Radiation damage to fullerite (C\textsubscript{60}) in the transmission electron microscope

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Electron energy-loss spectroscopy was used to monitor structural damage to solid C\textsubscript{60} as a function of electron exposure. The characteristic dose was found to be in the range 300–700 C/cm\textsuperscript{2} for incident energies in the range 100–200 keV and specimen temperatures between 100 and 300 K. The absolute value of this dose, and its energy and temperature dependence, suggest that the damage mechanism is predominantly electronic rather than knock-on displacement. © 1999 American Institute of Physics. [S0003-6951(99)04339-9]

Fullerene (C\textsubscript{60}) molecules can be condensed onto a substrate to form a thin film of the solid material (fullerite) whose structure changes from amorphous to crystalline as the substrate temperature (during deposition) is increased from 25 to 170 °C.\textsuperscript{1} Epitaxy has been reported for potassium iodide substrates held at 240 °C, based on transmission electron microscopy (TEM) studies.\textsuperscript{2} The fact that high-resolution TEM of C\textsubscript{60} is possible\textsuperscript{3} shows that the material is less radiation sensitive than typical organic solids. On the other hand, 1500 eV electrons are found to polymerize fullerite\textsuperscript{4} and C\textsubscript{60} films have been used as a negative electron-beam resist for nanolithography.\textsuperscript{5}

The aim of our work was to experimentally characterize the structural damage to fullerite at typical TEM incident energies and to investigate the mechanism of this damage. In doing so, we also address practical questions relevant to TEM microscopy of solid C\textsubscript{60}: can the damage incurred during image recording be avoided or minimized by choice of incident energy and specimen temperature?

Films of thickness 50–100 nm were made by subliming C\textsubscript{60} powder in vacuum onto potassium chloride substrates heated to 150 °C. Specimens were detached from the substrate by floating onto a water surface, prior to examination in a JEOL-2010 transmission electron microscope fitted with a Gatan model 666 electron energy-loss spectrometer. Spectra were recorded, in TEM image mode and with no angle-limiting objective aperture, as a function of irradiation time (over a period of typically 10 min), the recording time for each spectrum being of the order of 1 s. During irradiation, the TEM image was checked for specimen drift and the fluorescent-screen absorbed-current reading was monitored and converted to beam current, based on separate calibrations (using a Faraday cup) at each accelerating voltage. The incident-beam diameter at the specimen was adjusted to 1 μm, to provide current densities within the range 0.5–2.0 A/cm\textsuperscript{2}.

Irradiation damage was observed by monitoring the peak at 6.5 eV loss, due to π-electron resonance\textsuperscript{6} and characteristic of C—C bonding. Figure 1 shows spectra recorded at the beginning and end of an irradiation sequence, illustrating the progressive loss of intensity of the π-resonance peak. To quantify this effect, the electron intensity at 6.5 eV was divided by that at the subsequent minimum (9.5 eV), thereby correcting for any drift in beam current. The resulting "peak/valley ratio" was plotted logarithmically against electron dose D, given by multiplying current density by elapsed irradiation time. As illustrated in Fig. 2, the resulting plots were approximately linear, corresponding to an exponential decay of the π-peak intensity with a characteristic dose D\textsubscript{e} measurable from the downward slope of Fig. 2.

Four separate radiation series at an incident-electron energy of E\textsubscript{0} = 200 keV gave an average D\textsubscript{e} = 670 C/cm\textsuperscript{2}. In Table I, this value is compared with the dose required for various types of damage in fullerite, which we estimate from previous reports based on electron microscopy, high-resolution electron energy-loss spectroscopy (HREELS) and scanning tunneling microscopy (STM).\textsuperscript{4,5,7} Our value (670 C/cm\textsuperscript{2}) is within a factor of 3 of the dose reported for destruction of the π* carbon K-edge peak in the energy-loss spectrum\textsuperscript{8} but about a factor of 10\textsuperscript{4} larger than the dose which gives sufficient polymerization to allow C\textsubscript{60} to be used as a lithography resist.\textsuperscript{5}

