Structural modification of C_{60} films induced by 300-keV Xe-ion irradiation*

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The structural modification of C_{60} films induced by 300-keV Xe-ion irradiation was investigated. The irradiated C_{60} films were analysed using Fourier transform infrared spectroscopy, the Raman scattering technique, ultraviolet/visible spectrophotometry and atomic force microscopy. The analysis results indicate that the Xe-ion irradiation induces polymerization and damage of the C_{60} molecule and significantly modifies the surface morphology and the optical property of the C_{60} films. The damage cross-section for the C_{60} molecule was also evaluated.

Keywords: C_{60} films, ions irradiation, damage, polymerization

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1. Introduction

Since the discovery of C_{60}, the third carbon allotrope, investigations involving C_{60} have progressed rapidly in the areas of physics, chemistry and materials science due to its interesting properties[1] and its potential applications in fields related to superconductivity,[2,3] electronic devices,[4,5] medicine,[6] biology[7] and optics.[8] In the last 20 years, an important direction of research in the physics of fullerene is the structural modification of C_{60} under the bombardment of a variety of particles, including electrons and ions. Seraphin *et al.* showed a phase transformation from a crystalline phase to an amorphous phase after exposure of the crystalline C_{60} to a 200 keV electron beam.[9] Later, Onoe *et al.* suggested that electron beam irradiation could induce coalescence between adjacent C_{60} molecules.[10] The research result obtained by Palmetshofer and Kastner indicated that the polymerization of C_{60} took place at low fluences, and the C_{60} transformed to amorphous carbon after high-fluence irradiation with keV energy ions.[11] Zawislak *et al.* confirmed that the deposited energy density required for the complete destruction of a C_{60} molecule was about 0.5 eV/Å^3 with ion irradiation.[12] In 2006, ferromagnetic behaviour was confirmed in C_{60} films after irradiation with Ar and Si ions.[13]

Even after this progress, the C_{60} structural damage mechanism under the irradiation of a charge-particle is still not very clear because of the complexity of the kinetic procedure. Especially in low and medium energy regimes, the existence of synergistic effects between nuclear and electronic energy losses on structural modification has attracted much attention recently, and its mechanism remains unclear.[14,15]

In the present work, we investigated in detail the structural modification of thin C_{60} films (on quartz substrates) induced by 300-keV Xe-ion irradiation.

2. Experiment

The thin C_{60} films were deposited on pure quartz substrates in a vacuum of 2×10^{-5} torr by the evaporation (the temperature was close to 450 °C) of pure C_{60} (99.995%). The thickness of the thin C_{60} films was about 300 nm–600 nm.

The irradiation experiment of the thin C_{60} films was performed at room temperature with 300-keV Xe ions delivered by a 320-kV platform in Lanzhou. The ion flux was no more than 1×10^{10} cm$^{-2}\cdot$s^{-1} to avoid thermal effects. The irradiation fluences were in the range from 5×10^{11} cm^{-2} to 1×10^{13} cm^{-2}. Raman scattering and Fourier transform infrared (FTIR) spectroscopes were used to examine the structural

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modification of the C_{60} molecule. The Raman spectra were obtained using a JY-HR800 Raman spectrometer. The wavelength of the laser used in the Raman spectroscopy was 532 nm, corresponding to the energy of 3.8 eV. The FTIR measurements were carried out with a Nicolet NEXUS 670 system in reflection mode. Ultraviolet/visible spectrophotometry (UV–VIS, LAMBDA 900) was used to obtain the optical properties of the irradiated C_{60} films. Atomic force microscopy (AFM, SPM-RTESP) was used to investigate the change of the surface morphology of the C_{60} films due to ion bombardment. The experimental parameters are shown in Table 1.

Table 1. Parameters of 300-keV ^{129}Xe ion beams used for the irradiation of C_{60} films. The electronic (S_e) and the nuclear (S_n) stopping power are calculated via TRIM[16] simulation.

Ions	E/keV	S_n/eV·Å^{-1}	S_e/eV·Å^{-1}	R_p/nm
^{129}Xe	300	183	68	135

3. Results and discussion

3.1. AFM analysis

The AFM was applied to examine the surface morphology of the thin C_{60} films. Three dimensional AFM images of the thin C_{60} films, un-irradiated and irradiated with 300-keV Xe^{23+} ions of fluence 1×10^{13} cm^{-2}, are shown in Fig. 1. The difference between the unirradiated and irradiated samples is obvious. The surfaces of the bombarded samples become smoother compared to that of the as-deposited samples. The root-mean-square roughness (RMS) of the as-deposited and the irradiated samples is presented in Fig. 2. The roughness of the as-deposited C_{60} films is 2.36 nm. After the irradiation with 300-keV Xe^{23+} ions (1×10^{13} cm^{-2}), the RMS decreases to 1.85 nm, which is due to the sputtering induced by the incident ions.

