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Photoconductivity of solid fullerene C_{60} film modified by laser irradiation

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An improvement on photoconductivity of fullerene C_{60} film has been observed after modification of laser irradiation at room temperature or at about 100°C because some dimer, trimer and polymer of C_{60} have been formed under the laser irradiation. This leads to some change of charge transfer (CT) states and reduction on resistance to transport of photocarriers. Another important reason for the great increase on photoconductivity of C_{60} modified by laser irradiation at about 100°C (373 K) is thermal effect. Thermal treatment of the laser modified C_{60} thin film at above 100°C (373 K) for a few hours makes a great improvement on its photoconductivity because this treatment reduces trap centers for photocarriers resulted from an increase on its crystallinity and some change on its morphology. Oxygen has a great effect on photoconductivity reduction of the laser modified C_{60} thin film. © *2003 Kluwer Academic Publishers*

1. Introduction

C_{60} was discovered in 1985 [1]. Because the entire spherical surface of C_{60} is covered by rich π-conjugated electrons and it may be applied as novel photoelectric materials, much more attention has been paid to its optical and electrical properties, especially photoconductivity. The earliest works on photoconductivity of fullerene had been reported by Minami [2] and the other groups from mid to late of 1991 [3]. Thereafter, many researchers have investigated its photoconductive mechanism, including photocarrier generation from charge transfer excitons and carrier transport process [4–12]. Until present time, the transport mechanism of photocarriers in fullerene has not been made clear. In past a few years, some researchers have studied the dimerization, trimerization and polymerization of solid fullerene C_{60} film under laser irradiation [13–16]. Dimer, trimer and polymer of C_{60} could be synthesized after modification of laser irradiation with flux of 0.83–1200 w/cm^2 from -10°C to 130°C because some polymerized C_{60} molecules start to decompose if temperature is higher than 130°C [17]. As far as we know, nobody has reported on photoconductivity of laser modified C_{60} thin film.

In this paper, we prepared C_{60} film by deposition and carried out laser irradiation in the same chamber (kept in vacuum). Photoconductivity of C_{60} film was measured before and after modification of laser irradiation. Effect of thermal treatment and oxygen on photoconductivity of the laser modified C_{60} thin film has also been studied.

2. Experimental

2.1. Preparation of C_{60} films

Fullerene C_{60} powder with purity of 99.95% was purchased from SES Research Inc. Solid fullerene C_{60} films were directly deposited by sublimation of C_{60} powder under vacuum ($p = 1\text{–}4 \times 10^{-6}$ torr) on surface of quartz substrate with three pairs of coplanar Au electrodes, whose interelectrode gap is 5 μm. Crucible and substrate were kept at 306–310°C and 37–49°C during a whole deposition, respectively. Thickness of the C_{60} films was measured by TENCOR alpha-step 300 Meter. It ranges from 56 nm to 204 nm.

2.2. Laser irradiation

An argon laser machine with power of 110 mw (90 mw near sample) was applied to modify solid C_{60} films under vacuum ($1\text{–}4 \times 10^{-6}$ torr). The diameter of laser spot is about 1 mm and laser flux is about 11.5 w/cm^2.

2.3. Measurements

All photoconductivity measurements of solid C_{60} films were carried out at room temperature by use of Digital Electrometer Keithley 617 at the following conditions. Photon intensity is 2.0×10^{11} mm$^{-2} \cdot$ sec^{-1}. Wavelength ranges from 800 nm to 260 nm with an interval of 10 nm. Direct current voltage is 10 v. Wait, start, exposure and end time are 0, 2, 20 and 40 seconds, respectively.

JASCO NRS-2100 Laser Raman Spectrophotometer and Zeiss Spectrophotometer were applied to measure

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Raman and UV-visible absorption spectra of C_{60} films with and without laser irradiation.

