LASER ABLATION
OF
VARIOUS POLYMER MATERIALS

MASAMI INOUE, KEIKO ITO and NOBUHIKO OHMORI
MITSUBISHI ELECTRIC CORP., CENTRAL RESEARCH LABORATORY
Tsukaguchi Honmachi 8 Chome, Amagasaki, Hyogo, JAPAN

The laser ablative decomposition technique of various kinds of polymer materials is attracting attentions as one of the microfabrication techniques causing no thermal damages. We discuss here the etching process of polymer films such as polyimide, polystyrene, polymethylmethacrylate, polytetrafluoroethylene and tetrafluoroethylene-hexafluoropropylene copolymer, by the ablative decomposition using excimer laser and YAG laser. The etched depth per laser energy density and the morphology of etched surface depend on the polymer's absorption coefficient at the given laser wavelength. Each polymer has a specific threshold energy density for decomposition. The energy provided in extremely thin polymer surface by irradiation of threshold laser energy density correlates appreciably with the energy needed for raising to the volatile temperature on each polymer. It can therefore be presumed that the behavior of laser ablative decomposition depends on the optical and thermal properties of polymer.

1. INTRODUCTION

The material processings by the ultraviolet laser have attracted attentions as promising microfabrication, because of the rapid advance in the field of the excimer laser, and because of the broadened knowledge on the interaction between laser beam and various kind of materials. Recently, the laser ablative decomposition process of polymers using high intensity ultraviolet excimer laser has been expected for wide practical applications such as perforation of polymer insulators and removal of resist materials. This
process has good characteristics as follows;
(1) Photochemical process without any sign of thermal damage to the neighboring area of
the material. (2) Dry etching process in the ambient air. (3) Removal of fine area
in the material by reduced projection. (4) Selective removal of the material from the
underlying substrate being left virtually unaffected.

The behavior of the laser ablative decomposition will be discussed here based on the
observations of the polymer surfaces irradiated with various lasers which have different
wavelength region of ultraviolet to infrared, and the investigations of relationship
between polymer's decompositionability and it's characteristics.

2. METHODS

Commercial polymer films such as polypyrrole(PI), polystyrene(PS), polymethylmethacry-
late(PMMA), polytetrafluoroethylene(PTFE) and tetrafluoroethylene-hexafluoropropylene
copolymer(FEP) were used in the experiments. These polymers' optical properties such as
absorption coefficient and reflectivity were measured by spectrophotometer, and these
thermal properties were measured by thermal analyzer.

These polymers were irradiated with excimer laser( ArF: 193nm, KrF: 248nm and XeF:
351nm) and YAG short pulse laser( fundamental: 1064nm, second harmonic: 532nm and
fourth harmonic: 266nm) through a 1 mm diameter pinhole mask and a focusing quartz
lens. All the irradiation were performed in the ambient air. The pulse laser energy was
varied by use of ND filters and measured with a GenTec joule-meter at 1 Hz. The etched
holes at each experiment were measured for depth with a stylus profilometer. Surface
morphology of the polymers was observed with a scanning electron microscope(SEM).

3. RESULTS AND DISCUSSION

1. Polymer surface irradiated by laser

All the kinds of polymer were decomposed to be removed by irradiation of both excimer
lasers and YAG lasers, but the morphologies on the decomposed surface differ from one
another greatly. Figure 1 shows the SEM photographs of PI, PMMA and FEP film surfaces
irradiated by various lasers. The PI film surfaces irradiated by all the lasers used
except for fundamental YAG laser are smooth without thermal damage in appearance. The
PMMA film surface irradiated by the ArF excimer laser with the shortest wavelength is only very smooth. But the FEP film surface irradiated by every laser is very rough. In the cases of PI and PS which have aromatic ring structure of benzene, many conical remnants were left on the decomposed surface in certain conditions, and many carbon black particle adhered to the surroundings, as shown in Figure 2.

We discuss the mechanism responsible for the appearance of conical remnants in PI surface irradiated. With the number of pulse shots increasing, the remnants increase both in number and size. The remnants are found to decrease in number not only with increasing laser energy density per pulse, but also with decreasing irradiated area. By microscopic IR and X ray analyses, it was confirmed that the top of the remnant was covered with carbon black. In the initial stage, the clusters of the carbon black particles were generated and adhered to the polymer surface. And they prevented the polymer from being etched by succeeding laser pulses. In the results, many conical remnants were left on the etched surface.

Fig. 1 SEM photographs of various polymer films irradiated by various laser.
(a) 0.4 J/cm\(^2\), (b) 0.49 J/cm\(^2\), (c) 0.55 J/cm\(^2\), (d) 6.1 J/cm\(^2\), (e) 40 J/cm\(^2\), (f) 0.4 J/cm\(^2\), (g) 0.8 J/cm\(^2\), (h) 15 J/cm\(^2\), (i) 20 J/cm\(^2\), (j) 20 J/cm\(^2\), (k) 2.5 J/cm\(^2\), (l) 20 J/cm\(^2\), (m) 20 J/cm\(^2\), (n) 40 J/cm\(^2\), (o) 50 J/cm\(^2\).
Fig. 2. SEM photographs of PI surface irradiated by ArF excimer laser (0.4J/cm²).

