Polyimide Surface Modification by Pulsed Ultraviolet Laser Irradiation with Low Fluence

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ABSTRACT: Surface modification on a polyimide film by pulsed ultraviolet (UV) laser irradiation with a fluence below its ablation threshold was studied by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), and UV-vis spectroscopy. It was observed that a photochemical reaction occurred and hydrophilic groups, such as —OH and —COOH, formed on the polyimide surface after irradiation. In addition, a ripple microstructure formed on the surface when the angle of incidence of the laser beam was 20–50°. The contact angle of the polyimide surface with water decreased and the adsorption ability of the surface to a water-soluble dye clearly increased after laser irradiation. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 2739–2743, 2001

Key words: surface modification; polyimide; irradiation; Nd:YAG laser

INTRODUCTION

Polyimides have extensive applications ranging from aerospace to microelectronics, optoelectronics, composites, and fiber optics due to their excellent mechanical properties, electrical properties, and thermal resistance.[1] However, applications of polyimides are limited by their hydrophobic surfaces which result in poor wettability and poor adhesion.[2] Both wet chemical surface modification[3] and photochemical surface modification[4–6] of polyimides to increase their surface energy have been reported. Although ultraviolet (UV) light modification is a promising method without environmental pollution, it needs a large energy intensity and long exposure time.[2]

After the advent of the UV laser, laser-induced polymer surface modification has been the subject of numerous studies. In most reports,[2,7] the laser fluency used in surface modification exceeds the ablation threshold of polymers, which leads to the formation of deposited ablation products (debris) on the surface because of photodecomposition. The debris is not beneficial to most applications. Niino et al.[8] found that a photochemical reaction could also take place when the polymer surface was irradiated by an excimer laser at a fluence below the ablation threshold.

In this article, we report on the surface modification of polyimide using a pulsed UV laser with a fluence below the ablation threshold of polyimide. We found that the photochemical reaction occurring on the polyimide surface was different from that reported using a fluence above the threshold of the ablation.[7]We also observed that

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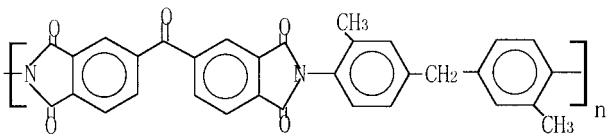

Scheme 1

the hydrophilicity of the surface was much improved after laser irradiation.

EXPERIMENTAL

Preparation of Polyimide Film

Polyimide (Scheme 1) was prepared from the polycondensation between 4,4′-diamino-3,3′-dimethyl diphenylmethane and benzophenone-3,3′-4,4′-tetracarboxylic acid dianhydride.[9] A *N*-methyl-2-pyrrolidone solution of polyimide was spin-coated onto glass substrates and then heated at 150°C for 1 h to remove the solvent.

Irradiation Procedure

All experiments reported here were carried out in air. The irradiation source was a Spectra-Physics Quanta-Ray GCR-4 Nd:YAG laser at wavelengths of 266 and 355 nm. The fluence of the laser beam was 10–45 mJ/cm^2 at a repetitive rate of 10 Hz and a pulse duration of 5 ns. The sample was fixed on an X–Y moving platform. The polyimide film was irradiated by scanning at a speed of 0.005 mm/s for the *X* direction and 5 mm/s for the *Y* direction. The incident angle of the laser beam was 20°–50°.

Characterization

X-ray photoelectron spectroscopic (XPS) analyses were conducted using a Perkin–Elmer PHI5500/5600 XPS spectrometer. FTIR spectra (KBr) were obtained on a Perkin–Elmer 710B infrared spectrophotometer. Atomic force microscopy (AFM) was used to detect the surface profile of the polyimide surface after laser irradiation. AFM analysis was conducted on a Digital Instrument Co. Multimode Nanoscope IIIa using a contact mode. The hydrophilicity of the polyimide surface was characterized by its contact angle with water and adsorption ability to a water-soluble dye (eosin Y). The contact angle was measured on a JJC-I contact-angle analyzer (manufactured by Shanghai No. 5 Optical Instruments Co., Shanghai, China).

