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Polymer Ablation with Excimer Lasers

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Polymer Ablation with Excimer Lasers

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Ablative photodecomposition of two polymers, poly(ethylene 2,6-naphthalate)(PEN) and polyethersulfone (PES), has been investigated for the surface modification. Regular granular microstructures appeared on the surface of PEN film after irradiation with excimer lasers (ArF, KrF, XeCl, and XeF). The microstructure formation of PEN film is explained by the growth of debris originated from the different etching rate between crystalline and amorphous region. In the case of PES, when irradiation with XeCl excimer laser was performed at a fluence of 750 mJ cm^{-2}, periodic wavy microstructures were formed. These surfaces modified by excimer laser ablation have potential application into alignment of liquid crystals and selective-area electroless plating.

Keywords: polymer, excimer laser, laser ablation, surface modification, photochemistry, microstructure

1. INTRODUCTION

When organic polymers are exposed to high intensity UV-pulsed lasers, ablative photodecomposition occurs on their surfaces. Laser ablation of polymers using excimer lasers has been investigated extensively since 1982.[1–3] At the first stage, most interest has focused on the mechanism including direct observation and analysis of ablated fragments.[4,5] From the viewpoint of application, excimer laser ablation has been established as novel techniques of material micromachining and medical surgery, because direct clean etching is attained photochemically without incurring thermal damage to the surrounding unirradiated region.

On the other hand, particular attention has been paid to surface morphological changes after polymer ablation, from both fundamental and applied aspects. In this paper, we report the microstructure formation on the surface of two polymer films: semicrystalline poly(ethylene 2,6-naphthalate) (PEN) and amorphous polyethersulfone (PES). In addition, two new technologies, alignment of liquid crystals in the cell composed of ablated PES films and selective-area electroless plating on an ablated polymer surface, are described, as practical applications of surface morphological microstructures.

2. EXPERIMENTALS

Materials: The polymers were commercially available films of PEN manufactured by Teijin Limited and PES manufactured by Mitsui Toatsu Chemicals, Inc. The

samples of stretched and unstretched PEN, and PES were 75 μm free-standing films in thickness.

Procedure: The source of radiations at 193(ArF), 248(KrF), and 351(XeF)nm was a Lambda Physik EMG 201MSC excimer laser, and the source at 308(XeCl)nm was an EMG 102MSC. These were generally operated at 1 Hz. The focused laser beam with quartz lens was incident on the samples perpendicularly unless otherwise noted. A desired fluence, determined by measuring the pulse energy with a pyroelectric joulemeter, was obtained by adjusting the distance between the lens and the sample so that the energy per pulse was constant, although the irradiated area was changed. All irradiations were conducted in air atmosphere.

3. RESULTS AND DISCUSSION

Despite extensive work performed on polymer ablation, there are still many important details of ablated surfaces that are incompletely understood. We have investigated the microstructure formation on the surface of polymer films.[6-12] Our samples described here are two polymers: PEN as an example of semicrystalline films and PES as an example of amorphous films. In these studies, we have used many kinds of experimental techniques for surface analysis, e.g., scanning electron microscopy (SEM), transmission electron microscopy (TEM), electron diffraction analysis, X-ray photoelectron spectroscopy (XPS), attenuated total reflection-Fourier-transfer IR spectroscopy (ATR-FTIR), and time-resolved light scattering system. However, detailed results measured by such methods were omitted in this report.

In general, the surface ablated with excimer lasers is modified physically and/or chemically, and may be of great value in industrial applications. Microstructure formation is one of the representatives of surface modification. We have found that our ablated polymer surface has potential applications into electronic materials. Two examples are shown here.

