Preparation of Semiconducting Polymer Films by High Intensity Photo-Chemical Processes with Excimer Laser Beams

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Excimer laser ablation (ELA) of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), 3,4,9,10-perylenetetracarboxylic diimide (PTCDI), 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) and perylene with 193(ArF), 248(KrF) and 308nm(XeCl) beams results in formation of amorphous semiconducting polymer thin films consisting of fine particles on several temperature-controlled substrates. The structure and electric conductivity of each prepared film depend considerably on the target material, ablation wavelength and substrate temperature. The films prepared on substrates at 300°C by ELA at 308nm from PTCDA and PTCDI partially contain polyperinaphthalene(PPN) structure with conductivity ranging from 10^{-1} to 10^{-2} Scm^{-1}.

Keywords: high intensity photo-chemical processes, laser ablation, excimer laser, amorphous semiconducting polymer thin films, polyperinaphthalene

1. Introduction

In recent years, high intensity photo-chemical processes with various kinds of laser beams are extensively studied in organic chemistry.[1-4] Especially, laser ablation method, which is widely applied to prepare inorganic thin films such as high Tc superconductor[5] and ferroelectric[6] thin films, is also recognized as one of the superior techniques for etching and surface modification of polymers, and studied vigorously both from fundamental and practical aspects.[7-13] Nevertheless, little attention has been given to application of this technique to preparation of organic thin films. However, since Hansen et al. reported the preparation of polymer films consisting of the same components as the target polymer materials using laser ablation for the first time[14], deposition of organic films by laser ablation[15-18] has gradually come into notice and to be considered as a good method for the preparation of novel functional organic thin films in view of the possible control of their chemical structures by selection of wavelength and fluence of the laser beams applied for ablation.

Along with this trend, Ouchi and Yabe[19] obtained fine particles with conductivities in the range 10^{-4}-10^{-9} Scm^{-1} by laser ablation of several condensed aromatic compounds such as 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA), 3,4,9,10-perylenetetracarboxylic diimide (PTCDI) and 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTCDA) with high power (more than 180mJ/pulse^{-1}) excimer laser beams of 193(ArF), 248(KrF) and 308nm(XeCl). Furthermore, Yudasaka et al.[20] prepared thin films of polyperinaphthalene (PPN), which is well known as one the low-dimensional conducting polymer[21,22], by ablation of PTCDA with fourth harmonic (266nm) of a Nd:YAG laser (fluence 10mJcm^{-2}).

In this paper, amorphous organic semiconductive thin films are prepared on temperature-controlled substrates (20-300°C) by excimer laser ablation (ELA) of PTCDA, PTCDI, NTCDA and perylene with 308, 248 and

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193nm laser beams. It is revealed that the structure and electric conductivity of the films are effectively controlled by appropriate selection of target material, wavelength of laser beam and, especially, substrate temperature in the deposition processes. The films prepared on substrates at 300°C by ELA of PTCDA and PTCDI at 308nm partially contain PPN structures with conductivity ranging from 10^{-1} to 10^{-2}\text{Scm}^{-1}.

2. Experimental

The experimental setup is shown in Fig. 1. A target material was ablated for 1-2 hours with a 308(XeCl), 248(KrF) or 193nm(ArF) pulsed excimer laser beam at a repetition rate of 5Hz in a reaction chamber evacuated below 10^{-3}\text{Torr} with rotary and mechanical booster pumps. The laser beam was focused on a target material. As a target material, PTCDA, PTCDI, NTCDA or perylene powder compressed into a disk (10 mm in diameter and 3mm in thick) was used. The molecular structure of each target material is shown in Fig. 2. Each target was spun with a motor, preventing a laser beam from concentrating on a fixed spot. Films were prepared on several types of substrates such as quartz, silicon and KBr, as required for the various characterization experiments described below. Each substrate was settled at a distance of 3cm from the target. The substrate temperature was controlled with a heater ranging between 20 and 300°C. The fluence of each laser beam applied was fixed to 250mJcm^{-2}\text{pulse}^{-1}.

Structure and electric property of the deposited films were investigated by scanning electron micrography (SEM), FT-IR, Raman, ultra violet-visible (UV-vis.) spectroscopy, X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR), X-ray diffraction (XRD) and electric conductivity measurement at room temperature with four probe method.

3. Results and discussion

3.1 Structures and electric conductivities of the films from PTCDA, PTCDI, NTCDA and perylene prepared on substrates at 20°C by ELA at 193, 248 and 308nm.