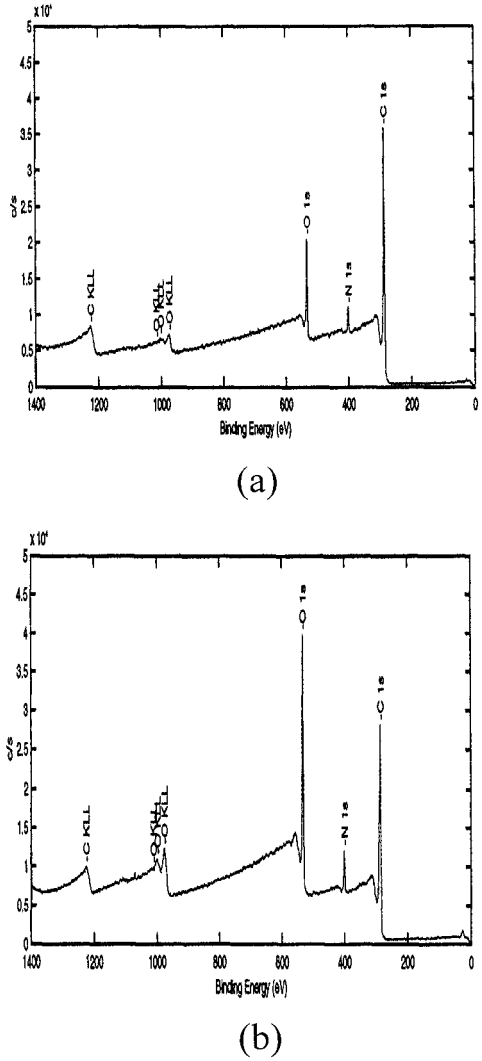

Figure 1 XPS spectra of polyimide surface (a) before and (b) after laser irradiation.

The adsorption of polyimide to eosin Y was characterized by measuring the ultraviolet-visible (UV-vis) spectra (Perkin–Elmer Lambda 20) of the polyimide films (before and after laser irradiation), which were immersed in a 1 wt % eosin Y/ethanol solution for 7 min and then washed with ethanol and dried.

Table I Concentration Ratios of Oxygen to Carbon and Nitrogen to Carbon Before and After Laser Irradiation

	O/C Ratio	N/C Ratio
Before irradiation	0.138	0.057
After irradiation	0.387	0.090

RESULTS AND DISCUSSION

XPS was used to obtain information on the chemical changes of the polyimide surface. For XPS measurements, the analytical depth is on the order of 50 nm and should therefore be more sensitive to surface modification than are other analytical techniques. The XPS spectra of (a) unradiated and (b) irradiated samples of polyimide are shown in Figure 1 and the results are listed in Table I. Significant changes are observed in the carbon 1*s* peak and the oxygen 1*s* peak after laser irradiation. After exposure, both the O/C and N/C ratios increased, indicating that an oxygen-rich surface was generated after the irradiation. This result differs from a carbon-rich surface, which was formed after UV laser exposure at a higher fluence.[7,10,11] This remarkable contrast indicates that the photochemical process, after exposure to a pulsed laser, is quite different for fluences above and below the threshold of the ablation process.

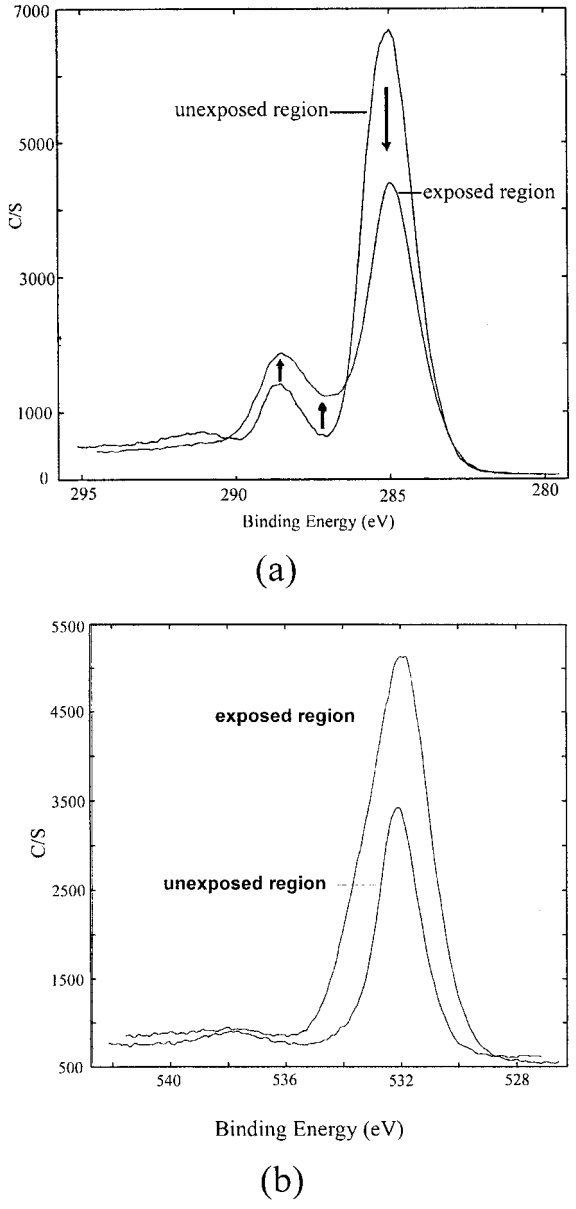

Figure 2 XPS spectra of polyimide surface: (a) C_{1s} core level; (b) O_{1s} core level.