3.1 Microstructure Formation on Surfaces of Semicrystalline Polymer Films by Excimer Laser Ablation

The threshold of KrF laser ablation for biaxially stretched PEN films was determined to be ca. 40 mJ cm^{-2} experimentally. Upon the exposure at high fluence 500 mJ cm^{-2}, the ablation showed topographical roughness on the surface of film. Figure 1 shows the growth of microstructures with the accumulation of laser shot. With the increase of laser shots, the ablated surface of PEN film revealed regular granular microstructures similar to those observed in the case of PET. Lazare and Srinivasan have speculated that the roughness developed upon successive absorption of laser pulses in the case of PET may well originate from the crystalline structure of the polymer subsurface.[13,14] In the case of PEN, Figure 1 shows similarly the growth of debris upon the accumulation of laser pulses.

Most incident energy by laser pulses is used for ablation. However, the lower energy than threshold is deposited on the deeper surface than the ablated region. Then, the thermal dispersion of the energy will produce a pool of molten materials

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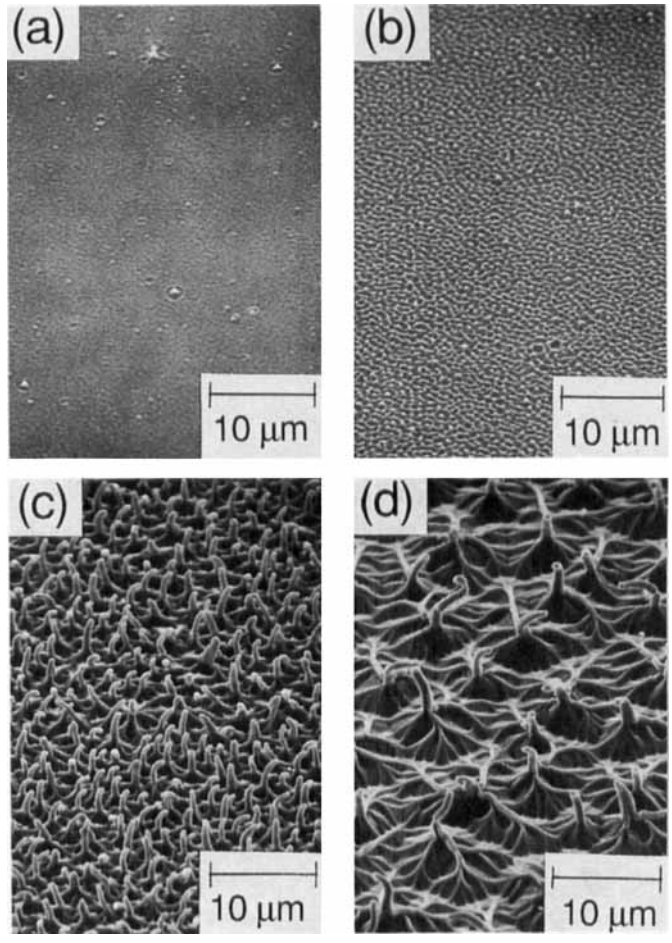

FIGURE 1 Surfaces of biaxially stretched PEN films after the exposure of KrF laser at 500 mJ cm^{-2}; (a) 1 shot, (b) 2 shots, (c) 10 shots, and (d) 100 shots.

containing reactive segments of polymer. We can speculate the growth of debris from the molten layer, as shown in Figure 2. The thermal contribution to the melting of polymer surface may be correlated to the penetration depth derived from Beer's law in a first approximation. When the exposures were carried out with 10 shots of ArF, KrF, XeCl, and XeF laser at the fluence of 500 mJ cm^{-2}, the size of debris was related to the penetration depth for their laser line, which varied inversely as the absorption coefficient (Table I). In the case of XeF laser irradiation, the biggest debris were formed. On the other hand, the smallest debris were given by ArF laser irradiation.

