Eur. Phys. J. D **24**, 385–388 (2003)
DOI: 10.1140/epjd/e2003-00150-5

**THE EUROPEAN PHYSICAL JOURNAL D**

# Effect of ion irradiation on $C_{60}$ thin films

## Ion-irradiation-induced resistance to photopolymerization

K. Narumi[1,a], Y. Xu[1], K. Miyashita[2], and H. Naramoto[1]

[1] Takasaki Branch, Advanced Science Research Center, Japan Atomic Energy Research Institute, 1233 Watanuki-machi, Takasaki, Gunma 370-1292, Japan
[2] Gunma Prefectural Industrial Technology Research Laboratory, 190 Toriba-machi, Maebashi, Gunma 371-0845, Japan

Received 10 September 2002

**Abstract.** We report a new effect of ion irradiation on $C_{60}$ thin films: $C_{60}$ thin films irradiated with 7-MeV $C^{2+}$ ions show resistance to photopolymerization. The resistance increases with increasing ion fluence of irradiation. The effect is qualitatively explained by the fact that the number of a $C_{60}$ pair satisfying the topochemical requirement for photochemical reaction in solids decreases by destruction of $C_{60}$ molecules accompanied by lattice disorder.

**PACS.** 61.48.+c Fullerenes and fullerene-related materials – 61.80.Jh Ion radiation effects – 82.35.-x Polymers: properties; reactions; polymerization

## 1 Introduction

Ion-irradiation effect of solid state $C_{60}$ has been investigated by many researchers and the primary effect is destruction of the molecule: energetic-ion impact leads to destruction of cage structure in a $C_{60}$ solid [1–5]. FTIR and Raman analyses have revealed that no intermediate fragments of a $C_{60}$ molecule are generated by ion impact, that is, each fullerene molecule completely decomposes into its constituent atoms in a single catastrophic event upon energetic-ion impact [1–4]; in consequence, transformation of a $C_{60}$ solid into a form of amorphous carbon was observed [1–4].

On the other hand, solid state $C_{60}$ can be transformed by UV-visible light to a polymeric phase [6]. It has been proposed that in the photopolymer, $C_{60}$ molecules are linked by covalent bonds *via* a photochemical 2 + 2 cycloaddition reaction in which the double bonds on neighboring $C_{60}$ molecules are broken and reformed as a four-membered ring. This process can be monitored by characteristic peak splittings and shifts in Raman and other vibrational spectra with regard to pristine $C_{60}$.

In the present study, ion-irradiation effect on photopolymerization in a $C_{60}$ solid is investigated with the use of Raman spectroscopy. We observe resistance of ion-irradiated films to the photopolymerization, which is explained by the fact that the number of a $C_{60}$ pair satisfying the topochemical requirement for photochemical reaction in solids decreases by ion-induced decomposition of the $C_{60}$ molecules accompanied by lattice disorder.

## 2 Experimental

Thin films of $C_{60}$ were prepared by molecular beam epitaxy on Si(111) substrates. A surface oxide of the substrate was removed by immersing in a 5% HF solution. Pure $C_{60}$ powder of 99.99% (Term USA) was loaded into a Knudsen cell in a deposition chamber whose base pressure was $1\times10^{-6}$ Pa and outgassed at 400 °C for more than 30 min before deposition. During the deposition, the temperature of the substrates was kept at 165 °C and a deposition rate was about 0.6 nm/min. The pressure in the chamber was lower than $5\times10^{-6}$ Pa during the deposition. All of the specimens used in the present study were prepared in the same one deposition run. X-ray-diffraction analysis indicated that $C_{60}(111)$ layers in an fcc crystal grew with its $\langle 111\rangle$ axis along to the $\langle 111\rangle$ axis of Si. After the deposition, the specimens were set in another irradiation chamber, whose base pressure was $1\times10^{-5}$ Pa. The specimens were then irradiated at room temperature with 7-MeV $^{12}C^{2+}$ ions from the 3-MV Tandem accelerator of JAERI/Takasaki. The films were about 190 nm thick so that almost all of C ions could pass through the film. The fluence was $1.0\times10^{12}$ to $1.0\times10^{15}$ /cm$^2$. Current density was carefully adjusted and it was around 200 nA/cm$^2$. Raman spectra were measured in air with Renishaw Ramascope 2000 $\mu$-Raman system using a fixed grating angle

