Collapse of a mass-selected C$_{60}$ ion beam collided on crystal surfaces

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Mass-selected C$_{60}$ ion beams were accelerated to different kinetic energies and deposited on the (0001) surface of highly oriented pyrolytic graphite and the (111) surface of a gold single-crystal. Scanning tunnelling microscopy (STM), Raman spectroscopy and laser desorption mass spectrometry were used to characterize the deposited species. The STM images showed that C$_{60}$ molecules colliding on the surface were not dissociated, but their cages collapsed and deformed to planar structures. The Raman spectra of the deposited species are different from the spectral feature of fullerene, and they were similar to that from the glassy carbon instead. The deposited species were desorbed and mass analysed. Both positive and negative C$_{60}$ ions were observed in the desorption mass spectra, confirming that the species collapsing on the solid surface were the C$_{60}$ clusters. It was also found that the collision energy resulting in the collapse of the cage structure of C$_{60}$ was around 400 eV, and that fragmentation of the collapsed species does not occur if the energy does not exceed 1 kV.

1 Introduction

The football geometry of C$_{60}$ was first proposed based on its remarkable signal intensity in the mass spectrum recorded; it implied a special stable structure.[11] Indeed, later dissociation experiments found that C$_{60}$ has a very high dissociation energy and is very hard to dissociate.[2] Once dissociated, it shrinks to smaller fullerenes with the loss of C$_2$ fragments.[3]

In addition to gas-phase studies, collision experiments were performed using a C$_{60}$ ion beam with different kinetic energies impacting on a solid surface. When the energy is less than about 500 eV, it was found that the colliding C$_{60}$ is still very stable and is not deposited onto, or into, the surface.[4] If the collision energy is in the 1 keV range, the deposited fullerene ions will fragment.[5,6] Gaher *et al.*[7] performed deposition experiments with an intense, highly ionized beam in the kilo-electronvolt energy range to form carbon thin films, which showed graphitic nanocrystallites embedded in amorphous carbon. However, in their experiments the deposited fullerene ions were not mass selected and formed a film with thickness ranging from 100 to 500 nm, so the possible structural changes for the individual C$_{60}$ molecules upon collision was very difficult to characterize.

In the experiments reported in this paper, special attention is focused on the structure on the collided C$_{60}$ molecules. The C$_{60}$ ion beams were produced by laser ablation and were mass selected on a home-made apparatus. The ions were then accelerated and collided onto a crystal surface. The deposition conditions were carefully controlled in the experiments so that the species deposited onto the surface were separated. Scanning tunnelling microscopy (STM), Raman spectroscopy and laser desorption mass spectrometry (LDMS) were used to characterize the deposition products.

2 Experimental

The C$_{60}$ ion beam was produced by laser ablating a sample of C$_{60}$ powder (purity 99.9%) on a home-made tandem time-of-flight mass spectrometer. Details of the apparatus are described elsewhere.[8] A second harmonic output from a Nd : YAG laser was used as the vaporization laser. The power density was carefully tuned to avoid the dissociation or coalescence of C$_{60}^+$ as much as possible. After acceleration

and flighting over a 2.5 m field-free drift tube, ions with different masses could be separated, and C$_{60}^+$ was selected by a pulsed electric field (the 'mass gate'). The selected ions were then decelerated and bombarded onto the chosen crystal substrate. The kinetic energy of the ion beam was varied by adjusting the acceleration and deceleration voltage. A microchannel plate (MCP) detector was set behind the substrate to monitor the mass-selection process.

In the deposition experiment, the C$_{60}$ ions generated by laser vaporization were collided onto the substrate by acceleration. The laser power density was controlled to approximately 5×10^7 W cm^{-2}. Each laser pulse could produce 10^6–10^7 C$_{60}$ ions after mass selection. The kinetic energy of the ion beam was tuned to between 200 and 900 eV. The pressure in the deposition chamber was 10^{-6} Torr. The (0001) surfaces of highly oriented pyrolytic graphite (HOPG) and the (111) surfaces of a gold crystal were chosen as the substrates for the deposition of the C$_{60}^+$ ion beam. The substrate surfaces were ground to remove the charges carried by the ion beam. By adjusting the deposition time, the deposited species could be maintained as a single monolayer on the substrate surface.

