Structural and electrical properties of an electron-beam-irradiated C_{60} film

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The structural and electrical properties of an electron-beam (EB)-irradiated C_{60} film have been examined at room temperature, using in situ infrared (IR) spectroscopy and ex situ four-probe measurements. IR results show that the irradiated film is neither graphite nor carbon nanotube-like but a peanut-shaped C_{60} polymer. Current–voltage curve shows that the polymer exhibits a metallic property with a drastically reduced resistivity of 7 Ω cm in comparison with 10^{8}–10^{14} Ω cm for solid C_{60}. This indicates the possibility of applying C_{60} molecules in EB nanofabrication processes and large potential for developing carbon-based nanodevices.

Since the first report on C_{60} photopolymerization,^{1} there have been several reports of methods to produce C_{60} polymers.^{2} In particular, C_{60} polymerization induced by light and electron-beam (EB) radiation is of great interest from a viewpoint of nanofabrication of C_{60}-based carbon materials.

Recently, we found, using in situ infrared spectroscopy and laser-desorption Fourier-transform mass spectrometer,^{3} that C_{60} molecules coalesce to form a peanut-shaped dimer (see Fig. 1) as a main product when irradiated with an EB for a few hours. When a C_{60} film is irradiated with an EB for a time longer than in previous works, a polymer based on this coalesced structure can be formed. This polymer can be regarded as a π-electron-conjugated system expected to exhibit a metallic property. In this letter, we report about an investigation of the structure of a C_{60} film irradiated with an EB for 20 h. The radiated film is examined by in situ infrared spectroscopy^{4} and the electron transport property of the EB-irradiated C_{60} film is investigated by four-probe measurements using electrochemically sharpened tungsten probes that are typically used for scanning tunneling microscopy.\(^{5}\) Using a four probe, we can extract the sheet resistance of films despite of unknown resistances at the electrical contacts between the probes and the film. Finally, the obtained results are compared with pristine solid C_{60}.

C_{60} films (70 nm thick) were formed on a CsI substrate in an UHV chamber (base pressure: 1 × 10^{-9} Torr) by sublimation of C_{60} powder. After formation of the C_{60} film, an EB with an incident energy of 3 keV was applied to the film using an EB gun connected to the UHV chamber. The details of the experimental conditions were described elsewhere.\(^{5}\) Before and after the EB irradiation, infrared (IR) spectra of the sample were measured in situ. The sample was subsequently taken out of the UHV chamber and the sheet resistance and I–V characteristics were measured at RT under normal atmospheric conditions.

Figure 2 shows the IR spectra of the C_{60} film before and after EB irradiation. Before irradiation (a), four intensive peaks corresponding to the fundamental IR-active modes of the C_{60} molecule were observed. After 10 h EB irradiation (b), while the four fundamental peaks decreased, an intensive broadband appeared around 1390 cm^{-1}. Furthermore, after 20 h irradiation (c), the broadband became more intensive and shifted to 1360 cm^{-1}. Besides this broadband, another weak peak appeared at 480 cm^{-1}. On the other hand, the fundamental peak of C_{60} at 1430 cm^{-1} disappeared completely. This IR peak originating only from the in-plane stretching motions of the C_{60} cage is very sensitive to any change in its cage structure, while the other fundamental peaks originating not only from the motion but also from the radial motion of the cage are not sensitive to any structural change in C_{60} (Ref. 6). The IR fundamental peak appearing at around 1430 cm^{-1} is, therefore, a good indicator for the change in the amount of C_{60}. Accordingly, the disappearance of the peak indicates that all C_{60} molecules in the film were...
coalesced by 20 h EB irradiation. As indicated by the arrows in Fig. 2(c), no IR peaks corresponding to graphite \(^{7} (868 \text{ and } 1588 \text{ cm}^{-1})\) and/or CNTs \(^{8} (874 \text{ and } 1600 \text{ cm}^{-1})\) were observed. We predicted that IR-active modes arising from the waisted region of the peanut-shaped dimers (see Fig. 1) appear in the range 1300–1400 cm\(^{-1}\), as indicated by the vector illustration below the IR spectra.\(^{9-11}\) Because, as polymerization proceeds, the frequency of the vibrational modes arising from a given structure does not change significantly (become broad) and their intensity becomes increased, the results of Fig. 3 suggested that the broad intensive IR band appearing around 1360 cm\(^{-1}\) is assigned to the in-plane stretching motion arising from the waisted region of the peanut-shaped C\(_{60}\) polymer.

