Disintegration of C_{60} by heavy-ion irradiation

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The changes in resistivity in fullerene (C_{60}) films subjected to 320-keV Xe ion irradiation are investigated as a function of ion dose. From a comparison of this dependence with similar data on Xe irradiated diamond and with data on C implanted fused quartz, it is concluded that upon ion impact C_{60} clusters completely disintegrate. This disintegration releases about 60 carbon atoms which disperse among the remaining intact C_{60} spheres giving rise to hopping conductivity between isolated C atoms. The present finding may explain the negative results in the search for fullerenes conjectured to exist in instellar dust and may establish limitations on the use of ion implantation to dope fullerenes with the aim of synthesizing new forms of high-T_c superconductors.

The most abundant fullerene cluster is C_{60}, which has a closed "soccer ball"-type structure similar to a geodesic dome in which each atom is sp^2 bonded to its neighbors.[1] In the solid form (single crystalline or amorphous) the C_{60} clusters are well separated and are only weakly bonded to each other by van der Waals forces, and the material as a whole is electrically insulating.[2]

In the present work we supply evidence that under ion impact, C_{60} breaks up into individual C atoms which disperse between the remaining C_{60} spheres, with the dispersed C atoms serving as centers for hopping conductivity. This conclusion is based on a comparison between the dose dependence of the electrical conductivity induced in C ion-implanted fused quartz and that induced in Xe bombarded C_{60}. We show that these two systems are remarkably similar in two respects. First, both exhibit the same functional form for the dependence of the induced conductivity on ion dose, a dependence which is consistent with a model of hopping conduction between isolated centers; and second the size of these centers is similar for both cases and is of the order of 0.1 nm. This shows that for both systems the conduction is due to hopping between isolated C atoms dispersed in an insulating medium. Furthermore, we show that the onset of conductivity for Xe irradiated C_{60} occurs at a dose about 60 times lower than for diamond irradiated with Xe ions under identical conditions. This can only happen if each fullerene "explodes" when struck by the Xe ion or by the products of the collision cascade releasing all of its 60 carbon atoms thus making them available for hopping conduction.

In our experiments the C_{60} films were prepared by evaporation of commercially obtained[3] C_{60}/C_{70} powder, containing more than 90% C_{60}, onto fused-quartz substrates. Raman measurements displayed peaks consistent with those reported for a film containing a mixture of C_{60} and C_{70}.[4] Typical film thicknesses were 300–500 nm, as determined by surface profilometry. Contacts for the electrical measurements were produced with Ag paint as two strips separated by a distance of about 0.5 mm. Samples were subjected to Xe ion irradiation at 320 keV ($R_p \pm \Delta R_p = 120 \pm 18$ nm) at room temperature and at 200 °C.

The Xe ion dose dependence of the resistivity was measured *in situ* in the evacuated chamber used for the ion irradiation employing an experimental arrangement very similar to that previously described for irradiation of diamond, amorphous hydrogenated carbon (*a*-C:H) films, and fused quartz.[5] This arrangement avoids the interference of the current integration and temperature control with the electrical measurements. A two-point measurement was employed using an electrometer capable of measuring up to 2×10^{12} Ω. The dose range covered was 10^{12}–10^{16} Xe/cm^2, which spans the range over which major modifications induced by heavy-ion implantation have been observed in related materials such as diamond and diamond thin films,[6] and amorphous hydrogenated carbon (*a*:C-H).[5] For the irradiation at 200 °C the resistance measurements were taken at this elevated temperature.

The resistance R versus Xe irradiation dose D for films irradiated at room temperature (RT) and 200 °C is shown in Fig. 1. The onset of conductivity occurs at a relatively low dose as compared to other carbon systems such as *a*-C:H (Ref. 5) and polymers.[7] The resistance displays a gradual decrease as a function of dose spanning four decades of ion dose. The effect of increasing the temperature of the sample during the implantation is small with the major difference being a lower saturation resistivity at high doses, being about a factor of 100 lower for the 200 °C implant than for the RT implant. Figure 1 also shows data for 100-keV C irradiation of fused quartz tak-

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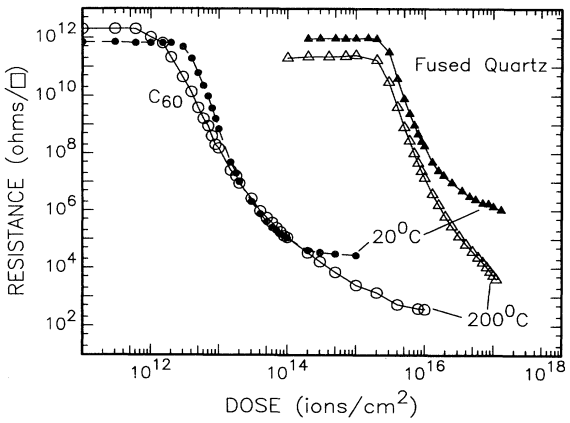

FIG. 1. Resistance vs dose for 320-keV Xe irradiation of C_{60} at room temperature (filled circles) and at 200 °C (open circles) and for 100-keV C irradiation of fused quartz at room temperature (filled triangles) and at 200 °C (open triangles).