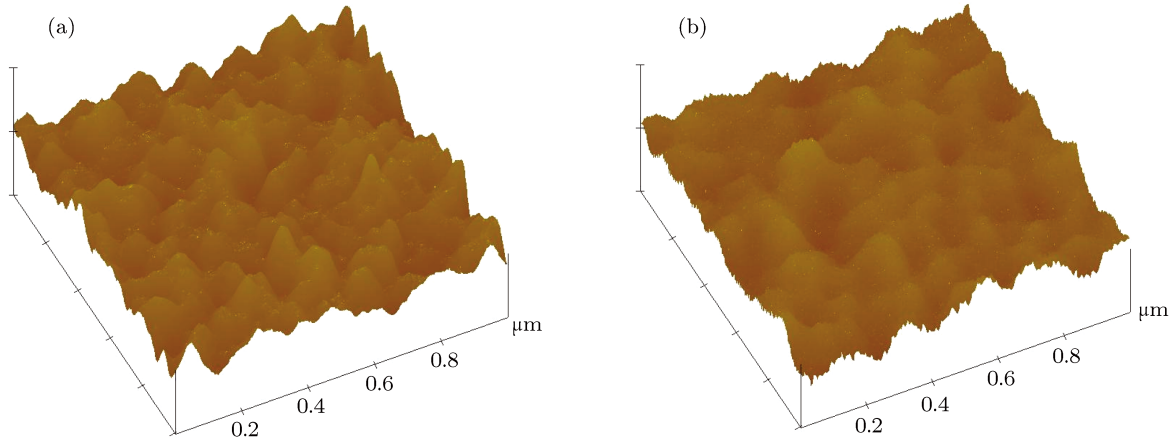


Fig. 1. (colour online) AFM images of C_{60} films: (a) unirradiated and (b) irradiated with 300 keV Xe^{23+} ions of fluence 1×10^{13} cm^{-2}.

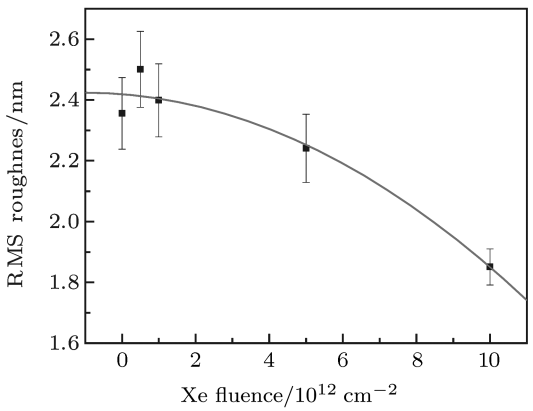


Fig. 2. Roughness versus fluence plot of as-deposited and irradiated C_{60} films.

3.2. UV–VIS analysis

Optical absorption is an important parameter for characterizing the optical and thermal properties of materials, because it can provide information about the energy level and the electron density of states.[17] Optical absorption spectra of as-deposited and Xe irradiated C_{60} films recorded over the range from 200 nm to 500 nm are shown in Fig. 3. Strong absorption peaks occur at 220 nm (5.636 eV), 268 nm (4.627 eV), and 346 nm (3.584 eV). It is observed that with the increasing irradiation fluence, the intensity of the absorption peaks gradually decreases.

When the fluence reaches 1×10^{13} cm^{-2}, the three absorption peaks almost disappear, which indicates that the Xe ion irradiation induces a modification of the electronic energy level.

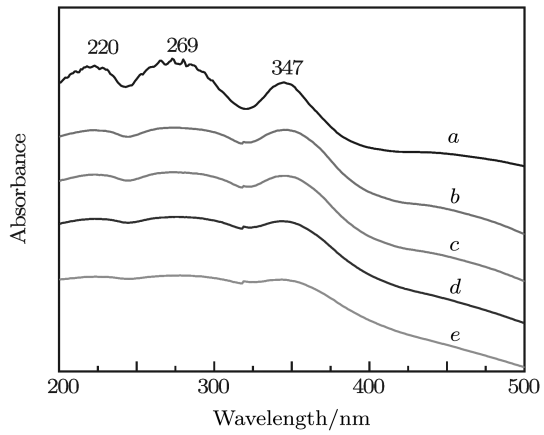


Fig. 3. UV–VIS spectra of as-deposited and irradiated C_{60} films, curve *a*: as-deposited, curve *b*: 5×10^{11} cm^{-2}, curve *c*: 1×10^{12} cm^{-2}, curve *d*: 5×10^{12} cm^{-2}, curve *e*: 1×10^{13} cm^{-2}.

