C_{60}-terminated Si surfaces: Charge transfer, bonding, and chemical passivation

P. Moriarty, M. D. Upward, A. W. Dunn, Y.-R. Ma, and P. H. Beton
Department of Physics, University of Nottingham, Nottingham NG7 2RD, United Kingdom

D. Teehan
Daresbury Laboratory, Daresbury, Warrington, Cheshire WA4 4AD, United Kingdom
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The interaction of C_{60} with the Si(111)-(7×7) and Si(100)-(2×1) surfaces has been investigated using synchrotron radiation core-level and valence-band photoelectron spectroscopy. C_{60} induces distinct spectral changes in the Si-$2p$ core-level emission from both surfaces, indicative of charge transfer to the adsorbed fullerene molecules. Our results suggest that C_{60} adsorption on Si(111) induces a redistribution of charge within the (7×7) unit cell involving electron transfer from rest atom to adatom dangling bonds. For a one monolayer coverage [on both Si(111) and Si(100)], broad C_{60}-induced chemically shifted components are present in the core-level spectra. Valence-band spectra, however, show no evidence for a high degree of electron occupation of the C_{60} lowest unoccupied molecular orbital. We present core-level data which illustrate that adsorption of a C_{60} monolayer inhibits ambient oxidation of the Si surface. [S0163-1829(98)03901-0]

I. INTRODUCTION

Fullerite, the bulk form of C_{60}, is a molecular solid in which bonding arises from weak van der Waals forces. The energy levels of individual molecules are therefore only weakly perturbed and the electronic structure of the solid is primarily determined by intramolecular covalent bonding. Photoelectron spectra from C_{60} molecules in the solid or gas phase therefore exhibit very similar spectral features.[1] In contrast, adsorption of C_{60} on metal and semiconductor surfaces may give rise to strong chemisorption bonds and a corresponding alteration of the molecular electronic structure. These changes in bonding and electronic structure may in turn be directly probed using photoelectron spectroscopy. Ohno *et al.*[2] have examined the interaction of C_{60} with metal and GaAs(110) surface using a combination of core-level, valence-band, and inverse photoemission. For adsorption on a range of metal surfaces, C_{60}-induced changes in the C-$1s$ core-level energy and line shape arose from a charge transfer from states near the metal Fermi level to the lowest unoccupied molecular orbital (LUMO). Considerable broadening of the C-$1s$ core level and its associated π-π^* shakeup features was observed, indicating a strong C_{60}-surface interaction.

The nature of the bonding between C_{60} and a solid surface may also be investigated by examining the effects of fullerene adsorption on the *substrate* core-level photoelectron spectra. Deposition of C_{60} on GaAs(110) was found not to affect the line shape of the As-$3d$ or Ga-$3d$ core levels.[2] This suggests a lack of chemical bonding and thus very weak C_{60}-surface interaction. In contrast, C_{60} adsorption on a number of metal surfaces causes a distinct modification of the core-level spectra, indicative of a strong chemisorption process.[2–4] Valence-band spectroscopy has been used to provide complementary information on the bonding and electronic structure of C_{60} submonolayers and monolayers including, for example, data on molecule-surface energy-level alignment[2] and molecular band occupancy.[2,5]

In this paper we present photoelectron spectroscopy data on the interaction of C_{60} with Si(111)-(7×7) and Si(100)-(2×1) surfaces. While a considerable amount of work on the structural properties of C_{60} submonolayers and monolayers on Si surfaces has been carried out using scanning tunneling microscopy (STM), very little direct information on the nature of the chemical bonds formed in these systems is available. We present a detailed analysis of the changes induced in Si-$2p$ core levels by the adsorption of C_{60} on Si(111) and Si(100) surfaces. For both surfaces our results may be explained by the chemisorption of C_{60} molecules via a charge transfer from Si atoms. However, valence-band spectra from C_{60} monolayers do not show any emission at the Fermi level, indicating that there is little occupation of the LUMO band. In addition, the possible application of C_{60} monolayers as passivating films for Si surfaces has been investigated by examining photoemission spectra following exposure of a monolayer-terminated Si surface to atmosphere.

