Electron-stimulated fragmentation mechanism for fullerene films on Si(111)-(7×7) surfaces: Dependence on thickness and electron flux

Leonid Bolotov* and Toshihiko Kanayama
Joint Research Center for Atom Technology, National Institute of Advanced Industrial Science and Technology (AIST), Higashi 1-1-1, Tsukuba, Ibaraki 305-8562, Japan
(Received 6 March 2003; published 9 July 2003)

We studied the fragmentation of ultrathin [1–6 ML (monolayer)] C_{60} films on Si(111)-(7×7) surfaces under intense pulse electron irradiation using a scanning tunneling microscope for field-emission electron irradiation below (20 eV) and above (45 eV) the fragmentation threshold energy. We assessed the fragmentation yield for various film thicknesses and electron fluxes. Fragmentation resulting in coalesced spheroid structures becomes less efficient in thinner films owing to faster energy transfer into the substrate. Our observation of flux dependence revealed that two-electron excitation causes fragmentation at sub-threshold energy when the excitation rate exceeds the excited-state decay rate ($\sim 10^9$ s^{-1} for 4-ML thickness).

DOI: 10.1103/PhysRevB.68.033404 PACS number(s): 73.61.Wp, 61.46.+w, 68.37.Ef, 82.30.Lp

The basic processes for electron-stimulated fragmentation of a cluster are of great interest from the viewpoint of electron-beam lithography applications, material chemistry, and the electron-assisted growth of quantum-size structures.[1,2] In particular, the electron irradiation of C_{60}, a cage carbon cluster, is of tremendous interest to alter its structural and electrical properties for not only technological applications,[3–5] but also for the creation of new forms of carbon with unique properties that have been predicted theoretically.[6–8] In the gas phase, electron irradiation initiates fullerene fragmentation by the emission of C_2 fragments caused by the single-electron excitation of the plasmon resonance of the molecule, when the electron energy exceeds a threshold of ~ 35 eV.[9–11] In the solid state, large carbon structures such as spirals, onions, and giant fullerenes have routinely been observed using transmission electron microscopes with high-energy electron beams that have an intensity as high as $\sim 1.25\times 10^7$ $nm^{-2}\,s^{-1}$.[12–16] In ultrathin C_{60} films subjected to electron beams at 0.5–3.3 keV, fragmentation-related changes in electron energy loss spectra appear when the electron flux is sufficiently large ($\sim 4\times 10^3$ $nm^{-2}\,s^{-1}$), leading the authors to conclude that electron-induced fragmentation of the C_{60} cage is caused by multiple electronic excitation of the molecule.[5,17] In our previous papers, we demonstrated the destruction of thin C_{60} films under intense pulse irradiation with 10–75 eV electrons extracted from a scanning tunneling microscope (STM) probe tip. Such irradiation led to the creation of large carbon structures (nanospheroids) as a result of coalesced C_{60} fragments produced by the electron excitation of fullerene molecules when the electron energy exceeded a threshold of ~ 35 eV.[18,19] We found spheroid formation below the threshold when the electron flux was as high as $\sim 10^9$ $nm^{-2}\,s^{-1}$, which suggests that the phenomenon has a strong dependence on electron flux.

In this Brief Report, we investigated the fragmentation phenomenon for various C_{60} film thicknesses and electron fluxes to clarify the excitation mechanism underlying the electron-stimulated fragmentation of C_{60} on Si(111)-(7×7) surfaces at an electron energy of 20–45 eV. We used a STM to both observe and modify the surface through field-emission (FE) electrons emitted from the STM probe tip in the field-emission regime. This enabled us to provide accurate control of the electron flux by adjusting field-emission conditions (retraction distance). We found that the incident electron flux, i.e., the excitation rate, had a decisive influence on the fragmentation yield of ultrathin films irradiated at low energy on account of the energy dissipated into the substrate.

