

Electron-beam-induced fragmentation in ultrathin C_{60} films on Si(100)- 2×1 -H: Mechanisms of cage destruction

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We demonstrate that irradiation of ultrathin (1–4 monolayer) films of C_{60} grown on Si(100)- 2×1 -H with 3.3 and 0.5 keV electron beams leads to substantial modification of the fullerene molecules and their ultimate destruction. The fragmented fullerenes coalesce under continued electron irradiation to form an amorphous material with graphitic local structure. No measurable desorption of fullerene or derived fragments is observed under the irradiation conditions used. At electron doses below those at which complete fullerene destruction occurs we observe evidence indicating polymerization, due to electronic excitation of the molecules, and fullerene hydrogenation by atomic hydrogen liberated by the incident electron beam. An examination of possible fragmentation mechanisms resulting from larger electron doses leads to the conclusion that decay of electronic excitations into vibrational modes of the molecule is the most likely route through which cage destruction occurs. [S0163-1829(99)02032-9]

I. INTRODUCTION

It is the closed-shell structure of the fullerenes¹ that leads to their stability relative to other forms of carbon clusters. However, as the very recent nature of their discovery¹ attests, they are far from abundant in the environment. It is now known that the fullerene molecules may be destroyed under a number of conditions, including irradiation by light in ambient atmosphere,^{2–5} heating to elevated temperatures,^{6–12} irradiation with energetic particles both in the solid^{13–22} and in the gas phase,^{23–33} absorption of photons,^{34–36} and electron and/or photon stimulated reaction with other molecules.^{37,38} This sensitivity to a wide variety of environmental conditions is the most likely explanation of the lack of environmental abundance of the fullerenes, despite the discovery of a number of methods by which they may be produced.^{39–41} By the study of the conditions under which fullerenes decompose and the likely mechanisms by which this decomposition takes place, it is not only possible to understand more completely the way in which fullerenes are removed from the environment but also the means by which they are formed. Despite great interest in this area,^{2–49} relatively little is still understood about the mechanisms by which the elegant structure of fullerene molecules can be destroyed, even though applications for irradiation-damaged fullerenes have already been discovered.^{47–49} This work focuses on the destruction of C_{60} molecules by bombardment with light, relatively low energy particles—electrons. By the use of low-mass, low-energy particles, damage by excitation of electronic degrees of freedom in the molecule may be isolated from that caused by direct transfer of kinetic energy to the nuclei.¹³ We have already demonstrated that fullerene destruction can be brought about by irradiation of films with ≈ 3 keV electrons.²² A detailed examination of a larger set of experimental results, considered together with those in the literature enables us to suggest the most likely means through which low-energy electron-induced fullerene cage opening and destruction occurs.

II. EXPERIMENT

Experiments were carried out in a multichamber ultrahigh vacuum (UHV) system, consisting of analysis and preparation chambers and a fast entry load lock. The analysis chamber, base pressure 1×10^{-10} Torr, is equipped with a high-resolution electron-energy loss spectrometer (Kesmodel LK3000), a low-energy electron diffraction (LEED) optics, and an electron gun and hemispherical analyser (VG100AX) for Auger electron spectroscopy (AES) measurements. A high-flux electron gun (VG LEG63) was mounted on the preparation chamber (with a base pressure of 5×10^{-9} Torr) and used to irradiate the C_{60} thin films.

The ultrathin C_{60} films were grown on hydrogen-passivated Si(100) substrates. The substrates were prepared *in situ* from n -type ($\rho > 15 \Omega \text{ cm}$) Si(100) samples about $12 \times 10 \text{ mm}^2$ in area. After thorough degassing in UHV the samples were flashed to 1400 K in the analysis chamber to remove the native oxide. Hydrogen passivation was then achieved *in situ* by dosing 1200 L of H_2 at 2×10^{-6} Torr in the presence of a hot Ta filament. During hydrogen exposure, the sample was held at a temperature of 600 K to suppress the formation of dihydride and trihydride phases.⁵⁰ Examination of the passivated surfaces by LEED showed the formation of a (2×1) surface structure. High-resolution electron-energy loss spectroscopy (HREELS) characterization of the surfaces confirmed the monohydride termination of the surface with spectra showing only losses associated with monohydride species.

High purity C_{60} (99.9%, MER corporation) was thoroughly degassed in UHV before being sublimed onto the substrates, also *in situ*, from a home-built Knudsen cell held at 425 °C. Typical chamber pressure during fullerene sublimation was 1×10^{-9} Torr. AES was used to determine fullerene coverage by comparison of the ratio of the Si L_{VV} peak at 92 eV with the C KLL peak at 272 eV to that obtained from a monolayer coverage of C_{60} on bare Si(100)- 2×1 .⁵¹

Vibrational spectra were obtained with a beam energy E_0 of 4.5 eV, with a resolution of 2.5–4 meV from an unirradiator.

ated fullerene film (the disorder induced by electron irradiation of the C_{60} films brought about a significant degradation in spectrometer resolution, as discussed below). The electronic excitations of the surface were measured at a beam energy of 20 eV, with the resolution degraded to approximately 20 meV, in order to obtain a good signal-to-noise ratio in the spectra in a reasonable space of time. The width of peaks in HREEL spectra due to electronic excitations of the C_{60} molecules are, apart from the vibrational fine structure of the exciton peaks, much greater than even the degraded instrumental resolution. Therefore, the peak shapes observed in the electronic excitation spectra suffer a negligible contribution from instrumental broadening. For clarity we shall refer to the spectra taken under conditions that lead to high resolution from an ordered film as HREEL spectra, and those taken with the settings appropriate for electronic excitations as EEL (electron energy loss) spectra.

C_{60} films were irradiated with electrons of 3.3 keV (0.5 keV) incident beam energy with sample currents in the range 12–50 μA (0.3 μA). The electron beam was scanned automatically over the entire sample surface in order to ensure even irradiation of the films. No correction was made for secondary electron emission from the surface, so that the electron beam doses quoted must be regarded as approximate.

III. RESULTS

A. Irradiation of multilayer C_{60} with 3.3 keV electrons

The effects of electron irradiation of a multilayer film of C_{60} are demonstrated in Fig. 1, which shows HREEL spectra obtained in the specular (55° , 55°) geometry as a function of the integrated dose of electrons, which were incident upon the film with an energy of 3.3 keV. The 4 ML-thick C_{60} film was grown on a Si(100)- 2×1 -H surface with the sample held at room temperature. Examination of the relative intensities of the vibrational modes in the spectrum obtained from the as-grown film, Fig. 1(a), indicates that the film is flat but does not display long-range order. This observation is supported by the absence of a LEED pattern, but the presence of a well-defined, relatively narrow specularly reflected electron beam. It is possible to increase the surface order in these films by annealing at moderate temperatures.⁵¹ However, since long-range ordering is unlikely to play a significant role in the fragmentation process and disorder will tend to reduce electron channeling effects, it was decided to use the films in their as-deposited form.