II. EXPERIMENT

The core-level and valence-band photoemission experiments were carried out on beam line 6.1 of the synchrotron radiation source, Daresbury, U. K. The synchrotron radiation was monochromatized by a 1200 lines/mm blazed grating and the energy distribution of the emitted photoelectrons measured using a hemispherical analyzer. Photon energies of 120 and 140 eV were chosen for Si-$2p$ core-level analysis with an overall instrumental resolution at those energies of approximately 0.3 eV. The core-level spectra were curve-fitted with spin-orbit-split Voight (a Gaussian convolved with a Lorentzian line shape) components using a nonlinear least-squares fitting routine.[6]

Preparation of clean Si(111)-(7×7) and Si(100)-(2×1) surfaces involved sample degassing at 600 °C for 8–12 h, followed by brief (''flash'') annealing at 1250 °C for 15–30 s. The sample temperature was monitored using an infrared

pyrometer and the pressure kept below 2×10^{-9} Torr during flashing. Surface order and cleanliness were determined from low-energy electron diffraction and the silicon surface core-level and valence-band spectra. C$_{60}$ (>99.9% purity) was sublimed from a resistively heated Ta envelope onto the Si surface (at room temperature). A chromel-alumel thermocouple was spot welded directly to the Ta envelope to monitor the C$_{60}$ source temperature.

An initial calibration of the evaporation rates for the source was carried out prior to the photoemission experiments in a separate system which housed a UHV STM.[7] An analysis of STM images enabled a direct estimate of surface coverages resulting from various source temperatures and deposition times. The source-sample geometry and source operating conditions in the photoemission UHV system were similar to those used in the STM system.

A second method used to estimate (submonolayer) C$_{60}$ coverages involved analysis of the decay of the bulk Si core-level intensity as a function of coverage. For Si samples with a multilayer C$_{60}$ coverage, annealing at temperatures in the 200–300 °C range results in the desorption of C$_{60}$ above the first monolayer.[8] Note that we define a C$_{60}$ monolayer as a complete single layer of fullerene molecules on the Si surface [and not as the molecular density with respect to the ideal (bulk-terminated) Si(111) or Si(100) surface]. For example, for Si(111)-(7×7), at 1 ML coverage there are 7 C$_{60}$ molecules per (7×7) unit cell[9] (i.e., 1.1×10^{14} molecules cm^{-2}). Similarly, for Si(100), assuming $c(4 \times 4)$ ordering of C$_{60}$ at a 1 ML coverage,[10] there are 0.25 molecules per (2×1) unit cell (8.5×10^{13} molecules cm^{-2}).

We have used the intensity ratio between the bulk component of the Si-2p core level from the clean and the C$_{60}$ monolayer-terminated surface to evaluate the electron escape depth. Taking this value (which we estimate as 7.8 ± 0.5 Å for 35 eV electrons) and assuming a Bier's law-dependent drop in the intensity of the bulk Si component as the C$_{60}$ coverage increases to 1 monolayer, enables a determination of submonolayer coverages. The value for the escape depth that we estimate is slightly larger than that determined in previous studies.[11,12] This may possibly be related to defects and vacancies in the C$_{60}$ monolayer, as discussed below. However, we find that the coverages determined using this method agree well with the values expected from the STM-based calibration of the source.

III. RESULTS AND DISCUSSION

A number of recent scanning tunneling microscopy (STM) studies have focused on the bonding sites and ordering of C$_{60}$ molecules deposited onto Si(111) and Si(100) surfaces.[13–20] Both Wang *et al.*[13] and Chen and Sarid[14] found that for room-temperature adsorption on Si(111)-(7×7), C$_{60}$ molecules are randomly distributed across the substrate exhibiting no tendency to bond at step edges or defects nor to coalesce to form islands. The strong molecule-surface interaction implied by these observations was proposed to arise from charge transfer from the adatoms of the Si(111)-(7×7) reconstruction to the C$_{60}$ LUMO. STM images showing a reduction in the local density of states for adatoms located close to the adsorbed molecules provided evidence for Si-C$_{60}$ charge transfer.
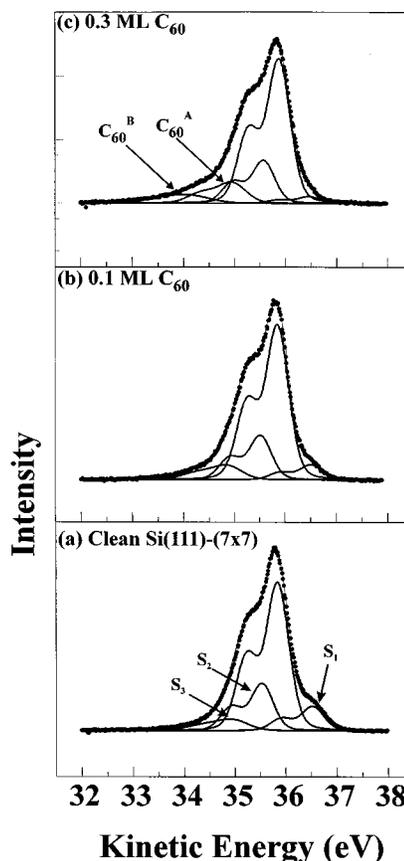
FIG. 1. Si 2p core-level spectra for the (a) clean Si(111)-(7×7) surface, (b) the (7×7) surface with a 0.1 ML coverage, and (c) with a 0.3 ML coverage. The photon energy was 140 eV for all spectra.

