Ablation of metal-containing perylene tetracarboxylic dianhydride with third harmonic of Nd:YAG laser

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Abstract. Deposited films were prepared by ablation of disk-like targets of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) and mixed targets of PTCDA with cobalt (PTCDA-Co) and copper powders (PTCDA-Cu) using the third harmonic of a Nd:YAG laser (355 nm) at fluences ranging from 0.1 to 1.0 Jcm⁻²pulse⁻¹. FT-IR and Raman spectroscopy showed that ablation of PTCDA-Cu at more than 500 mJcm⁻²pulse⁻¹ led to an effective elimination reaction of the anhydride groups of PTCDA as well as PTCDA-Co at more than 700 mJcm⁻²pulse⁻¹. In ablation of PTCDA-Co and PTCDA-Cu, plasma emission was observed around 500 nm. With increasing fluence, addition to the plasma emission, peaks at 437, 469, 513 and 550 nm coming from C₂ radicals were observed, suggesting that PTCDA was partially decomposed into C₂. TOF mass spectra in ablation of PTCDA-Co showed fragments of PTCDA without one or two anhydride groups as well as CoCₙ⁺ (n=0-5) and Co(CO)ₓ²⁻.

1. Introduction
Preparation of polyperinaphthalenic organic semiconductor (PPNOS), which is promising as organic electronic devices and energy storage materials has been tried by laser ablation. [1-4] The authors succeeded to prepare PPNOS nanoparticles by laser ablation of mixed targets of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) with cobalt powders using third harmonic of Nd:YAG laser (355nm) through effective elimination reaction of the anhydride groups of PTCDA.[5,6]

In this study, ablation of PTCDA targets with copper particles as well as cobalt particles were carried out using 3rd harmonic of a Nd:YAG laser in order to investigate the mechanism of elimination reaction of the anhydride groups of PTCDA as shown in figure 1.

Figure 1. Scheme of elimination reaction of the anhydride groups of PTCDA.
2. Experiment
Disk-like PTCDA targets and mixed targets of PTCDA with cobalt and copper powders with an average diameter of 4 μm, PTCDA-Co and PTCDA-Cu, respectively, were ablated and deposited on substrates in a reaction chamber at ca. 10⁻³ Pa. The third harmonic of a Nd:YAG laser (355 nm) was employed for ablation at fluences ranging from 0.1 to 1.0 Jcm⁻²pulse⁻¹. The target materials were irradiated for 20 minutes at a repetition rate of 10 Hz. The molecular structures of the deposits were investigated by FT-IR and Raman spectroscopy. In addition, emission spectra were measured in ablation of PTCDA-Co and PTCDA-Cu. Furthermore, fragments in ablation of PTCDA-Co were analysed by time-of-flight (TOF) mass spectroscopy.

3. Results and discussion
3.0. Molecular structure of deposited films prepared by ablation of PTCDA-Co and PTCDA-Cu
Deposited films were prepared by ablation of PTCDA, PTCDA-Co and PTCDA-Cu. From FT-IR measurements, it was revealed that the anhydride groups of PTCDA were effectively eliminated, in case of ablation of PTCDA-Co at more than 300 mJcm⁻²pulse⁻¹ and PTCDA-Cu at more than 700 mJcm⁻²pulse⁻¹. In contrast, ablation of pure PTCDA did not in the removal of the groups for any laser fluence. [5] FT-IR spectra of the films prepared by ablation of PTCDA-Cu at various fluences are shown in figure 2. The spectrum at 100 mJcm⁻²pulse⁻¹ is quite similar to that of an evaporated film of PTCDA. Intensity of the broad band from around 1730 to 1800 cm⁻¹ related to the anhydride groups of PTCDA is decreased with increasing fluences from 500 mJcm⁻²pulse⁻¹. Peaks at 1600, 1360 and 1290 cm⁻¹ were clearly detected in the Raman spectrum for ablation of PTCDA-Cu at less than 500 mJcm⁻²pulse⁻¹, which were characteristic of perylene skeleton, indicating that anhydride groups of PTCDA were eliminated without decomposition of perylene skeleton.

Intensity ratios at 1763 cm⁻¹ against at 1593 cm⁻¹, \( I_{1763\text{cm}^{-1}}/I_{1593\text{cm}^{-1}} \) were plotted as a function of fluence to compare the efficiency of elimination reaction of the anhydride groups among PTCDA, PTCDA-Co and PTCDA-Cu. The results are shown in Figure 3. It is found that elimination reaction occurs more effectively for PTCDA-Cu than for PTCDA-Co. This is probably due to thermal effects induced after the laser beam was absorbed by the metal particles. Average temperature rise in laser-beam absorption by metal particles, \( \Delta T \) is estimated following equation 1[7], under the assumption that laser beams are completely absorbed by metal particles.