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![Graph showing electron energy-loss spectra](image-url)
The characteristic dose for structural damage considerably exceeds that for organic compounds, for which \( D_c \) is usually below 1 C/cm\(^2\) and an electronic mechanism (following inelastic scattering of the primary electron) is involved. Therefore it might be supposed that the damage derives from knock-on displacement processes (due to elastic scattering) which occur at higher incident-electron energies in the case of metals and many inorganic compounds. The collapse of carbon nanotubes under 800 keV irradiation has been attributed to this knock-on process.\(^9\) Cui, Li, and Huang have modeled the displacement damage to C\(_{60}\) by means of molecular-dynamics simulations.\(^10\) They find that the threshold energy \( E_d \) for carbon-atom displacement varies between 44 and 21.5 eV, depending on the direction of the momentum exchange, an average value being \( E_d = 29 \) eV.

Knowing \( E_d \) it is possible to calculate a cross section (\( \sigma_d \) per atom) for atomic displacement by electrons of kinetic energy \( E_0 \) by integrating the differential cross section \( d\sigma/d\Omega \) over scattering angle \( \theta \), from a minimum angle \( \theta_{\text{min}} \) to its maximum value of \( \pi \) radians (head-on collision). Conservation of energy and momentum gives:\(^11\)

\[
1 - \cos(\theta_{\text{min}}) = 2 \sin^2(\theta_{\text{min}}/2)
= 2E_d(496A)/[E_0(E_0 + 1022)],
\]

\( \text{TABLE I. Estimates of the dose required for various types of electron-beam damage to solid C}_{60}\) Values have been scaled to 200 keV incident energy, taking the dose to be proportional to the square of incident-electron velocity (see discussion).

<table>
<thead>
<tr>
<th>Dose (C/cm(^2))</th>
<th>Observed effect</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.065</td>
<td>Polymerization (electron-resist properties)</td>
<td>b</td>
</tr>
<tr>
<td>80</td>
<td>Loss of HREELS structure (graphization)</td>
<td>c</td>
</tr>
<tr>
<td>400</td>
<td>Speckled patches seen in STM images</td>
<td>a</td>
</tr>
<tr>
<td>780</td>
<td>63% decay of 6.5 eV energy-loss peak</td>
<td>e</td>
</tr>
<tr>
<td>2000</td>
<td>50% decay of 285 eV K-loss peak</td>
<td>d</td>
</tr>
<tr>
<td>9000</td>
<td>Substantial fading of diffraction spots</td>
<td>d</td>
</tr>
<tr>
<td>27000</td>
<td>63% displacement damage (calculated)</td>
<td>e</td>
</tr>
</tbody>
</table>

\( E_d \) in eV, \( E_0 \) is in keV and the atomic weight \( A \) \( \approx 12 \) for carbon. For atomic number \( Z < 20 \), the differential cross section for elastic scattering is given by\(^11\)

\[
d\sigma/d\Omega = r(10^{-3}Za_0R/E_0)^2[(1 + E_0/511)/
(1 + E_0/1022)]^2 \sin^2(\theta/2)^{-2},
\]

where the Bohr radius \( a_0 = 52.9 \) pm, Rydberg energy \( R = 13.6 \) eV and \( E_0 \) is again in keV. The Mott factor \( r \), which takes into account electron spin, is given by\(^11\)

\[
r = 1 - (v^2/c^2)\sin^2(\theta/2) + \pi(Z/137)(v/c)\sin^2(\theta/2)
\times[1 - \sin(\theta/2)],
\]

where \( v \) is the speed of the incident electron and \( c \) is the speed of light in vacuum.