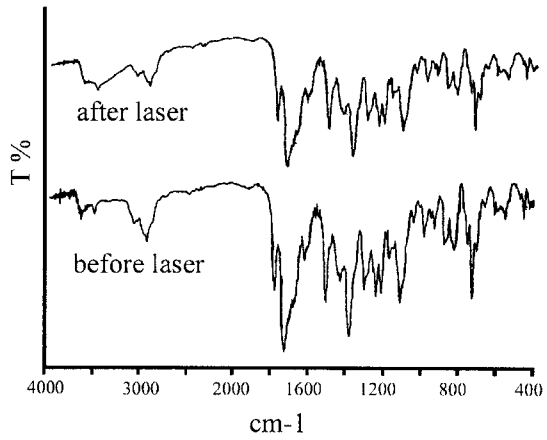

Figure 3 FTIR spectra of polyimide before and after laser irradiation.

To observe more clearly the chemical changes induced by the pulsed laser irradiation on the polyimide surface, XPS spectra of C_{1s} and O_{1s} signals are shown in Figure 2. After laser irradiation, the C_{1s} peak at 285 eV [Fig. 2(a)] from C—H, C—C, or C—N is decreased and the peak at 287.8 eV assigned to C═O is increased. Moreover, the C_{1s} curve rises from its minimum at about 286 eV, indicating the occurrence of a new peak at about 286 eV after laser irradiation. This new peak is assigned to a C—O peak. Therefore, we suggest that part of the hydrophobic groups, such as C—H, C—C, or C—N bands, was transformed to hydrophilic groups, such as —OH and —COOH, after UV laser irradiation. Figure 2(b) shows that the O_{1s} band of the polyimide film after laser irradiation broadens and the center of the band shifts slightly to a high binding energy in comparison with the band of the nonirradiated film. This suggests that photooxidation might occur on the polyimide surface during laser irradiation.

Figure 3 shows the transmittance FTIR spectra of polyimide. The absorption peak at 3500 cm^{-1}, which is due to —OH stretching, is increased after laser irradiation. This result further verifies the existence of photooxidation on the

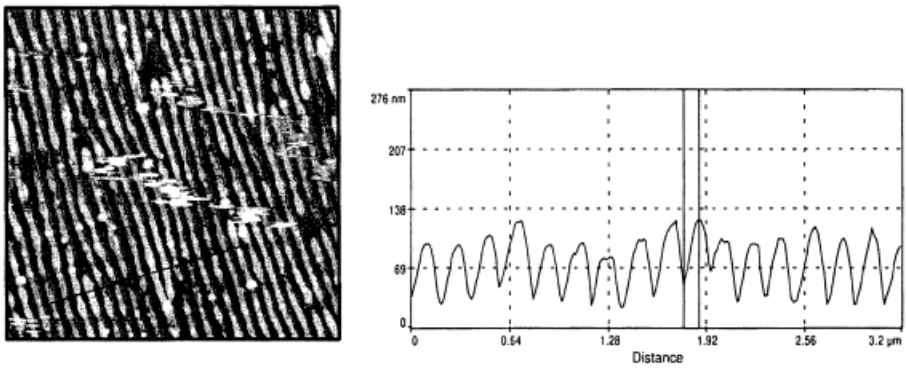

Figure 4 AFM micrograph of UV-irradiated polyimide surface at 40 mJ/cm^2.

polyimide surface during laser exposure. Moreover, the absorption peak attributed to the methyl and methylene groups at 2900–3100 cm^{-1} is decreased after laser exposure, which may indicate that part of the methyl groups might be oxidized to —COOH. Only a small difference was observed in the FTIR spectra of polyimide before and after laser irradiation, indicating that the oxidization occurs only on the surface of the polyimide.

AFM was also used to investigate the surface profiles of laser-irradiated polyimide films and the results are shown in Figure 4. It is observed that ripples are formed on the polyimide surface after irradiation. These ripples may contribute to improvement of the wettability of the polyimide. Under our experimental conditions, the ripples could only be obtained while keeping the angle of incidence of the laser beam between 20° and 50°. Laser irradiation was carried out at fluences of 20, 30, and 40 mJ/cm^2. The amplitude of the ripple (the distance from the minimum to the maximum) measured with AFM is 17, 20, and 67 nm, respectively, and increased nonlinearly with the fluence independent of the angle of incidence of the laser beam. In addition, the ripples start to break up when the fluence exceeds 45 mJ/cm^2, which may be regarded as the ablation threshold for the polyimide studied (Fig. 5). It must be noted that this ablation threshold was obtained when the polyimide film was irradiated with a scanned laser beam, while the widely used ablation threshold for Kapton film was measured when the laser beam was fixed on one point.[12,13] The ripples obtained on this polyimide surface were widely believed to be caused by the interference between the incoming polarized laser beam and its surface scattering wave.[14,15]

