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DEGRADATION OF C_{60} NANOCRYSTALS ON Si(111)-(7×7) SURFACES UPON LOW-ENERGY ELECTRON IMPACT

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Electron irradiation of thin (4–6 monolayers) nanocrystals of C_{60} fullerenes formed on Si(111)-(7 × 7) substrates were performed with intense flux of field-emission (FE) electrons (10^5–10^8 electrons $nm^{-2} s^{-1}$) extracted at 10–100 V from probe tips of a scanning tunneling microscope (STM). At extraction voltage of 10–30 V, stimulated migration of C_{60} caused long-lasting changes of morphology of nanocrystals on a time scale of minutes after irradiation. With increase of extraction voltage beyond 40 V, fragmentation of C_{60} became dominant leading to creation of large carbon structures with apparent height of 0.4–1.5 nm as a result of coalescence of fragments. The contributions of different phenomena including polymerization and evaporation to nanocrystal degradation vary with electron energy and dose.

Keywords: fullerenes; silicon; electron-stimulated fragmentation; scanning tunneling microscopy

INTRODUCTION

Electron beam irradiation of fullerenes is not only of technological importance on using fullerenes as a resist material for electron-beam lithography [1,2] but also of scientific interest in creation of new forms of carbon predicted theoretically [3–6].

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Several phenomena such as polymerization, disordering and fragmentation were shown responsible for degradation of C_{60} films exposed to electron beams at an energy range of 0.5–22 keV [1,2,9]. Even at electron energy of 3–5 eV, modification of C_{60} layers grown on GaAs(110) and Si(111)-(7×7) surfaces was produced with concentrated flux of electrons injected from probe tips of scanning tunneling microscopes (STM) in tunneling regime [7,8]. This change was attributed to formation of C-C bonds bridging adjacent fullerenes [12,14]. In order to elucidate a particular role of different phenomena involved in degradation of fullerenes, we examined morphology of fullerene nanocrystals upon irradiation with 10–100 eV electrons under different excitation conditions.

EXPERIMENTAL

Fullerene nanocrystals with a thickness of 4–6 monolayers (MLs) were prepared on Si(111)-(7×7) surfaces of Si wafers (n-type, 0.001 Ohm.cm, Sb doped) by thermal evaporation of C_{60} powder from a Al_2O_3 crucible at 350–400°C with deposition rate of 3–10 ML per min. When the coverage was larger that 3 ML, C_{60} nanocrystals of 20–70 nm in diameter were formed.

Electron irradiation of fullerene nanocrystals was performed by applying a series of short (less than 1 s) voltage pulses with amplitude of 10–100 V between the sample surface and the probe tip when the tip had been retracted to a distance of 10–50 nm away from the surface (field-emission regime). The structural changes were observed in a 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 less than 10 nm and treated *in-situ* with field-ion microscopy. The above technique provided us with both accurate irradiation of a single nanocrystal and detailed images of produced morphology changes on an atomic scale. Details of the method have been described elsewhere [10,11].

ELECTRON IRRADIATION EFFECT

Field-emission (FE) electrons produced distinct changes of C_{60} nanocrystals depending on the electron energy and dose. Black molecules with an internal structure seen in Figure 1(a) occurred after irradiation of a nanocrystal with low density of electrons extracted at 10–30 V. Similar black molecules have already been observed and attributed to polymerized C_{60} molecules as a result of C_2-C_2 bridging adjacent molecules [7,8]. With increase of electron dose, growth of an additional layer became apparent as well as crystal shape change [Fig. 1(b)]. Such behavior was produced by mobile C_{60} molecules, indicating that electronic excitation gives the mobility to the molecule.