Although deposition of C$_{60}$ on Si(100)-(2×1) also results in a random distribution of molecules indicating that the molecular mobility at room temperature is small, it has recently been argued that the C$_{60}$-Si(100) and C$_{60}$-Si(111) interactions are fundamentally different.[15–17] A model based on a physisorption mechanism involving dipole-dipole interactions (and negligible charge transfer) between C$_{60}$ molecules and Si(100) surface dimers has been proposed.[15] This model suggests that the strength of the C$_{60}$-Si(100) surface bonding is of the same order of magnitude as the van der Waals interaction in the fullerite crystal. Klyachko and Chen[16] have recently further developed this model to account for the uniaxial incommensurate C$_{60}$ overlayers they observed on Si(100) and Ge(100) surfaces.

In the following, we detail the Si-2p core-level changes induced by C$_{60}$ adsorption on Si(111)-(7×7) and Si(100)-(2×1) surfaces. For both surfaces, the modification of the core-level line shape and the observation of an intense chemically shifted component following C$_{60}$ deposition strongly suggests that in each case the molecules are chemisorbed.

C$_{60}$/Si(111)-(7×7): Submonolayer coverages

Figure 1 shows the Si-2p core-level spectrum acquired with a photon energy of 140 eV for the Si(111)-(7×7) surface and also illustrates the changes induced following ad-

TABLE I. Core-level fitting parameters for the Si-2p spectrum from the Si(111)-(7×7) surface.

Gaussian width	0.45 eV
Lorentzian width	0.09 eV
Spin-orbit splitting	0.602 eV
Branching ratio	0.498
S_1 (Δ BE)	−0.69 eV
S_2 (Δ BE)	+0.31 eV
S_3 (Δ BE)	+0.90 eV

sorption of submonolayer C_{60} coverages. The fitting parameters for the spectrum from the clean (7×7) surface [Fig. 1(a)] are listed in Table I. To achieve the best fit to the experimental data, four Voight curves, the bulk and three surface core-level shifted (SCLS) components, were necessary. Very high resolution (~70 meV) Si-2p spectra from the Si(111)-(7×7) surface have been obtained by Karlsson *et al.*[21] where five surface components were resolved in the core-level data. With much lower (~300 meV) resolution the spectra may be fitted with only three surface components as shown in Fig. 1(a) and also found by a number of other groups.[22,23]

The SCLS components in Fig. 1(a) are labeled S_1, S_2, and S_3. S_1 is shifted to lower binding energy (BE) [corresponding to higher kinetic energy in Fig. 1(a)] with respect to the bulk peak by 0.70 eV and may be identified with the rest atoms of the (7×7) reconstruction following the work of Karlsson *et al.*[21] The shift to lower binding energy has been explained in terms of a charge transfer from the (7×7) unit-cell adatoms to the rest-atom dangling bonds. This results in fully occupied (lone pair) states associated with the rest atoms, while the adatom dangling bonds are almost empty. Karlsson *et al.*[21] attributed a peak at +0.53 eV BE to core-level emission from adatoms, and, in addition, resolved a component at +0.24 eV which they proposed arose from second layer pedestal atoms. The poorer resolution associated with the spectrum shown in Fig. 1(a) leads to an inability to separate the adatom and pedestal-related curves. As was the case for the (7×7) Si-2p core-level analysis reported by Poncey *et al.*[22] the adatom and pedestal contributions are accounted for by a SCLS contribution at +0.3 eV BE (labeled S_2) and the bulk component. A third broad [Gaussian full width at half maximum (FWHM)=0.88 eV] SCLS component, S_3, at +0.9 eV is required to provide a good fit to the "tail" on the high BE side of the spectrum. Although a number of groups have also observed a similar weak feature in Si-2p spectra from the (7×7) surface,[24–26] its precise origin has not been determined to date.

