Laser Processing of Polymer Materials:
New Techniques to Prepare Advanced Materials
by using Excimer Lasers

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Development of excimer lasers brought new phenomena for processing of polymer materials. Polymer ablation has already been utilized for micromachining in industry. In these years investigations on laser processing of polymer materials are extending to not only micromachining but also thin film preparation and surface modification. This paper reviews new techniques to prepare advanced polymer materials and discusses new directions of polymer processing.

Keywords: excimer laser, laser ablation, micromachining, deposition, surface modification

1. Introduction

Development of excimer lasers, which can emit pulsed high-intensity ultraviolet lasers such as ArF (193 nm), KrF (248 nm), XeCl (308 nm) and XeF (351 nm), brought many new phenomena in polymer science. These are based on laser ablation (ablative decomposition) and excimer laser-induced photochemical reaction (Fig. 1).

It has passed 15-years since polymer ablation was reported by Kawamura [1] and Srinivasan [2] in 1982. Polymer ablation is an interesting phenomenon from viewpoints of both basic science and applied technology (Table 1) and many investigations including diagnostics by various analytical methods have been reported so far.[3] Nowadays polymer ablation has been established as industrial technologies such as fabrication of multi-chip modules, ink jet nozzles, wire stripping and so on.[4-7] Applications of polymer ablation are important not only in micromachining of polymer materials but also in deposition of thin films and in surface modification (Fig. 2).

On the other hand the irradiation to polymers with excimer lasers at fluences below ablation
threshold can induce photochemical reactions onto polymer surfaces. These reactions are different from conventional photochemical reactions by using lamps and have some advantages for processing of polymer materials.

In this paper we wish to review prominent papers reporting new interesting techniques based on the interaction of excimer lasers with polymer materials, and to discuss new directions of laser processing for polymer materials.

2. Etching : Micromachining

Micromachining of polyimide (PI) for thin film packaging structures and polyethersulfone (PES) for ink jet nozzles has been already commercialized in industry by using conventional excimer lasers. For development of manufacturing technology, three key technologies, ablation process, mask technology and tooling, were overcame. Most of engineering polymer materials having significant absorbance in the uv-region can be etched precisely without thermal damage by laser ablation with conventional excimer lasers. Next subjects for these micromachining of polymers are improvements in cost of ownership and throughput. For these requirements, recently, laser makers developed high repetition rate system with output stability by using a solid state power module in stead of a traditional thyatron.

In case of such polymers as polytetrafluoroethylene (PTFE) and polyethylene (PE) having no significant absorption in the uv-region, photo-ablation must be irradiated with specific lasers such as \( \text{F}_2 \) laser [8,9] and ultra-short pulsed excimer lasers [10]. On the other hand, IBM group (Davis and Egitto) prepared

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**Table 1. Research subjects of polymer ablation.**

<table>
<thead>
<tr>
<th>Basic science</th>
<th>Applied technology</th>
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| (1) Photochemistry in condensed phase  
(a) multiphoton excitation  
(b) high-density absorption | (1) Etching  
(a) microdrilling  
(b) marking |
| (2) Polymer reaction  
(a) photolysis of main/side chain  
(b) surface reaction | (2) Surface processing  
(a) surface modification  
(b) marking |
| (3) Ultrafast phenomena  
(a) point explosion  
(b) plasma science | (3) Deposition of ablated fragments  
(a) thin film preparation  
(b) fine particle preparation |
PI-doped PTFE and they found that it could be etched without thermal damage even if by XeCl excimer laser ablation.[11-13] The content of PI is around 0.2-5% and its thermal property remains that of non-doped PTFE.

As a new application of polymer ablation, excimer laser lithography has been investigated by Hitachi group (Suzuki, Hayashi et al.).[14, 15] This is a process of direct patterning and removal of a resist polymer film and does not need a development process and realizes a non-vacuum dry removal of resist. As the results of developments for new resist, polyurethane resins are selected because they show high ablation rate at 248 nm KrF laser irradiation, high resolution and well resistant to etching. This technique aims for manufacturing of TFT-LCD.

Lippert reported the new polymer film which was designed for high resolution laser ablation at a specific irradiation wavelength.[16,17] Triazeno polymer film is ablated by mainly photochemical mechanism (Fig. 3). The gaseous products of the photochemical decomposition were assumed to assist the material removal, and to prevent the redeposition of solid products which would contaminate the surface.

Fig.3. Structural unit of triazeno polymer

3. Deposition: Thin Film Preparation

Although deposition of metal and metal oxide by laser ablation has been extensively investigated since mid-1980s, little attention has been paid to polymer films. As only one paper in 1980s Hansen and Robitaille reported the thin film deposition of such polymers as poly(methylmethacrylate) (PMMA), Nylon-6,6, polycarbonate (PC), and PI by ablation with ArF, KrF, or Nd:YAG laser. [18] However PTFE and PE could not be applied by this technique.

Deposition of PTFE thin film was carried out by ablation with F\textsubscript{2} laser (157 nm) and FHG of Nd:YAG laser (266 nm). Blanchet and co-workers succeeded in preparation of PTFE thin films by ablation with 266 nm laser beam under argon or CF\textsubscript{4} gas atmosphere.[19-22] On the other hand, Kannari and co-workers prepared crystalline PTFE thin films by using F\textsubscript{2} laser.[23-25] Moreover they developed a new technique to prepare functional PTFE film dispersed semiconductor particles (CdTe) or organic molecules (copper-phthalocyanine and 4-dialkylamino-4-nitrostilbene) by a dual laser ablation method using a F\textsubscript{2} laser and a KrF excimer laser (Fig. 4).