3. Results and discussion

3.1. Photoconductivity of C_{60} modified by laser irradiation

After deposition of C_{60} film (thickness of 133 nm), its photoconductivity was measured. Then, we carried out laser irradiation on this film for 13 hrs at room temperature. Photoconductivity versus wavelength curves of the C_{60} film with and without laser irradiation for 13 hrs are shown in Fig. 1. According to its variation from short wavelength to long wavelength, the photocurrent curve of C_{60} without laser irradiation is divided into three ranges: 260 nm–410 nm (top of peak at 320 nm), 410 nm–550 nm (top of peak at 450 nm), and 550–800 nm (top of peak at 580 nm). The curve shape of C_{60} modified by laser irradiation for 13 hrs is similar with that without laser irradiation besides a little shift on its top of peak. However, the photocurrent values of the laser modified C_{60} are higher than those before laser modification, especially in range of 260 nm–550 nm.

From Fig. 2, peak at 1467 cm^{-1} in Raman spectrum of C_{60} film (thickness: 204 nm) shifts to 1462 cm^{-1} after the modification of laser irradiation. Some difference on their UV-visible absorption spectra in range of 300–700 nm is also observed (Fig. 3). According to references [13–16], peak at about 1469 cm^{-1} in Raman spectrum of C_{60} shifted to 1459 cm^{-1} after modification of laser irradiation. Ma *et al.* [18] had also reported some difference among UV-visible absorption spectra of C_{60}, C_{60} dimer and polymer solutions. So, these results indicate that some dimer, trimer and polymer of C_{60} in laser irradiation spot have been formed. Generally, photoconductivity is a photoelectric process that involves two important steps: photogeneration of charge carriers and their transport through solid. Since optical excitation is the first event preceding any photogeneration step, electric structure of ground and excited states should be related greatly with photoconductive properties. Compared Fig. 1 with Fig. 3a, photocurrent curves (shown in Fig. 1) of solid film C_{60} without laser irradiation almost folllow the corresponded UV-visible absorption spectra in the whole measurement range. This result indicates that photocarrier generation proceeds via excitation of C_{60}. According to reference [4] and [10], photocarriers generation of solid C_{60} film occurs predominantly through intermolecular charge transfer (CT) states through interband transition above 2.3 ev (<539 nm). Photogenerated carriers are

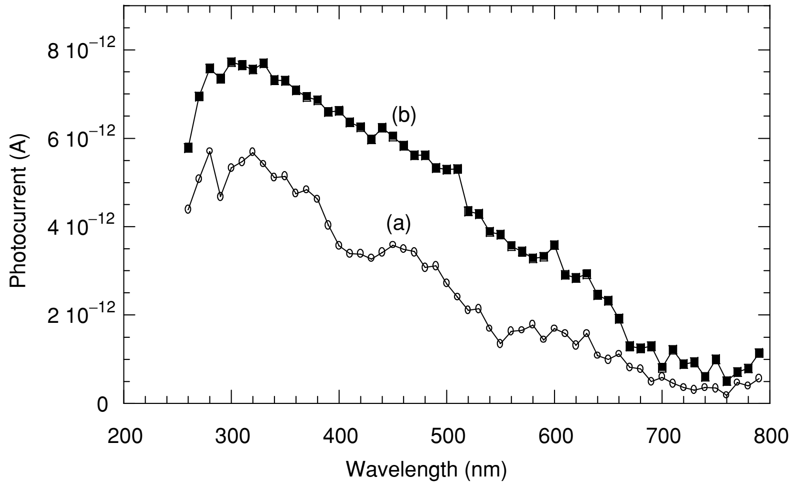

Figure 1 Photocurrent vs. wavelength of C_{60} film (133 nm) (a) before and (b) after 13 hrs laser irradiation.