Figure 6 shows the relationship between the contact angle of the irradiated polyimide surface with water and the irradiation fluence at a wavelength of 355 nm. It is very clear that the increased fluence leads to a decreased contact angle and increased hydrophilicity. Figure 7 shows UV-

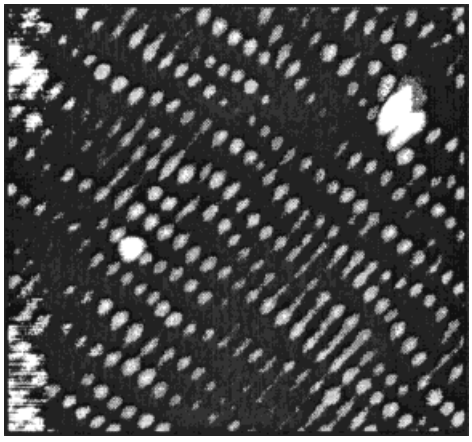

Figure 5 AFM micrograph of UV-irradiated polyimide surface at 45 mJ/cm^2.

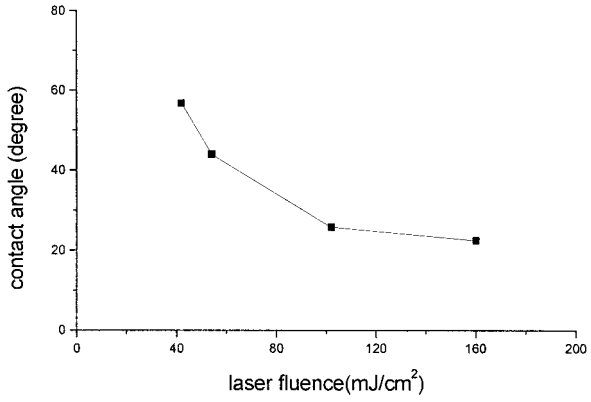

Figure 6 Contact angle of water on the laser-irradiated polyimide surface.

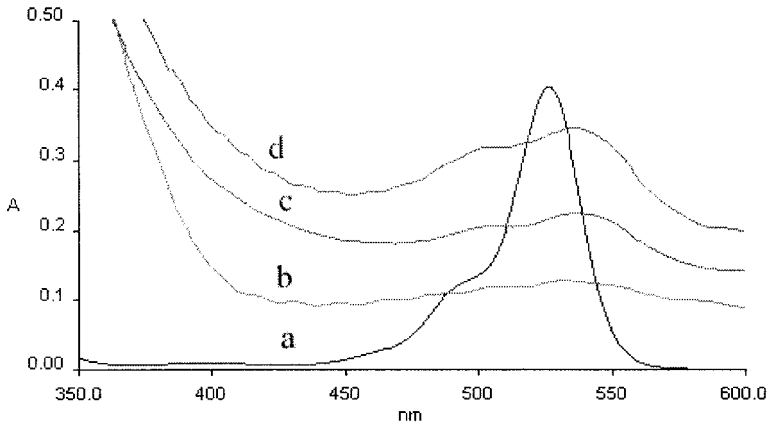

Figure 7 UV-vis spectra of laser-irradiated polyimide films after being immersed in an eosin Y/ethanol solution: (a) eosin Y/ethanol solution; (b) 0 min; (c) 4 min; (d) 5 min.

vis spectra of the 355-nm laser-irradiated polyimide film after being treated with an eosin Y/ethanol solution. Spectrum "a" is from the eosin Y/ethanol solution and the absorption maximum of eosin Y is at 470–550 nm. Spectrum "b" is from the nonirradiated polyimide film after treatment with the eosin Y/ethanol solution, which shows no absorption of eosin Y. When the polyimide film was irradiated with the laser, for various times before the treatment with the eosin Y/ethanol solution, the absorption of eosin Y clearly increased with increase of the laser irradiation time. This clearly suggests that the laser irradiation increases not only the hydrophilicity of the polyimide surface but also its adsorption ability to the dye.

CONCLUSIONS

We studied the surface modification of polyimide film by a pulsed UV laser at a fluence below the ablation threshold. A photochemical reaction occurs and hydrophilic groups, such as —OH and —COOH, are formed on the polyimide surface. A ripple microstructure forms on the polyimide surface when the angle of incidence of the laser beam is 20°–50°. Therefore, the pulsed laser can achieve chemical and physical surface modifications on polyimide. The obtained polyimide surface has much improved hydrophilicity: The contact angle with water decreased and the adsorption ability of the dye increased.

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