Temperature dependence of the electronic and vibrational excitations of C_{60} adsorbed on $Si(100) - 2 \times 1$

LETTER TO THE EDITOR

Temperature dependence of the electronic and vibrational excitations of C$_{60}$ adsorbed on Si(100)-2×1

Michael R C Hunt†

Laboratorio Tecnologie Avanzate Superfici e Catalisi, Dell'Istituto Nazionale per la Fisica della Materia (TASC-INFM), Padriciano 99, I-34012, Trieste, Italy

Abstract. Electron spectroscopic studies of C$_{60}$ monolayers adsorbed on a Si(100)–2 × 1 surface as a function of annealing temperature indicate three adsorption states. At room temperature C$_{60}$ interacts weakly with the surface and in consequence the electronic and vibrational excitations of the molecule are only slightly perturbed. Above 873 ± 10 K changes in electronic and vibrational excitations indicate that, although the molecule remains intact, the nature of the surface–molecule bond changes, leading to what may be regarded as a strongly chemisorbed 'precursor' state to cage opening and destruction. Beyond 1048 ± 10 K the fullerene molecules begin to break up, with some carbon atoms remaining on the substrate surface in the form of a carbide.

Possible exploitation of C$_{60}$ in electronic devices, as a precursor in the production of Si–C structures [1], and as an enhancer for the CVD growth of diamond films [2] has meant that the adsorption of C$_{60}$ on silicon surfaces has received significant attention [3–15]. Recent STM experiments [15] have indicated that C$_{60}$ bonds weakly to the Si(100)–2 × 1 surface at room temperature. When the adsorbed molecules were subjected to an 873 K anneal a change in bonding geometry was observed, and the molecules became more difficult to move, indicating formation of a stronger substrate–adsorbate bond.

Further evidence of strong surface–molecule bonding above $\approx$870 K is provided by observation of cage opening and fragmentation of C$_{60}$ adsorbed on silicon when subjected to a high temperature ($>$1000 K) anneal [9, 10, 14]. Similar fragmentation phenomena have been observed for C$_{60}$ adsorption on transition metals [16].

In this letter the temperature dependence of the electronic structure and vibrational modes of C$_{60}$ monolayers adsorbed on Si(100)–2 × 1 is studied with electron energy loss spectroscopy (EELS), Auger electron spectroscopy (AES) and high-resolution electron energy loss spectroscopy (HREELS).

Experiments were undertaken in an ultra high vacuum (UHV) system consisting of preparation and instrumentation chambers with base pressures of 1×10^{-10} mbar and 5×10^{-11} mbar respectively. *n*-type, P-doped (2×10^{18} cm^{-3}) silicon was used as a substrate. The silicon was suspended between two tantalum clamps which enabled direct resistive heating by passing current through the sample. Sample temperature was monitored by a thermocouple held onto the sample surface by one of the clamps and, for temperatures in excess of 873 K, by an infra-red pyrometer.

† Current address: Nanoscale Physics Research Laboratory, School of Physics and Space Research, University of Birmingham, Birmingham B15 2TT, UK.

L229

Sample surfaces were prepared by cycles of Ne^+ ion sputtering (ion energy 1.2 keV) and annealing to 1300 K. Cleanliness was monitored by AES, which was also used to determine adsorbate coverage from the ratio of substrate and overlayer Auger peaks. Surface order was examined with a low-energy electron diffraction (LEED) optics. After sputtering and annealing cycles the substrate showed a clear (2×1) diffraction pattern and the Auger signal from any contamination was always below 0.5% of the Si LVV peak height.

99% pure C_{60} from Texas Fullerenes, degassed in UHV, was sublimated onto the sample from an open tantalum crucible held at 700 K. During evaporation the sample was held ∼2 cm away from the crucible. The pressure during dosing remained between 2×10^{-10} and 6×10^{-10} mbar. The C_{60} coverage was calibrated by measuring the ratios between the carbon KLL peak at 272 eV and the Si LVV peak at 92 eV. One physical C_{60} monolayer (1 ML) was *defined* by the coverage produced by saturating the Si(100)–2×1 surface with C_{60} at a temperature of 900 K—above that required for desorption of the multilayer [9].