Figure 2 shows the electronic excitation spectra obtained from the same film. The EEL spectrum from the pristine film shows the well-defined energy loss peaks characteristic of the C_{60} molecule. The leading feature at 2.2 eV corresponds to the excitation of transitions between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the fullerene molecule, both of which are π -orbital-derived.⁵² The structure seen on the low-energy side of the peak corresponds to excitation into discrete excitonic states, which eventually converge to the band edge. The broad peak at about 3 eV and those at 3.6 and 4.7 eV can be attributed to π - π^* transitions.⁵²

Irradiation of the C_{60} film brings about substantial changes to both the vibrational and the electronic structure,

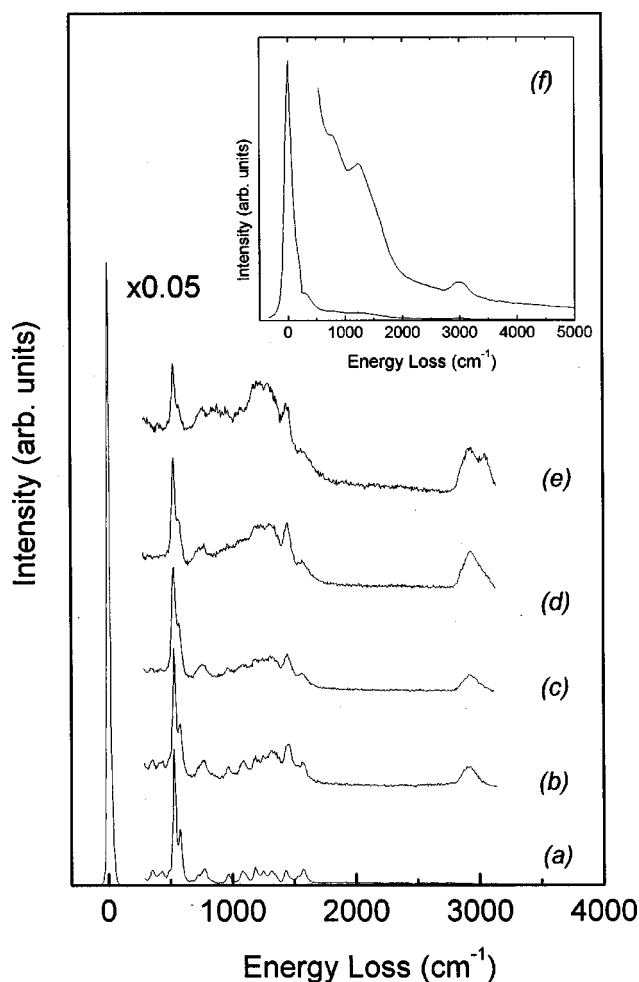


FIG. 1. HREEL spectra from a 4 ML-thick C_{60} film grown on Si(100)- 2×1 -H as a function of total electron dose at 3.3-keV energy: (a) zero; (b) 2.5×10^{-3} C cm^{-2} ; (c) 7.5×10^{-3} C cm^{-2} ; (d) 1.7×10^{-2} C cm^{-2} ; (e) 6×10^{-2} C cm^{-2} ; and (f) 2.2 C cm^{-2} . The spectra were obtained in specular geometry (55° , 55°) at a primary beam energy of 4.5 eV, and are normalized to the elastic peak intensity. The spectrum obtained at the largest electron dose is shown in an inset due to the substantial change in elastic peak shape and width which occurs after this degree of irradiation.

even with a relatively small electron dose. Upon irradiation of the film with electrons to a dose of 2.3×10^{-3} C cm^{-2} one immediately observes a new vibrational band, Fig. 1(b), at ≈ 2910 cm^{-1} . The position of this mode corresponds to that which would be expected from C-H stretching vibrations involving sp^3 hybridized carbon atoms.⁵³ Contamination may be ruled out as the source of this new vibration: Test experiments, which involved irradiating a single spot of an identical fullerene film under exactly the same conditions (rather than rastering the electron beam over the surface) showed no detectable changes in either electronic or vibrational excitations of the molecular film. If the C-H stretching vibration arose due to the presence of hydrocarbon contamination from the residual gases present in the chamber one would expect to see it just by exposure of the surface to the same environment without the effects of electron-beam irradiation. Therefore, the C-H stretching peak arises from a disruption of the intramolecular carbon-carbon bonds of the fullerene molecules and the formation of new bonds involving hydrogen. The new carbon-hydrogen bonds may either arise from

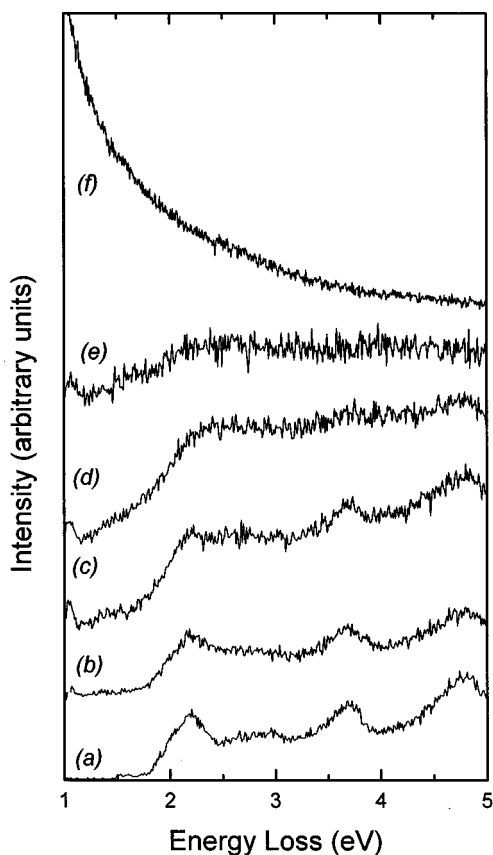


FIG. 2. EEL spectra from a 4-ML C_{60} film deposited on Si(100)- 2×1 -H as a function of electron irradiation at 3.3 keV: (a) zero; (b) 2.25×10^{-3} $C\text{ cm}^{-2}$; (c) 7.5×10^{-3} $C\text{ cm}^{-2}$; (d) 4×10^{-2} $C\text{ cm}^{-2}$; (e) 6×10^{-2} $C\text{ cm}^{-2}$; (f) 2.2 $C\text{ cm}^{-2}$. Spectra are obtained in the specular (55° , 55°) geometry at a primary beam energy of 20 eV. Spectra are normalized to elastic peak intensity, except (f), which is multiplied by a factor of 0.2.