While the energies of the SCLS components in the spectrum shown in Fig. 1(a) are in excellent agreement with earlier (7×7) Si-2p core-level analyses, the relative intensities of the S_1 and S_2 components are somewhat larger (S_1/S_2 ~0.45) than that reported in a number of previous studies.[27–29] It is important to note, however, that a range of values for this ratio [ranging from 0.10 (Ref. 27) to 0.33 (Ref. 28)] have been quoted. It might be argued that the difference in the rest-atom component intensity between the present study and earlier work is related to surface contamination or defects. However, it has been shown that very
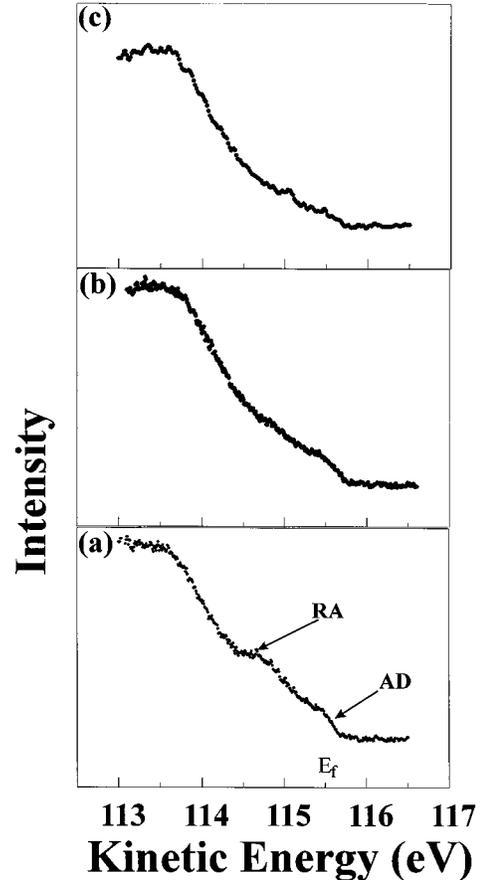
FIG. 2. Valence-band spectra from the Si(111)-(7×7) surface. (a) Spectrum from the clean surface prior to C_{60} deposition, (b) following 0.1 ML C_{60} deposition, and (c) 0.3 ML C_{60} deposition. The photon energy was 120 eV for all spectra.

small amounts of surface contamination[22,30] can completely remove the adatom contribution at the Fermi level. The valence-band spectrum shown in Fig. 2(a) clearly exhibits the adatom- and rest-atom-related features expected for the clean (7×7) surface.[22,23] The valence-band contribution due to the partially filled adatom dangling bonds appears as an edge (labeled AD) crossing the Fermi level, while the rest-atom state (labeled RA) is visible as a shoulder approximately 1 eV higher in binding energy. The sharpness of the Fermi edge observed in Fig. 2(a) would suggest that an appreciable amount of surface contamination was not present.

Considerable changes in both the core-level and valence-band spectra occur following the deposition of submonolayer coverages of C_{60} on the (7×7) surface. A comparison of Figs. 1(a) and 1(b) indicates that, following deposition of 0.1 ML C_{60}, the rest-atom-related core-level feature labeled S_1 is attenuated (and shifts slightly to +0.65 eV BE), while there would appear to be no significant change for peak S_2. There is a slight apparent increase in the intensity of the S_3 component—the origin of this increase is described below. The preferential attenuation of the rest-atom core-level component is mirrored in the valence-band spectrum where the shoulder at 0.8 eV below the Fermi level observed for the clean (7×7) surface [labeled RA in Fig. 2(a)] is barely visible in Fig. 2(b). Importantly, the Fermi edge due to the

partially filled adatom dangling bonds remains largely unaffected by the adsorption of 0.1 ML of C$_{60}$. Deposition of an additional 0.2 ML C$_{60}$ results in a further strong attenuation of the S_1 component (accompanied by an energy shift to +0.6 eV BE) in the core-level spectrum [Fig. 1(c)]. At this coverage (0.3 ML) a broad shoulder on the high BE side of the Si $2p$ peak is visible and is due to the presence of two C$_{60}$-induced components shifted by 0.95 eV (labeled C$_{60}^A$) and 1.9 eV (labeled C$_{60}^B$) from the bulk peak. There is no evidence of a rest-atom- or adatom-related feature in the valence-band spectrum following adsorption of 0.3 ML C$_{60}$ [Fig. 2(c)].