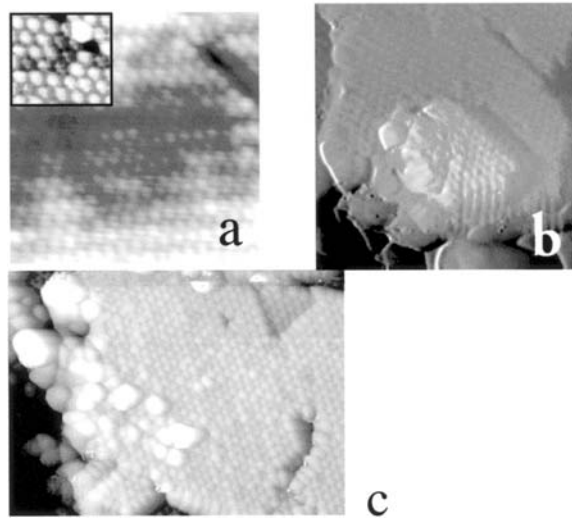

FIGURE 1 STM images of C_{60} nanocrystals exposed to electrons extracted at 15 V and (a) ~76 nC, and (b) ~200 nC. The inset in (a) shows a chain of polymerized C_{60}. (c) The large carbon structures were produced by electrons extracted at 45 V and ~200 nC. The irradiated areas is ~10 nm (a-b) and 30 nm (c). (−3.7 V, 0.2 nA).

At higher electron energy, creation of globules, large carbon structures, [Fig. 1(c)] became dominant accompanying with reduction of the nanocrystal diameter. Globule size was 0.4–1.5 nm in height and 2–5 nm in diameter. Once produced globules were stationary and firm in contrast that C_{60} islands were not rigid in shape, indicating that they were formed by coalescence of fragmented fullerenes. It has been reported previously that spirals and giant onions of various diameters were predominantly produced by destruction of carbon sheets under high-energy electron beams of a transmission electron microscope (TEM) [13–16]. Thus they are most likely products in our experiments.

Competitive contribution of several phenomena including evaporation was evaluated by determining the critical dose where each phenomenon became apparent. For instance, Figure 2(a) shows dynamic changes of nanocrystal morphology plotted as a function of time for a nanocrystal irradiated repeatedly with electrons at 25 V. The density of polymerized fullerenes increased upon each electron impact. Thus there is no critical dose for polymerization. When the dose was ~120 nC, dramatic shrink of the nanocrystal was observed, indicating the presence of critical dose for C_{60} evaporation/migration.

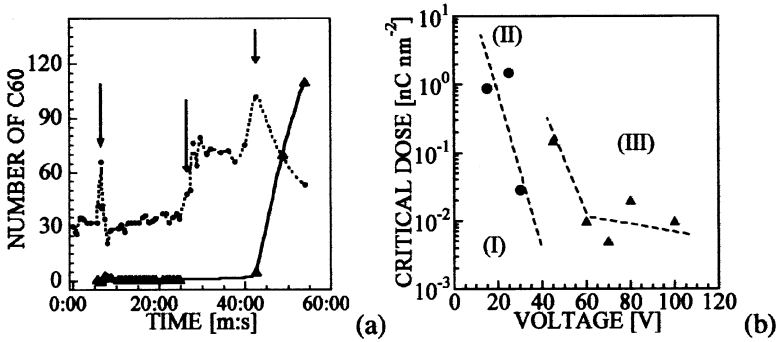

FIGURE 2 (a) Number of polymerized (circles, dot line) and migrated molecules (triangles, solid line) as a function of time. The arrows indicate moments of electron irradiation performed at 25 V and the increasing dose of ~40, ~60 and ~120 nC. (b) The critical dose for migration (circles) and fragmentation (triangles) as a function of extraction voltage. The letters denote regions of polymerization (I), evaporation/migration (II) and fragmentation (III). The lines are eye-guides.