Important factors responsible for the formation of microstructures are features of polymer film, in particular, crystallinity and stress. In the case of unstretched amorphous PEN film, no debris was observed on the surface of remaining polymer at the entire bottom of the etched region when the exposure was performed at much higher fluence above the threshold. On the other hand, the ablation for

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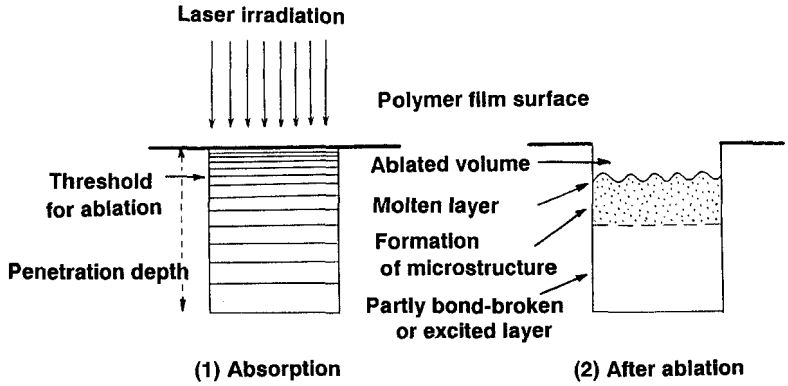

FIGURE 2 Schematic process of microstructure formation after polymer ablation on the surface of polymer film. Spacing of lines corresponds to the density of absorbed photons.

TABLE I

Absorption coefficient of spun-on PEN film (thickness: 28 nm)

Wavelength(nm)	Absorption coefficient (cm^{-1})
193 (ArF)	68,000
248 (KrF)	200,000
308 (XeCl)	38,000
351 (XeF)	25,000

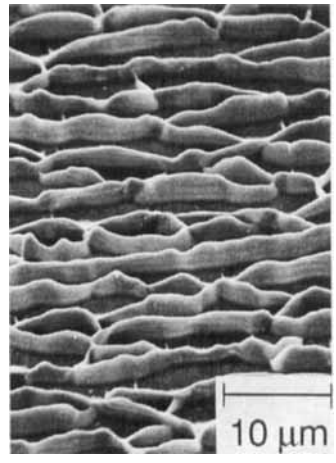

FIGURE 3 Surface of monoaxially stretched PEN film after the exposure with KrF laser of 10 shots at 500 mJ cm^{-2}.

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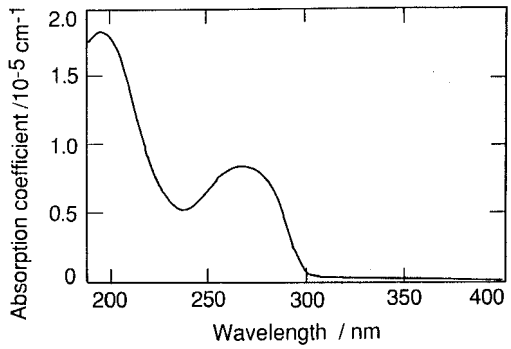

FIGURE 4 Electronic absorption spectrum of spun-on PES film (thickness: 67 nm).

monaxially stretched PEN film emerged periodic roll structures quite different from that of biaxially stretched film above described. An anisotropic structure whose orientation is perpendicular to a stretching direction is shown in Figure 3. It becomes apparent that surface roughness depends on the subsurface situation between crystalline and amorphous phases. The influence of stress fields was reported by Bahners and Schollmeyer.[15–17] Excimer laser radiation for the PET fiber, which had the stress imposed during a spinning process and was blocked by a network of crystallites, yielded a highly oriented and regular roll structure. The orientation of the rolls was strictly perpendicular to the fibrillar orientation (given by the stress axis) of the fiber.

3.2 Microstructure Formation on Surface of Amorphous Polymer Film by Excimer Laser Ablation

The formation of microstructures upon polymer ablation has been considered to be specific phenomena originated from the presence of crystallinity as described previously in the cases of semicrystalline PET and PEN films.[18] Actually, amorphous PES film yields a smooth surface upon ablation with KrF excimer laser. However, if exposed with the XeCl laser at a fluence of more than 500 mJ cm^{-2}, PES film revealed curious topographical structures in the bottom of the trench. Figure 4 shows the uv-vis absorption spectrum of a spun-on PES film. The values for the absorption coefficient are about 140 and 6.1 $\times$ 10^4 cm^{-1} at 308 and 248 nm, respectively. The threshold fluence of XeCl and KrF laser ablation was experimentally determined to be about 100 and 20 mJ cm^{-2}, respectively.