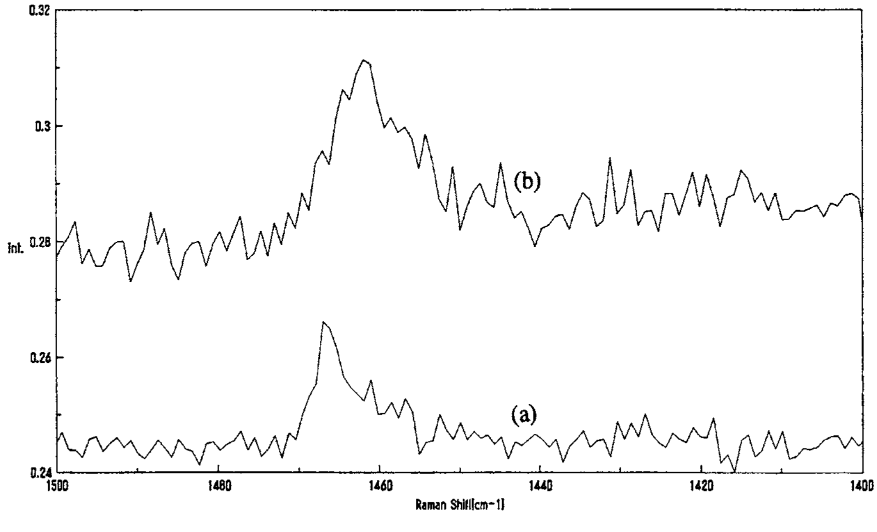

Figure 2 Raman spectra of C_{60} film (204 nm) (a) without laser irradiation and (b) with 13 hrs laser irradiation at room temperature.

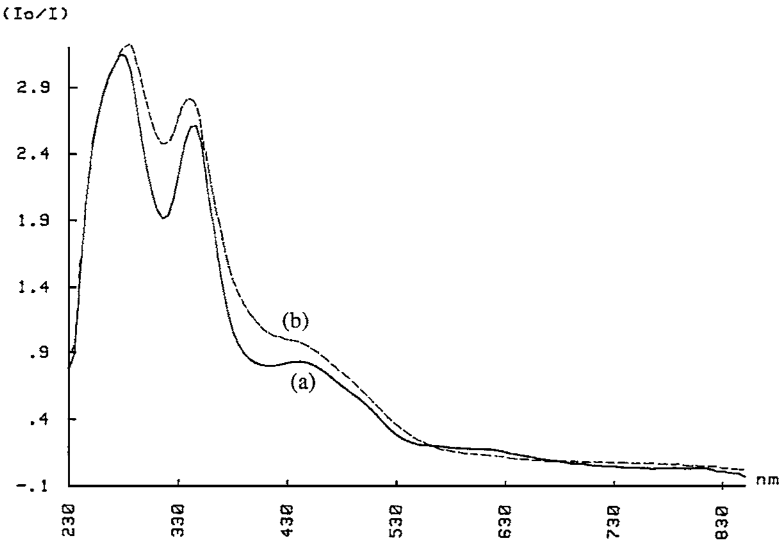

Figure 3 UV-visible absorption spectra of C_{60} film (204 nm) (a) without laser irradiation and (b) with 13 hrs laser irradiation at room temperature.

ascribed to intramolecular Frenkel-excitons by exciton-exciton collision ionization below 2.3 ev (>539 nm). Minami had reported [19] that solid state specific absorption of C_{60} at about 450 nm was related to intermolecular interaction between adjacent C_{60} molecules. From Fig. 3, it is easily noted that the specific absorption peak at about 450 nm of C_{60} became indistinct and its intensity increased by modification of laser irradiation. This result means interaction among molecules of the laser modified C_{60} is slightly stronger than that among C_{60} molecules. Ma had also reported that photoinduced electron-transfter properties of C_{60} dimer are somewhat different from those of C_{60} [18]. From above discussion, there may be some difference on CT states of C_{60} and the laser modified C_{60}. This leads to high efficiency of photocarriers in the laser modified C_{60} thin film above 2.3 ev (<539 nm). On the other hand, some dimer, trimer and polymer of C_{60} have been formed under laser irradiation and the distance between two bucky balls in these polymerized C_{60} should be shorter than that of two isolated C_{60} molecules. This causes reduction of resistance to photocarriers. Therefore, the photoconductivity of C_{60} is improved by the modification of laser irradiation, especially in range of 260–539 nm.

In order to study effect of temperature on modification of C_{60} by laser irradiation, C_{60} film (thickness: 56 nm) was irradiated for 13 hrs at room temperature (RT), then 3 hrs (total 16 hrs) and 3 hrs (total 19 hrs) at about 100°C (HT). Their photocurrent versus wavelength curves are given in Fig. 4. After laser irradiation for 13 hrs at RT, its photocurrent values from 260 nm to 640 nm are higher than those before laser irradiation. Its photocurrents with sharp peak at about 280 nm after laser irradiation for 16 hrs (including 3 hrs at about 100°C) are much higher than those after laser irradiation for 13 hrs at RT from 260 nm to 400 nm. These values increase with laser irradiation time. However, peak positions of the laser modified C_{60} at HT are similar with those just before laser irradiation. Because thermal treatment has much influence on improvement of photocurrent of the laser modified C_{60} (shown in Figs 5 and 7 and discussed in next section), high photocurrent values of the laser modified C_{60} at HT might be mainly ascribed to thermal effect.