LDMS analysis was performed on the same apparatus.[8] For the purpose of desorption, the powder density of the laser beam was tuned to less than 10^7 W cm^{-2}. The desorbed ions were then accelerated at 1 kV and mass analysed based on their flight times. Mass resolution of the mass spectrometer exceeds 400 ($m/\Delta m$).

The Au(111) surface was prepared following a well known flame annealing method.[9,10] Briefly, a gold wire of 0.8 mm in diameter was fed into an O$_2$ and H$_2$ flame to form a molten sphere, this was followed by slow crystallization. A gold single crystal with octahedral (111) faces was thus obtained. It has been shown that atomically flat terrace-step structures are consistently observed on the Au(111) surface. One of the Au(111) facets was chosen as the substrate surface after being annealed at 600 °C for 10 min.

For comparison, a gold crystal sample with C$_{60}$ molecules adsorbed on its (111) surface was also examined by STM and Raman spectroscopy. To prepare this reference adsorption sample, a drop of C$_{60}$ solution (toluene 1 µg ml^{-1}) was transferred to a clean Au(111) surface, leaving a mono- or bi-layer of C$_{60}$ molecules after evaporation of the solvent.

STM examinations were carried out in air on a Nanoscope IIIa STM (Digital Instruments) with electrochemically etched tips of either W or Pt–Ir. STM images were recorded with the data type of current.

Raman measurements were performed with a confocal microprobe Raman system (LabRam I). A single spectrograph with a holographic notch filter and a Peltier cooled CCD detector (1024×256 pixels) gave high spectral sensitivity. The slit and pinhole used were 100 and 400 µm, respectively. The power of the probe laser (632.8 nm) delivered to the sample was about 11 mW. A $100\times$ objective was used for the experiment.

3   Results

3.1   STM results

Fig. 1(a) shows the STM image of the HOPG(0001) surface after receiving collisions from accelerated C_{60} ions with 900 eV kinetic energy for 10 min. An image of the enlarged area is given in the lower right corner showing the configuration of the deposited species with the atoms of the HOPG substrate surface clearly resolved. The observed species is about 2 nm across and nearly 0.2 nm in height on the surface. From the atomic resolution image of the background graphite, one could easily estimate that the clustering atom number of the

species is around 60. This result suggests that after colliding on the solid surface, the cage structure of the C_{60} molecule breaks and the C_{60} collapses forming a nearly planar structure. The STM image in Fig. 1(b) was recorded after a 90 min deposition time. As can be seen on the image, the collapsed species do not completely fragment and are still bonded to the surface as clusters, which are well oriented on the surface. The distance between adjacent clusters is about 3 nm.

The interactions between the fullerene molecules and the HOPG surface are usually rather weak. No STM image of the monolayer C_{60} molecules on the HOPG surface have been obtained. However, the kinetic energy used for deposition in the above experiment is known to be sufficient to dissociate or deform the C_{60} molecules.[6] In the present work, it has been shown that the deposited molecules are strongly adsorbed on the HOPG surface and adhere even after continuous scanning at 0.6 nA with a tip bias of 0.4 V for some hours. This is another indication that the deposited species do not keep the original cage structure characteristic of fullerene molecules as they appear to be so well adsorbed on the HOPG surface.

The accelerated ion beam may also cause damage to the HOPG surface.[11] In order to verify further if the bright spots on the STM images are the deposited species or just damage, we raised the tunnelling current used during the STM measurement. When the current was raised to 1 nA, it was found that the deposited species could be swept away by the tip, thereby restoring the perfect HOPG surface, see Fig. 2. Therefore, it is certain that the observed humps on the STM topography must be the species deposited from the energetic C_{60}^{+} beam. This result also excludes the possibility that the C_{60} molecules are inserted into the subsurface of the HOPG.