Fig.4. Setup for the fabrication of PTFE thin films containing semiconductor microcrys-tallities.
There are many papers reporting preparation of diamond and diamond-like carbon films by laser ablation of graphite, but they are not included this article because they are not polymer processing. Hiraoka succeeded in preparation of crystalline diamond by ArF excimer laser ablation of PMMA and poly(methacrylic acid) doped with TiCl₄.[26] The important parameters to get crystalline diamond are the substrate surface, temperature, laser fluence and target polymer composition.

Nishio and coworkers succeeded in the preparation of conducting polymer films by laser ablation of polyacrylonitrile (PAN).[27] The films prepared by ablation at 308 nm essentially maintained the original structure of PAN. On the other hand, the structures of films deposited by ablation at 248 and 193 nm were quite different, and, in particular, π-conjugated systems were developed by ring closure of nitrile groups with increasing laser fluence. The films gave electric conductivity on the order of $10^{-2}$ S cm$^{-1}$. Moreover, they prepared polyacenic semiconducting thin films by ablation of bulk phenol-formaldehyde (PF) resin and PAS given from a heat-treated PF resin.[28]

Deposition from gas phase under irradiation with excimer laser was studied for specific polymers. Fuchigami and coworkers reported a deposition of bis(ethynylstyryl)benzene (BESB) having reactive sites of triple bonds as the end group under KrF excimer laser irradiation by a molecular beam technique (Fig. 5).[29] The laser irradiation to the film surface after and during deposition caused cis-to-trans photoisomerization and gave amorphous film due to disordering of the molecular arrangement. On the contrary, the photoisomerized trans-trans isomer crystals were found to be grown upon the irradiation during deposition at the substrate temperature of 60 °C. Further study on polymerization is expected.

Itadani and coworkers have studied on a preparation of thin film of liquid crystalline polymer by chemical vapor deposition with polarized excimer laser (Fig. 6).[30] The deposited film showed anisotropy, suggesting the direction of side chains of the polymer was parallel to the electric vector of the laser beam. Molecular orientation of this liquid crystalline polymer film took place on the polyimide layer exposed a linearly polarized laser.[31] This technique is interesting in micron-sized control of molecular orientation.

![Fig. 5. Molecular structure of BESB (cis-cis)](image)

![Fig. 6. Scheme of molecular orientation of the thin film deposited by CVD.](image)
4. Surface Reaction: Surface Modification

In recent decades, together with the establishment of micromachining by ablation techniques, a modification of the surface of polymer materials has attracted considerable interests in science and technology. [32,33]

Although the first paper of polymer ablation by Srinivasan reported morphological changes on the ablated polymer surface, Niino and Yabe have extensively studied on physical and chemical changes on the surface by ablation. [34-41] They found not only morphological changes but also changes of surface potential and generation of radicals. Recently, in a collaboration work with NOK Co., it has been reported that morphological changes on the surface of composite material, carbon black/elastomer, are useful for tribology control of sealing and packing materials. [42]

Morphological changes of bio-materials was studied by laser ablation. Tezuka and coworkers reported the formation of periodic ndmicrostructures on the surface of collagen film by ArF excimer laser. [43] The size and shape were dependent on the laser fluence and number of pulses. They analyzed the roughness by using surface topography and AFM images.

One of the most challenging subjects on surface modification of polymers is improvement of hydrophilic and adhesive properties for fluorocarbon resins. Murahara and Okoshi reported that the surface of fluorocarbon polymer became lipophilic and hydrophilic by the surface reaction with trimethylborane and trihydroxyborane, respectively, upon ArF excimer laser irradiation. [44,45] They showed also improvement of adhesion.

Niino and Yabe found that the surface of poly(tetrafluoroethylene) (PTFE) became hydrophilic enough to be metallized by chemical plating upon the ArF laser irradiation under the atmosphere of hydrazine (Fig. 7). [46-49] The metallized pattern showed higher resolution than 100 μm and a strong adhesive strength of 150 kgf cm⁻² for nickel and 80 kgf cm⁻² for copper. The laser-treated surface of PTFE showed high adhesion strength through epoxy or cyanoacrylate adhesive for steal. The tensile strength at breaking point was over 12 MPa almost comparable to that of PTFE itself.

Fig. 7. Schematic diagram of surface modification of PTFE film under hydrazine gas atmosphere.

Fukumura and coworkers reported a novel method to dope solid polymers with aromatic molecules without using solvents. Laser ablation of PMMA film doped with pyrene gave a target polymer film implanted with pyrene. This method will open a new technique to prepare electro-optic devices doped functional organic compounds. [50,51]
5. Summary

Interaction of excimer lasers with polymer materials has induced various phenomena which could not be opened by other traditional methods or physical techniques. Most distinctive characteristics of excimer lasers is a source of high-quality and high-intensity ultraviolet photons, which makes possible to excite high electronic levels by multiphoton excitation mechanism. We can design and expect new reactions through higher excited levels for various starting materials including polymers. These possibilities will give useful processing of polymer materials if we correspond to industrial needs and design the most suitable reaction fields.

References