The PES surface irradiated by the 750 mJ cm^{-2} XeCl laser was shown in Figure 5. The laser beam was focused with a planoconvex quartz lens and incident on the film perpendicularly. This phenomenon cannot be ascribed to a diffraction effect caused by passing the laser beam through a slit, because the slit (17 $\times$ 5 mm^2) was located between the laser and the focusing lens at a position which gave a homogeneous fluence in the beam. A definite spacing pattern, oriented at random, appeared more than 30 shots. The spacing of microstructures remained constant

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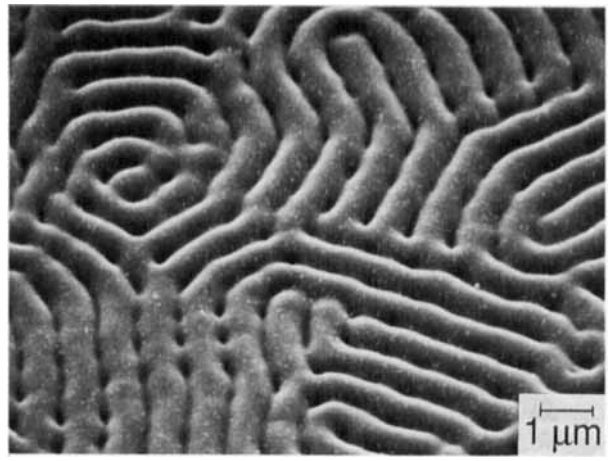

FIGURE 5 Surface of PES film after the exposure with XeCl laser of 100 pulses at the fluence of 750 mJ cm^{-2} at the incident angle of 0°.

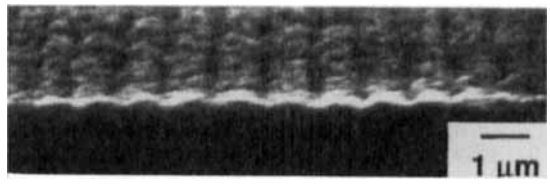

FIGURE 6 Cut-surface of PES film after the exposure with XeCl laser of 100 pulses at the fluence of 750 mJ cm^{-2} at the incident angle of 0°.

with subsequent irradiation after 30 shots, although the growing amplitude of debris was observed in the cases of PEN and PET. With the exposure at a fluence below 500 mJ cm^{-2}, a smooth surface can be obtained on the film.

The spacing of wavy microstructures is strictly regular at every position as shown in Figure 6. We found the dependence of the spacing on the fluence of the beam. The spacing, which is measured by a diffraction pattern from a coherent He-Ne laser, is plotted as a function of fluence (on a logarithmic scale) shown in Figure 7. The spacing can be increased with an increase of the fluence. SEM measurements of cross-section in the ablated film showed that the depth of microstructures was minute compared to the grating pitch, about 0.2 μm in the case of 1 μm pitch.

Interestingly, it was discovered that the pattern could be controlled by varying the angle of the incident radiation on the film. Figure 8 shows the pattern when the XeCl laser beam was incident on the sample at 45°. The orientation of the microstructure-like grating was parallel to the plane of the incidence of the ablating beam. The wavy structure changed gradually from the random pattern to the periodic ripple-like as the film was inclined from 0° to 57°, while the spacing is similar to that formed by perpendicular exposure.

Upon the exposure with a plane-polarized XeCl laser, the grating appeared on the film even at the incident angle of 0°. Its orientation was perpendicular to the electric field (E field) vector of the polarized beam. When nonpolarized beam is

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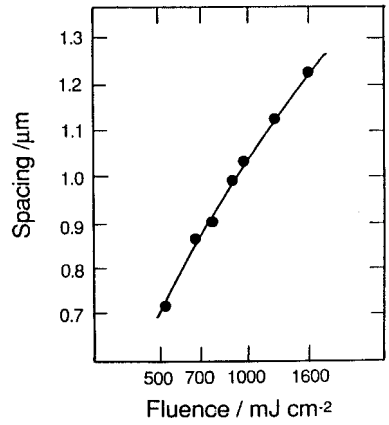

FIGURE 7 Plots of the spacing of the wavy microstructures in the PES film vs the fluence when exposured with XeCl laser perpendicularly.