the fragmentation of C_{60} molecules and the satisfaction of dangling bonds by hydrogen, or hydrogenation of intact fullerene cages. The formation of $C_{60}H_x$ (x up to 24) by hydrogenation of C_{60} with atomic hydrogen has been observed both in solid films⁵⁴ and in cold matrices.⁵⁵ Atomic hydrogen may be generated by the incident electron beam either from the residual gases of the chamber (hydrogen formed the dominant component), or evolved from the interface between the C_{60} and the hydrogenated Si surface. As far as the former possibility is concerned, it is quite reasonable to assume that hydrogen from the ultrahigh vacuum ambient can diffuse into the fullerene film, as has been observed in condensed gas films at low temperatures,⁵⁶ which thereby provides the proximity necessary to allow reaction between fullerene molecules (or their fragments) and atomic hydrogen liberated by incident electrons. Apart from the presence of the extra modes associated with the C-H bond both infrared⁵⁵ and neutron scattering⁵⁷ spectra of hydrogenated C_{60} are rather similar to those of pristine molecules. In Fig. 1(b), one can also clearly observe a small, but significant, reduction in the relative intensity of the dipole-active T_{1u} modes at 527 and 575 cm^{-1} with respect to those that are dipole forbidden, indicating that a measurable reduction in the order of the surface region occurs. A disordering of the film suggests that the carbon cages of some fullerene mol-

ecules may be significantly damaged, fragmentation occurring in competition with the formation of $C_{60}H_x$.

Increased electron doses are accompanied by rapid further evolution of the vibrational spectra, Figs. 1(c)–1(f). As irradiation of the molecular film increases the relative intensity of the dipole active T_{1u} vibrations at 527 and 575 cm^{-1} decrease still further with respect to modes that are dipole forbidden (there are two other dipole active T_{1u} modes at 1182 and 1475 cm^{-1} respectively,⁵⁸ but the oscillator strengths associated with these vibrations is such that they do not appear more intense than dipole forbidden modes except in films with a high degree of long-range ordering⁵⁹). The angular width of the specular HREELS beam, which provides a useful measure of the surface order,^{53,59} further increases with electron dose, demonstrating that the surface of the C_{60} film begins to roughen under exposure to the electron beam.

The reduction in the relative intensity of the dipole active vibrations can be explained by disordering and/or a reduction in the number of species that possess this mode. Comparison between off-specular spectra from pristine and irradiated films should resolve this issue. The wider dipole lobe associated with a disordered surface implies that, for a given geometry sufficiently off-specular, the relative intensity of the dipole allowed transitions should be greater in a spectrum from a disordered surface than from a pristine surface. If, however, the off-specular spectrum from an ordered film presents a higher relative intensity for the dipole active modes compared to the irradiated film this indicates that modification or destruction of the fullerene molecules has occurred in addition to disorder. Figure 3 shows spectra obtained from (a) a pristine 4-ML film and (b) one irradiated to 3×10^{-2} $C\text{ cm}^{-2}$ with 0.5-keV electrons (the irradiation with lower energy electrons will be discussed in more detail below). One can clearly see that the relative intensity of the peak derived from the two lowest energy T_{1u} modes is significantly weaker, in comparison to the dipole-forbidden modes, in the off-specular spectrum of the irradiated film when compared with that of the undamaged film. This indicates a likely reduction in the number of species exhibiting these modes in the thin film and that fragmentation occurs in addition to hydrogenation.

As well as the relative decrease in the intensity of the dipole active modes upon irradiation mentioned above, the higher energy region of the vibrational spectrum also undergoes a substantial evolution as a function of exposure to the electron beam, Figs. 1(c)–1(e). The vibrational modes become noticeably broader, which may indicate a reduction in the symmetry of the fullerene molecules. In addition to the broadening of the vibrations in the 800–1800 cm^{-1} region their relative intensities change dramatically. A strong, broad peak appears at about 1300 cm^{-1} with a weaker shoulder at about 1570 cm^{-1} . The position and breadth of these peaks makes it tempting to identify them with the Raman active D and G bands of amorphous carbon,^{4,60} especially as these bands have been observed in the Raman spectrum of C_{60} amorphized by Ar-ion laser irradiation under ambient atmospheric conditions.⁴ Between these bands lies a sharp mode at about 1455 cm^{-1} that may possibly be the Raman-active $A_g(2)$ mode of C_{60} shifted by overlap with the ‘‘ D -band’’

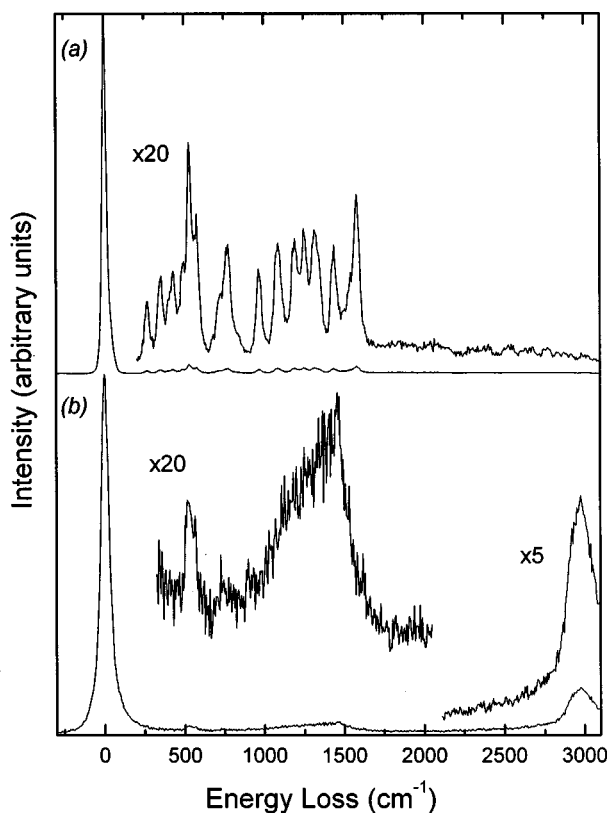


FIG. 3. HREEL spectra obtained 20° off-specular (incident angle 55° , reflection angle 35°) from (a) pristine 4 ML-thick C_{60} film on Si(100)- 2×1 -H, and (b) after irradiation with 0.5 keV electrons at a dose of $3 \times 10^{-2} \text{ C cm}^{-2}$. The lower relative intensity of the dipole-active modes at 527 and 575 cm^{-1} in (b) suggests that in addition to inducing disorder (see text) irradiation brings about destruction of the fullerene molecules. The spectra are normalized to the elastic peak intensity.

peak and by the effects of polymerization [for polymerized C_{60} the $A_g(2)$ mode lies at 1458 cm^{-1}].^{61,62}

The C-H stretching region also undergoes substantial changes: At low doses, Fig. 1(b), a single peak at $\approx 2910 \text{ cm}^{-1}$ appears, but with more electron irradiation a second peak, visible as a weak shoulder at a dose of $7.5 \times 10^{-3} \text{ C cm}^{-2}$, Fig. 1(c), grows in intensity until it matches that of the first, Fig. 1(e). The lower frequency C-H mode at 2910 cm^{-1} may be attributed to the vibrations of hydrogen bound to sp^3 -hybridized carbon⁵³ and is similar to that observed for C_{60} thermally hydrogenated by hydrogen from a passivated Si surface (at 2930 cm^{-1}).⁵¹ This indicates that for lower electron doses hydrogen bonds either to complete fullerene molecules or to relatively large molecular fragments, as discussed above. The new vibrational mode that appears at a frequency of $\approx 3050 \text{ cm}^{-1}$ is much higher than that reported for hydrogenated C_{60} and is characteristic of the vibrations of hydrogen bonded to sp^2 -hybridized carbon atoms.⁵³ The appearance of this peak indicates that at this point destruction of the fullerene cages must have occurred, since to bond to hydrogen and remain fully incorporated in an intact C_{60} cage a carbon atom must form four bonds, and hence be sp^3 hybridized rather than sp^2 hybridized.