Figure 3 shows the \(I-V\) characteristics and sheet resistance of the C\(_{60}\) polymer formed after 20 h EB irradiation. The open circles represent \(I-V\) characteristics measured by probes 1 and 4 (outer probes), while the open rectangles represent the sheet resistance derived from voltages measured by probes 2 and 3 (inner probes). Inset in this figure shows the optical micrograph taken during the corresponding four-probe measurement. Interpole distances were set in the range 8–40 \(\mu\)m, ensuring appropriate film thickness for four-probe measurement,\(^{12}\) and in the particular case of Fig. 3, the distance was 35 \(\mu\)m. As shown in Fig. 3, the sheet resistance fluctuated around 0 V. This was due to the diminished measurement accuracy for small currents and/or small voltages in the present system. The sheet resistance and \(I-V\) characteristics of pristine C\(_{60}\) film could not be obtained, because sheet resistance was beyond the measurement range of the present system.

As shown in Fig. 3, there is no prolonged plateau around \(V=0\), and that the \(I-V\) curve is linear. In other words, no Schottcky barrier formation is apparent between the film and the metal probes. This indicates the metallic property of the peanut-shaped C\(_{60}\) polymer. The resistance directly derived from the \(I-V\) curve included large contact resistances due to the small contact area between the sharp tungsten probes and the film, and it is actually difficult to measure the contact resistances. So, the sheet resistances of the film were measured using voltage difference between inner two probes.\(^{12}\) Here, it is noted that the contacts of the inner probes to the film were ohmic. Sheet resistance of 1 M\(\Omega\) in Fig. 3 corresponds to a resistivity of 7 \(\Omega\) cm (in this case film thickness...
was 70 nm). We performed four-probe measurements at several locations on the same film and on the different film of 160 nm thick, and the resistivity was distributed in the range 1–10 Ω cm. Therefore, we concluded that the resistivity of the EB induced C\textsubscript{60} polymer is considerably smaller than pristine C\textsubscript{60} by a factor of 10\textsuperscript{8}–10\textsuperscript{14} (Refs. 13 and 14). It is noted that the EB induced C\textsubscript{60} polymer exhibited a metallic property at RT in air and the metallic character remained unchanged after air exposure for at least 2 weeks. This indicates that the present metallic C\textsubscript{60} polymer was very stable in the presence of oxygen and water vapor and could be easily applied to conventional LSI nanofabrication processes.

The temperature dependence of resistance should be measured for the EB induced C\textsubscript{60} polymer in order to distinguish between metal (or semimetal) and semiconductor. The present experimental setup, however, achieved the temperature variation only from RT to about 100 °C, which was not enough to discuss the origin of metallic behavior shown in Fig. 3. To reveal the origin of the metallic property is a further study of the present work. In this letter, the most fascinating finding is that insulating C\textsubscript{60} films show a metallic property in air at RT after EB irradiation.

In summary, we have demonstrated that EB irradiation of C\textsubscript{60} films forms a metallic C\textsubscript{60} polymer. It is interesting to note that the metallic property of the EB-irradiated film was originally observed at RT in air and remained unchanged after at least 2 weeks of air exposure. Because EB is currently used for nanolithography and the EB induced C\textsubscript{60} polymer is insoluble in organic solvents, the present work indicates the possibility of applying C\textsubscript{60} molecules in conventional LSI nanofabrication processes and great potential for developing carbon-based nanodevices.

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12. When an interprobe distance \(L\) is much larger than the film thickness \(t\), the sheet resistance \(R_s\) of the film was evaluated in terms of \(R_s = 4.532^t (V/I)\), and the resistivity \(\rho\) was calculated from \(\rho = R_s t\). Here, \(V\) is the voltage difference between the inner two probes and \(I\) is the current flow between the outer two probes.
14. J. Mort, R. Ziolo, M. Machonkin, D. R. Huffman, and M. I. Ferguson, Chem. Phys. Lett. 186, 284 (1991). In this letter, the samples were not purified and, although dominantly C\textsubscript{60}, undoubtedly contained substantial amounts of C\textsubscript{70}. It is assumed that the controlling molecule is C\textsubscript{60}. 