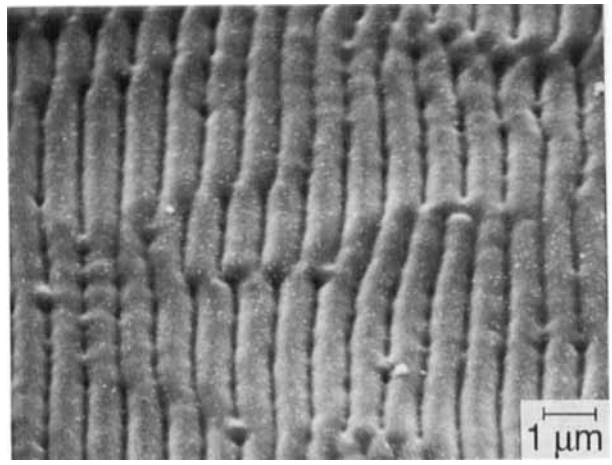

FIGURE 8 Surface of PES after the exposure of 100 pulses XeCl laser at the incident angle of 45°.

incident on the film at 57°, the penetrating beam into the PES film has an elliptical polarization with dominant direction of the E field vector perpendicular to the plane of the incidence. The anisotropy of the micropattern on the PES film depends on the degree and direction of the polarized beam for ablation.

The microstructure formation of amorphous PES film is limited to precisely specified transient heating provided with the exposure of XeCl laser at relatively high fluences (5 E_T). That is to say, the XeCl laser beam can deeply penetrate into the films under the ablated area because the XeCl laser line corresponds the absorption edge of the polymer films. Then, the local temperature on the surface of the irradiated region would be rapidly raised and a pool of fluidized material would be formed. Finally, it can be assumed that intrinsic properties of polymer such as glass transition temperature are highly responsible for the formation of microstructures from the fluidized layer. Although thermal loading on polymer

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films is popular phenomenon in excimer laser ablation, the strictly defined fluidized layer is indispensable for this type of microstructure formation.

3.3 Applications of Surface Modifications

3.3.1 Alignment of nematic liquid crystals on polymer films. We found that the ablated PES film having periodic grating-like microstructure is of potential importance not only for grating but also for alignment of liquid crystals.

As shown in Figure 9, the PES films for a cell of liquid crystal were fabricated by the XeCl laser irradiation of 30 pulses at the fluence of 750 mJ cm^{-2}. The nematic liquid crystals (LC:Merck E7) were inserted into the cell comprised of two ablated PES films, together with anthraquinone dye (AQ:BDH Limited D5) which was used as a dichromatic dye for measuring of nematic LC orientation.

Figure 10 shows the polarized visible spectra of the anthraquinone dichromatic dye contained in the LC cell (1 wt%). In the case of the grating-like microstructure as shown in Figure 8, the dichromic ratio D ($D = A_{\parallel}/A_{\perp}$, at 594 nm) of AQ was about 3.2, and LC aligned uniformly parallel to the groove direction of the anisotropic micropattern. Our experimental results were similar to those previously reported using grating.[19] Nematic LCs align homogeneously on a grooved surface according to the magnitude of the elastic strain energy density of LC produced by the grating pitch.

On the other hand, for the pattern oriented at random as shown in Figure 5, the dichromic ratio of AQ was about 1.2, owing to the distortion of the nematic LC on the surface. It was obvious that the nematic LC was much affected by the anisotropy of microstructures on the ablated PES film.