Comparison of the attenuation of the silicon LVV peak at 92 eV, due to deposition of a C_{60} monolayer, with that of the Au 69 eV peak for saturation of a Au(110) surface at ∼600 K [17], known to produce a complete close-packed monolayer, indicates that the saturation coverage for the Si(100)–2×1 surface is close to that of a close packed C_{60} monolayer (i.e. approximately 1×10^{14} C_{60} molecules/cm^2 which would be 0.3 ML in standard notation). Hamza and Balooch [9] have estimated a saturation coverage of 0.4 physical monolayers, but this was based on the assumption that a full C_{60} monolayer would *completely* attenuate the substrate Auger signal.

Monolayers of C_{60} were heated to their final annealing temperature over a period of 5–7 min and then held at that temperature for 5 min, before being slowly cooled below 400 K over the same timescale.

After characterization by LEED and AES, vibrational and electronic excitations of the surface were measured using a Leybold–Hereaus ELS-22 high-resolution electron energy loss spectrometer (HREELS). Vibrational spectra were acquired at a beam energy of 8 eV in the specular geometry with incident and reflection angles of 72° to the sample normal. Electronic excitation spectra were acquired in specular geometry, with incidence and reflection angles of 72° at an incident beam energy of 12 eV. For electronic excitation spectra spectrometer resolution was degraded to around 60 meV to obtain a good signal-to-noise ratio.

Spectra showing low-energy electronic excitations of 1 ML C_{60} on clean Si(100)–2×1 are shown in figure 1, as a function of annealing temperature. Comparison with the spectrum from a multilayer shows that for the adsorption of C_{60} at 300 K the higher-lying electronic excitations are not strongly perturbed. However, the first strong feature, which corresponds to the transition between highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), is broadened. The weak, sloping, background between about 1.1 and 1.8 eV probably arises from the silicon substrate, whilst the sharp feature at 720 meV is associated with C–H bearing contaminants and increased in intensity as a function of time. The observed electronic excitations were the same both in the presence and absence of this contamination, indicating that the contaminant molecules present do not perturb the C_{60}–Si system.

That the spectra are representative of single monolayer films rather than a superposition of spectra from C_{60} molecules in direct contact with the substrate and those in multilayer islands can be seen by appeal to STM results from C_{60} adsorbed on both the Si(100)–2×1 [5] and Si(111)–7×7 [12] surfaces, where monolayer completion is observed before second layer growth, a result of the much larger self-diffusion of C_{60} when compared to the diffusion of the molecules over the silicon surface.
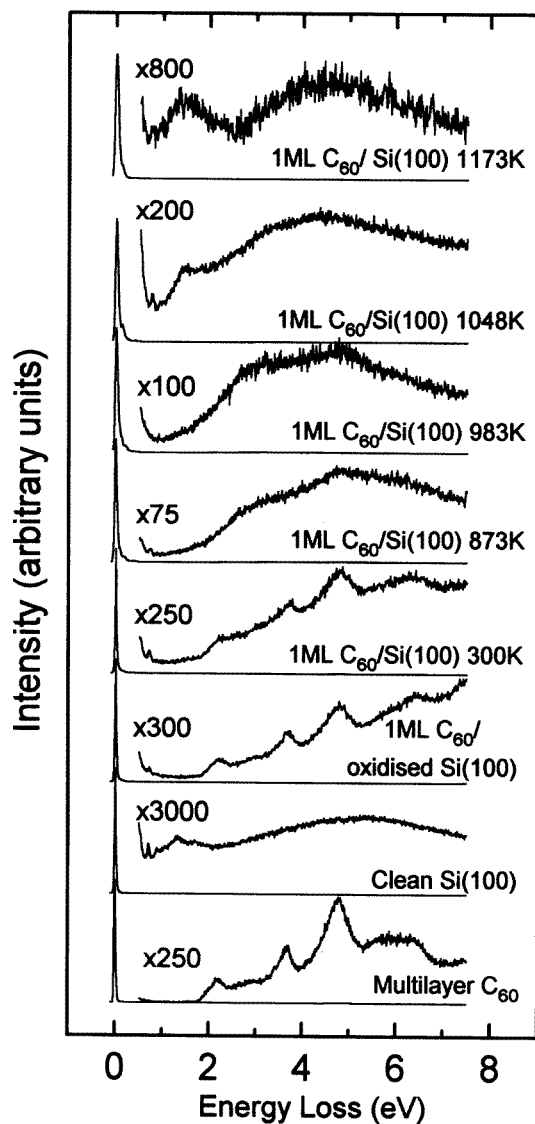
Figure 1. Electron energy loss spectra of: multilayer C_{60} clean Si(100)–2 × 1, a C_{60} monolayer on an oxidized Si(100) surface and monolayers of C_{60} on clean Si(100)–2 × 1 annealed to various temperatures. The spectra were taken in the specular geometry at an incident beam energy of 12 eV and are normalized to the elastic peak intensity.