In order to compare the behaviour of the collapsed and the adsorbed C_{60} molecules and to verify further the observation on HOPG, both deposition and adsorption experiments were carried out on the Au(111) surfaces, on which C_{60} molecules are more strongly adsorbed. For the deposition experiment, the C_{60} ion beams were accelerated and bombarded onto the Au(111) surface but for the adsorption experiments the C_{60} molecules were prepared as a solution and dropped onto the crystal surface. The STM images shown in Fig. 3 correspond to the species deposited and adsorbed onto the Au(111) surface, respectively. Fig. 3(a) shows the species deposited on the Au(111) surface using a C_{60}^{+} beam with a 900 eV kinetic energy for 120 min. The deposited species observed on the image have essentially the same size and height as those in Fig. 1 except that their arrangement on the gold surface is disordered. The C_{60} molecules adsorbed onto the Au(111) surface, on the other hand, display the hexagonal character of the C_{60} array with an intermolecular distance of 1.1 nm and a height of 0.4 nm, which are exactly what is observed in previous measurements.[12] A conclusion can be drawn at this stage that in comparison with the original C_{60} molecule the deposited species are much flatter. In other words, the C_{60} molecules collapsed on colliding with the crystal surface.

3.2   Raman spectroscopic results

While STM images can provide topographic information of the collapsed species, Raman spectral characterization can gain deeper insight into the detailed structure of the species. Fig. 4 shows a set of Raman spectra of the collapsed C_{60} on the HOPG surface after colliding with 900 eV kinetic energy and with different deposition times in comparison with a C_{60} microcrystal on the surface and the blank HOPG samples. For Fig. 4A the 1461 cm^{-1} band can be assigned to the A_g mode of C_{60}, which is the characteristic band of C_{60} and one that can be red-shifted by several wavenumbers under different conditions.[13,14] The sharp peak at 1585 cm^{-1}, which also appears on the other spectra, is assigned to the E_{2g} mode of the single-crystal graphite. In the spectra of the deposited
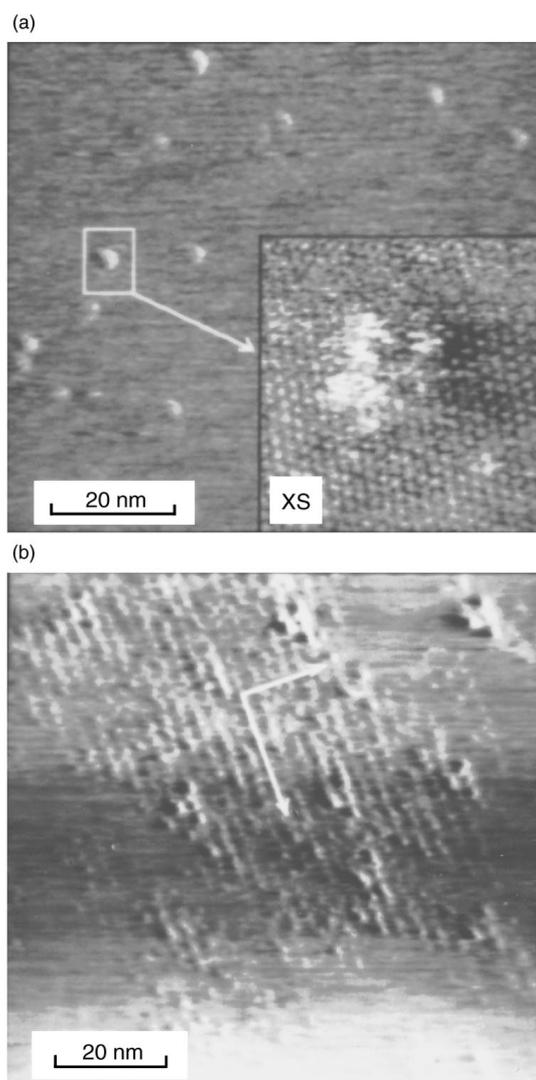

(a)

20 nm   XS

(b)