On first examination, our core-level and valence-band data would suggest that the C$_{60}$ molecules interact most strongly with the rest atoms of the (7×7) reconstruction. However, STM images of submonolayer C$_{60}$ coverages on Si(111)-(7×7) clearly show that the molecules are not adsorbed at rest-atom sites[13,14] but bond predominantly to sites close to the three midadatoms in either half of the unit cell.[14] These sites do not have a Si rest atom at their center. A plausible explanation for this apparent discrepancy between the STM and photoemission data is that C$_{60}$ adsorption induces a charge redistribution in the (7×7) unit cell. One possibility is that excess charge from the second layer Si rest atoms may be transferred back to the adatoms which are involved in bonding to a C$_{60}$ molecules. A rest-atom–adatom ''reverse'' charge transfer has also been proposed for the NH$_3$/Si(111)-(7×7) (Ref. 31) and K/Si(111)-(7×7) (Ref. 32) systems.

Two C$_{60}$-induced core-level components are clearly visible in Fig. 1(c) (labeled C$_{60}^A$ and C$_{60}^B$). The C$_{60}^A$ component (Gaussian FWHM: 0.76 eV) has a relative BE of +0.95 eV and therefore overlaps to some extent with the S_3 component of the clean (7×7) surface. This overlap causes the apparent increase in the intensity of the S_3 component following deposition of 0.1 ML C$_{60}$. The appearance of a component at higher binding energy is consistent with the charge transfer from Si surface atoms to the fullerene LUMO discussed above. A second very broad C$_{60}$-related component (Gaussian FWHM: 1.4 eV) C$_{60}^B$ is visible at a BE of +1.9 eV in Fig. 1(c) and is necessary to account for the tail on the high BE side of the spectrum. Finally, as expected, both the C$_{60}^A$ and C$_{60}^B$ components increase in intensity as the C$_{60}$ coverage increases (see section on monolayer C$_{60}$ coverage below).

Chemisorption of C$_{60}$ on Si(100)-(2×1)

Consensus on the structure of the Si(100)-(2×1) surface, following long-standing debate, has recently been reached. The low-temperature STM results of Wolkow[33] provided convincing evidence that the Si(100) surface dimers are asymmetric or ''buckled.'' Accompanying the buckling of the surface dimer is a charge transfer from the atom displaced towards the bulk (the ''down'' atom) to the atom moved towards the vacuum (the ''up'' atom). The ''up'' atom therefore acquires a net negative charge. Landemark et al.[34] decomposed the Si(100)-(2×1) Si-$2p$ core level into a bulk and three SCLS components (with a resolution of less than 70 meV). These components were attributed to the ''up'' dimer atom (at a relative BE of −0.49 eV), the ''down'' dimer atom (+0.06 eV relative BE) and second
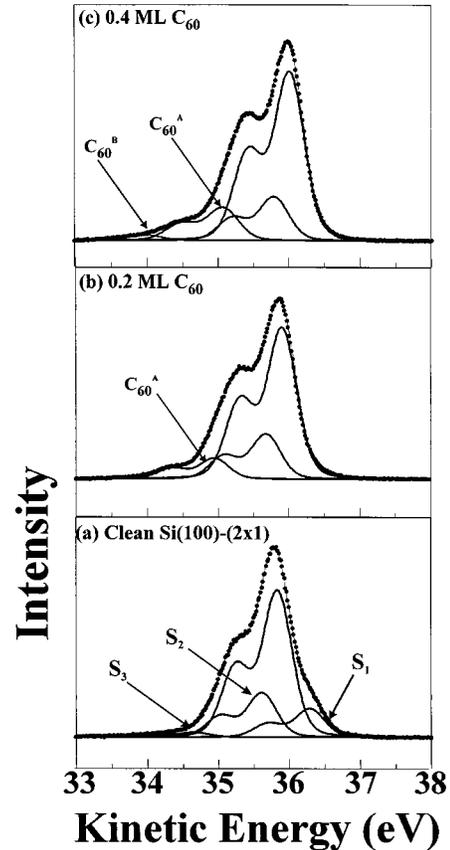
FIG. 3. Si $2p$ core-level spectra for the (a) clean Si(100)-(2×1) surface, (b) the (2×1) surface with a 0.1 ML coverage, and (c) with a 0.3 ML coverage. The photon energy was 140 eV for all spectra.

layer Si atoms (+0.22 eV relative BE). For the core-level experiments described in this paper the total instrumental resolution is approximately 0.3 eV. Therefore, while we can resolve the ''up'' atom and second layer components [labeled S_1 and S_2 in Fig. 3(a)], the ''down'' atom component is not resolved. In common with Poncey et al.,[22] we found it necessary to include a third broad component (S_3) to account for the tail on the low kinetic energy side of the spectrum. The fitting parameters for the clean Si(100)-(2×1) surface are shown in Table II.