The rather small perturbation of the HOMO–LUMO transition in the C_{60} monolayer indicates that there is relatively weak substrate–adsorbate interaction in comparison with C_{60} on metal surfaces [18, 19]. To explore the nature of the silicon–C_{60} bond we exposed a clean Si(100) surface to O_2 at 300 K. After 1500 L exposure the surface was saturated and no more oxygen uptake was observed. Onto this substrate we dosed 1 ML C_{60}, again at 300 K, as shown in figure 1. It has been shown that the silicon oxide surface is inert
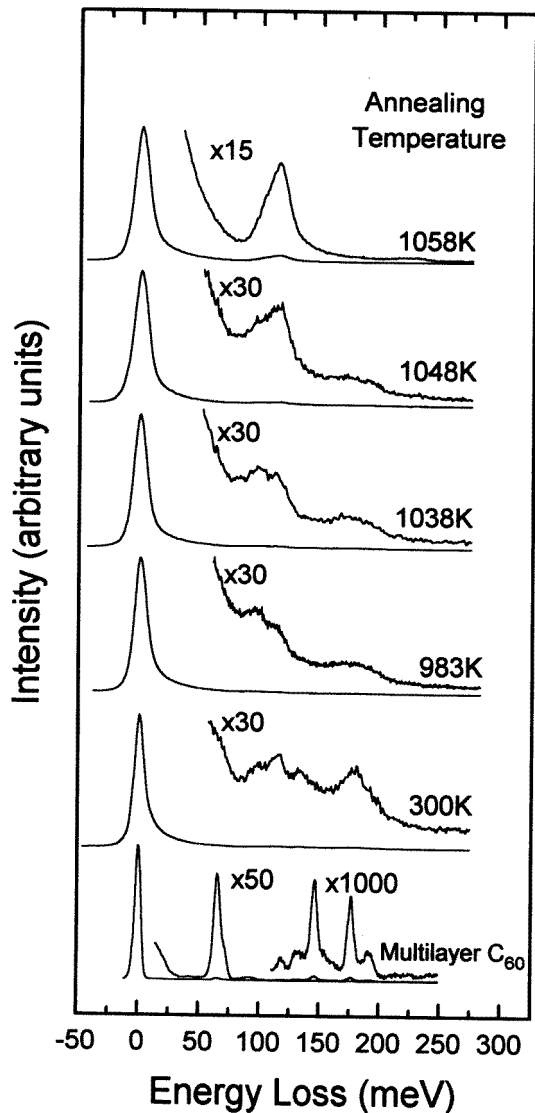
Figure 2. HREEL spectra from 1 ML of C_{60} on Si(100)–2 × 1 as a function of annealing temperature compared to that from a C_{60} multilayer. Spectra were obtained at a primary energy of 8 eV in the specular geometry and are normalized to elastic peak intensity.

to C_{60} adsorption [20] and our EEL spectra, exactly the same as those from a thick C_{60} film [6, 18, 19], confirm this. The positions of the energy loss features in the monolayers on both the clean and oxidized silicon surfaces are the same, but the lowest energy transition is narrower and more well defined for the latter.

The C_{60} monolayers on both the clean and oxidized silicon surfaces are disordered (no LEED pattern was visible), so that difference in the peakshape of the HOMO–LUMO excitation cannot be explained in terms of symmetry breaking due to disorder. Given that

changes in the Si LVV Auger peakshape also occur upon fullerene adsorption on the clean surface (attributed to carbon–silicon bonding [9]) it seems likely that a weak chemisorption, rather than physisorption [15], bond forms between the clean Si(100) substrate and the adsorbate.

Upon annealing a C_{60} monolayer to 873 ± 10 K dramatic changes are observed to occur in the energy loss spectrum, figure 1. A strong broadening of all the observed electronic transitions occurs and in particular the HOMO–LUMO transition is completely washed out. A new feature appears as a shoulder at about 2.6 eV, and a broad peak centred at about 4.8 eV, close to a transition of multilayer C_{60} (4.7 eV), is also visible. The large alteration in the electronic structure measured from the surface cannot be explained in terms of a decrease of the C_{60} signal with respect to a modified substrate signal because Auger spectra (discussed below) show that, for this temperature, no significant C_{60} desorption occurs. Nor can the changes at this temperature be attributed to opening of the C_{60} cage for which Auger spectra and STM [14, 15] indicate the requirement of a higher annealing temperature. In the absence of desorption or fragmentation we are therefore left with a change in the nature of the surface–adsorbate bond as an explanation for the temperature-induced changes in electronic structure.