Fullerene films with a thickness of 1–6 ML (monolayer) were prepared on the Si(111)-(7×7) surfaces of Si wafers (*n* type, 0.001Ω cm, Sb doped) at room temperature by thermally evaporating C_{60} powder at a deposition rate of 3–10 nm/min (1-ML coverage corresponded to a thickness of 1 nm). When the coverage was less than 3 ML, the films were structureless, whereas C_{60} nanocrystals 20–70 nm in diameter were formed at greater coverage. Details of the technique to irradiate the sample surface with FE electrons emitted from the STM probe tip have been described elsewhere.[20,21] Here, we extracted FE electrons by applying a series of short (0.01–0.9 s) voltage pulses between the surface and the probe tip that had been retracted 6–50 nm away from the sample surface (a field-emission regime). Every single irradiation event (an extraction voltage pulse) was well separated in time in order to minimize local heating. The FE electron energy was determined from the extraction voltage subtracting a work function of tungsten of ~ 4.8 eV. The electron flux was regulated by changing the retraction distance and calculated from the FE current assuming that the diameter of the irradiated area is equal to the retraction distance.[21] The structural changes that resulted were observed with the STM in the tunneling regime with a sample bias of -3.5 V and a tunnel current of 0.18–0.30 nA. We used W(111) tips having radii of less than 10 nm after treating them *in situ* with field-ion microscopy.

The effects of pulse electron irradiation of multilayer films of C_{60} are demonstrated in Fig. 1, which shows STM images of C_{60} nanocrystals modified by FE electron irradiation. For 6-ML coverage, irradiation with FE electrons at 40 eV led to the creation of large carbon structures (carbon spheroids) less than 2 nm in height, which was accompanied

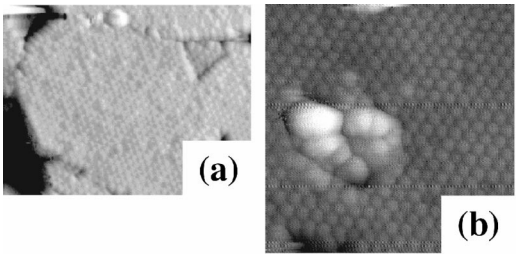

FIG. 1. STM images of C_{60} nanocrystals exposed to FE electrons at ~20 eV and ~60 nC, taken (a) before and (b) after irradiation. The diameter of the irradiated region is ~6 nm. The image sizes are 30×23 nm^2 (a) and 15×15 nm^2 (b). Images were acquired at a sample bias of −3.5 V with a tunneling current of 0.18 nA.

by irradiated nanocrystal shrinkage owing to the agility of C_{60}.[18] When the diameter of the irradiated areas was as small as 6 nm resulting in an electron flux of $\sim10^9$ nm^{-2} s^{-1}, spheroids were formed even with ~20 eV electrons as can be seen in Fig. 1(b). The mean spheroid diameter was 1.0 ± 0.3 nm, which corresponded to a carbon structure merged from three to five fragmented fullerenes. The spheroids were immobile on the timescale of the experiment and no further coalescence was observed. They appeared immediately after irradiation in less than 20 s (limit of our time resolution), while long-lasting migration of fullerenes displaced by electron excitation yielded growth of aggregates and ordered C_{60} islands for irradiation at an electron energy of below 30 eV and lower electron flux.[18]

As defects and crystal boundaries may be involved in spheroid nucleation as seen in Fig. 1(b), we selected wide, perfect crystals of C_{60} for this study of dependence on flux and thickness.