If the electron dose is increased dramatically to 2.2 C cm^{-2} , as shown in Fig. 1(d), the vibrations that are ob-

served become weak and sit on a strong loss background decreasing in intensity with increasing loss energy. This low-energy tail is very similar to that which has previously been seen in HREELS studies of the graphite (0001) (Refs. 63 and 64) surface, indicating that in the limit of high doses the fullerene film has a graphitic local structure. The presence of a broad vibrational loss at about 3000 cm^{-1} indicates that hydrogen remains included in the film even after graphitization. The formation of disordered material with a local graphitic structure after long electron bombardment demonstrates conclusively that electron irradiation leads ultimately to the destruction of the C_{60} molecules.

Changes in the vibrational spectra of the fullerene films as a function of electron irradiation are accompanied by related changes in the electronic excitation spectra. The changes wrought in the EEL spectrum for an irradiation dose of $2.25 \times 10^{-3} \text{ C cm}^{-1}$, Fig. 2(b), in comparison to the pristine film, Fig. 2(a), are rather less pronounced than those observed in the vibrational spectrum. This indicates the greater sensitivity of vibrational spectroscopy in observing a low concentration of modified species, no doubt partly arising from the greater cross section afforded by vibrational excitations in comparison to electronic excitations (evidenced by the requirement of a degraded resolution in the latter case in order to obtain good counting statistics), and also from the fact that the vibrational excitations are less broad than electronic excitations and hence offer a greater definition. The initial effect of irradiation on the electronic excitations of the molecular film is to further broaden the π - π^* transition located at about 3 eV, Fig. 2(b), this broadening increases with further electron dose, Fig. 2(c), until the excitation is no longer visible as a pronounced peak above the broad underlying continuum of electronic excitations, Fig. 2(d). The higher-lying electronic excitations also rapidly lose their definition as the electron dose increases and become replaced by a broad continuous range of electronic excitations, Figs. 2(d) and 2(e), which indicates a significant change in the nature of the surface species. This change is mirrored in the broadening of the onset of the electronic transitions at about 2 eV and the appearance of significant loss intensity in the region below, which represents the band gap of the pristine film. Taken together, the smearing out of the electronic transitions and the presence of intensity in the band-gap region are in perfect accord with what would be expected if the molecular symmetry was strongly broken by fragmentation of the fullerene cages. Indeed, studies of exohedral fullerene compounds have shown that the HOMO-LUMO transition observed by HREELS (Ref. 65) is broadened by the reduction in molecular symmetry brought about by the addition of a chemical group to the exterior of the carbon cage. However, while it is possible that the spectra from films subject to relatively modest doses could be explained, at least in part, by electron-stimulated attachment of hydrogen to the fullerene molecular cages and/or polymerization, the evolution of the electronic excitation spectra with higher electron doses point (as do the vibrational spectra) to ultimate destruction of the fullerene molecules. The destruction of the fullerene molecules is manifested in the development of a smooth background characteristic of graphite observed in the electronic excitation spectrum after long irradiation, Fig. 2(f). This background is also seen in the vibrational

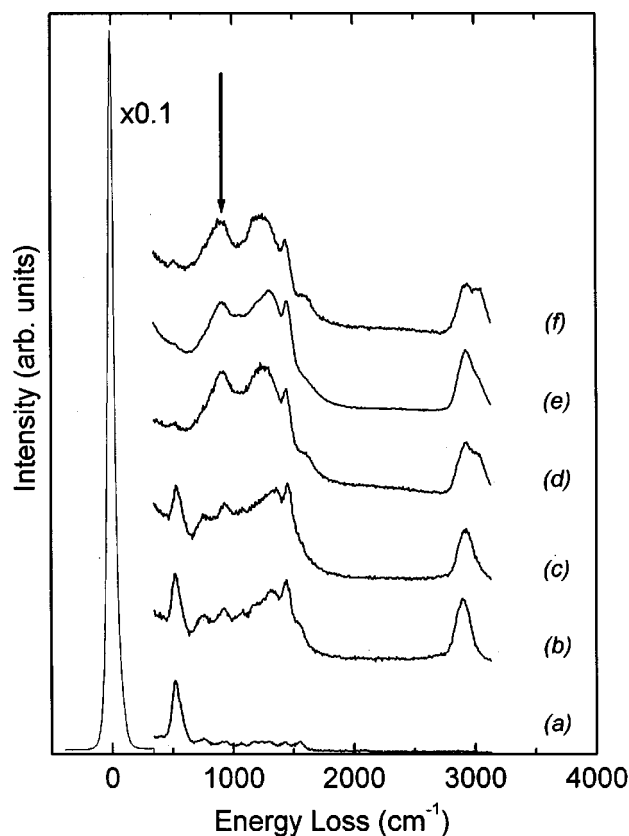


FIG. 4. HREEL spectra of 1-ML C_{60} grown on Si(100)- 2×1 -H, as a function of irradiation with 3.3-keV electrons: (a) zero; (b) 7.5×10^{-2} C cm $^{-2}$; (c) 1.5×10^{-1} C cm $^{-2}$; (d) 3×10^{-1} C cm $^{-2}$; (e) 6×10^{-1} C cm $^{-2}$; (f) 9×10^{-1} C cm $^{-2}$. A new mode at about 910 cm^{-1} , absent from the thicker irradiated films is marked with a vertical arrow. Spectra were acquired at a 4.5 eV primary energy in the specular (55° , 55°) geometry.

spectrum after the same electron dose, Fig. 1(f). The smooth featureless decay of intensity with increasing energy loss shows none of the electronic excitations of C_{60} ,⁵² lending further strong support to the hypothesis of cage break up and transformation of the C_{60} into an amorphous “graphitic” material.