Annealing the C_{60} monolayer to temperatures below 1048 ± 10 K does not lead to any further significant change in the surface electronic structure, as evidenced by the spectra in figure 1. However, for anneals at or above this temperature major changes in electronic structure, accompanied by significant desorption (see below), occur. The most notable point about the spectra for the high-temperature anneals is that they are essentially the same as those from silicon contaminated by carbon from the residual gases of the chamber. This observation coincides with a point made previously [9] that after fragmentation of C_{60} on a Si(100)–2 × 1 surface the remaining carbon behaves in the same manner as 'contamination'.

The chemical interaction between C_{60} and Si(100)–2 × 1 (and the absence of interaction on the oxidized surface) is further illustrated by lineshape changes of the Si LVV and C KLL peaks under C_{60} adsorption. Changes in Auger spectra for C_{60} adsorption on clean Si(100)– 2 × 1 and Si(111)–7 × 7 have already been addressed by Hamza and Balooch [9, 10], and we shall therefore limit discussion to a brief consideration of changes in relative intensities of carbon and silicon Auger peaks as a function of annealing temperature.

Upon annealing the sample above 1048 ± 10 K significant alterations to the Auger spectra occur. Strong desorption of C_{60} or molecular fragments is evidenced by a significant reduction in the ratio between the C KLL and Si LVV Auger peaks. In an AES study of C_{60} fragmentation on Si(100)–2 × 1, Hamza and Balooch [9] observed initial fragmentation only at higher annealing temperatures than those reported here. This apparent discrepancy can be explained by kinetic limitations to the cage opening process: at 1048 ± 10 K the cage breaking rate may be high enough to produce a detectable change over a period of 300 s but not over, say, 5 s. Kinetic limitations to the desorption of C_{60} fragments may also lead to the shape of the plot of carbon/silicon peak ratio to annealing temperature previously observed [9], which we did not reproduce: rapid sample cooling may trap C_{60} fragments, of higher carbon density than the intact molecules, on the surface. These fragments will then suppress the Auger signal from the substrate leading to the reported curve.

HREEL spectra as a function of annealing temperature are presented in figure 2. There are two particularly strong differences between the spectra from the multilayer film and that of the monolayer adsorbed on silicon. In the multilayer spectrum there is a strong peak centred at 66 meV due to two closely spaced dipole-active vibrational modes. These modes appear as a weak shoulder, less intense than the other modes, in the spectrum of the C_{60} monolayer. The disorder in the monolayer film will reduce the intensity of dipole-

active modes with respect to dipole-forbidden modes, but off-specular spectra from ordered films [17, 18] suggest that the intensities of dipole-active and forbidden modes should be comparable.

Suto *et al* [7] have seen a much stronger loss associated with the 66 meV dipole-active peak of submonolayers of C_{60} on Si(100)–2 × 1, which could be a result of differences in coverage calibration or a resonance effect [21, 22] due to different incident beam energies.

The monolayer spectrum also exhibits a strong peak at 109 meV not readily apparent in pristine C_{60} films [3, 6, 18, 19] and which appears to be associated with the interface region [7]. This peak cannot be attributed to either C or H contamination of the silicon surface, nor to contaminants arising from the residual gases in the vacuum chamber (the relative intensity of this peak does not change with time), and may therefore be a mode of the C_{60} cage with intensity enhanced by the substrate–adsorbate bond or cage distortion induced by it.

Annealing to temperatures above 873 ± 10 K produces a strong reduction in the intensity of the feature at 109 meV compared to that at 94 meV, reflecting the change in the surface–molecule bond suggested above. The broad vibrational band between 150 and 200 meV is characteristic of the modes of sp^2 bonded carbon networks—graphite [23] and the fullerenes [3, 6, 7, 8, 18, 19, 22]—and provides an indication that cage fragmentation has not yet occurred at this temperature.