Since spheroid growth originates in the electron-stimulated fragmentation of C_{60} molecules, we evaluated fragmentation yield through the number of created spheroids. Figure 2 shows the change in fragmentation yield (the number of spheroids per total dose) as a function of film thickness *d*. The fragmentation yield obtained for an electron flux of $\sim4\times10^{-2}$ nA nm^{-2} decreases sharply for $d\leqslant3$ nm,

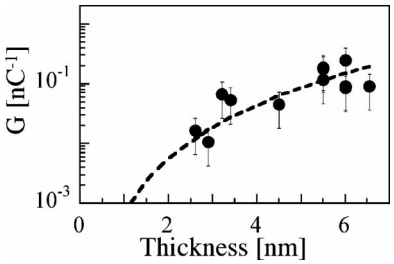

FIG. 2. Fragmentation yield *G*, i.e., the number of spheroids produced per electron dose, as a function of film thickness for irradiation at ~45 eV, a dose of ~0.6 nC nm^{-2} and an electron flux of $\sim4\times10^{-2}$ nA nm^{-2}. The thicknesses obtained from STM images were corrected by adding 0.8 nm for the presence of the chemically bonded C_{60} monolayer (Ref. 22). The broken line is a fit to a power function to the order of 3.

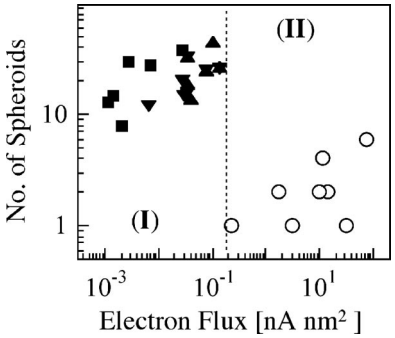

FIG. 3. The number of spheroids created as a function of electron flux for irradiation at ~45 eV (closed symbols) and ~20 eV (open circles). At every electron flux intensity, a virgin nanocrystal of C_{60} was exposed to a dose of ~300 nC. The different closed symbols represent data obtained for different values of *d* from 4 nm to 6 nm. The open circles correspond to a thickness of ~4.2 nm. The vertical line indicates the threshold separating regions where excitation by single (I) or two electrons (II) is dominant.

whereas it is almost constant for thicker films. The best fit of the data to a power function of *d* was obtained with an order of 3. For 1-ML coverage, we were unable to create spheroids under the excitation used. Since C_{60} forms strong chemical bonds with the surface Si atoms,[22,23] the coupling of C_{60} and Si surface atoms provides rapid energy dissipation from C_{60} into the substrate and it is responsible for the reduced fragmentation yield. For $d\leqslant2.4$ nm, the spheroids might be formed but disordered film structure and numerous aggregates of C_{60} hindered accurate counting of the number.

To assess the energy dissipation rate, we changed the excitation rate, i.e., the electron flux intensity, while keeping the total dose constant. Figure 3 shows the number of spheroids created at an electron energy of ~20 eV and ~45 eV as a function of electron flux for 4–6 ML coverage. At an electron energy of 45 eV, the number of spheroids slightly increased with an increase in the electron flux from 10^{-3} to 10^{-1} nA nm^{-2}. The weak dependence on electron flux is consistent with the fact that fragmentation occurs upon single-electron excitation of the molecule. At increasingly larger flux, we were unable to accurately count the number of spheroids because of significant desorption of the material. The weak dependence on electron flux seen in Fig. 3 and the presence of the energy threshold for spheroid creation,[18] both rule out heating effect by FE electrons as possible mechanism of spheroid formation. Insignificant heating occurred in our case because both long mean free path of phonon (~5 nm) in bulk C_{60} crystals[24] and the irradiation procedure used here provide efficient heat dispersion.

Spheroids appeared even at an electron energy of ~20 eV, i.e., fragmentation took place, only when the electron flux exceeded a threshold of $\sim2\times10^{-1}$ nA nm^{-2}. As the electron energy is about half the energy required for fragmentation by single-electron excitation, this result indicates that two electrons are necessary to provide sufficient energy to the molecule to initiate fragmentation that is similar to multiphoton adsorption.[9,25–27] Above the flux threshold, electron excitation happens twice in a C_{60} molecule within an

interval that is shorter than the lifetime of the excited state. As a result, the number of spheroids gradually increased with the flux, being consistent with the mechanism whereby the fragmentation probability is proportional to the product of the flux and the lifetime of the excited state.