To investigate the optical property of the irradiated C_{60} samples, we use the relationship between the absorption coefficient (α) and the photon energy ($h\nu$):[18]

$$\alpha h\nu = A(h\nu - E_{\rm g})^r, \tag{1}$$

where A is a constant, r is an index, and $E_{\rm g}$ is the band gap. In this study, $r = 1/2$, which results from an allowed direct transition. The absorption coefficient α can be calculated using the Urbach rule:[18]

$$I_t = I_0\,{\rm e}^{-\alpha t}, \tag{2}$$

where I_0 and I_t are the intensities of the incident and the transmitted light, respectively, and t is the film thickness. The absorption coefficient square of the as-deposited and the Xe irradiated C_{60} films as a function of the photon energy is plotted in Fig. 4. The band gaps can be deduced from the intersections of the extrapolated lines, which are based on the linear parts of the curves, with the axis of the photon energy. The band gap of the as-deposited C_{60} films obtained in this way is 2.38 eV, which decreases to 2.36 eV after the irradiation of 1×10^{13} cm^{-2}. The reduced band gap at higher fluences appears to be a result of defect energy levels below the conduction band created by the ion irradiation.[20]

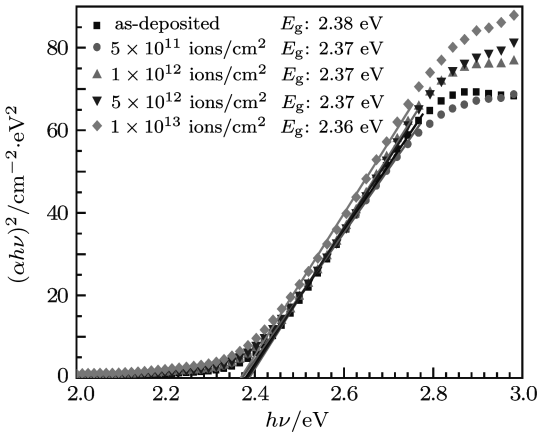


Fig. 4. The $(\alpha h\nu)^2$ versus energy plots of as-deposited and irradiated C_{60} films.

3.3. Raman & FTIR analysis

Raman spectroscopy is an important tool to study structural modification induced by ion irradiation.[21] The C_{60} molecule forms a truncated icosahedron, whose symmetry is characterized by the I_h point group. There are 10 Raman active modes, two of which are non-degenerate A_g modes and the remaining are five-fold degenerate H_g modes.[22–23] Figure 5 shows the Raman spectra of the as-deposited C_{60} and the C_{60} irradiated with 300-keV Xe^{23+} ions of different fluences ranging from 5×10^{11} cm^{-2} to 1×10^{13} cm^{-2}. It is observed that the intensities of all active modes decrease gradually with the increasing fluence of the Xe ion, indicating that the Xe-ion irradiation reduces the icosahedral symmetry of the C_{60} molecule and damages the C_{60} films. In addition, with the increasing fluence of the Xe ion, the decrease and the damage are gradually enhanced.

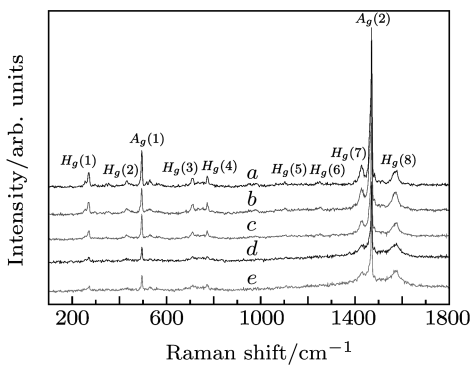


Fig. 5. Raman spectra of as-deposited and irradiated C_{60} films, curve *a*: as-deposited, curve *b*: 5×10^{11} cm^{-2}, curve *c*: 1×10^{12} cm^{-2}, curve *d*: 5×10^{12} cm^{-2}, curve *e*: 1×10^{13} cm^{-2}.