Based on Eqs. (1)–(3), the integrated cross section \( \sigma_d \) for atomic displacement is shown in Fig. 3 for several values of displacement energy, including the maximum expected value (44 eV), the minimum value (21.5 eV) and the average value \( E_d = 29 \) eV.\(^10\) More appropriately, each square data point in Fig. 3 corresponds to an effective cross section obtained by averaging ten values of \( \sigma_d \) calculated from the ten values of \( E_d \) given by Cui, Li, and Huang for different directions of momentum transfer.\(^10\) The square data points indicate that displacement damage begins at a threshold energy of about 115 keV; at \( E_0 = 200 \) keV, the value of \( \sigma_d \) is about 6 barn \( (6 \times 10^{-24} \) cm\(^2\) \) per atom.

If the damage mechanism is predominantly knock-on displacement, the characteristic dose \( D_c \) should be inversely related to the displacement cross section

\[
D_c = e/\sigma_d,
\]

where \( e = 1.6 \times 10^{-19} \) C is the electronic charge. Equation (4) gives \( D_c \approx 27,000 \) C/cm\(^2\) for \( E_0 = 200 \) keV. As illustrated in Table I, this value is much higher than our value for \( \pi \)-peak decay. Moreover, the discrepancy with experiment is even greater at lower values of incident energy; see Fig. 4.
We therefore conclude that knock-on displacement is only a minor component of the structural damage to fullerite. This conclusion is supported by the fact that our measured characteristic dose decreased as the incident energy was reduced to 100 keV, whereas the displacement dose would increase (see Fig. 4) and there should be no knock-on displacement below the 115 keV threshold energy. Even at $E_0 = 1$ MeV, it appears unlikely that knock-on effects make a significant contribution: Eqs. (1)–(4) predict that the required dose would be $D_e \approx 13\,000\, C/cm^2$.

Damage by fast electrons must therefore involve an electronic mechanism, as in the case of organic compounds and some inorganic ones (e.g., alkali halides). If so, the characteristic dose is expected to be roughly proportional to the square of the speed $v$ of the incident electron. Within experimental error, our measurements (made at 100, 160, and 200 keV) are consistent with this trend; see Fig. 4.

Using a Gatan model 613 cooling holder, we also measured the temperature dependence of $\pi$-peak fading. $D_e$ decreased by a factor of 2 as the specimen temperature was lowered from 300 to 100 K, which is typical of the temperature dependence of structural damage in organic materials and is therefore consistent with an electronic mechanism. In the case of knock-on damage, the cross section and characteristic dose should be independent of temperature.

The situation in $C_{60}$ appears different to that in graphite, where supposedly only knock-on damage is possible. The reason may be that covalent bonds in $C_{60}$ are strained relative to the lower-energy planar configuration in graphite. When bonds are broken as a result of inelastic scattering, it may be energetically profitable to form out-of-plane bonds with other molecules, leading to polymerization and the loss of double bonds within each molecule.

In organic materials, inelastic scattering leading to valence-electron excitation is believed responsible for the permanent breaking of chemical bonds, manifested as radiation damage. But in the case of some aromatic compounds, there is evidence that structural damage requires carbon $K$-shell ionization, which would result in Auger-electron emission, a doubly ionized molecule and greater structural reorganization. Indirect evidence for this mechanism is sometimes deduced from similarity between the cross sections for damage and for $K$-shell ionization. In the present case, however, the $K$-shell cross section is a factor of 70 higher than the damage cross section ($K$-shell $D_e$, a factor of 70 lower; see Fig. 4), implying that most $K$-shell ionizations do not result in permanent damage.

In summary, we have measured structural damage in thin films of $C_{60}$ by monitoring loss of intensity of the $\pi$-resonance energy-loss peak. The characteristic dose $D_e$ for this process is one to two orders of magnitude less than that calculated for knock-on atomic displacement, indicating that an electronic mechanism is involved. The observed temperature and incident-energy dependence of $D_e$ are consistent with this conclusion. In consequence, structural damage cannot be avoided by reducing the incident-electron energy below some threshold value. A modest reduction in radiation sensitivity is possible by cooling the specimen.

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**References**