Figure 3(b) shows the changes in the Si-$2p$ spectrum that occur following the deposition of 0.2 ML of C$_{60}$. The S_1 component is removed and a C$_{60}$-induced chemically shifted component (C$_{60}^A$) appears at 0.90 eV higher binding energy. As the coverage is increased to 0.4 ML, the C$_{60}$-induced

TABLE II. Core-level fitting parameters for the Si-$2p$ spectrum from the Si(100)-(2×1) surface.

Gaussian width	0.43 eV
Lorentzian width	0.09 eV
Spin-orbit splitting	0.599 eV
Branching ratio	0.501
S_1 (Δ BE)	−0.47 eV
S_2 (Δ BE)	+0.22 eV
S_3 (Δ BE)	+1.04 eV
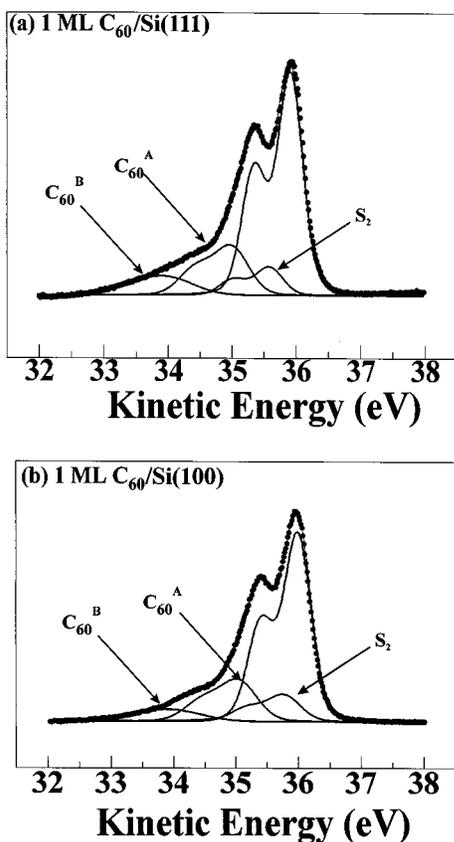
FIG. 4. Si $2p$ core-level spectra for a 1 ML C_{60} coverage on (a) the Si(111)-(7×7) surface and (b) the Si(100)-(2×1) surface. Photon energy=140 eV in both cases.

component increases in intensity and a second component (at +1.9 eV BE) related to C_{60} absorption (C_{60}^B) begins to appear. Interestingly, the binding energies of these C_{60}-related components are very similar to those for the Si(111)-(7×7) case. It is important to note that if C_{60} were physisorbed on the Si(100)-(2×1) surface as has been argued by a number of authors,[15–17] we would not expect to observe such significant changes in the Si-$2p$ core-level spectrum. The distinct spectral changes we observe for C_{60}/Si(100)-(2×1) indicate a strong valence electron charge redistribution consistent with a chemisorption of the fullerene molecules.

In an initial state picture, the shift to higher BE of the C_{60}-induced component is indicative of a charge transfer from the Si surface atoms to the adsorbed C_{60} molecules. While we cannot rule out the possibility of final-state or screening effects contributing to the measured C_{60}-induced core-level shift, it is important to note that C_{60} adsorption produces no change in the BE of the Si(100)-(2×1) S_2 component [see Figs. 3(a), 3(c), and Fig. 4]. As shown by Pehlke and Scheffler,[35] the 0.22 eV shift of the S_2 component is predominantly due to final-state screening effects. If C_{60} adsorption strongly modified the surface screening we might expect the BE of the S_2 component to change.

An alternative explanation for the C_{60}-induced core-level shift we observe is the formation of C_{60}-Si covalent bonds. In that case, the electronegativity difference between carbon and silicon atoms gives rise to an effective charge transfer from Si to C. We believe that covalent bond formation for room temperature C_{60} adsorption is unlikely since the magnitude of the core-level shift is much greater than that expected for C-Si covalent bonds.[28,36]

The disappearance of the S_1 component (arising from the "up" atom of the Si dimer) following deposition of only 0.2 ML of C_{60} is surprising. The average separation of molecules for a 0.2 ML coverage is approximately 60 Å (i.e., between 15 and 20 dimer sites). While we do not fully understand the complete removal of the S_1 component at a relatively low C_{60} coverage, the implication is that C_{60} adsorption is associated with relatively long-range dimer-dimer interactions. However, STM images of submonolayer coverages (~0.01 to 0.03 ML) of C_{60} on Si(100)-(2×1) indicate that the molecules are adsorbed between buckled dimer rows. If dimer buckling was induced by C_{60} adsorption, we should not observe a decrease in the intensity of the S_1 component.