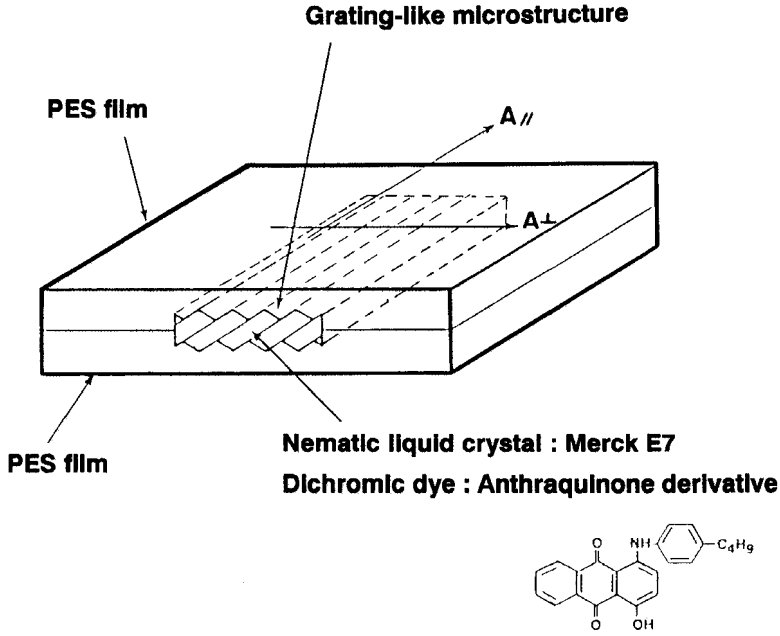

FIGURE 9 Schematic set-up of LC cell for alignment of liquid crystals.

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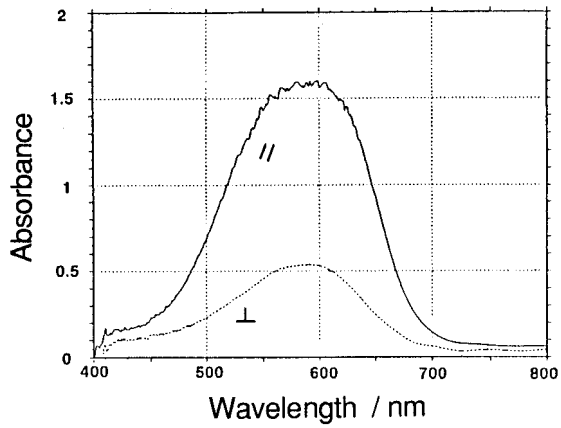

FIGURE 10 Polarized visible spectra of *AQ* in the LC cell comprised of two ablated PES films having a grating-like microstructure as shown in Figure 8.

3.3.2 Electroless plating of metals on polymer surfaces. So far, interest in polymer ablation has been mainly directed toward etching of plastic materials, from the viewpoint of application in industry. In addition, we can expect to exploit functional polymers modified by laser ablation. Various chemical and physical changes have been observed on the surface of polymer after ablation. We noticed the change in surface potential on the film before and after ablation.

The surface potential of polymer film was measured with an electrostatic voltmeter. In the case of PET film, although the surface potential before irradiation is almost neutral between +0.5 to −0.5 V, it changes to +2.5 to 3.0 V after irradiation with a XeCl laser in air. This behavior was similarly observed in such polymer films as PEN, polyimide, PES, and poly(methyl methacrylate).

The positively-charged area which was ablated with laser beam was selectively metal-plated with electroless plating procedure as follows. The procedure consists of three steps. First, the polymer film was ablated by the irradiation of excimer laser (ArF, KrF, XeCl, or XeF) with 10 to 100 pulses through a patterning mask in ambient air. Second, the ablated film was dipped into the aqueous solution containing a negative charged colloid composed of palladium (Pd) and surfactant as an activation process.[20] Finally, the dipped film was rinsed with de-ionized water and immersed in an electroless plating bath of copper (Cu) or nickel (Ni).