Interestingly, in region (II) (see Fig. 3) where two-electron excitation causes fragmentation at 20 eV, desorption becomes apparent for 45-eV irradiation. This indicates that desorption is also induced by two-electron excitation. The threshold separating the two regions corresponds to an excitation rate of $\sim 1.3\times 10^{9}$ s^{-1} per single molecule. The value agrees well with the lifetime of the lowest excited singlet state ($\sim 1.3\times 10^{-9}$ s) for C_{60} isolated in organic solvents at room temperature.[9,28] The excitation rate is larger than the unimolecular dissociation rate of 10^{3}–10^{5} s^{-1} obtained for gas phase C_{60} with an internal energy of ~ 40 eV.[9–11] The obtained excitation threshold reflects the balance between excitation rate and dissipation decay that is determined by C_{60}-C_{60} interaction and energy transfer to the conductive substrate. Because of the short penetration depth of 20–40 eV electrons, excitation almost always occurs at the topmost C_{60} layer and dissipates into the bulk substrate depending on the distance, i.e., the film thickness d. The dependence of decay rate on the molecule-substrate distance has been reported for organic molecules located in a range from 1 nm to 20 nm outside a conductive surface, where the rate of nonradiative energy transfer for optically excited molecules decreases with the distance as $\sim d^{-3}$ for bulk transfer and as $\sim d^{-4}$ for surface transfer in accordance with the classical dipole damping model.[29,30] For C_{60} /alkanethiol/Au sandwich structures, the energy decay rate was 10^{10} s^{-1} for $d=1.5$ nm and 2×10^{9} s^{-1} for $d=2.5$ nm.[29] Both the power-law fit (see Fig. 2) of our data for 3–6 nm films and the threshold of $\sim 10^{9}$ s^{-1} obtained for $d\sim 4.2$ nm are consistent with the damping model, indicating that energy transfer from excited C_{60} into the substrate reduces the fragmentation yield. This implies that C_{60}-C_{60} intermolecule interaction does not play a significant role in the phenomenon.

For films thinner than 3 ML, we must take other factors into account, i.e., disordering of the film structure. Disorder in the structure may hinder the diffusion of fragments and, consequently, their coalescence and spheroid growth. Eventually, this gives rise to amorphous graphiticlike films such as those reported for 1–4 ML C_{60} films subjected to 500-eV electrons at a high dose.[5] However, as spheroid formation is extremely localized at the irradiated position [see Fig. 1(c)], we can rule out this effect as a major cause of the thickness dependence seen in Fig. 2.

In conclusion, electron-stimulated fragmentation of fullerenes on Si(111)-(7×7) surfaces results in the formation of carbon spheroids under intense pulse irradiation with FE electrons. The fragmentation yield decreases in ultrathin (1–6 ML) films, which is explained by fast energy transfer into the substrate. The evidence of flux dependence led us to conclude that two-electron fragmentation is achieved by subthreshold electrons of 20 eV when the excitation rate exceeds the excited-state decay rate into the substrate.

The authors wish to thank Professor E. Osawa of the NanoCarbon Research Institute, Ltd. and Professor K. Maeda of the University of Tokyo for their invaluable discussions. This work was supported in part by the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

*Present address: Advanced Semiconductor Research Center, AIST. Electronic address: bolotov.leonid@aist.go.jp