Increasing the temperature to 1038 K leads to the growth of a peak at 112 meV, to almost the same strength as that at 94 meV. This frequency is that of the C–Si bond in surface silicon carbide obtained by pyrolysis of either CO [24] or C_2H_4 [25], which demonstrates that the C_{60} molecules are beginning to be destroyed by the annealing process and break up into individual carbon atoms which form bonds with the surface. The relative intensity of this mode increases with anneal temperature whilst that of all the other modes decreases, a result of the increasing rate of cage breakup. When a temperature of 1058 ± 10 K is reached all evidence of the C_{60} derived modes vanishes leaving only the Si–C mode and its overtone band (about 220 meV). Destruction of C_{60} and formation of a 'surface' silicon carbide accords with the electronic excitation spectra discussed above—when the fullerene molecules break up they leave behind a surface carbide similar to that formed by pyrolysis of other carbon containing molecules.

In conclusion, it has been shown that when C_{60} is deposited on a Si(100)–2 × 1 surface at 300 K its electronic and vibrational structure is only weakly perturbed, consistent with 'weak chemisorption'. Upon annealing to 873 K, changes in the electronic structure and vibrational density of states of the adsorbed molecules indicates that a change in surface–molecule bonding occurs, without the destroying of the C_{60} cage structure, forming what may be regarded as a chemisorbed 'precursor' to fragmentation. Further annealing to 1048 K and beyond leads to cage breaking and significant carbon desorption, leaving behind a surface layer of SiC.

References

[1] Balooch M and Hamza A V 1994 *J. Vac. Sci. Technol.* B **12** 3218
[2] Meilunas R J, Chang R H, Liu S and Kappes M 1991 *Appl. Phys. Lett.* **59** 3461
[3] Gensterblum G, Pireaux J J, Thiry P A, Caudano R, Vigneron J P, Lambin Ph, Lucas A A and Krätschmer W 1991 *Phys. Rev. Lett.* **67** 2171

[4] Li Y Z, Chander M, Patrin J C, Weaver J H, Chibante L P F and Smalley R E 1992 *Phys. Rev.* B **45** 13 837
[5] Hashizume T, Wang X-D, Nishina Y, Shinohara H, Saito Y, Kuk Y and Sakurai T 1992 *Japan. J. Appl. Phys.* **31** L880
[6] Lucas A A, Gensterblum G, Pireaux J J, Thiry P A, Caudano R, Vigneron J P, Lambin Ph and Krätschmer W 1992 *Phys. Rev.* B **45** 13 694
[7] Suto S, Kasuya A, Ikeno O, Horiguchi N, Achiba Y, Goto T and Nishina Y 1993 *J. Electron Spectrosc. Relat. Phenom.* **64/65** 877
[8] Suto S, Kasuya A, Ikeno O, Hu C-W, Wawro A, Nishitani R, Goto T and Nishina Y 1993 *Japan. J. Appl. Phys.* **33** L1489
[9] Hamza A V and Balooch M 1993 *Chem. Phys. Lett.* **201** 404
[10] Balooch M and Hamza A V 1993 *Appl. Phys. Lett.* **63** 150
[11] Xu H, Chen D M and Creager W N 1993 *Phys. Rev. Lett.* **70** 1850
[12] Chen D, Chen J and Sarid D 1994 *Phys. Rev.* B **50** 10 905
[13] Wang X-D, Hashizume T, Shinohara H, Saito Y, Nishina Y and Sakurai T 1992 *Japan. J. Appl. Phys.* **31** L983
[14] Chen D and Sarid D 1994 *Phys. Rev.* B **49** 7612
[15] Chen D and Sarid D 1995 *Surf. Sci.* **329** 206
[16] Cepek C, Goldoni A and Modesti S 1996 *Phys. Rev.* B **53** at press
[17] Hunt M R C 1995 *PhD Thesis* University of Cambridge
[18] Hunt M R C, Modesti S, Rudolf P and Palmer R E 1995 *Phys. Rev.* B **51** 10 039
[19] Modesti S, Cerasari S and Rufolf P 1993 *Phys. Rev. Lett.* **71** 2469
[20] Moalem M, Balooch M, Hamza A V, Siekhaus W J and Olander D R 1993 *J. Chem. Phys.* **99** 4855
[21] Palmer R E and Rous P J 1992 *Rev. Mod. Phys.* **64** 383
[22] Hunt M R C and Palmer R E 1996 *Surf. Rev. Lett.* **3** at press
[23] Oshima C, Aizawa T, Souda R, Ishizawa Y and Sumiyoshi Y 1988 *Solid State Commun.* **65** 1601
[24] Froitzheim H, Köhler U and Lammering H 1984 *Phys. Rev.* B **30** 5771
[25] Widdra W, Huang C, Briggs G A D and Weinberg W H 1993 *J. Electron. Spectrosc. Relat. Phenom.* **64/65** 129