Multilayer and monolayer C_{60} coverages

The Si-$2p$ core-level spectra for a 1 ML C_{60} coverage on Si(111) and Si(100) are shown in Figs. 4(a) and 4(b), respectively. In both cases there are two intense C_{60}-related components (C_{60}^A and C_{60}^B) at binding energies of +0.95 [Si(111)] and 0.90 eV [Si(100)] and +1.9 eV (both surfaces). In addition, in order to achieve satisfactory fits of the experimental data it was necessary to include the S_2 components (albeit with lower intensity) of the clean surface spectra. The retention of these clean surface-related features for C_{60} coverages of 1 ML indicates that fullerene adsorption does not induce a large amount of surface structural rearrangement. This result is in good agreement with x-ray diffraction[37] studies of thick C_{60} films on Si(111) and Si(100) which indicated that the (7×7) and (2×1) reconstructions were preserved at the fullerene-Si interface.

Multilayer films were grown by continuing the deposition of C_{60} until Si-$2p$ core-level emission was no longer observed. STM data indicates that for all low index Si surfaces[9,38,39] C_{60} molecules above the first (chemisorbed) monolayer interact via van der Waals forces and generally adopt the hexagonal close packing found in the bulk fullerite crystal.[9,10] A valence-band spectrum of a multilayer C_{60} film grown on Si(111) is shown in Fig. 5(a). [Multilayer C_{60} films grown on Si(100) produced identical valence-band spectra]. The spectrum shown in Fig. 5(a) is characteristic of thick C_{60} films and, as discussed by Weaver et al.,[40] the highest energy valence-band peaks may be attributed to π-related molecular orbitals [the HOMO and HOMO-1 bands, labeled in Fig. 5(a)], with lower-lying peaks related to more localized σ_p and σ_s-related orbitals.

Annealing of the multilayer sample at a temperature of 300 °C results in the desorption of the weakly bonded molecules above the first monolayer. C_{60} molecules in the first monolayer remain chemisorbed. The valence-band spectrum from a C_{60} monolayer, Fig. 5(b), consists of the molecular orbital features seen in Fig. 5(a) superimposed on the emission from the Si(111) valence band. We do not observe any emission at or near the Fermi level suggesting a very low electron occupation of the LUMO. This observation is in conflict with a number of estimates of the amount of Si(111)-C_{60} charge transfer based on both experimental[41] and theoretical[42] work. Yamaguchi[42] estimated that 3.35 elec-
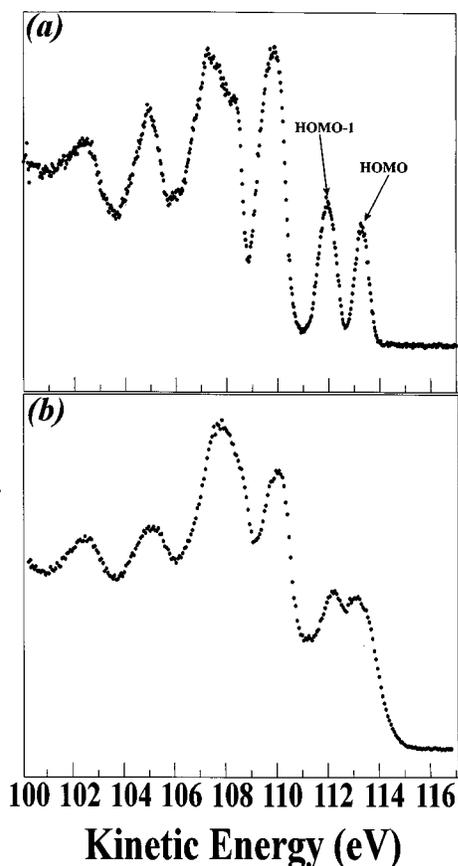
FIG. 5. Valence-band spectra from (a) a thick (bulklike) C$_{60}$ film on Si(111) and, (b) from a 1 ML C$_{60}$ coverage on Si(111). Photon energy=120 eV.

FIG. 6. The effects of exposure to atmosphere on the Si-2p core level from a C$_{60}$-monolayer terminated Si(111) surface. The uppermost spectrum is from a clean Si(111)-(7×7) surface exposed to air for 5 min.

trons, on average, were donated from the Si(111)-(7×7) surface atoms to the C$_{60}$ molecule. A transfer of approximately three electrons would result in the threefold degenerate LUMO being half-filled and, in the absence of electron-electron correlation effects, having metallic characteristics with a very high density of states at the Fermi level. Our valence-band spectra rule out a high degree of charge transfer and suggest that only fractional electronic charge is donated to the C$_{60}$ molecule from the Si(111) surface atoms.