B. Irradiation of 1-ML C_{60} on Si(100)- 2×1 -H with 3.3-keV electrons

In order to obtain more information about the fragmentation process and hence to shed more light on the possible mechanisms of fullerene degradation under electron beam exposure we also carried out experiments in which we irradiated a monolayer film with 3.3-keV electrons, and multilayer films with 0.5-keV electrons. Dealing with the results obtained from the monolayer first, we show in Fig. 4 the results of electron irradiation of a single monolayer of C_{60} grown on the Si(100)- 2×1 -H surface. The molecules in the monolayer film are physisorbed⁵¹ and, since the films were grown at room temperature, are flat, but display no long-range ordering. Upon irradiation similar changes occur in the monolayer film to those described above for the multilayer. Namely, a reduction in the intensity of the two lowest energy dipole-active T_{1u} modes at 527 and 575 cm^{-1} , a change in the form of the higher energy intramolecular

vibrations to resemble those of the Raman spectrum of laser amorphized fullerenes, and the appearance of a C-H stretching mode corresponding to hydrogen bonded to sp^3 -hybridized carbon atoms followed by the growth of a second C-H stretching mode corresponding to bonding with sp^2 -hybridized carbon atoms. However, these spectra display an additional strong, broad, feature at about 910 cm^{-1} [marked by the arrow in Fig. 4(c)]. This peak starts to become visible at the lowest exposures shown. The frequency of this mode corresponds closely to that expected of a Si-C bond,⁶⁶ implying that hydrogen desorbs or is displaced from the hydrogen-passivated Si surface under electron bombardment. The fullerene molecules, or fragments derived therefrom can then bond to the bare Si surface giving rise to the observed vibration.

The electron doses, uncorrected by secondary electron emission, required to bring about a given change in a monolayer fullerene film are about an order of magnitude higher than those for the 4 ML-thick fullerene film. There are two possible reasons for the dependence of spectral evolution on electron dose: (a) that the secondary electron emission coefficient is substantially different between C_{60} and the Si surface, the consequences of which we will discuss below, or (b) that the processes that lead to fragmentation are partially quenched by the close proximity of the substrate surface to the C_{60} molecules.

C. Irradiation of multilayer C_{60} with 0.50-keV electrons

Irradiation of a 4-ML C_{60} film with 0.5-keV electrons also brings about broadly the same changes observed when 3.3-keV electrons are employed, as shown in Fig. 5. However, there are some subtle differences that exist between these spectra and those for 3.3-keV electron irradiation shown in Fig. 1. It should be noted that limitations on the efficiency of the electron gun resulted in electron fluxes at 0.5 keV which were about an order of magnitude lower than those possible at 3.3 keV incident beam energy. While the secondary electron emission from the C_{60} film and the underlying substrate is likely to change between the different incident beam energies this variation will be relatively small.⁶⁷ Hence, even though measurements of the total electron dose at 3.3 and 0.5 keV may correspond to different “real” doses this variation between doses measured at higher and lower incident beam energies should be negligible in comparison to the range of doses studied.

The most prominent difference between irradiation of a fullerene multilayer with 3.3-keV electrons, Fig. 1, and 0.5-keV electrons, Fig. 5 is that, for a given electron dose, the vibrational peak at 1455 cm^{-1} is much more pronounced for the lower energy electron beam irradiation. Overlap with the strong intensity of this peak causes the whole of the vibrational region between 1000 and 2000 cm^{-1} to seem significantly more intense in comparison with the two lowest-lying dipole active modes at 527 and 575 cm^{-1} than for a similar irradiation at 3.3 keV [compare, for example, Figs. 1(c) and 5(c)]. As described above, it is tempting to attribute the vibrational mode at 1455 cm^{-1} to the $A_g(2)$ -derived mode of polymerized C_{60} molecules^{61,62} within the film. Such an attribution then suggests that the greater (relative) intensity of this mode for a given electron dose at lower beam energy

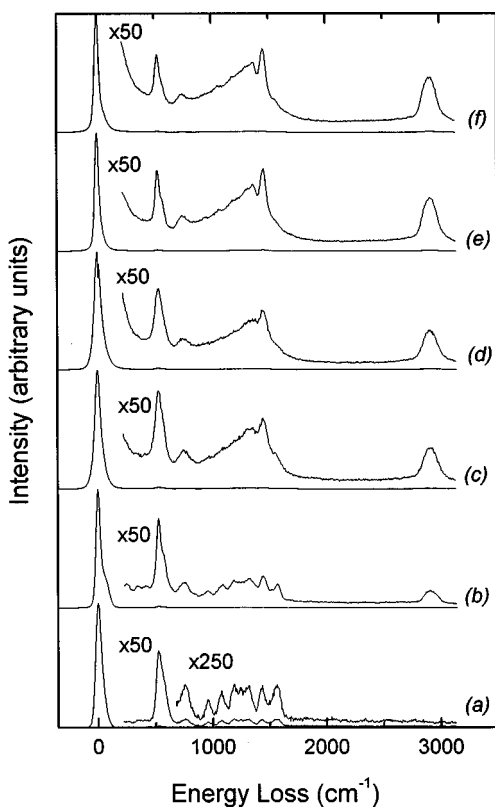


FIG. 5. Specular (55° , 55°) HREEL spectra from a 4 ML-thick C_{60} film on Si(100)- 2×1 -H, irradiated with 0.5-keV electrons to: (a) 0 C cm^{-2} ; (b) $4.5\times 10^{-4}\text{ C cm}^{-2}$; (c) $9\times 10^{-4}\text{ C cm}^{-2}$; (d) $1.8\times 10^{-3}\text{ C cm}^{-2}$; (e) $1.1\times 10^{-2}\text{ C cm}^{-2}$; (f) $3\times 10^{-2}\text{ C cm}^{-2}$. Spectra were acquired with a 4.5-eV incident beam energy and are normalized to the elastic peak height.

arises due to polymerization becoming more favorable (with respect to fragmentation) with decreasing electron beam energy or flux density.⁶⁸ However, Raman studies of laser irradiated fullerite⁴ undertaken in conditions, which would suppress the formation of polyfullerene displayed a very similar strong, Raman active, mode at about 1464 cm^{-1} in addition to those associated with amorphous carbon. It was suggested⁴ that this peak arose from links between fullerene molecules brought about by reaction with cage fragments. A similar, Raman-active mode was observed when fullerite was irradiated with high-energy ions (energies of the order of 100 keV), and in that case the peak was attributed to polyfullerene formation due to electronic energy transfer.¹⁶ Since electronic excitation of the C_{60} molecules is likely to bring about a substantial population of the long-lived lowest-lying excitonic state (which has triplet character in the free molecule⁶¹) it is likely that C_{60} molecules will be able to polymerize provided the electronic excitations are long-enough lived. Therefore, we propose that polymerization brought about by electronic excitation is in competition with electron beam-induced destruction, either as a function of incident electron flux or energy, or both. It is also noticeable that only a single C-H stretching mode is observed even at the largest nominal electron doses employed, which suggests that the cross section for fragmentation is reduced under the conditions used for lower energy electron irradiation. These observations may explain why Zhao and coworkers⁶⁹ observed thermally reversible changes when irradiating