20 nm

Fig. 1   STM images of the (0001) HOPG surface after deposition by mass-selected C_{60} ions accelerated with 900 eV kinetic energy for: (a) 10 min and (b) 90 min
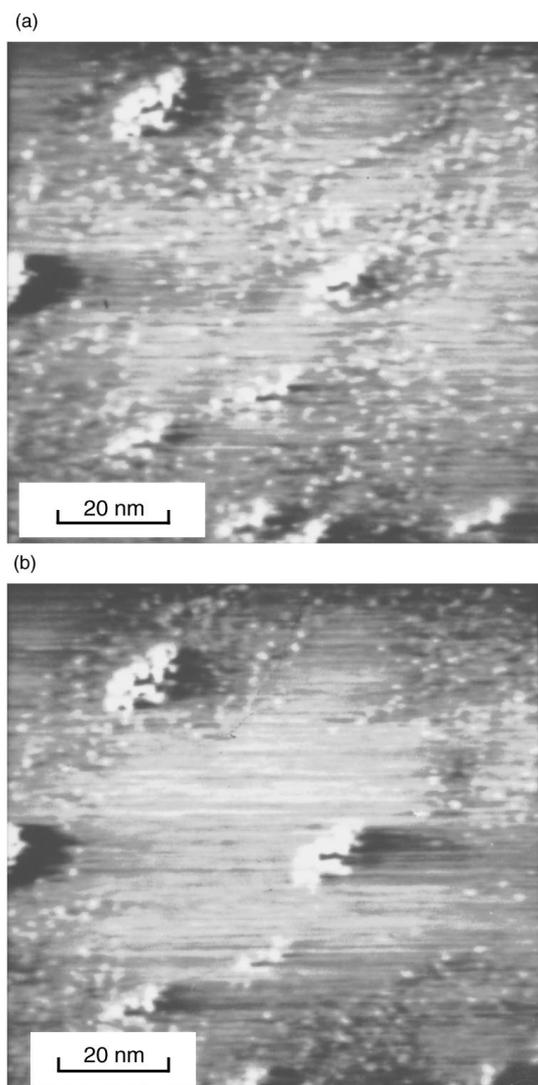
Fig. 2 STM images of HOPG surface (a) before and (b) after the deposition products were swept off by the STM tip. For sweeping out the products the tunnel current was raised to 1 nA. In image (b), the swept species are accumulated on the edge of the sweeping area and the bare HOPG surface is exposed.

species, the 1461 cm^{-1} band of the A_g mode of C_{60} was no longer observed, but a new peak at 1332 cm^{-1} appeared instead. The new peak is the characteristic vibration mode of amorphous carbon in sp^3 hybridization, and its intensity increases with the ion deposition time. The conclusions reached based on these Raman results are that the deposited species do not keep the original cage structure of the C_{60} molecules and that some of their component carbon atoms are converted to sp^3 hybridization.

Since both graphite and C_{60} are different forms of elementary carbon, some spectral bands may overlap. In order to characterize the collapsed species in detail, we changed the substrate to the Au(111) surface, and the Raman spectra are shown in Fig. 5D. As a reference, Fig. 5A and E display the spectra of pristine C_{60} and glassy carbon, respectively. The collapsed species exhibit two bands centred at around 1332 and 1585 cm^{-1}. The latter represents the vibration of carbon atoms in sp^2 hybridization. This band was indeed overlapped by the intense bands (E_{2g}) of the HOPG in Fig. 4. The Raman spectra reveal that the structure of the collapsed species is different from that of the pristine C_{60} molecules and contains both sp^2 and sp^3 carbon atoms just like the structure of glassy carbon. In fact, the spectrum is very similar to that of the glassy carbon surface as shown in Fig. 5E.
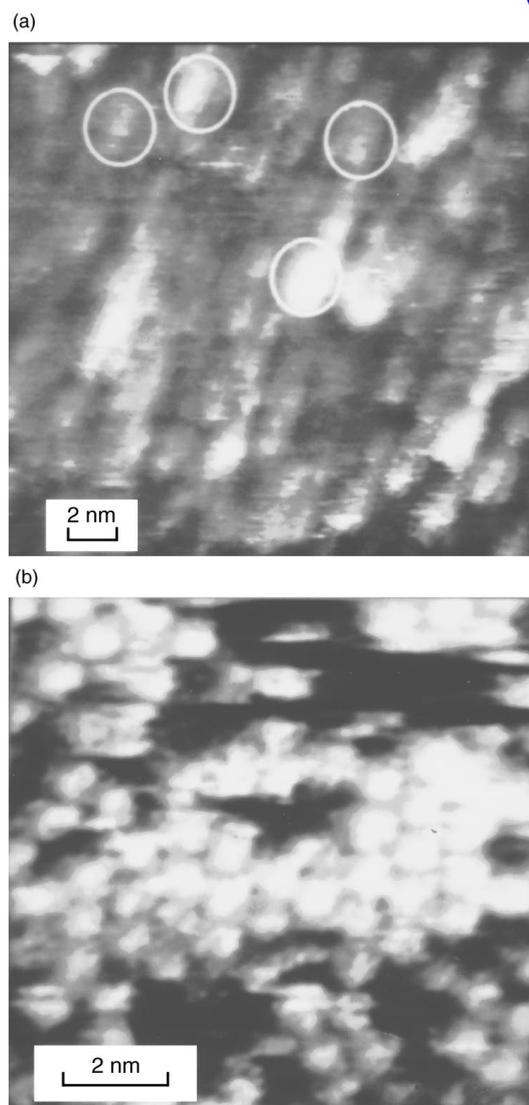