ELA of each aromatic compound target with 193, 248 and 308nm beams results in formation of homogeneous organic thin films on substrates at 20°C. No remarkable difference in surface morphologies are observed between the films prepared by ablation of PTCDA, PTCDI, NTCDA and perylene. Each film consists of

<table>
<thead>
<tr>
<th>Target Material</th>
<th>Ablation Wavelength (nm)</th>
<th>Conductivity (S\text{cm}^{-1})</th>
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<tbody>
<tr>
<td>PTCDA</td>
<td>308</td>
<td>2.4\times10^{-4}</td>
</tr>
<tr>
<td>PTCDA</td>
<td>248</td>
<td>7.1\times10^{-5}</td>
</tr>
<tr>
<td>PTCDA</td>
<td>193</td>
<td>6.3\times10^{-4}</td>
</tr>
<tr>
<td>PTCDI</td>
<td>308</td>
<td>3.6\times10^{-6}</td>
</tr>
<tr>
<td>PTCDI</td>
<td>248</td>
<td></td>
</tr>
<tr>
<td>PTCDI</td>
<td>193</td>
<td>8.3\times10^{-7}</td>
</tr>
<tr>
<td>NTCDA</td>
<td>308</td>
<td>&lt;1.0\times10^{-7}</td>
</tr>
<tr>
<td>NTCDA</td>
<td>248</td>
<td>&lt;1.0\times10^{-7}</td>
</tr>
<tr>
<td>NTCDA</td>
<td>193</td>
<td>&lt;1.0\times10^{-7}</td>
</tr>
<tr>
<td>perylene</td>
<td>308</td>
<td>&lt;1.0\times10^{-7}</td>
</tr>
<tr>
<td>perylene</td>
<td>248</td>
<td>&lt;1.0\times10^{-7}</td>
</tr>
<tr>
<td>perylene</td>
<td>193</td>
<td>&lt;1.0\times10^{-7}</td>
</tr>
</tbody>
</table>

Table I. Electric conductivities at room temperature for the films prepared on substrates at 20°C from PTCDA, PTCDI, NTCDA and perylene by ELA at 308, 248 and 193nm.
Electric conductivity at room temperature for each film prepared on a quartz substrate at 20°C from each target with different ablation wavelength is listed in Table I. Conductivities ranging from $10^{-6}$ to $10^{-5}$ S cm$^{-1}$ and from $10^6$ to $10^{-7}$ S cm$^{-1}$ are obtained for the films from PTCDA and PTCDI, respectively. Films from other targets are insulators with electric conductivities less than $10^{-7}$ S cm$^{-1}$.

Figure 3 shows FT-IR spectra of the films from PTCDA, PTCDI, NTCDA and perylene with various ablation wavelengths together with those of evaporated films of the target materials. For the films from PTCDA and NTCDA by ablation at 308 nm, spectra virtually similar to those of evaporated films indicate that the films intrinsically consist of their target materials, except for an increase of peak intensity at 1730 cm$^{-1}$ in each film from NTCDA. This peak is probably due to formation of carbonyl groups after leaking the reaction chamber by reaction of radicals yielded by ablation with oxygen in air. In the films with 248 and 193 nm irradiation,
change in peak intensities between 1780 and 1730 cm\(^{-1}\) or broadening of the peaks at 1300 cm\(^{-1}\) and 1000 cm\(^{-1}\), which are all related to carboxylic anhydride groups in PTCDA and NTCDA, are observed, indicating the bond breaking of carboxylic anhydride groups in PTCDA and NTCDA. Considerable damage of main frame for the film prepared from perylene is observed even at 308 nm. In particular, disappearance of the peak at 1500 cm\(^{-1}\) and remarkable increase of the peak intensity at 1700 cm\(^{-1}\) in each spectrum suggest the formation of radicals by bond breaking of perylene skeleton. Structure of the target material is, on the other hand, kept for the film from PTCDI with each wavelength, considering from resemblance of spectra to that of the evaporated film of PTCDI apart from a slight broadening.

Raman spectra (excited by 514 nm) for the films from PTCDA with 193, 248 and 308 nm, shown in Fig. 4, give us further information on their structural changes. While only two broad peaks around 1600 and 1380 cm\(^{-1}\), characteristic of amorphous carbon, are observed for films by ELA with 193 and 248 nm, the spectrum of the film with 308 nm light shows sharp peaks at 1600 cm\(^{-1}\) due to aromatic rings, 1400 and 1280 cm\(^{-1}\) due to in-plane C-H bending. It is interesting to note, here, that we could obtain a clear Raman spectrum of the film by ELA at 308 nm, although vacuum deposition film of PTCDA gave only a broad band due to fluorescence.

Comparison of FT-IR spectra involving 1780, 1730, 1300 and 1000 cm\(^{-1}\) related to carboxylic anhydride groups and UV-vis. spectra showing a \(\pi-\pi^*\) band around 500 nm for the film prepared at 308 nm with those for the film by vacuum deposition of PTCDA indicates that the components of the film prepared by ELA at 308 nm are essentially PTCDA monomers.

Halo pattern around \(2\theta=20^\circ\) of XRD spectrum without any sharp peaks indicates the amorphous nature of this film.

3.2 Dependence on substrate temperature of structure and electric conductivity of the films prepared from PTCDA, PTCDI and NTCDA by ELA at 308 nm.