fullerene films adsorbed on GaAs(110) with 1.5-keV electrons from the electron gun of a LEED system, and 5-eV electrons from an scanning tunneling microscopy tip. In the former case, whilst the electron beam energies and total sample currents used are comparable to those we have employed to obtain the results presented here, the flux density of electrons from a LEED gun is likely to be some orders of magnitude below those we obtained with our focused scanning electron gun. Indeed, we found that irradiation of a 4-ML C_{60} film on Au(110) with a LEED gun at $6\text{ }\mu\text{A}$ sample current, beam energies between 1.5 and 3 keV, and a spot diameter measured to be 3 mm (corresponding to an electron flux density of $\approx 1\times 10^{14}\text{ cm}^{-2}\text{ s}^{-1}$, in comparison with a nominal maximum of $\approx 4\times 10^{17}\text{ cm}^{-2}\text{ s}^{-1}$ from our scanning electron gun) produced no changes observable with HREELS, even after relatively large electron doses.⁷⁰

D. Annealing of an irradiated C_{60} multilayer

A further question to address is that of the nature of the products formed by electron beam irradiation of the fullerene films. It appears clear that the final product of irradiation with a large number of electrons is an amorphous carbon film with a graphitic local structure, but the nature of the intermediate products is less clear. In particular, it is interesting to determine whether the perturbed molecules or fragments are discrete, or form a network even at relatively low-electron doses. To shed some light on this issue, we annealed a 4-ML C_{60} film that had been exposed to an electron dose of $3\times 10^{-2}\text{ C cm}^{-2}$ at a beam energy of 500 eV, Fig. 6. AES showed that upon heating significant desorption of carbon-containing species occurred indicating that the hydrogenated fullerenes or fullerene fragments formed in the initial stages of electron beam irradiation are volatile and thus rather small. The desorption of some of the electron beam modified species after gentle annealing to 500 K for 4.5 h is borne out by the HREEL spectrum in Fig. 6(b). The relative intensity of the first two dipole active T_{1u} modes is now much stronger with respect to the dipole-forbidden modes. The strong peak at about 1455 cm^{-1} is also much reduced in intensity, although this may also be a function of the break up of any C_{60} polymer units in the film into monomers at elevated temperature. The form of the spectrum is similar to that of Fig. 1(b), suggesting that the remaining monolayer of C_{60} is substantially less damaged than the upper layers of the film, which have desorbed. Reduced damage of the lower layers is entirely consistent with attenuation of the incident electron beam as it passes through the 4 ML-thick film, which results in lower-lying layers being exposed to smaller electron fluxes than the outer layers of the fullerene film.

In addition to reducing the intensity of the C-H stretching mode at about 2900 cm^{-1} , a second effect of annealing is to shift this peak from the value of $\approx 2910\text{ cm}^{-1}$ in the irradiated 4-ML film to $\approx 2930\text{ cm}^{-1}$ in the annealed film. This latter frequency is the same as that of the C-H vibration observed when a C_{60} film on Si(100)- 2×1 -H is annealed to 600 K for 5 min,⁵¹ attributed to hydrogenation of the adsorbed fullerene molecules by atomic hydrogen from the passivated surface. This indicates that a substantial proportion of the C_{60} molecules that remain on the surface after the anneal are hydrogenated but intact. However, a small shoul-

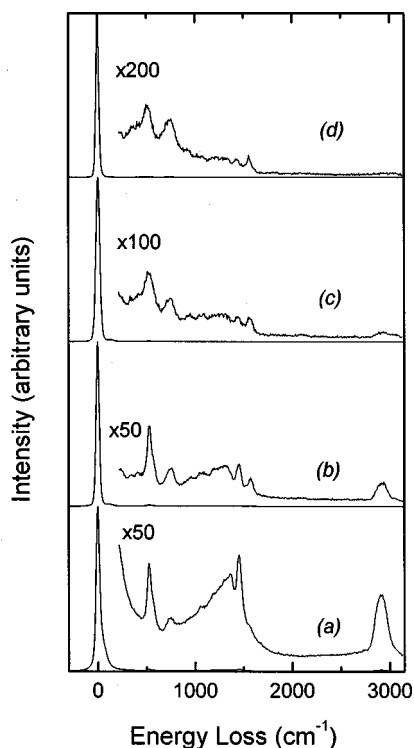


FIG. 6. HREEL spectra acquired from a 4-ML C_{60} film on $Si(100)-2\times 1-H$, irradiated with $3\times 10^{-2} C cm^{-2}$ with 0.5-keV electrons as a function of annealing: (a) as irradiated; (b) after annealing to ≈ 500 K for 4.5 h; (c) after a further 30 min at ≈ 650 K; (d) after a further 30 min at ≈ 720 K; Spectra were obtained with a 4.5-eV incident beam energy in specular ($55^\circ, 55^\circ$) geometry, and are normalized to the elastic peak intensity.

der can be seen on the high-energy side of the C-H stretch of the hydrogenated molecules, at about $3060 cm^{-1}$. As remarked upon previously, this frequency corresponds well with the stretching of hydrogen bonded to an sp^2 -hybridized carbon atom, showing that some fragments resulting from the destruction of fullerene molecules remain on the surface. Contamination from hydrocarbons can be ruled out as the source of the hydrocarbon-related vibrations since it is well known that C-H contaminants desorb after annealing C_{60} films to about 450 K.⁵⁹

Whilst hydrogen still remains on the surface of the silicon after annealing a pristine film as described, only a small broad bump is observed in the Si-H vibrational region at $2100 cm^{-1}$ in Fig. 6(b), which may correspond to some residual hydrogen termination of the silicon surface. The greater decrease in residual hydrogen termination of the silicon surface is mirrored by the greater relative intensity of the mode at $2930 cm^{-1}$ with respect to the C_{60} vibrational peaks compared to that observed for the annealed pristine film in Ref. 51. The increased desorption of hydrogen produced by annealing the irradiated film compared with the results of annealing a pristine film may arise either due to the longer annealing time (albeit at a lower temperature) of the former, or the liberation of atomic hydrogen from the passivated silicon surface under exposure to electron irradiation. Particularly notable is that even in the absence of the passivating hydrogen the positions of the first T_{1u} modes at 530 and $575 cm^{-1}$ are unaltered. Modes at higher energy are shifted, but nonrigidly, these changes might be induced by hydrogenation

or a weak chemical interaction with the surface. It is to be expected that the higher-energy modes, with primarily tangential displacement patterns that involve substantial deformation of the fullerene double bonds, should be more sensitive to subtle chemical changes in the molecule than the lower energy, primarily radial vibrational modes.