Figure 2(b) represents the critical dose as a function of electron energy and outlines the conditions for each effect to occur. We see that polymerization is dominant at the extraction voltage below 30 V. At the voltage beyond ~40 V, i.e. the electron energy of ~35 eV, creation of large carbon structures becomes efficient. The electron energy range corresponds well to the energy at which efficient fragmentation by electron-stimulated emission of C_2 units has been observed for gas-phase fullerenes due to multiple excitation of the giant plasmon resonance (~20 eV) [17,18]. In high-intensity laser irradiation studies, both contraction of C_{60} molecules and creation of large-mass fullerenes were obtained through multi-photon excitation of the plasmon resonance of C_{60}, when a single fullerene absorbed dozen of photons (~3.14 eV) and increased its internal energy to ~39 eV [14,19–21]. Similarly, when the electron energy exceeds 35 eV, electron-stimulated fragmentation of fullerene molecules occurs. In contrast to gas-phase fullerenes, the fragmentation of C_{60} molecules in solid state leads to not only creation of smaller-mass fullerenes but also coalescence of the fragments and ultimately growth of large carbon structures such as spirals and onions.

SUMMARY

Electron irradiation of thin C_{60} nanocrystals formed on Si(111)-(7 × 7) substrates has been performed with FE electrons extracted at 10–100 V from

the STM probe tip. Concentrated flux of FE electrons (10^5–10^8 electrons $nm^{-2} s^{-1}$) produces morphological changes of C_{60} nanocrystals attributed to several competitive mechanisms depending on electron energy and dose. Degradation of C_{60} nanocrystals by fragmentation and growth of large carbon structures becomes apparent for electron energy larger than $\sim$35 eV, whereas polymerization is dominant for lower energies.

REFERENCES

[1] Tada, T. & Kanayama, T. (1996). *Jpn. J. Appl. Phys.*, *35*, L63.
[2] Hunt, M. R. C., Schmidt, J., & Palmer, R. E. (1999). *Phys. Rev. B*, *60*, 5927.
[3] Mackay, A. L. & Terrones, H. (1991). *Nature*, *352*, 762.
[4] Menon, M., Richter, E., & Subbaswamy, K. R. (1998). *Phys. Rev. B*, *57*, 4063.
[5] Fujita, M., Umeda, T., & Yoshida, M. (1995). *Phys. Rev. B*, *51*, 13778.
[6] Vanderbilt, D. & Tersoff, J. (1992). *Phys. Rev. Lett.*, *68*, 9511.
[7] Zhao, Y. B., Poirier, D. M., Pechman, R. J., & Weaver, J. H. (1994). *Appl. Phys. Lett.*, *64*, 577.
[8] Nakamura, Y., Mera, Y., & Maeda, K. (2000). *Appl. Phys. Lett.*, *77*, 2834.
[9] Robinson, A. P. G. *et al.* (1998). *Chem. Phys. Lett.*, *289*, 586.
[10] Becker, R. S., Higashi, G. S., Chabal, Y. I., & Becker, A. J. (1990). *Phys. Rev. Lett.*, *65*, 1917.
[11] Shibata, M., Nitta, Y., Fujita, K., & Ichikawa, M. (1998). *Appl. Phys. Lett.*, *73*, 2179.
[12] Rao, A. M. *et al.* (1993). *Science*, *259*, 955.
[13] Iijima, S. (1980). *J. Cryst. Growth*, *50*, 675.
[14] Dresselhaus, M. S. (1996). *Science of fullerenes and carbon nanotubes*, Academic Press, p. 158 and 209.
[15] Ru, Q. *et al.* (1996). *Chem. Phys. Lett.*, *259*, 425.
[16] Fuller, T. & Banhart, F. (1996). *Chem. Phys. Lett.*, *254*, 372.
[17] Foltin, M. *et al.* (1993). *J. Chem. Phys.*, *98*, 9624.
[18] Hathiramani, D. *et al.* (2000). *Phys. Rev. Lett.*, *85*, 3604.
[19] Ulmer, G. *et al.* (1991). *Chem. Phys. Lett.*, *182*, 114.
[20] Yoo, R. K., Ruscic, B., & Berkowitz, J. (1992). *J. Chem. Phys.*, *96*, 911.
[21] Hunsche, S. *et al.* (1996). *Phys. Rev. Lett.*, *77*, 1966.