Fig. 3 STM images of Au(111) surface with: (a) deposition products of C_{60} ions with 900 eV kinetic energy and 120 min deposition time (marked by the circles in the figure with sizes about 2 nm); (b) monolayer of C_{60} molecules (with both the diameter and height of the adsorbed C_{60} molecule about 0.7–0.8 nm and hexagonally arranged on the surface with 1.1 nm distance)
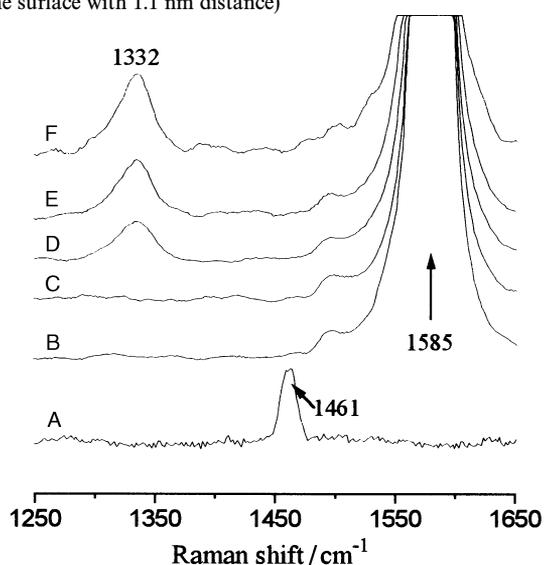

Fig. 4 Raman spectra of: A, microcrystal of C_{60} and B, blank HOPG crystal. Deposition products on (0001) HOPG surfaces with 900 eV kinetic energy and various deposition times: C, 10 min; D, 90 min; E, 120 min and F, 480 min.
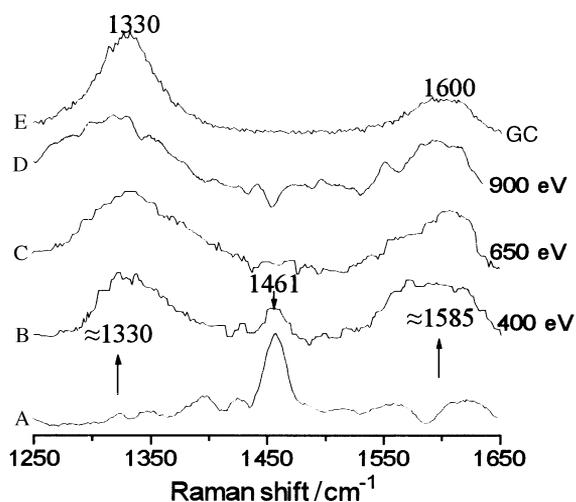
Fig. 5 Raman spectra of: A, microcrystal of C_{60}; deposition products with 120 min deposition time and different kinetic energies: B, 400 eV; C, 650 eV; D, 900 eV and E, glassy carbon (GC)

Fig. 6 Time-of-flight mass spectra of positive and negative ions desorbed from the gold crystal surface. The desorbed species were deposited on the surface with 900 eV kinetic energy and 120 min deposition time.

cage structures when they were vaporized by the desorption laser.

4 Discussion

The collisions with a solid surface of energetic C_{60} ions with different kinetic energies have been studied.[6,15] It was found that if the collision energy is above a certain threshold value, the C_{60} molecules might fragment or deform.[15] Lill et al.[6] thought the value to be about 500 eV, because C_{60} ions having this energy were not reflected upon collision but were deposited on the surface much more tightly than the pristine C_{60} molecules. Based on Raman spectroscopy measurements, Gaher et al.[7] showed that if C_{60} ions were accelerated by 300–400 V, only part of the C_{60} molecules was decomposed during deposition.