From above discussion, the photoconductivity of C_{60} film has been improved by the modification of laser irradiation at room temperature or at about 100°C because some dimer, trimer and polymers of C_{60} have been formed during laser irradiation.

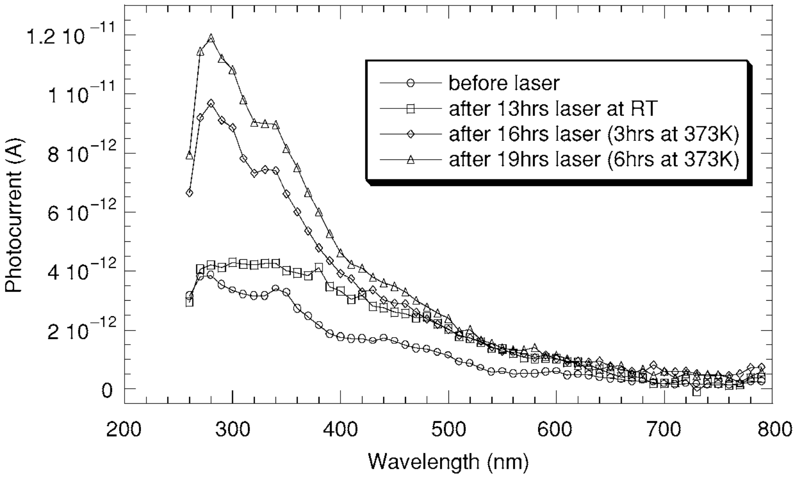

Figure 4 Photocurrent vs. wavelength of C_{60} film (56 nm) before and after laser irradiation for 13 hrs, 16 hrs and 19 hrs.

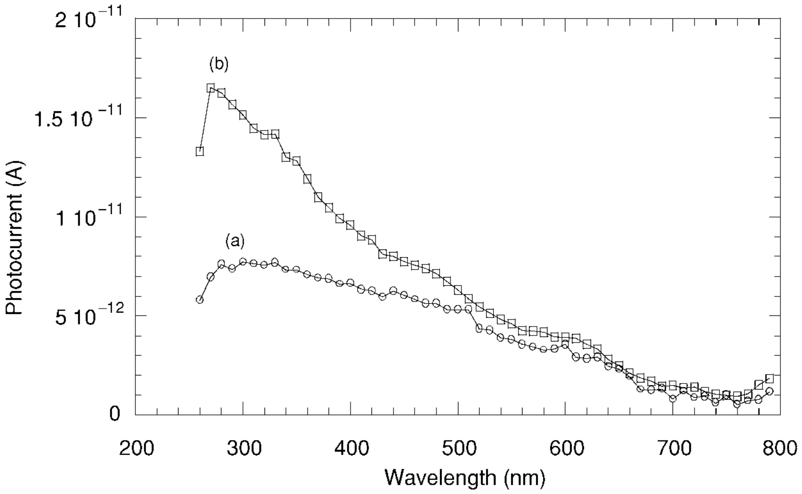

Figure 5 Photocurrent of laser modified (13 hrs) C_{60} film (133 nm) (a) before and (b) after thermal treatment (125°C/1 hr).