If the irradiated film is then further annealed to a temperature of about 650 K for 30 min, further evolution of the HREEL spectrum occurs, Fig. 6(c). There is a significant loss in the intensity of the C-H stretching mode at $\approx 2910 cm^{-1}$ suggesting that dehydrogenation of intact C_{60} molecules occurs. However, unlike the result of Schmidt *et al.*⁵¹ where dehydrogenation at of the C_{60} molecules at 800 K was accompanied by strong bonding with the underlying $Si(100)$ surface (from which the passivated hydrogen had also desorbed), no shift in the position of the dipole-active T_{1u} modes at 530 and $575 cm^{-1}$ occurs, merely a broadening due to a degradation of instrumental resolution (possibly related to surface roughening). Annealing further to 720 K for 30 min leads to almost complete dehydrogenation of the fullerene molecules. Only a weak very broad feature remains in the C-H region, possibly from a low concentration of hydrogenated molecular fragments remaining on the surface. The peak derived from the lowest-lying dipole-active modes shifts from 530 to about $514 cm^{-1}$. The reduction in frequency of the dipole-active modes can be attributed to charge transfer from, and hybridization with, the silicon substrate accompanied by the molecular distortions associated with increased substrate-adsorbate bonding.^{51,71} Therefore, in addition to dehydrogenation there is a clear indication that a change in bonding occurs between the adsorbed fullerene molecules and the substrate with increasing temperature as observed previously for C_{60} adsorption onto clean $Si(100)-2\times 1$.¹²

IV. DISCUSSION

Before turning to the possible mechanisms by which electron impact could induce the destruction of C_{60} molecules we first show that thermally induced effects can be eliminated as the cause of the changes that we have observed. The temperature of the base of the sample holder was measured during the electron irradiation process, and rose only by 25 K above room temperature after the largest electron doses reported here (which required approximately 12 h to obtain). Even if the sample itself were substantially hotter it is unlikely that the temperature gradient between sample and sample holder base could reach levels that would enable thermally induced fullerene damage. Furthermore, the products formed as the result of thermal annealing of a multilayer film of C_{60} on $Si(100)-2\times 1-H$ (Ref. 51) are significantly different from those observed in this study. To briefly recapitulate, the annealing process in the case of a multilayer leads initially to desorption of the multilayer and reaction of hydrogen with the C_{60} molecules in the remaining monolayer, these molecules chemisorb to the surface. Further heating then dehydrogenates the fullerene molecules leading to a chemisorbed phase the same as that formed for deposition of C_{60} onto a clean $Si(100)-2\times 1$ surface.¹² Finally, decomposition and carbide formation occurs.^{12,51} None of these effects was seen under electron irradiation. Indeed, Auger elec-

tron spectroscopy indicated that no measurable desorption occurred during irradiation of the fullerene film, demonstrating that the majority of the material resulting from electron-induced destruction of the C_{60} remained incorporated in the film.

There are a number of possible mechanisms that may be invoked to describe the process of fragmentation of C_{60} molecules, the merits of which we will consider in turn. Each of the mechanisms considered should apply equally to the destruction of any polymerized or hydrogenated molecule formed within the film in competition with fragmentation during the early stages of irradiation. These mechanisms can be thought of as falling into two broad classes: those involving “direct” energy/momentum transfer to the internal motion of the molecular cage and those in which the process is mediated by electronic excitation. Considering the former first, experiments involving the irradiation of carbon nanotubes with an 800-keV electron beam⁷² have implicated “knock-on” collisions as the primary means by which the nanotubes are destroyed under such conditions. These collisions can be envisaged at the simplest level as a two body collision between an incident electron and the nucleus of a carbon atom. If enough energy and momentum are imparted to the atomic nucleus the ejection of the target atom from the nanotube can occur. It has been estimated from molecular-dynamics simulations that a minimum energy of about 15 eV is required to eject a carbon atom from the surface of a nanotube.⁷² The structural similarity that exists between C_{60} and nanotubes implies that it is reasonable to assume that a similar energy is required for the ejection of a carbon atom from a C_{60} cage (although it should be noted that the thermal activation energy for fullerene fragmentation is much smaller, measured to be about 4 eV in the gas phase⁸). While an incident electron from a 3.3 keV beam certainly has the energy to eject a carbon atom from a C_{60} cage under these assumptions, a treatment of the interaction between the incident electron and the carbon nucleus in terms of two-body classical scattering demonstrates that the transfer of 15 eV energy from an electron with 3.3 keV kinetic energy to a stationary carbon nucleus would violate the law of momentum conservation.⁷³ Therefore, we can conclude that destruction by “knock-on” collision does not represent a good model of the fragmentation process.

Electronic excitation of C_{60} molecules by incident electrons or photons can bring about the emission of secondary electrons from a fullerene film. A C_{60} film is an insulator with a band gap of about 2.2 eV, so at first glance it would seem a reasonable assumption that C_{60} molecules in a film may become ionized to such a degree that the on-molecule Coulomb energy increases to such a degree that fragmentation of the molecule is possible. This phenomenon, which has been observed in gas-phase atomic clusters is known as “Coulomb explosion.”⁷⁴ However, this scenario requires that each of the fragmented fullerene molecules can build up a high degree of charge whilst present in the thin film. For this to happen, the opportunities for neutralization must be small. Therefore, one would expect that in a photoemission experiment or a low-energy electron scattering experiment (where the secondary electron emission coefficient is small) that the C_{60} film should begin to charge. It has been demonstrated in photoemission experiments from a C_{60} film on

Au(110), Al(111), and Al(110) using synchrotron radiation that the onset of steady-state charging is at a C_{60} coverage of 3-4 ML,⁷⁵ the maximum used in these experiments—indeed we observe fragmentation in a single monolayer.

In addition to the rather minimal likelihood of substantial fullerene charging in thin films, the stability of fullerene positive ions needs to be taken into account. Calculations indicate that isolated fullerene ions up to a charge state of +6 should be stable against symmetric dissociation.⁷⁶ In fact, gas-phase measurements on highly charged fullerene ions have demonstrated that rather asymmetric charge separation takes place involving the ejection of charged C_2 units.²⁹ The energy released in the fragmentation process led to the calculation that the intercharge distance in the transition state before fragmentation is greater than the radius of the parent C_{60} ion. This led in turn to the suggestion that a neutral C_2 dimer is initially ejected from the C_{60} cage followed by a charge-transfer interaction between the dimer and the C_{58} unit.²⁹ Consequently, the low probability that sufficiently highly charged fullerene ions be created in the thin film, the theoretical stability of fullerene ions, and the observation of charge separation via dimer ejection rather than more symmetric “explosion” suggest that although Coulomb explosion is a common phenomenon in gas-phase atomic clusters, it does not offer a convincing explanation as to the means by which fullerene destruction under electron beam irradiation occurs.

