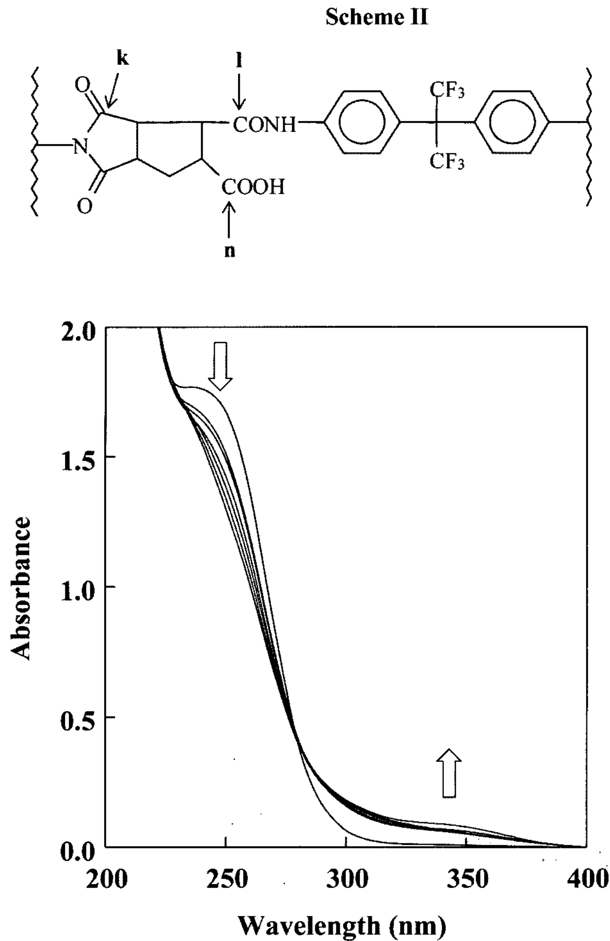


Figure 5. UV absorption spectral changes of a polyimide-I film containing 5 wt% benzophenone and 30 wt% BOHD at the irradiation doses of 0, 1, 2, 3, 4, 5, 6 J/cm^2.

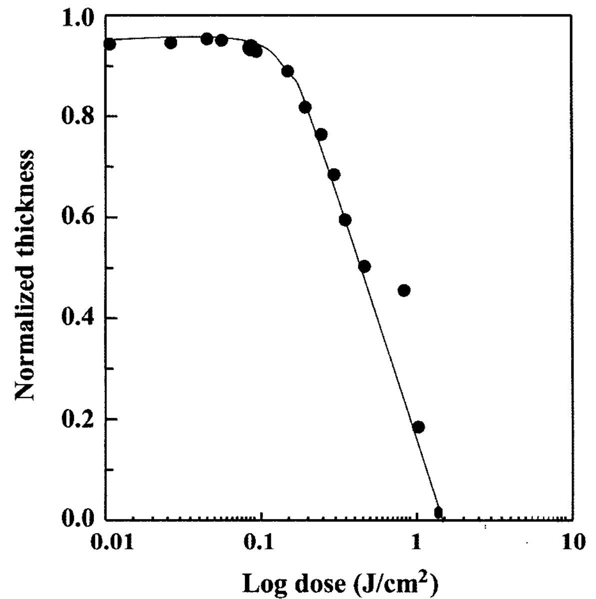


Figure 6. Normalized thickness of a polyimide-I film on a silicon wafer as a function of exposure doses of 310 nm UV light. Development was carried out in 0.2 wt% TBAH in water/ethanol (1/10, v/v).

The solubility change of a polyimide-I film induced by the photochemically produced amine from BOHD was utilized for the preparation of a PSPI. Figure 6 displays a normalized thickness of a polyimide-I film on a silicon wafer, which was estimated from the IR absorption band, as a function of the irradiation doses. A typical positive type irradiation doses vs. normalized thickness curve was obtained. The sensitivity (D_c) was calculated from the exposure doses when normalized thickness is zero. The sensitivity (D_c) and contrast (γ_p), obtained from the slope of the curve, were 1.2 J/cm^2, and 1.08, respectively.