As for C$_{60}$/Si(111), emission at the Fermi level was not observe for a C$_{60}$ monolayer on Si(100), again indicating that very little charge transfer occurs. This is in contrast to the tunneling spectroscopy measurements and theoretical calculations of Wang et al.,[43] which indicated that a C$_{60}$ monolayer on Si(100) was metallic. Günster et al.[44] have also found, using 21.2 eV photons from a He lamp, that the valence-band spectra for C$_{60}$ adsorbed on Si(100) do not exhibit any features relating to a high density of states at the Fermi level.

It is interesting to note that the position of the HOMO band at 2.1±0.1 eV below the Fermi level is the same for the multilayer and monolayer spectra [from both the C$_{60}$/Si(111) and C$_{60}$/Si(100) samples]. For C$_{60}$ adsorbed on Au surfaces[45] a 0.5 eV shift of the HOMO position was observed for a C$_{60}$ monolayer compared to a thick film. This shift was attributed to the difference in screening of the core hole for C$_{60}$ molecules in a bulklike environment and C$_{60}$ molecules at the

surface of the Au crystal. For the latter case the high degree of electron occupancy of the lowest unoccupied molecular orbital leads to an enhanced screening and thus a shift in the HOMO position towards lower binding energy. The lack of a HOMO shift for thick C$_{60}$ layers compared to a C$_{60}$ monolayer on the Si surfaces investigated in the present work indicates that there are no significant differences in screening for molecules in a bulklike environment or at a Si surface. This may in turn be directly related to the small degree of surface-molecule charge transfer suggested by the lack of a LUMO-related feature in the valence-band spectrum.

Ambient oxidation of C$_{60}$-monolayer-terminated surfaces

We have recently examined the effectiveness of a C$_{60}$ monolayer in providing a chemically unreactive termination of the Si(111)-(7×7) surface.[8] Our STM results showed that deposition of a single C$_{60}$ monolayer significantly inhibits corruption of the Si(111)-(7×7) surface by water and atmospheric oxygen. We have used photoelectron spectroscopy to provide complementary chemical information on the interaction of C$_{60}$/Si(111) with atmospheric oxygen. Figure 6 shows the evolution of the Si-2p core level with progressively longer exposure to atmosphere. (The spectra shown in Fig. 6 are for a sample that was repeatedly exposed to air for increasing periods of time). The uppermost spectrum [Fig. 6(v)] is, for comparison, from a clean Si(111)-(7×7) surface that was exposed to air for 5 min. In this spectrum, the broad peak located at approximately 4 eV lower kinetic energy than the bulk Si peak is due to SiO$_2$ (Ref. 46) arising from the formation of a native oxide layer.

Figure 6(i) is the core-level spectrum from the C$_{60}$ monolayer-terminated surface before exposure to atmosphere. Following exposure for 5 min, a comparison of Figs. 6(ii) and 6(v) indicates that the C$_{60}$ monolayer significantly inhibits oxidation of the Si surface. However, a small contribution to the spectrum due to SiO$_2$ formation is visible on the low kinetic energy side of the bulk Si-2p peak and this steadily grows in intensity as the sample is exposed to air for progressively longer periods. Following an exposure time of

1 h, a clear peak due to oxide formation is observed [Fig. 6(iv)]. Although not shown here, very similar core-level changes for the air-exposed C_{60} monolayer terminated Si(100) surface were observed. If the passivation mechanism for the C_{60} monolayer arises from the inability of air molecules to pass through the fullerene film,[8] the presence of areas where the ideal close packing of the molecules is disturbed will significantly degrade the protection of the underlying Si. This in turn suggests that the effectiveness of the C_{60} monolayer chemical passivation will be critically dependent on the degree of molecular ordering.

IV. CONCLUSIONS

The photoelectron spectroscopy data presented in this paper provide strong support for models of C_{60} adsorption on Si(111)-(7×7) and Si(100)-(2×1) involving chemisorption via Si-C_{60} charge transfer. A comparison of the photoemission data for C_{60}/Si(111)-(7×7) with previous STM studies suggests that C_{60} adsorption induces a charge redistribution in the (7×7) unit cell. We find that the amount of charge transfer for both the C_{60}/Si(111) and the C_{60}/Si(100) systems is significantly less than previously suggested. Finally, termination of both Si(111) and Si(100) with a C_{60} monolayer leads to a significant reduction in the Si surface oxidation rate.

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