[1] G. Dujardin, R.E. Walkup, and Ph. Avouris, Science **255**, 1232 (1992).
[2] A.D. Kent, T.M. Shaw, S. von Molnar, and D.D. Awschalom, Science **262**, 1249 (1993).
[3] J.-M. Coquel, M.R.C. Hunt, L. Šiller, and R.E. Palmer, J. Appl. Phys. **84**, 4603 (1998).
[4] T. Tada and T. Kanayama, Jpn. J. Appl. Phys., Part 2 **35**, L63 (1996).
[5] M.R.C. Hunt, J. Schmidt, and R.E. Palmer, Phys. Rev. B **60**, 5927 (1999).
[6] M. Menon, E. Richter, and K.R. Subbaswamy, Phys. Rev. B **57**, 4063 (1998).
[7] M. Fujita, T. Umeda, and M. Yoshida, Phys. Rev. B **51**, 13 778 (1995).
[8] D. Vanderbilt and J. Tersoff, Phys. Rev. Lett. **68**, 511 (1992).
[9] M.S. Dresselhaus, G. Dresselhaus, and P.C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, San Diego, 1996), pp. 157-158, 209, 483, and 860.
[10] M. Foltin, M. Lezius, P. Scheier, and T.D. Mark, J. Chem. Phys. **98**, 9624 (1993).
[11] D. Hathiramani, K. Aichele, W. Arnold, K. Huber, E. Salzborn, and P. Scheier, Phys. Rev. Lett. **85**, 3604 (2000).
[12] T. Füller and F. Banhart, Chem. Phys. Lett. **254**, 372 (1996).
[13] S. Iijima, J. Cryst. Growth **50**, 675 (1980).
[14] H. Kroto, Science **242**, 1139 (1988).
[15] D. Ugart, Nature (London) **359**, 707 (1992).
[16] Q. Ru, M. Okamoto, Y. Kondo, and K. Takayanagi, Chem. Phys. Lett. **259**, 425 (1996).
[17] A.P.G. Robinson, and R.E. Palmer, Chem. Phys. Lett. **289**, 586 (1998).
[18] L. Bolotov and T. Kanayama, Appl. Phys. Lett. **81**, 1684 (2002).
[19] L. Bolotov and T. Kanayama, Mol. Cryst. Liq. Cryst. Sci. Technol., Sect. A **386**, 129 (2002).
[20] R.S. Becker, G.S. Higashi, Y.J. Chabal, and A.J. Becker, Phys. Rev. Lett. **65**, 1917 (1990).
[21] M. Shibata, Y. Nitta, K. Fujita, and M. Ichikawa, Appl. Phys. Lett. **73**, 2179 (1998).
[22] S. Suto, K. Sakamoto, D. Kondo, T. Wakita, A. Kimura, A. Kakizaki, C.-W. Hu, and A. Kasuya, Surf. Sci. **438**, 242 (1999).
[23] X. Yao, T.G. Ruskell, R.K. Workman, D. Sarid, and D. Chen, Surf. Sci. **366**, L743 (1996).
[24] R.C. Yu, N. Tea, M.B. Salamon, D. Lorents, and R. Malhotra, Phys. Rev. Lett. **68**, 2050 (1992).
[25] G. Ulmer, E.E.B. Campbell, R. Kuhnle, H.G. Busmann, and I.V. Hertel, Chem. Phys. Lett. **182**, 114 (1991).
[26] R.K. Yoo, B. Ruscic, and J. Berkowitz, J. Chem. Phys. **96**, 911 (1992).

[27] S. Hunsche, T. Starczewski, A. l'Huillier, A. Persson, C.-G. Wahlstrom, H.B. van Linden van den Heuvell, and S. Svanberg, Phys. Rev. Lett. **77**, 1966 (1996).
[28] J.W. Arbogast, A.P. Darmanyan, C.S. Foote, Y. Rubin, F.N. Diederich, M.M. Alvarez, S.J. Anz, and R.L. Whetten, J. Phys. Chem. **95**, 11 (1991).
[29] K. Kuhnke, R. Becker, M. Epple, and K. Kern, Phys. Rev. Lett. **79**, 3246 (1997).
[30] A.P. Alivisatos, M.F. Arndt, S. Efrima, D.H. Waldeck, and C.B. Harris, J. Chem. Phys. **86**, 6540 (1987).