<table>
<thead>
<tr>
<th>(1) 1 shot</th>
<th>(2) 10 shots</th>
<th>(3) 50 shots</th>
<th>(4) 150 shots</th>
</tr>
</thead>
<tbody>
<tr>
<td>100 nm</td>
<td>100 nm</td>
<td>100 nm</td>
<td>1 μm</td>
</tr>
<tr>
<td>(5) 10 shots</td>
<td>(6) 100 shots</td>
<td>(7) 500 shots</td>
<td>(8) 1000 shots</td>
</tr>
<tr>
<td>100 μm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 3. SEM photographs of surface and side wall of PI films irradiated by various lasers. (a) 0.4J/cm², (b) 6.1J/cm², (c) 41.5J/cm²
Furthermore, Figure 3 shows the detailed observation, that is, the SEM photographs of surface and wall of PI film irradiated by ultraviolet, visible and infrared ray lasers. As shown in this Figure, the surface irradiated by excimer laser is the smoothest of all without thermal damage, and the irradiated surface becomes rough because of thermal damage with increasing wavelength of laser.

As can be seen from these results, the morphologies of polymer surface irradiated by laser may be ascribed to the removed volume per laser pulse and may depend on the penetrating depth of laser beam into polymer.

2. Etched depth of polymer irradiated by laser

We discuss the laser ablation behavior on the basis of the data of etched depth. All the kinds of polymers were decomposed to be removed by the irradiation of laser beam, but the removed volume differed from one another. For every polymer, a linear relationship between the etched depth and the number of laser pulses existed at any magnitude of the pulse energy density. When the laser energy density per pulse increased, the etched depth per pulse became large. In other words, the etched depth per pulse at given pulse laser energy was invariant with depth of the etched hole. Figure 5 shows the relationship between the etched depth per pulse and the laser energy density for PI film irradiated by various laser.

Every polymer has a threshold energy for the ablative decomposition and the etched depth becomes abruptly large over a certain energy density per pulse, as shown in Figure 6. We assume that the threshold energy is the smallest value of energy density which can be measured with a stylus profilometer. Table 1 shows the threshold laser energy density values and the absorption coefficients of various polymers at the given laser wavelength.

Therefore, threshold laser energy density values are found to be arranged in the descending order of the absorption coefficient. It is considered that the etched depth of the polymer per pulse laser energy density depends on the absorption coefficient of the polymer at the given laser wavelength. These experiments reveal that the irradiated polymer surface is smooth without thermal damage in the case of polymer with large absorption coefficient (about 10⁹ cm⁻¹) and that small absorption causes the thermal damage.
Fig. 4. Plots of etched depth per pulse versus log laser energy density for PI irradiated by various lasers.

Fig. 5. Plots of etched depth per pulse versus log laser energy density for various polymer films irradiated by ArF excimer laser.
even if ArF excimer laser is used.

3. Influence of polymer’s thermal properties on laser ablation

As mentioned previously, the laser ablation behaviors depend on optical properties of polymer. Next, we discuss the influence of polymer’s thermal properties on laser ablation behavior, because the thermal damage appears even in polymer film irradiated by excimer laser. We estimate both the energy needed for raising to volatile temperature of polymer and the energy provided in polymer surface by irradiation of threshold laser energy density. Table 2 shows the physical properties and the energy(Q) needed for raising to volatile temperature(Tv) of these polymer used in this experiment. This energy(Q) is determined with the following equation(1).

\[ Q = \rho ( c \Delta T + \Delta H_m ) \quad (1) \]

\( \rho \) : density, \( \Delta T \) : raising temperature from initial temperature(25°C)
\( c \) : specific heat, \( \Delta H_m \) : fusion energy

On the other hand, the energy required for ablative decomposition of polymer is above the threshold energy. Then, the energy(\( \Delta E_{\text{surf}} \)) provided by laser irradiation on polymer surface is determined with the following equation(2).

\[ \Delta E_{\text{surf}} = \alpha ( 1 - R ) E_t \quad (2) \]

\( \alpha \) : absorption coefficient, \( R \) : reflectivity
\( E_t \) : threshold laser energy density

Figure 6 shows the relationship between \( Q \) and \( \Delta E_{\text{surf}} \). As shown in this figure, the
energy given by threshold laser energy density correlates well with the energy needed for raising to the volatile temperature on each polymer. It can therefore be presumed that the behavior of laser ablative decomposition depends on photo-thermal transformation.

Table 2. The physical properties and the energy needed for raising to volatile temperature of various polymer

<table>
<thead>
<tr>
<th></th>
<th>PS</th>
<th>PMMA</th>
<th>PI</th>
<th>FEP</th>
<th>PTFE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflectivity(R) (300nm)</td>
<td>0.03</td>
<td>0.06</td>
<td>0.083</td>
<td>0.021</td>
<td>0.002</td>
</tr>
<tr>
<td>Density(ρ) g/cm³</td>
<td>1.11</td>
<td>1.15</td>
<td>1.42</td>
<td>2.12</td>
<td>2.14</td>
</tr>
<tr>
<td>Specific heat(c) J/g·°C</td>
<td>1.2~2.4</td>
<td>1.25~2.5</td>
<td>1.09</td>
<td>1.17</td>
<td>1.17</td>
</tr>
<tr>
<td>Fusion energy(ΔHm) J/g</td>
<td>-</td>
<td>-</td>
<td>20.0</td>
<td>34.2</td>
<td></td>
</tr>
<tr>
<td>Volatile Temp.(Tv) °C</td>
<td>300</td>
<td>270</td>
<td>550</td>
<td>420</td>
<td>425</td>
</tr>
<tr>
<td>ρ(cΔT+ΔHm) J/cm³</td>
<td>528</td>
<td>559</td>
<td>813</td>
<td>947</td>
<td>998</td>
</tr>
</tbody>
</table>

![Fig. 6. Relationship between the energy (ΔEsuf) given by threshold laser energy density and the energy(Q) needed for raising to volatile temperature.](image)

4. CONCLUSION

It can be concluded that the behaviors of the laser ablative decomposition depend on both photo-absorption property and thermal property that each polymer has respectively. Using the laser processing, we must adopt the laser fitted to the objective material.