---

[a] e-mail: `narmi@taka.jaeri.go.jp`

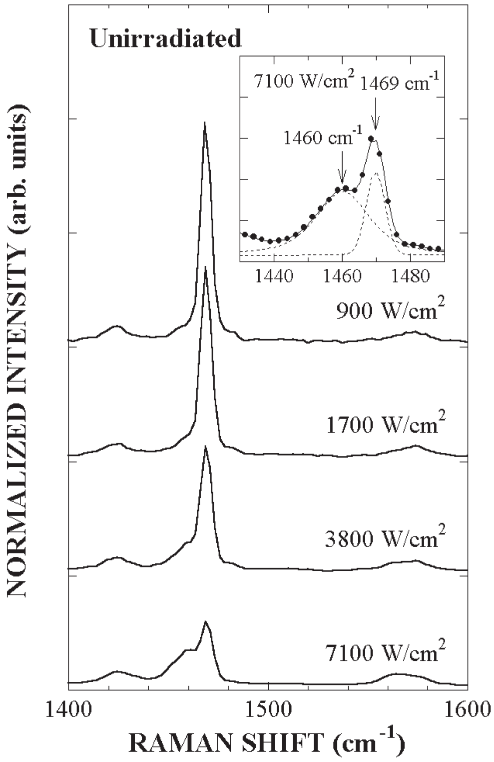

**Fig. 1.** Dependence of Raman spectra for an unirradiated specimen on power density of the Ar$^+$ laser. Inset shows Lorentzian-line-fit analysis of the Raman spectrum measured with 7100 W/cm$^2$.

and 514.5 nm radiation from an Ar$^+$ laser. The spot size of the laser was estimated to be about 3 $\mu$m.

## 3 Results and discussion

Figure 1 shows dependence of Raman spectra around the "pentagonal pinch" mode for an unirradiated film on power density of the Ar$^+$ laser. Each of the spectra was measured with accumulation time of 120 s with the power density indicated in the figure. The Ar$^+$ laser illuminated the specimen just only during the accumulation of a spectrum. The Raman intensity of the line at 1469 cm$^{-1}$ decreases with increasing power density, while a shoulder at the lower-frequency side of the line becomes prominent. The result of Lorentzian-line-fit analysis for the spectrum measured with 7100 W/cm$^2$ is shown in the inset, which demonstrates that the shoulder is attributed to the Raman band at 1460 cm$^{-1}$ due to a polymeric phase of $C_{60}$ [7]. Figure 1 indicates that the Ar$^+$ laser illumination photopolymerizes $C_{60}$ in the film during the collection of a spectrum although the laser illuminates the film in air.

The result shown in Figure 1 appears to be inconsistent with the previous results [7,8]: under UV-visible light in the presence of oxygen, photo-enhanced diffusion of $O_2$ into interstitial voids in the $C_{60}$ lattice occurs and intercalated $O_2$ hardens $C_{60}$ against photopolymerization. However, the photopolymerization and the $O_2$ diffusion into the crystal progress simultaneously under laser illumination in air; furthermore, the rate of the photopolymerization at room temperature has been shown to be proportional to the laser intensity [9]. Although effect of laser intensity on the diffusion process of $O_2$ has not been known in detail yet, the present result can be understood as a result of competition between photopolymerization and $O_2$ diffusion: under laser illumination with enough intensity, photopolymerization overwhelms $O_2$ diffusion.

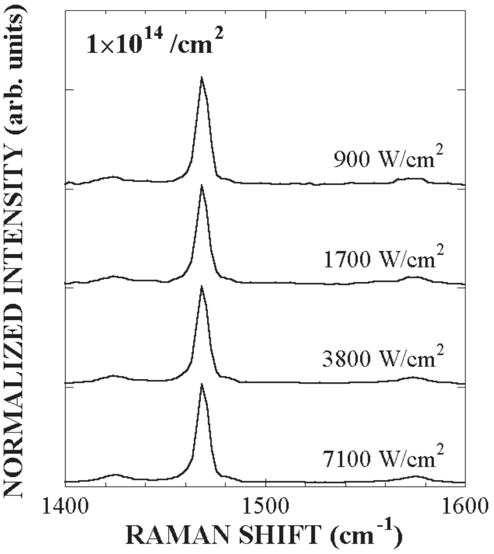

**Fig. 2.** Dependence of Raman spectra for a specimen irradiated with the fluence of $1.0 \times 10^{14}$/cm$^2$ on power density of the Ar$^+$ laser.

On the other hand, Figure 2 shows the change of the Raman spectrum for a $C_{60}$ film irradiated with $1.0 \times 10^{14}$/cm$^2$, where all of the spectra were measured on the same conditions as those in Figure 1. Contrary to the result shown in Figure 1, the spectra do not depend on the laser power and the Raman band due to a polymeric phase is hardly observed, which indicates that the film is resisting the photopolymerization. As discussed above, the unirradiated film was photopolymerized under the laser illumination with the same intensity even in air; thus it can be concluded that this resistance to the photopolymerization is not attributed to the oxygen effect.