Finally, we are left with the coupling of electronic excitations of the fullerene molecules to intramolecular vibrational modes as the cause of cage destruction. Electronic, more specifically multiple plasmon, excitation of C_{60} molecules leading to cage destruction has previously been proposed to explain the fragmentation patterns observed when C_{60} molecules at low density in the gas phase are exposed to high energy (420-625 MeV), highly ionized Xe ion beams.²⁷ Multiple excitation of the $\sigma + \pi$ plasma resonance of the C_{60} valence electrons by the electromagnetic field of the incident ion leads to “catastrophic disintegration” of the molecules. A similar excitation pathway has been proposed for fullerene destruction by multiphoton absorption.³⁶ It was clearly seen that multiphoton absorption corresponding to a single excitation of the $\sigma + \pi$ plasmon led to single ionization of the target molecules, whereas absorption corresponding to a double excitation of the plasmon resonance led to the possibility of multiple ionization and cage fragmentation. The absence of delayed ionization or fragmentation³⁶ attested to the strong coupling of the plasmon with the ionization and fragmentation decay channels. Coupling of electronic excitations to molecular vibrational excitations, sharing deposited energy among the fullerene vibrational modes is quite a reasonable assumption in the light of the large “kinetic shift” (the extra energy necessary to bring about fragmentation in a C_{60} molecule in a given time over the binding energy of a C_2 unit) observed in gas-phase electron-beam induced fullerene fragmentation studies.²⁴

We propose that the mechanisms advanced for fullerene destruction under ion²⁷ and photon³⁶ irradiation in the gas phase, described above, are equally applicable to the case of electron beam irradiation of a solid fullerene film. As in the gas phase, multiple plasmon (and conceivably other electronic) excitation of the molecules by the incident electron

beam can excite multiple electronic transitions, part of the energy of which may become partitioned into vibrational modes as the molecule equilibrates. The creation of a highly vibrationally excited state is equivalent to a local heating of an individual molecule, and one can imagine that under these circumstances the cage atoms quite literally evaporate, perhaps by ejection of C_2 units or by complete (“catastrophic”) disintegration, bringing about the destruction of the molecules. The dissipation of the energy associated with intramolecular vibrations into the film is limited by the fact that the intermolecular vibrations are of rather low energy⁷⁷ arising from a weak coupling between adjacent molecules. If enough energy could be transferred into intermolecular modes significant molecular desorption from the film would occur as predicted in molecular-dynamics simulations of low-energy ion bombardment of C_{60} films.²¹ Desorption (measurable by changes in C *KLL* line intensity in Auger spectra) is not observed in our experiments. It may, of course, be argued that if ejection of C_2 dimers from fullerene cages were a dominant decay channel, this should also lead ultimately to some reduction in the number of carbon atoms within the fullerene film. However, measurements of the kinetic-energy distributions of dimers resulting from electron impact on fullerenes in the gas phase show that the average kinetic energy of dimer ions is always about 0.45 eV regardless of the electron impact energy.²⁶ The very low-kinetic energies of the released ionic fragments strongly indicate that they would be unable to escape from the surface of a solid film due to the attractive polarization forces that would be induced by their charge state.

The requirement for the population of highly electronically excited states before enough energy is distributed into the fullerene intramolecular modes for destruction to occur fits well with the observed flux dependence of molecular fragmentation, which is discussed in Sec. III C. Although it is of course possible for a single incident electron of sufficient energy to excite multiple plasma modes of a single molecule, the aggregate probability of multiple excitation will increase with increasing incident electron flux. Therefore, although our proposed mechanism for electron-beam induced destruction of C_{60} in the solid phase remains somewhat speculative, circumstantial evidence strongly supports this dissociation channel.

V. SUMMARY

Using the results described in Sec. III, we can formulate a description of the processes that go on under electron beam irradiation. The basic changes that occur initially under electron beam irradiation are the same whether a monolayer or a multilayer film and a high or a low-incident beam energy is used. There is a marked surface roughening that is manifested in a broadened dipole scattering lobe in HREELS and a decrease in the relative intensity of dipole active with respect to dipole forbidden modes. As described in Sec. III A, some of this reduction in the intensity of the dipole-active vibrations occurs due to fullerene destruction. New C-H bonds are formed, which can be interpreted as arising from the satisfaction of the dangling bonds of fullerene fragments and by hydrogenation of fullerene molecules by hydrogen radicals either originating from the passivated Si surface or

from residual chamber gases. The occurrence of the aforementioned surface roughening⁷⁸ and the presence of C-H vibrations associated with sp^3 -hybridized carbon atoms, indicate that although irradiation-induced hydrogenation may occur at low doses at higher electron doses fragmentation becomes the dominant form of damage.

The increasing strength of the vibrational mode at 1455 cm^{-1} in the HREEL spectra during the early stages of irradiation, under all the irradiation conditions studied (Figs. 1, 4, and 5) and the similarity of this peak position to that of the Raman-active $A_g(2)$ mode of polymerized C_{60} (Refs. 61 and 62) suggests that polymerization may occur in competition with fragmentation. As pointed out earlier (Sec. III C) the presence of a similar vibration has been observed when fullerene films have been irradiated with ions¹⁶ or laser light.⁴ Although a similar evolution of spectral features is seen under all the irradiation conditions observed it is notable that the “polyfullerene” vibrational mode is significantly stronger for irradiation at lower electron fluxes, indicating that these conditions may favor polymer formation over fragmentation and explain why irradiation under conditions of relatively low flux can give rise to either thermally reversible changes,⁶⁹ or none at all.⁷⁰

As the degree of irradiation of the fullerene films continues, molecular destruction becomes manifest, first in the presence of a second C-H stretching vibration at about 3050 cm^{-1} [for example in Fig. 1(e)]. This mode corresponds to the stretching of a bond between an H atom and an sp^2 -hybridized carbon atom,⁵³ demonstrating that some of the carbon-carbon bonds within the C_{60} cage are broken. In addition irradiation of a monolayer film of C_{60} gives rise to a new mode at about 910 cm^{-1} , corresponding to an Si-C vibration,⁶⁶ marked with an arrow in Fig. 4(f). Ultimately, irradiation of a multilayer leads to the appearance of a smooth loss background, Figs. 1(f) and 2(f), characteristic of a graphitic material, demonstrating that the fullerene molecules are destroyed and their fragments coalesce into an amorphous material with a graphitic local structure, perhaps not unlike those predicted by the simulations of Serra *et al.*⁴

Several possible models which could be employed to describe the mechanism of electron-irradiation-induced fullerene fragmentation were considered in turn in Sec. IV. It was demonstrated that of the models considered, multiple electronic excitation of the molecule followed by partition of some of the excitation energy into the internal vibrational modes of the molecule leading to fragmentation offered the most attractive explanation of the experimental results. The necessity for multiple excitation of the molecules neatly explains the observation of a strong dependence of irradiation-induced changes on the incident electron flux, although it would be interesting to determine if the fragmentation process involves sequential dimer emission or a complete “explosion” of the carbon cage.

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