Organic semiconductive thin films are prepared on substrates at 20°C and 300°C by ELA of PTCDA, PTCDI and NTCDA with
Table II. Electric conductivities at room temperature for the films prepared on substrates at 300°C from PTCDA, PTCDI and NTCDA by ELA at 308nm.

<table>
<thead>
<tr>
<th>Target material</th>
<th>Conductivity (S cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PTCDA</td>
<td>2.7×10⁻¹</td>
</tr>
<tr>
<td>PTCDI</td>
<td>8.6×10⁻²</td>
</tr>
<tr>
<td>NTCDA</td>
<td>1.5×10⁻¹</td>
</tr>
</tbody>
</table>

308nm light. In every case, surface morphology consists of smaller particles and it becomes more compact when prepared on substrates at 300°C compared with that prepared at 20°C. Surface morphologies of the films prepared on substrates at 20 and 300°C by ELA of PTCDI are shown in Fig. 5.

Electric conductivities at room temperature are listed in Table II for the films prepared by ELA with a 308nm beam on substrates at 300°C from PTCDA, PTCDI, NTCDA. Although each film prepared on a substrate at 20°C by ELA of each target shows electric conductivity in the order of 10⁻⁴ S cm⁻¹, at most, as mentioned in the previous section, each film prepared on a substrate at 300°C show more than 10⁻² S cm⁻¹. For the films prepared on substrates at 300°C by ELA of PTCDA and NTCDA, the electric conductivities reach up to 10⁻¹ S cm⁻¹.

Fig. 6. FT-IR spectra of the films prepared on substrates at 300°C by ELA at 308nm from (a) PTCDA, (b) PTCDI and (c) NTCDA.

FT-IR spectra in Fig. 6 show decrease of peak intensities between 1780 and 1650 cm⁻¹ related to the side groups and/or carboxyl groups formed after leaking for the films prepared on substrates at 300°C by ELA of each target.

XPS and ESR results for the film by ELA of PTCDI indicate that the binding energy of C1s is shifted from 284.6 to 284.3 eV with the spin concentration decreasing from 9.2×10¹⁸ to 1.9×10¹⁸ spins cm⁻³ with increasing substrate temperature from 200 to 300°C, suggesting that a π-conjugated system develops by effective recombination of radicals with increasing substrate temperature.

Figure 7 shows the Raman spectra for the films by ELA of each target. While the spectrum for NTCDA shows broad bands reminiscent of amorphous carbon, strong peaks at 1380 and 1280 cm⁻¹ still survive for both PTCDA and PTCDI.

As for the films prepared by ELA of PTCDA and PTCDI, FT-IR and Raman results allow us to conclude that polymerization occurs by eliminating the side groups with preserving perylene skeleton to form polyperinaphthalene (PPN) structure partially. Actually, these Raman spectra are quite similar to that for PPN prepared by Murakami et al. with vapor polymerization method.[21]

Fig. 7. Raman spectra of the films prepared on substrate at 300°C by ELA at 308nm from (a) PTCDA, (b) PTCDI and (c) NTCDA.

Development of PPN structure on the
substrate at 300°C is not due to thermal scission of side groups after deposition of PTCDA and PTCDI monomers, since these monomers do not decompose at a temperature lower than 400°C. (Both monomers sublime at 360°C without decomposition.) Moreover, monomers are sparingly deposited on such a high-temperature surface. Rupture of side groups must have occurred during the ablation event, and "naked" perylene skeleton reach the substrate. High temperature (300°C) assists their polymerization to PPN. Namely, increase of substrate temperature contributes to selective deposition of the fragments containing perylene skeleton without side groups.

4. Conclusion

ELA of PTCDA, PTCDI, NTCDA and perylene with 193, 248 and 308nm beams results in formation of amorphous organic thin films consisting of fine particles on several temperature-controlled substrates.

Selection of target material, ablation wavelength and substrate temperature allows us to obtain organic films with different structures and electric conductivities. While the films prepared on a substrate at 20°C by ablation of PTCDA at 193 and 248nm, for example, are amorphous carbon, the components of the film at 308nm are essentially PTCDA monomer. Moreover, the films prepared on a substrate at 300°C by ELA of PTCDA and PTCDI partially contain polyperinaphthalene structure with conductivity more than $10^{-2}$ Scm$^{-1}$. Increase of substrate temperature contributes to selective deposition of the ablatant containing perylene skeleton without carboxylic anhydride groups as well as to acceleration of the recombination reaction of radicals. Further improvement will lead to PPN films without structural defects.

As a conclusion, potential control of structure and electric property in preparing organic films by ELA is demonstrated in this study. Detailed discussion on the ablation and deposition mechanisms should be made for minute control of ELA. Probing of ablating species by time-of-flight mass spectroscopy, absorption and emission spectroscopy and temperature measurements during the ablation/deposition processes are now in the planning.

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References