Figure 3 shows ratio of integrated peak intensity of the Raman band due to a polymeric phase to that of the line at 1469 cm$^{-1}$ as a function of the laser power for four different ion fluences. Integrated peak intensity was determined by the Lorentzian-line-fit analysis of the obtained Raman spectra. As inferred easily from Figure 1, the ratio for the unirradiated film increases with increasing power density of the laser. Such a change is also observed except for the film irradiated with $1 \times 10^{14}$/cm$^2$ and the variation becomes smaller as the ion fluence increases. On the other hand, for the film irradiated with $1 \times 10^{14}$/cm$^2$, the ratio is so small and hardly depends on the power density of the laser as inferred from Figure 2.

Figure 3 clearly indicates that ion-irradiated films are resistant to photopolymerization and that the resistance

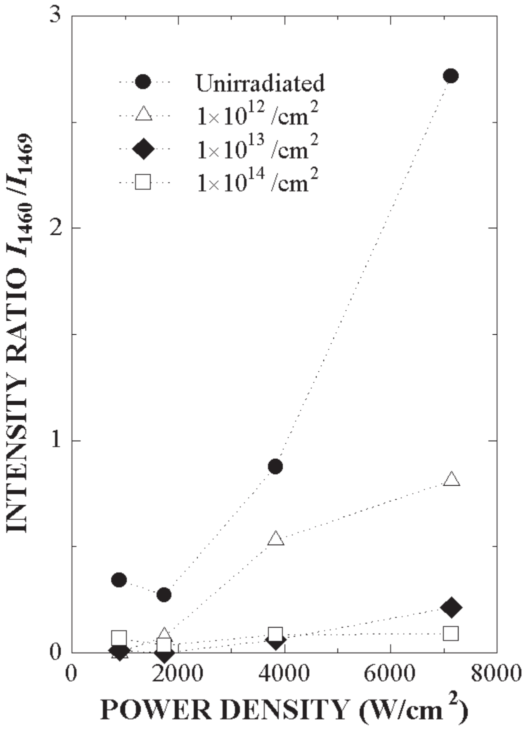

**Fig. 3.** Laser-power dependence of integrated-intensity ratio of the Raman band due to a polymeric phase to that of the line at 1469 cm$^{-1}$ peak for four different fluences. Broken lines are guide to the eye.

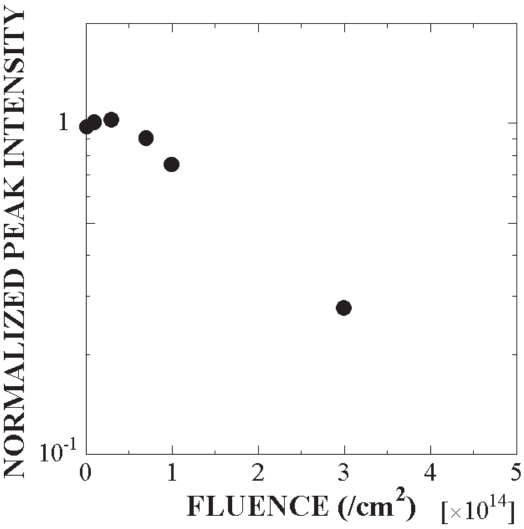

**Fig. 4.** Fluence dependence of the integrated peak intensity of $A_g(2)$. The intensity is normalized by that of the unirradiated film. The power density of the Ar$^+$ laser was 900 W/cm$^2$.