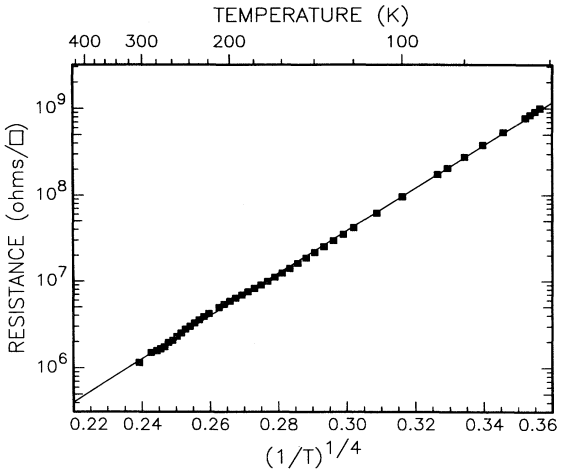

FIG. 2. Resistance vs temperature for C_{60} irradiated with 5×10^{13} Xe/cm^2 (320 keV) at room temperature. The straight line is a least-squares fit to the data.

en under similar experimental conditions.[8] Note the close similarity of the features described above for Xe irradiated C_{60} to those of C implanted quartz, except that the dose of C required to produce a given resistivity is about 1000 times higher in fused quartz than the dose of Xe required to produce the same resistivity in C_{60}.

In order to determine the nature of the conductivity in the irradiated films *ex situ* measurements of the resistance (R) as a function of temperature (T) were performed. The results of such a measurement for a C_{60} film irradiated with a dose of 5×10^{13} Xe/cm^2 are plotted in Fig. 2 as $\log_{10}(R)$ vs $(1/T)^{1/4}$. The fact that all the data points follow a straight line in this presentation proves that the conduction for the damaged film is well described by variable range hopping.[9] For a C_{60} film irradiated with 1×10^{16} Xe/cm^2 at 200 °C the resistivity displays an almost flat dependence on temperature, typical of graphite metalliclike conduction, and is similar to that obtained in heavily ion-implanted diamond.[10]

Having verified that the conduction mechanism is hopping we now examine the dose dependence of the resistivity with a view to estimating the size of the hopping centers. In systems in which the conduction occurs by hopping between isolated conducting centers, the conductivity should depend on the average interatomic spacing between these centers. The concentration dependence of the conductivity, σ, is governed by the tunneling probability between a pair of states separated by a typical distance of the order of $N^{-1/3}$, which is the average distance between hopping centers whose volume concentration is N. The expected functional dependence[11] is

$$R \propto 1/\sigma \propto \exp(\gamma N^{-1/3}\lambda^{-1}) , \quad (1)$$

where γ is a numerical coefficient of the order of unity, and the parameter λ is the characteristic dimension of a localized state on a hopping center. For conducting centers introduced by ion implantation N is proportional to the ion dose, and follows the simple relation

$$N=\beta\times D/W , \quad (2)$$

where D is the dose (in ions/cm^2), W is the thickness of the implanted region (in cm), and β is a numerical factor equal to the number of hopping centers created by each incident ion. By combining Eqs. (1) and (2) it is evident that for hopping conduction a plot of $\log_{10}(R)$ vs $D^{-1/3}$ should yield a straight line.

Figure 3, in which the data of Fig. 1 have been replotted as $\log_{10}(R)$ vs $D^{-1/3}$, shows that this is indeed the case for both Xe irradiated C_{60} and carbon implanted fused quartz. The excellent fit to this functional form proves that the hopping model for conduction described by Eq. (1) holds for both these systems.

Information about the size of the centers responsible for the hopping conduction is contained in the parameter λ in Eq. (1), which can be deduced from the slope, S, of

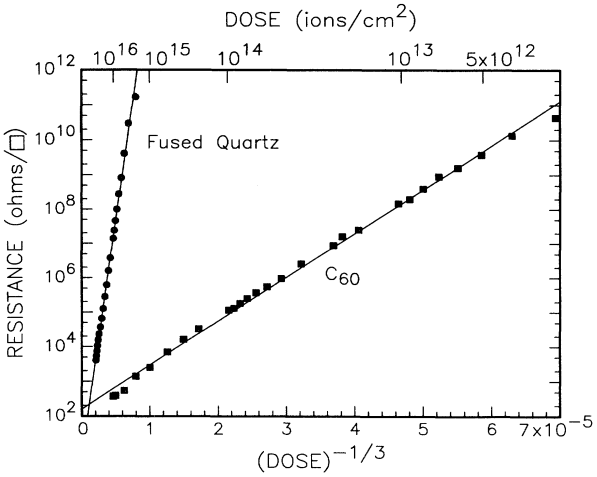

FIG. 3. The data of Fig. 1 replotted as $\log_{10}$(resistance) vs (dose)$^{-1/3}$ for 100-keV C implanted fused quartz (circles) and 320-keV Xe implanted C_{60} (squares). Both implantations were performed at 200 °C. The straight lines are least-squares fits to the data.