Our experimental results suggest that the threshold value is about 400 eV, which agrees well with previous experiments.[6,15] However, our results also indicate that if the collision energy is in excess of this value, the deposition C_{60} clusters do not dissociate but simply collapse on the deposited surface. In our experiments, the collided species are kept separate on the crystal surface, so their topography can be characterized by STM. As revealed by the STM images, the deposited species are of roughly the same sizes, 2 nm in diameter and 0.2 nm in height. The space they occupy on the surface is almost equivalent to that occupied by a 60 carbon atom plane. Since the species were deposited from the mass-selected C_{60}^{+} ions, they should consist of 60 carbon atoms as well. The corresponding Raman spectra do not show any peaks that can be assigned to C—O, C—H or other C—X groups. In fact, when the species were desorbed from the substrate, they were detected as C_{60} clusters. As no buffer gas was introduced in the desorption experiment, it is very unlikely that new C_{60} molecules can be formed by laser desorption. It is therefore reasonable to assume that the collapsed species are still C_{60}, but they do not preserve the cage structure of pristine C_{60} molecules (as shown by the STM and Raman spectroscopy observations).

It is of special interest that the STM images show that the collided C_{60} molecules have collapsed to form a nearly two-dimensional structure. This structure was further characterized by Raman spectroscopy. It was deduced from the spectra that the deposition products consist of both sp^2 and sp^3 carbon atoms, such as in the glassy carbon. Amaratunga et al.[16] reported that a hard, elastic thin film of pure carbon could be created by depositing closed, hollow graphitic carbon nanoparticles, nanotubes and onions onto a substrate at high velocity. The particles are apparently disrupted on

In order to characterize the threshold value of the collision energy required to collapse the cage of a C_{60} molecule, we measured the Raman spectra of the deposited species with different collision energies by adjusting the acceleration energy of the C_{60} ion beam. Owing to the space distribution of the C_{60} ions in the acceleration zone of the apparatus, the kinetic energy of the ion beam has a distribution of around 10% of the acceleration voltage. Fig. 5B, C and D are Raman spectra of the products deposited on the gold surface with several different kinetic energies. Fig. 5B corresponds to a collision energy of 400 eV. Characteristic bands of both fullerene and the collapsed species can be observed in the spectrum. When the kinetic energy was raised to about 650 eV, the Raman spectrum recorded is identical to that obtained with an energy of 900 eV, which is high enough to collapse all the colliding C_{60} molecules. This infers that all the deposited species collapse with a collision energy of more than 400 eV.

It is necessary to emphasize that the spectral range recorded is from 350 cm^{-1} to 3700 cm^{-1} and that there is no indication of the formation of any chemical bonds between carbon and any other atoms, confirming that the collapsed species are pure carbon clusters.

3.3 Desorption results

The deposition products were further characterized by LDMS. The products were deposited from a C_{60}^{+} beam with 900 eV kinetic energy, which is known to be high enough to deform the C_{60} molecules. The substrates for the sample were the HOPG (0001) and Au(111) surfaces. In the recorded mass spectra, a peak with $m/z = 720$ can be observed. This confirms that the collapsed species are composed of 60 carbon atoms. As HOPG itself can produce C_{60} clusters after laser ablation, the result from the gold substrate sample is required to provide more evidence. Fig. 6 displays the spectra of both positive and negative ions from the sample. In addition to the peaks from $C_{60}^{\pm}$, mass peaks from gold ions can also be observed in the spectra.