increases with increasing ion fluence. This can be qualitatively explained by the topochemical requirement for the photochemical 2 + 2 cycloaddition reaction in solids and destructive collisions of the $C_{60}$ molecules with energetic ions accompanied by lattice disorder. At first, let us consider photochemical reaction in a $C_{60}$ solid. According to the topochemical requirement for photochemical reaction in molecular solids, the photopolymerization is active when two carbon double bonds on adjacent molecules are oriented parallel to one another and separated by less than 0.42 nm [10,11]. In the fcc structure of a $C_{60}$ crystal, the distance between adjacent molecules is as small as 0.29 nm [12]. A $C_{60}$ molecule has 30 double bonds and spins freely about randomly oriented axes on fcc lattice positions at room temperature; thus the probability that two double bonds on adjacent molecules are oriented parallel to one another is high. Therefore, the topochemical requirement is satisfied in a $C_{60}$ crystal. On the other hand, ion irradiation of $C_{60}$ films leads to complete decomposition of each molecule into its constituent atoms [1–3]. In the present study, the number of the $C_{60}$ molecule surviving ion bombardment decreases exponentially with increasing ion fluence: Figure 4 shows change of normalized peak intensity of the line at 1469 cm$^{-1}$ and it was estimated that about 30% of $C_{60}$ molecules in an as-deposited film was destroyed after the irradiation of the fluence of 1×10$^{14}$/cm$^2$. Thus the number of the molecules involved in photopolymerization decrease with increasing ion fluence. Furthermore, the decomposition of molecules induces lattice disorder. According to the reference [2], $C_{60}$ molecules surviving ion bombardment are supposed to fill the gaps left by the missing molecules, which is similar to a box filled with balloons stacked in an ordered fashion: if some of the balloons are allowed to explode at random throughout the volume, the rearrangement of the remaining balloons leads to disorder of the stack. The disorder of the crystal lattice induces change of the distance between adjacent molecules. Because of these two reasons, the number of the adjacent-molecule pairs satisfying the topochemical requirement decreases with increasing ion fluence. Therefore, the photopolymerization is suppressed for the ion-irradiated films.

Finally, we mention two: one is another possible cause of resistance to photopolymerization. Judging from the fact that a peak characteristic of amorphous carbon is observed in Raman spectra for films irradiated with high fluence, constituent atoms of a destroyed $C_{60}$ molecule are supposed to be scattered between $C_{60}$ molecules as small pieces of amorphous carbon at low fluence. Such amorphous pieces might have some effect on photopolymerization: for example, the molecules might be prevented from spinning. The other is that the same effect as observed in the present study is expected in the case of pressure-induced polymerization, because the covalent linking between the $C_{60}$ molecules has also been proposed to be *via* the 2 + 2 cycloaddition reaction in the pressure-induced $C_{60}$ polymers [13].

## 4 Concluding remarks

We observed resistance of ion-irradiated films to the photopolymerization. The resistance increased with increasing ion fluence of irradiation. This is a secondary effect of ion irradiation of a $C_{60}$ solid and it can be attributed to destruction of $C_{60}$ molecules by ion impact. In conclusion, we mention application of the effect: it has potential to make it possible to control polymerization although the effect accompanies the destruction of the molecules.

The authors are grateful to the crew of the 3-MV Tandem accelerator of JAERI/Takasaki for their detailed control of beam intensity. They also thank Tokyo Instruments, Inc. for their assistance in the Raman-spectroscopy measurements.

## References

1. R.G. Musket, R.A. Hawley-Fedder, W.L. Bell, Radiat. Eff. Defects **118**, 225 (1991)
2. S. Prawer, K.W. Nugent, S. Biggs, D.G. McCulloch, W.H. Leong, A. Hoffman, R. Kalish, Phys. Rev. B **52**, 841 (1995)
3. J. Kastner, H. Kuzmany, L. Palmetshofer, Appl. Phys. Lett. **65**, 543 (1994)
4. K. Narumi, H. Naramoto, Surf. Coat. Technol. **158-159C**, 363 (2002)
5. A. Yogo, T. Majima, A. Itoh, Nucl. Instrum. Meth. B **193**, 299 (2002)
6. A.M. Rao, P. Zhou, K.-A. Wang, G.T. Hager, J.M. Holden, Y. Wang, W.-T. Lee, X.-X. Bi, P.C. Eklund, D.S. Cornett, M.A. Duncan, I.J. Amster, Science **259**, 955 (1993)
7. P.C. Eklund, A.M. Rao, P. Zhou, Y. Wang, J.M. Holden, Thin Solid Films **257**, 185 (1995)
8. P. Zhou, A.M. Rao, K.-A. Wang, J.D. Robertson, C. Eloi, M.S. Meier, S.L. Ren, X.-X. Bi, P.C. Eklund, M.S. Dresselhaus, Appl. Phys. Lett. **60**, 2871 (1992)
9. Y. Wang, J.M. Holden, Z.-H. Dong, X.-X. Bi, P.C. Eklund, Chem. Phys. Lett. **211**, 341 (1993)
10. K. Venkatesan, V. Ramamurthy, *Photochemistry in organized & Constrained Media*, edited by V. Ramamurthy (VCH, Weinheim, 1991)
11. P. Zhou, Z.-H. Dong, A.M. Rao, P.C. Eklund, Chem. Phys. Lett. **211**, 337 (1993)
12. M.S. Dresselhaus, G. Dresselhaus, P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic Press, San Diego, 1996)
13. M. Núñez-Regueiro, L. Marques, J.-L. Hodeau, O. Béthoux, M. Perroux, Phys. Rev. Lett. **74**, 278 (1995)