In order to further understand the damage process, we quantitatively analyse the Raman spectra around the $A_g(2)$ mode. In the previous studies,[24,25] the $A_g(2)$ mode of C_{60} has been proven to be sensitive to polymerization and alkali-metal doping in solid state. Figures 6 and 7 show the Raman spectra around the $A_g(2)$ mode of the C_{60} films irradiated with 300-keV Xe^{23+} ions of fluences 5×10^{11} and 1×10^{13} cm^{-2}, respectively. The experimental data ranging from 1380 cm^{-1} to 1620 cm^{-1} were carefully fitted with Lorentz equations, and six individual components located at 1578 cm^{-1} ($H_g(8)$), 1468 cm^{-1} (G band), 1470 cm^{-1} ($A_g(2)$), 1465 cm^{-1}, 1460 cm^{-1}, and 1427 cm^{-1} ($H_g(7)$) were obtained. It is well known that solid state C_{60} is susceptible to polymerization under suitable photon radiation[21] as well as temperature and pressure.[26] A downshift of about 5 cm^{-1} is found for the formation of one intermolecular covalent bond per C_{60} molecule.[27,28] Ion beam irradiation could also provide a similar local condition and has been shown to induce the polymerization of a C_{60} molecule.[11,29] Hence, the appearance of 1465 cm^{-1} and 1460 cm^{-1}components in the irradiated C_{60} films might be attributed to ion-induced polymerization. The two fitted components might correspond to dimers and linear chains,[30] respectively.

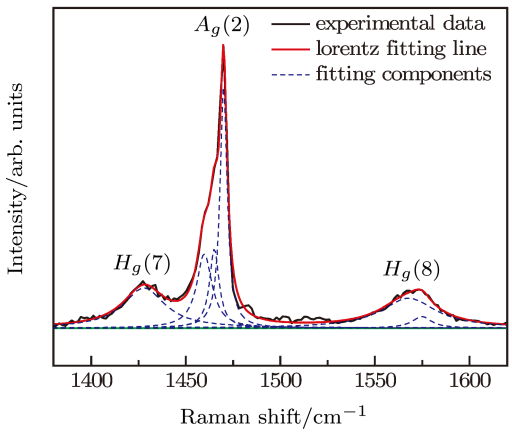


Fig. 6. (colour online) Raman spectrum of C_{60} films irradiated with 300 keV Xe^{23+} ions of fluence 5×10^{11} cm^{-2}. The dashed curves represent individual fitted components.

The damage and the polymerization processes of the C_{60} films were investigated in detail by measuring the integrated intensities of the 1460 cm^{-1}, 1465 cm^{-1}, and 1470 cm^{-1} lines. A plot of survival and polymerization ratios versus the irradiation fluence is shown in Fig. 8. It can be seen that with the increasing irradiation fluence, the survival ratio of C_{60} molecule decreases, while the polymerization curve exhibits a different behaviour. At the fluence of 5×10^{11} cm^{-2}, the polymerization ratio achieves the maximum, at which about 50% of the C_{60} molecule is polymerized. With the increasing fluence up to 1×10^{13} cm^{-2}, the polymerization ratio decreases to no more than 10%. The results indicate that the polymerization of C_{60} takes place at low fluences and the damage effect becomes significant at high fluences.

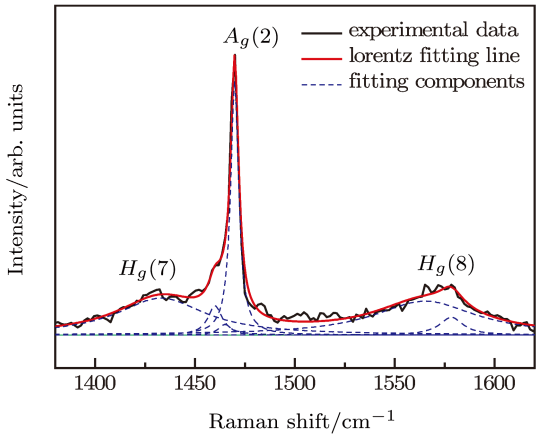


Fig. 7. (colour online) Raman spectrum of C_{60} films irradiated with 300 keV Xe^{23+} ions of fluence 1×10^{13} cm^{-2}. The dashed curves represent individual fitted components.

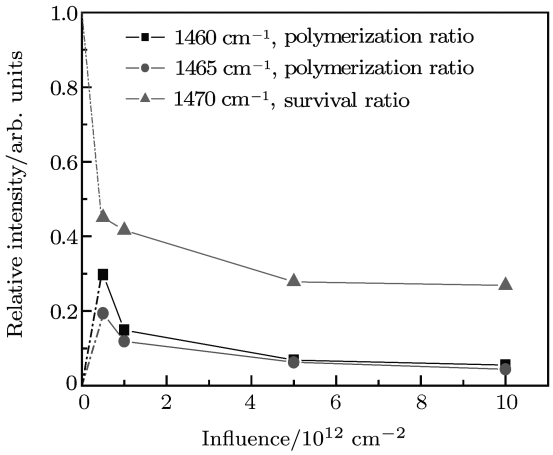


Fig. 8. Survival and polymerization ratios of the molecule as a function of irradiation fluence.