Mass spectrometry can define the mass of different species. For elementary clusters, such as carbon clusters, it can also define the size of the cluster. Therefore, provided that a coalescence reaction does not occur in the desorption process, which is very unlikely under the present experimental conditions, the LDMS results here confirm that the collapsed species are C_{60} clusters. However, the mass spectrum does not provide structural information on the samples, so we cannot confirm whether the collapsed species recovered their pristine
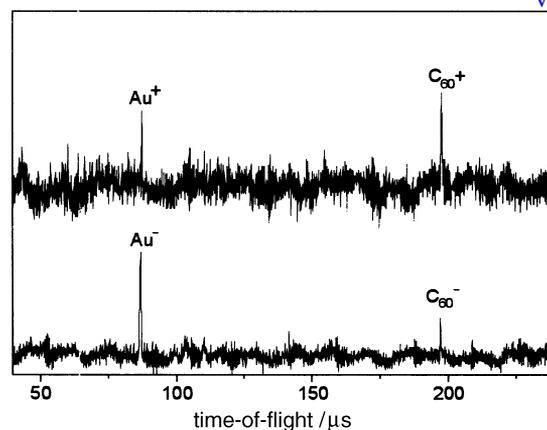
impact, causing them to link up. Electron-energy-loss spectra[16] reveal a reduction in π bonding in the intersecting regions of the nanoparticles, suggesting that they are covalently linked by tetrahedral sp^3 bonds. Gaher *et al.*[7] characterized the film deposited from an energetic fullerene ion beam and deduced, from the Raman spectrum, which is very similar to that shown in Fig. 5D, that the deposition product has an overall percentage of sp^3 bonds of 35%, which might correspond to 50% sp^3 bonding in the amorphous material. Although the product studied in this work was deposited from the mass-selected C_{60} ions, they might have similar structures.

A major difference of our deposition experiment, as compared with conventional techniques, is that the deposited ions were produced by laser ablation and mass selected on a homemade apparatus. In addition, the deposited species were desorbed with much lower laser power and mass analysed on the same apparatus. The desorption result confirms that the collapsed species is still a C_{60} cluster, but we cannot determine from the mass spectrometry whether the collapsed C_{60} cluster has recovered its pristine cage structure. It will be of interest to find out if the collapse process is reversible. A further study on this process is in progress.

References

1   H. W. Kroto, J. R. Heath, S. C. O'Brien, R. F. Curl and R. E. Smalley, *Nature* (*London*), 1985, **318**, 162.

2   D. J. Klein, T. G. Schmaiz, T. G. Hite and W. A. Seitz, *J. Am. Chem. Soc.*, 1986, **108**, 1301.

3   J. F. Christian, Z. M. Wan and S. L. Anderson, *J. Chem. Phys.*, 1993, **99**, 3468.

4   R. C. Mowray, D. W. Brenner, B. I. Dunlap, J. W. Mintmire and C. T. White, *J. Phys. Chem.*, 1991, **95**, 7138.

5   H. G. Busmann, B. Reif, I. V. Hertel and H. G. Maguire, *J. Chem. Phys.*, 1993, **98**, 7574.

6   Th. Lill, H. G. Busmann, B. Reif and I. V. Hertel, *Appl. Phys. A*, 1992, **55**, 461.

7   H. Gaher, H. G. Busmann, R. Hiss, I. V. Hertel, H. Romberg, J. Fink, F. Bruder and R. Brenn, *J. Phys. Chem.*, 1993, **97**, 8244.

8   R. B. Huang, Z. Y. Liu, H. F. Liu and L. S. Zheng, *Int. J. Mass Spectrom. Ion Processes*, 1995, **105**, 55.

9   J. Clavilier, D. Armand and B. L. Wu, *J. Electroanal. Chem. Interfacial Electrochem.*, 1982, **135**, 159.

10 H. Honbo, S. Sugawara and K. Itaya, *Anal. Chem.*, 1990, **62**, 2424.

11 G. Brauchle, S. Richardschneider, D. Illig, R. D. Beck, H. Schreiber and M. M. Kappes, *Nucl. Instrum. Methods Phys. Res. Sect. B*, 1996, **112**, 105.

12 R. J. Wilson, G. Meijer, D. S. Bethune, R. D. Johnson, D. D. Chambliss, M. S. de Vries, H. E. Hunziker and H. R. Wendt, *Nature* (*London*), 1990, **348**, 621.

13 Y. Hamanaka, S. Nakashima, M. Hangyo, H. Shinohara and Y. Saito, *Phys. Rev. B*, 1993, **48**, 8510.

14 L. Holz, M. Pfeiffer, H. Gaber and A. Lau, *Appl. Phys. A*, 1995, **61**, 171.

15 Y. Shi, X. J. Fan, H. X. Guo and Q. Fu, *Solid State Commun.*, 1996, **99**, 445.

16 G. Amaratunga, M. Chhowalla, C. J. Kiely, I. Alexandrou, R. Aharonov and R. M. Devenish, *Nature* (*London*), 1996, **383**, 321.