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\Delta T = \frac{F \pi r^2}{CVd} (1 - R)
\]
where $F$ is the laser fluence, $r$ is the radius, $C$ is the specific heat, $V$ is the volume, $d$ is the density and $R$ is the reflectivity of the metal particles. Figure 4 shows the dependence of $\Delta T$ on $F$ for Co and Cu. The values of $r$, $C$, $d$, and $R$ for Co and Cu particles to estimate $\Delta T$ are listed in Table 1. $\Delta T$ for Cu at each fluence is higher than that for Co. It is reported that the elimination temperature of anhydride groups of PTCDA is 516ºC.[1] $\Delta T$ exceeds the value at $F$ of 500 and 700 mJcm$^{-2}$pulse$^{-1}$ for Cu and Co, respectively. These results support the results from the FT-IR measurement described above, suggesting that thermal effects of metal particles heated by laser irradiation are dominant for elimination of the anhydride groups of PTCDA.

### 3.1. Emission spectra in ablation of PTCDA-Co and PTCDA-Cu

Emission spectra in ablation of PTCDA, PTCDA-Co and PTCDA-Cu at 100 mJcm$^{-2}$pulse$^{-1}$ are shown in Figure 5. Lack of lines in the range 660-680 nm and 730-750 nm is owing to defects in the detector. In the spectrum in ablation of PTCDA, broad bands around 500 nm and 650 nm are due to plasma emission and fluorescence of PTCDA, respectively. In ablation of PTCDA-Co and PTCDA-Cu, the intensity of the fluorescence is decreased and, at the same time, the intensity of plasma emission is increased compared with that in ablation of PTCDA.

In ablation of PTCDA at more than 300 mJcm$^{-2}$pulse$^{-1}$, emission peaks at 437, 469, 513, and 550 nm coming from C$_2$ radicals [8] were detected. The intensity of these peaks was increased with increasing fluence. Addition to these peaks, emission peaks at 390, 400, 412, 455 and 460 nm related to Co atoms were observed in ablation of PTCDA-Co at more than 300 mJcm$^{-2}$pulse$^{-1}$.[9] Similarly, for ablation of PTCDA-Cu at more than 300 mJcm$^{-2}$pulse$^{-1}$, peaks related to Cu atoms were detected at 407, 428, 454, 459, 511, 515 and 521 nm.[9]

### 3.2. TOF mass spectra in ablation of PTCDA-Co

TOF mass spectra of fragments by ablation of PTCDA/Co at 2.5 mJcm$^{-2}$pulse$^{-1}$ and 5.0 mJcm$^{-2}$pulse$^{-1}$ are shown in Figure 6 together with that by ablation of PTCDA at 2.5 mJcm$^{-2}$pulse$^{-1}$. It should be noted that the fluence employed in TOF mass spectroscopy is much lower than that in film deposition. This is due to high sensitivity of a detector employed in TOF mass spectroscopy, preventing us from making direct comparison. However informative results for elucidation of the ablation mechanism were obtained. Although PTCDA monomers were main products for ablation of the PTCDA target, fragments with m/z of 320 and 248, which were corresponding to elimination of either and both anhydride groups of PTCDA, respectively, were detected. Furthermore, larger mass numbers such as 496 and 568 were also observed with increasing fluence. These were formed by dimerization of fragments of PTCDA without just one or two anhydride groups. Some of the fragments less than m/z of 100 were identified as CoC$_n^-$ (n=0-5) and Co (CO)$_2^-$.

### Table 1. The values of $r$, $C$, $d$, and $R$ for Co and Cu particles.

|     | $r$ (µm) | $C$ (mJg$^{-1}$K$^{-1}$) | $d$ (gcm$^{-3}$) | R  |
|-----|----------|--------------------------|------------------|----|
| Co  | 2        | 420                      | 8.90             | 0.542 |
| Cu  | 2        | 390                      | 8.96             | 0.410 |

Figure 4. Dependence of average temperature rise in laser beam absorption by metal particles $\Delta T$ on fluence $F$ for Co and Cu.
4. Conclusion

Deposited films were prepared by ablation of PTCDA, PTCDA-Co and PTCDA-Cu with the third harmonic of a Nd:YAG laser (355 nm) at fluences ranging from 0.1 to 1.0 Jcm⁻²pulse⁻¹. The anhydride groups of PTCDA were eliminated more effectively in ablation of PTCDA-Cu than PTCDA-Co. In ablation of PTCDA-Co and PTCDA-Cu, emission of plasma was observed around 500 nm. The intensity was increased with increasing fluence. At the same time, peaks at 437, 469, 513 and 550 nm coming from C₂ radical were observed, suggesting that PTCDA was partially decomposed into C₂. TOF mass spectra in ablation of PTCDA-Co showed fragments of PTCDA without one or two anhydride groups as well as CoCₙ⁺ (n=0-5) and Co(CO)₂⁺.

A series of these experiments allowed us to conclude that elimination of the anhydride groups of PTCDA was induced mainly due to the thermal effect of metal powders by laser irradiation. In addition, chemical effects to form carbon clusters with Co and Co-carbonyl complexes are also concerned for ablation of PTCDA-Co. In order to obtain higher qualitative PPNOS, formation of C₂ radicals should be reduced.

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