the lines in Fig. 3, and is given by

$$S=\gamma\times(\beta/W)^{-1/3}\lambda^{-1}\ . \tag{3}$$

For C implanted fused quartz, $S=3.2\times10^6$ cm$^{2/3}$, and obviously $\beta\simeq1$ since each implanted carbon atom contributes at most one hopping center. Taking γ to be of the order of unity, $\beta=1$, and $W=140$ nm (i.e., the width of the implant distribution), λ is found to be 0.76 Å. This value is comparable to the size of a single carbon atom. This result is not surprising, especially at low doses, as the implanted C atoms are isolated from one another since diffusion is negligible at these temperatures. For Xe implantation into C_{60}, β is not known *a priori*. However the data in Fig. 1 show that the onset of the conductivity for Xe implanted C_{60} occurs at a dose 1000 times lower than that required to induce the same conductivity in C implanted quartz, meaning that $\beta\simeq1000$ for Xe irradiated C_{60}. From Fig. 3, $S=2.9\times10^5$ cm$^{2/3}$ for Xe irradiated C_{60} and taking $\beta=1000$ and $W=140$ nm (i.e., the thickness of the ion-beam modified region), we obtain a value of λ of 0.83 Å.[12] This value indicates in the case of Xe implanted C_{60} the center responsible for the hopping conduction is again most likely a single C atom, and shows that the C_{60} clusters have completely disintegrated upon ion impact with no large-sized fragments surviving to act as conducting centers. One would therefore expect 60 carbon atoms to be made available for conduction upon each C_{60} cluster disintegration.

This expectation is indeed verified by comparing the dose dependence of the conductivity of Xe irradiated C_{60} with similar published data on the conductivity induced in Xe implanted diamond[6] for which each carbon atom, when dislodged, is expected to contribute at most one hopping center. In the case of diamond the onset of conductivity occurs at a dose of about 1.5×10^{14} Xe/cm^2, whereas for Xe irradiated C_{60} it occurs at 2.5×10^{12} Xe/cm^2. Thus the dose required for the onset of conductivity in Xe irradiated diamond is a factor of about 60 higher than that required for the onset of conductivity in Xe irradiated C_{60}, exactly as expected if the C_{60} cluster disintegrates when hit by either an incident Xe ion or an energetic C recoil, releasing all of its 60 carbon atoms. Once free, these carbon atoms most likely diffuse into the spaces between the remaining C_{60} spheres thus contributing to the conductivity as individual hopping centers randomly dispersed in the insulating environment of nondamaged C_{60}.

The present finding, that C_{60} disintegrates into individual carbon atoms, may at first appear surprising in view of the results from other energy deposition processes, which show that fullerenes fragment into smaller even-numbered clusters.[13] However, it should be borne in mind that the passage of an energetic heavy ion in a solid is unique in that it is accompanied by a thermal spike at least 1 nm in diameter. This dimension is comparable to the size of an individual C_{60} cluster. Calculations suggest that within this spike extremely high temperatures, lasting for a few picoseconds, prevail. In a regular solid most material within the ion track recrystallizes during the cooling down process. However this is not expected for a van der Waals solid such as C_{60} since each fullerene is only weakly interacting with its surrounding environment and once raised to an extremely high temperature it is unlikely to reform upon cooling in the absence of a template to guide the regrowth. Indeed the energy delivered to each fullerene during the slowing down of a single 320-keV Xe ion is estimated to be of the order of 1 keV, which corresponds to about 16 eV per carbon atom, an energy which far exceeds the binding energy of carbon in any of its known forms. The same arguments also hold for other less stable fullerenes (such as C_{70}) which may have been present in the films in small quantities.

Our results are consistent with those recently reported for proton irradiated C_{60} films.[14] In that work the IR peaks typical of C_{60} were found to decrease with ion dose without significant changes in peak positions or peak width as would be expected if fragments were formed. Based on this evidence the authors of Ref. 14 speculate that each C_{60} cluster is destroyed by the proton impact. The present work not only proves this speculation but furthermore provides information about *how* this disintegration occurs and about the "fate" of the remnants of the disintegration, viz., that the C_{60} molecule "explodes" into about 60 isolated carbon atoms, each of which contributes individually to the electrical conductivity of the bombarded film.

The disintegration of C_{60} upon heavy-ion impact found here has important ramifications for prospects to dope fullerenes by ion implantation as a means of synthesizing new high T_c superconducting materials.[15] Obviously, these attempts will have to take into account the damaging effect of the ion beam and the contribution to the electrical conductivity of the "loose" carbon atoms which are liberated by the ion impact. Furthermore, the present finding may explain the absence of fullerenes conjectured to exist in interstellar dust.[16] In light of the present work, this absence does not necessarily mean that such clusters were never formed. Rather, it may mean that the fullerenes formed were destroyed by collisions with heavily damaging energetic particles likely to occur in space.

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