3.2. Effect of thermal treatment on photoconductivity of the laser modified C_{60} thin film

Photocurrent values of the laser modified (laser irradiation for 13 hrs at RT) C_{60} thin film (thickness: 133 nm) are improved by thermal treatment at 125°C for 1 hour, its highest value is about 2 times of that before the thermal treatment and the shape of its photocurrent versus wavelength curve is also changed after the thermal treatment (shown in Fig. 5), which is much more coincided with its UV-visible spectrum (Fig. 6b). There is much difference on UV-visible absorption spectra of C_{60} film with and without laser irradiation even if they were thermally treated at the same conditions (Fig. 6). Thermal treatments at 102°C/2 hrs and 155–159°C/1 hr on the laser modified (laser irradiation for 19 hrs, including 13 hrs at RT and 6 hrs at about 100°C) C_{60} thin film (thickness: 56 nm) were carried out. From Fig. 7, photocurrent values of the laser modified C_{60} are improved slightly by thermal treatment at 102°C/2 hrs because it has been modified by laser irradiation at about 100°C for 6 hrs just before this thermal treatment. After its thermal treatment at 155–159°C/1 hr, photocurrent values of the laser modified C_{60} thin film have been increased greatly and its highest value rises by 8 times compared with that before this treatment. According to reference [20], size of C_{60} crystals could be increased with the temperature of substrate and defects in crystals could be reduced. We also found that C_{60} film prepared at high substrate temperature (above 100°C) exhibited high photoconductivity. An initial study on structure alteration and chemical stability of the heated C_{60} film showed that C_{60} film annealed at 160°C or 200°C for some time created a close packed lattice and its crystallinity was also increased [21]. So, thermal treatment of the laser modified C_{60} thin film at high temperature ($\geq$100°C) for some time could make an increase on its crystallinity or some change on its morphology and reduce defects of crystals. The trap centers of photocarriers in the laser modified C_{60} thin film are reduced as a result of the decrease of defects in its crystals. Therefore, the thermal treatment at above 100°C could

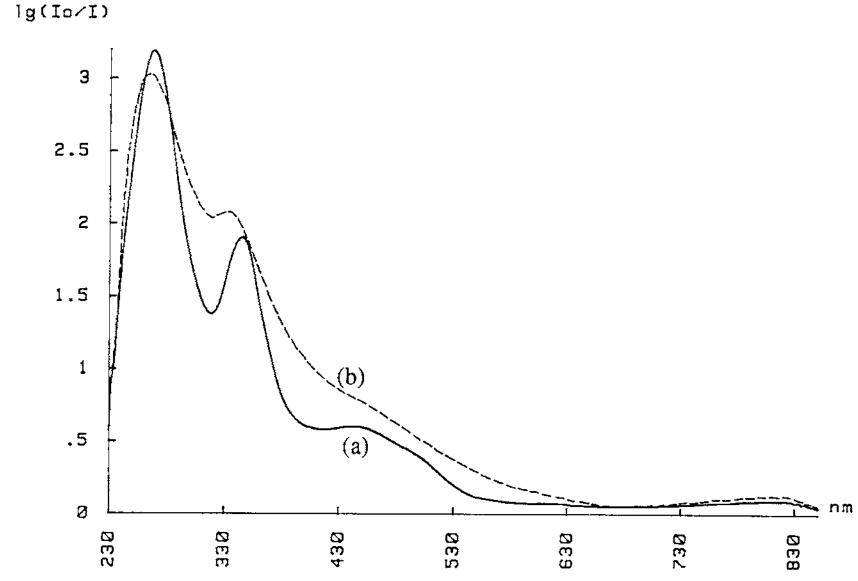

Figure 6 UV-visible absorption spectra of C_{60} film (133 nm) after thermal treatment at 125°C for 1 hr (a) without laser irradiation and (b) with 13 hrs laser irradiation at room temperature.