Process for selective-area electroless plating on laser-ablated polymer film

Treatment	Surface potential (in PET)
(1) Polymer film	neutral (−0.5 ~ +0.5 V)
(2) Laser ablation	positive (+2.5 ~ +3.0 V)
(3) Washing with deionized water	positive (+16 ~ +25 V)
(4) Dipping in negatively charged Pd colloid solution	
(5) Dipping in electroless plating solution	

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4. CONCLUSIONS

Many laser-induced chemical reactions and techniques have been discussed for past several decades. Among these, the discovery of polymer ablation in 1982 has led to both scientific and industrial interests. Extensive work on polymer ablation has directed toward direct etching so far and little attention has been paid to ablated surface of polymer.

We showed some interesting microstructures on the ablated surface of polymer film by excimer laser irradiation. The formation mechanism of microstructures has not been elucidated. Elementary photophysical and photochemical processes in the exposure of excimer laser to polymer films are very complicated because of many channels such as bond-breaking, thermal relaxation, and energy dispersion. In addition, properties of polymers influence dynamical changes after the exposure. The mechanism of morphological changes on the surface by polymer ablation is far from being completely understood. However, some experiments showed a few type of microstructures which should be correlated to the irradiation conditions or the polymer properties.

From the viewpoint of industry, we showed that the ablated surface of polymer has great potential for surface modification. So far many techniques have been applied for surface modification to polymers; e.g., chemical or mechanical treatment, radiation with high-energy beam, or plasma etching. We believe that polymer ablation is one of the greatest promising techniques for surface modification of polymer films. In the near future more widespread techniques will be developed.

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References

1. Y. Kawamura, K. Toyoda and S. Namba, *Appl. Phys. Lett.*, **41**, 374 (1982).
2. R. Srinivasan and V. Mayne-Banton, *Appl. Phys. Lett.*, **41**, 576 (1982).
3. R. Srinivasan and W. J. Leigh, *J. Am. Chem. Soc.*, **104**, 6784 (1982).
4. R. Srinivasan and B. Braren, *Chem. Rev.*, **89**, 1303 (1989).
5. S. Lazare and V. Granier, *Laser Chem.*, **10**, 25 (1989).
6. H. Niino, A. Yabe, S. Nagano, and T. Miki, *Appl. Phys. Lett.*, **54**, 2159 (1989).
7. H. Niino, M. Nakano, S. Nagano, A. Yabe, H. Moriya, and T. Miki, *J. Photopolym. Sci. Technol.*, **2**, 133 (1989).
8. H. Niino, M. Nakano, S. Nagano, and A. Yabe, *Appl. Phys. Lett.*, **55**, 510 (1989).
9. H. Niino, Y. Kawabata, and A. Yabe, *Jpn. J. Appl. Phys.*, **28**, L 2225 (1989).
10. H. Niino, M. Nakano, S. Nagano, H. Nitta, K. Yano and A. Yabe, *J. Photopolym. Sci. Technol.*, **3**, 53 (1990).
11. H. Niino, M. Shimoyama, and A. Yabe, *Appl. Phys. Lett.*, **57**, 2368 (1990).
12. H. Niino and A. Yabe, *J. Photochem. Photobiol. A: Chem.*, in press.
13. Srinivasan and S. Lazare, *Polymer*, **26**, 97 (1985).
14. Lazare and R. Srinivasan, *J. Phys. Chem.*, **90**, 24 (1986).
15. T. Bahners and E. Schollmeyer, *Angew. Makromol. Chem.*, **151**, 19 (1987).

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16. T. Bahners, A. Bossman, and E. Schollmeyer, *Angew. Makromol. Chem.*, **170**, 203 (1989).
17. T. Bahners and E. Schollmeyer, *J. Appl. Phys.*, **66**, 1884 (1989).
18. Y. Novis, J. J. Pireaux, A. Brezini, E. Petit, R. Caudano, P. Lutgen, G. Feyder, and S. Lazare, *J. Appl. Phys.*, **64**, 365 (1988).
19. J. Cognard, *Cryst. Liq. Cryst.*, Suppl. **1**, 53 (1982).
20. Y. Nakao and K. Kaeriyama, *J. Colloid Interface Sci.*, **110**, 82 (1986).

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