Figure 7 shows a tapping mode AFM image of a positive micropattern obtained with a polyimide-I film on a silicon wafer after exposure to 310 nm UV light over 3.2 J/cm^2. The area of the image is 25 × 25 μm in the x, y-plane with an expanded z-axis. A very fine micropattern with a line width of 5 μm and depth of 204 nm was obtained. The result clearly demonstrates that the polyimide-I film containing benzophenone and BOHD, can be applied in the preparation of a positive type PSPI. Moreover, the micropattern can be de-

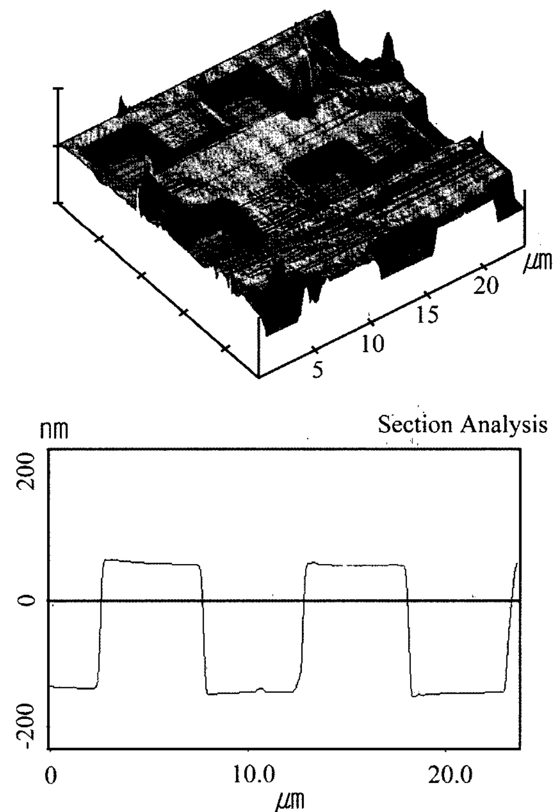
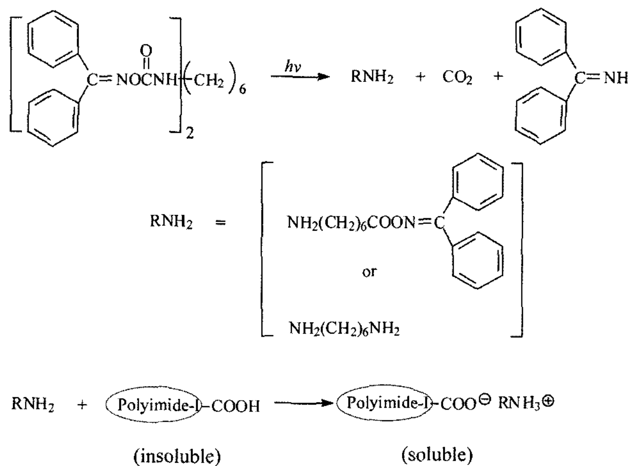


Figure 7. A tapping mode AFM image of a positive micropattern of a polyimide-I film containing 5 wt% benzophenone and 30 wt% BOHD, and its depth profile. Development was carried out in 2.38 wt% TBAH in water.

Scheme III



veloped by using the conventional alkali developing solvent - 2.38 wt% TBAH in H_2O.

The dissolution mechanism of the polyimide-I film upon irradiation, in the presence of benzophenone and BOHD, can be explained as shown in Scheme III. Irradiation of a polyimide-I film containing benzophenone and BOHD led to the formation of an amine through the photosensitized decomposition reaction of oxime-urethane groups in BOHD. The photochemically produced amine from BOHD reacts with the pendant -COOH groups in the chemically imidized polyimide-I to form carboxylic acid - amine salts inducing solubility increase in the developing solvent.

The polyimide-I is soluble in THF, but insoluble in ethanol. On the contrary, the salt of polyimide-I and n-butylamine is insoluble in THF, but good soluble in ethanol or 0.2 wt% TBAH in H_2O /ethanol (1:10, v/v) solution. The irradiated area in the polyimide-I film became more soluble than the non-irradiated area due to the formation of acid - amine salt inducing accelerated penetration of the developer into the polyimide film. Thus, a polyimide, which is not intrinsically photosensitive, can become photosensitive through the addition of a photobase generator containing oxime-urethane groups as a photosensitive compound.

Conclusions

The present study clearly demonstrates that a chemically imidized polyimide film, which is not intrinsically photosensitive, became photosensitive through the addition of a photobase generator containing oxime-urethane groups as a photosensitive compound. It is very likely that the amine, which was produced by the photodecomposition of a photobase generator, reacts with the pendant -COOH groups of the chemically imidized polyimide to form carboxylic acid - amine salts inducing solubility increase in the irradiated area of the polyimide-I film in a developing solvent. The function of the photobase generator in this PSPI seems to be in analogy with that of naphthoquinone azide in the novolak photoresist system, which produces acid upon irradiation.

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