The structural damage of the irradiated C_{60} can also be observed in the FTIR spectra (Fig. 9). The peaks characterizing the C_{60} IR modes are located at 526 cm^{-1}, 576 cm^{-1}, 1182 cm^{-1}, and 1430 cm^{-1}, which are consistent with those previously reported in literature.[31] With the increasing irradiation fluence, the intensities of the IR modes gradually de-

crease, which also indicates that the irradiation induces a decrease of the icosahedral symmetry of the C_{60} molecule and damage of the C_{60} films.

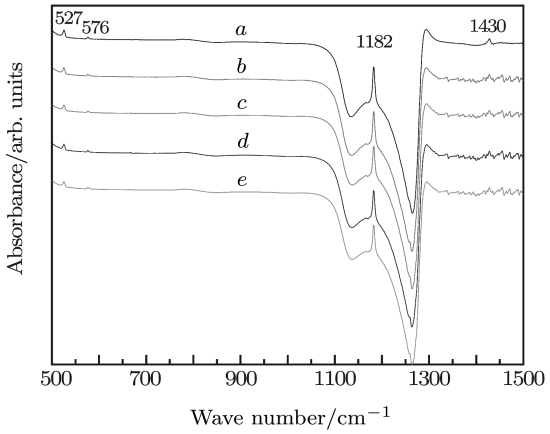


Fig. 9. IR spectra of as-deposited and irradiated C_{60} films, curve *a*: as-deposited, curve *b*: 5×10^{11} cm^{-2}, curve *c*: 1×10^{12} cm^{-2}, curve *d*: 5×10^{12} cm^{-2}, curve *e*: 1×10^{13} cm^{-2}.

With the experimental data given in Figs. 5 and 9, the damage cross-section σ of the C_{60} molecule can be extracted by fitting the intensity of the Raman and the IR modes to an exponential function:[32]

$$I_\varphi = I_0\,\mathrm{e}^{-\Phi\sigma}, \tag{3}$$

where I_0 and I_φ are the Raman (or the IR) intensities before and after ion irradiation with a fluence of Φ.

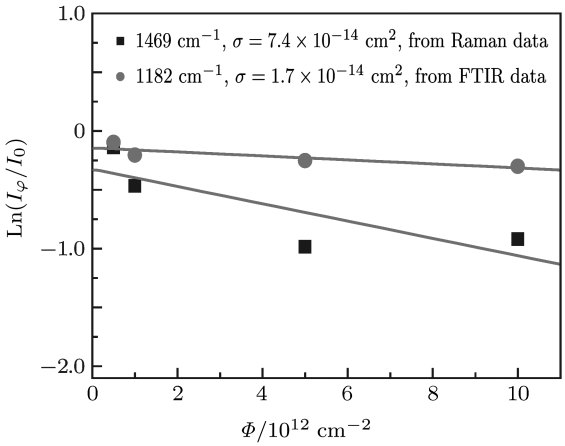


Fig. 10. The Ln(I/I) with the fluence Φ for the 1469 cm^{-1}, 1182 cm^{-1} modes Φ.

Figure 10 shows Ln(I_φ/I) as a function of the fluence. Obviously, the slope of the Ln(I_φ/I_0) versus Φ curve should be the damage cross section. In the present study, the damage cross sections extracted from the Raman and the IR data are 7.4×10^{-14} cm^2 and 1.7×10^{-14} cm^2, respectively. The cross section measured from the IR spectra is somewhat lower than that from the Raman spectra. A possible reason for the difference was discussed by Prawer *et al.*[32]

In this work, the nuclear energy loss is 186 eV/Å, which is about three times larger than the electronic energy loss, hence the damage process is dominated by the nuclear collision.

4. Summary

In summary, the structural modification of C_{60} films induced by 300-keV Xe-ion irradiation was investigated using AFM, UV–VIS spectrophotometry, Raman and FTIR spectra. This study shows that the Xe ion in the nuclear collision domain induces a significant modification of the C_{60} films (surface morphology and optical property) and of the C_{60} molecule (polymerization and damage). The polymerization of C_{60} takes place at low fluences and the damage effect becomes significant at high fluences. The damage cross-sections deduced from the Raman and the IR data are 7.4×10^{-14} cm^2 and 1.7×10^{-14} cm^2, respectively.

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