Effect of Cobalt Powder on Elimination Reaction of the Side Group of 3,4,9,10-Perylenetetracarboxylic Dianhydride during Laser Ablation at 355 nm

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1. Introduction

Polyperinaphthalene (PPN) has been expected to be a promising material for a variety of electric/electronic devices.[1] Since the first synthesis was reported by Murakami et al.,[2] some attempts have been made to prepare films or nanoparticles of this material.[3,4] Among them, we had succeeded to prepare films basically consisting of PPN nanoparticles by excimer laser ablation (ELA) of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) with XeCl beams (308 nm).[4] The urgent key subject to obtain well-defined PPN is effective preparation of the high qualitative intermediate species without the side groups of PTCDA as shown in Scheme I. Recently, we have found remarkable enhancement of elimination efficiency for the side groups by ELA of mixture targets of PTCDA with cobalt (Co) powder (PTCDA/Co) [5,6] to obtain the intermediate species effectively, though it still contained some structural defects.

It is interesting to study the effect of Co in ablation at longer wavelengths on the elimination reaction of the anhydride groups of PTCDA for preparation of the higher qualitative intermediate species. In this report, laser ablation of PTCDA/Co as well as PTCDA was carried out using the third harmonic wavelength of a Nd:YAG laser at various

fluences.

2. Experimental

The third harmonic wavelength (355 nm) of a Nd:YAG laser was employed for ablation. Disk like targets of PTCDA and PTCDA/Co at 1/4 in molar ratio were ablated at fluences ranging from 0.2 to 1.0 Jcm⁻²pulse⁻¹ in a reaction chamber evacuated to ca. 10⁻³ Pa and deposited on KBr and glass substrates at a substrate temperature (*T_s*) of 27°C. The morphology and molecular structure of the deposition were investigated by a scanning electron microscope (SEM), FT-IR and Raman spectroscopies as well as micro elemental analysis.

3. Results and discussion

Laser ablation of both PTCDA and PTCDA/Co targets with 355 nm beams enabled us to obtain thin films consisting of various sizes of nanoparticles. A surface SEM image of a film deposited by the ablation of PTCDA/Co is shown in Fig. 1. The diameter of the particles is roughly ranging from 50 to 100 nm.

Scheme I

Fig. 1. Surface SEM image of a film prepared by the ablation of PTCDA/Co at 0.5 Jcm⁻²pulse⁻¹.

Fig. 2. FT-IR spectra for films prepared by the ablation of PTCDA at (a) 0.2, (b) 0.5 and (c) 1.0 Jcm⁻²pulse⁻¹.

Figure 2 shows FT-IR spectra for films prepared by the ablation of PTCDA at 0.2, 0.5 and 1.0 Jcm⁻²pulse⁻¹. Large peaks at 1765 and 1735 cm⁻¹ related to the anhydride groups of PTCDA can be observed independent of the laser fluences applied, indicating that the ablation of PTCDA with 355 nm beams does not allowed us to remove the side groups.

On the contrary, the ablation of PTCDA/Co showed a prospective result. In the FT-IR measurement, large peaks related to the anhydride groups of PTCDA could be found for a film prepared at 0.2 Jcm⁻²pulse⁻¹. However, drastic decrease in the peak intensity was observed with increasing fluence up to 0.5 Jcm⁻²pulse⁻¹. Figure 3 shows FT-IR and Raman spectra for a film prepared at 0.5 Jcm⁻²pulse⁻¹. In the FT-IR spectrum (Fig. 3(a)), the peaks related to the side groups almost completely disappeared. The fact that elimination of the side groups of PTCDA can be achieved at T_s of 27°C suggests that almost all the monomers ablated lost their side groups before landing on substrates by interaction with Co particles included in the targets. Although such a phenomenon could be observed in our previous studies with XeCl excimer laser beams[5,6], the threshold of the fluence for

Fig. 3. (a) FT-IR and (b) Raman spectra for a film prepared by the ablation of PTCDA/Co at 0.5 Jcm⁻²pulse⁻¹.

the complete removal of the side groups was 1.0 Jcm⁻²pulse⁻¹, twice of the present study using 355 nm beams. On the other hand, the Raman spectrum for the film prepared at 0.5 Jcm⁻²pulse⁻¹ (Fig. 3(b)) shows a quite sharp peak at 1290 cm⁻¹ assigned to a C-H in-plane bending mode of a perylene skeleton together with peaks at 1560 and 1360 cm⁻¹ characteristic to condensed aromatic rings. The full width of half maximum (FWHM) of the peak at 1290 cm⁻¹ was 21 cm⁻¹, smaller than that prepared with XeCl beams (22 cm⁻¹).[5] These results indicate that the intermediate species without the anhydride groups as well as with a better-defined perylene skeleton are effectively produced by the ablation of PTCDA/Co with 355 nm beams at 0.5 Jcm⁻²pulse⁻¹. Actually, [H]/[C] estimated by micro elemental analysis of the deposition was 0.42, almost in accordance with that of the theoretical value for the species (0.40).

4. Conclusion

PTCDA and PTCDA/Co targets were ablated using the third harmonic wavelength of a Nd:YAG laser to obtain thin films consisting of various size of nanoparticles. Although the anhydride groups could not be removed by the ablation of PTCDA regardless of the fluences applied, the most part of the side groups were scavenged by the ablation of PTCDA/Co at 0.5 Jcm⁻²pulse⁻¹. The Raman spectrum for the film showed a quite sharp peak assigned to a C-H in-plane bending mode of a perylene skeleton. These results indicate that the intermediate species for preparation of PPN without the anhydride groups as well as with a better-defined perylene skeleton are effectively produced by the ablation of PTCDA/Co with 355 nm beams at 0.5 Jcm⁻²pulse⁻¹.

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