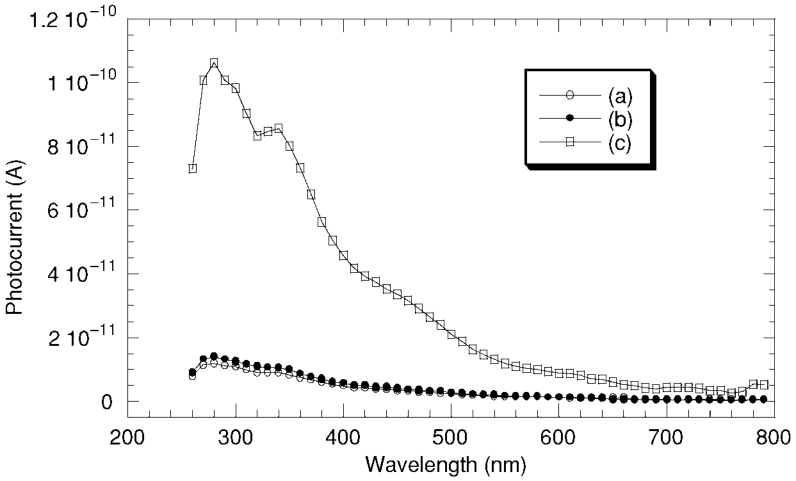

Figure 7 Photocurrent vs. wavelength of C_{60} film (56 nm) modified by laser irradiation for 19 hrs (13 hrs at RT and 6 hrs at about 100°C) before (a) and after thermal treatment ((b) 102°C/2 hrs and (c) 155–159°C/1 hr).

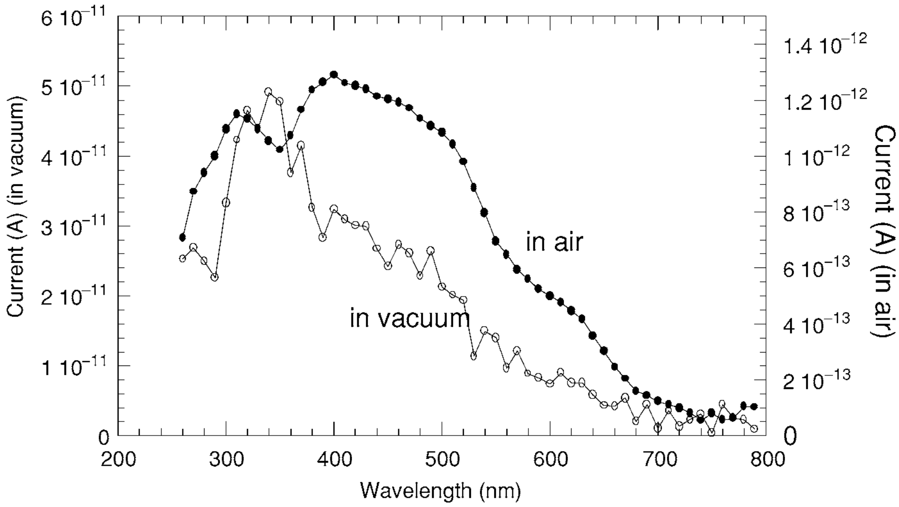

Figure 8 Photocurrent vs. wavelength of C_{60} film (204 nm) modified by laser irradiation for 13 hrs in vacuum and in air.

effectively enhance photoconductivity of the laser modified C_{60} thin film.

3.3. Effect of oxygen on photoconductivity of laser modified C_{60} thin film

Photocurrent versus wavelength curves of the laser modified (laser irradiation for 13 hrs) C_{60} thin film (thickness: 204 nm) in vacuum and air are given in Fig. 8. Its photocurrent values decrease greatly by exposure in air. The photocurrent decreases by factors of about 45. The shape of photocurrent versus wavelength curve of the laser modified C_{60} thin film is also changed by exposure in air. The major charge carriers in C_{60} solid film are electrons. If laser irradiation on C_{60} film was carried out in air, its photocurrent became so small that the electron meter could not measure them because laser irradiation could enhance the diffusion of oxygen in C_{60}. Oxygen with strong affinity with electrons could work as a carrier trap or recombination center [22–25].

4. Conclusions

Photoconductivity of fullerene C_{60} film has been improved after modification of laser irradiation at room temperature because some dimer, trimer and polymer of C_{60} have been formed under laser irradiation. This leads to some change of charge transfer (CT) states and reduction of resistance to transport of photocarriers. The reasons that photoconductivity of C_{60} modified by laser irradiation at about 100°C (373 K) has a great increase are thermal effect except of the formation of some dimer, trimer and polymer among C_{60} molecules under laser irradiation. Thermal treatment of the laser modified C_{60} thin film at above 100°C (373 K) for a few hours make a great improvement on its photoconductivity because this treatment causes reduction of trap centers for photocarriers resulted from an increase on its crystallinity and some change on its morphology. Oxygen could greatly reduce photoconductivity of the laser modified C_{60} thin film.

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