Surface Science 603 (2009) 2896–2901

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

C_{60} submonolayers on the Si(1 1 1)-(7 × 7) surface: Does a mixture of physisorbed and chemisorbed states exist?

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ARTICLE INFO

Article history:
Received 12 June 2009
Accepted for publication 29 July 2009
Available online 4 August 2009

Keywords:
Silicon
C_{60}
Interface
Scanning tunnelling microscopy
Adsorption

ABSTRACT

We have carried out a combined X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy(UPS), and scanning tunnelling microscopy (STM) study of the C_{60}-Si(1 1 1) interaction where the XPS/UPS spectrometer and STM are integrated on a single UHV system. This enables a direct comparison of the XPS/UPS spectra with the STM data and eliminates any uncertainty in C_{60} coverage measurements. X-ray standing wave measurements and density functional theory calculations have been used to support and interpret the results of the XPS/UPS/STM experiments. Our data conclusively rule out models of C_{60} adsorption which involve a mixture of physisorbed and chemisorbed molecules [K. Sakamoto, et al., Phys. Rev. B 60 (1999) 2579]. Instead, we find that *all* molecules, up to 1 monolayer coverage, bond to the surface via Si–C bonds which are predominantly of covalent character.

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1. Introduction

There exists a significant body of literature covering the adsorption of C_{60} on the Si(1 1 1)-(7 × 7) surface. Although this work spans a range of both experimental and theoretical techniques – including scanning tunnelling microscopy (STM) [1–4], photoelectron spectroscopy [5–7], electron energy loss spectroscopy [8,9], surface X-ray diffraction [10], linear combination of atomic orbital theory [11], and density functional theory (DFT) [12,13] – complete consensus has, somewhat surprisingly, yet to be reached on the nature of the C_{60}/Si(1 1 1)-(7 × 7) interaction. Our understanding of this system has evolved considerably over the last eighteen years or so, with initial work suggesting that fullerene molecules bond to the Si(1 1 1)-(7 × 7) surface in a manner analogous to that observed on metal surfaces, i.e. via a transfer of substrate electrons into the lowest unoccupied molecular orbital (LUMO) of C_{60}. Subsequent photoemission spectroscopy measurements [5–7] showed that there was negligible LUMO occupation and prompted the proposal [6,7] that C_{60} is covalently bound to silicon surfaces. Lee and Kang [13], using DFT in the local density approximation, found that the C_{60}-Si(1 1 1) interaction is predominantly covalent in character. Earlier theoretical work by Sànchez-Portal et al. [12] indicated that covalent bond formation between C_{60} and the (7 × 7) surface is accompanied by a significant amount of charge transfer due to local hybridisation of the fullerene orbitals with Si(1 1 1) surface states. This is a rather different picture of charge transfer as compared to the LUMO filling proposed in early studies of C_{60} adsorption on Si(1 1 1)-(7 × 7).

This brief summary, however, somewhat simplifies the picture of the C_{60}/Si(1 1 1)-(7 × 7) interaction that at present emerges from the literature. There are two opposing schools of thought involving rather different interpretations of spectroscopic (largely photoemission) data. In a significant number of publications [7,14–19] it has been suggested that 1.00,0.00,0.00 for deposition at room temperature onto both Si(1 1 1)-(7 × 7) and Si(1 0 0)-(2 × 1), C_{60} chemisorbs only up to a relatively low submonolayer coverage. For the Si(1 1 1)-(7 × 7) surface this coverage is ~30%. Sakamoto et al. [17–19] argue that all fullerene molecules adsorbed above this threshold coverage are *physisorbed*. To date, and to the best of our knowledge, an explanation of the "quenching" of chemisorption above a 0.30 ML coverage has not been put forward. The alternative proposal [5,6,20,21] is that *all* fullerene molecules in a monolayer are chemisorbed and it has been suggested [20] that the apparent switch of the adsorption state from chemisorption

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doi:10.1016/j.susc.2009.07.043

to physisorption above a critical coverage arises from improper coverage calibration.

Given the continued interest in the exploitation of fullerene molecules as a core element of both fundamental and applied nanoscientific research, the precise adsorption state of C_{60} remains an important question to address. Through a combination of photoelectron spectroscopy and STM measurements, carried out on the same sample in the same UHV system, we show that there are significant differences in the He-I (21.2 eV) valence band spectrum for a 1 ML coverage of C_{60} on Si(1 1 1) we measure and that reported elsewhere [7,19]. In particular, we observe a significantly more intense spectral peak arising from Si–C bonding at close to 1 ML coverage than was found in these earlier studies. A non-linear least squares fitting analysis of the lineshapes of the highest occupied molecular orbital (HOMO)- and the next highest occupied molecular orbital (HOMO-1)-derived peaks in the valence band spectrum for coverages of 0.25 ML and 0.9 ML does not yield evidence for a coverage-dependent switch in the adsorption character of the C_{60} molecules. Despite the covalent bonding of buckminsterfullerene to the Si(1 1 1)-(7 × 7) surface, however, X-ray standing wave analysis reveals that C_{60} adsorption does not strongly perturb the positions of the underlying silicon atoms, in line with previous surface X-ray diffraction results [10].

2. Experimental

All combined photoemission-STM experiments were carried out within a multi-chamber ultra-high-vacuum (UHV) system supplied commercially (Omicron Nanotechnology GmbH). The preparation chamber (base pressure $\sim 1 \times 10^{-10}$ mbar) is equipped with a C_{60} evaporation source, a helium discharge tube as a source of ultraviolet (UV) photons, and a hemispherical electron energy analyzer (Scienta). A second, connected, chamber (base pressure $\sim 5 \times 10^{-11}$ mbar or better) is equipped with an Omicron low temperature STM-Qplus AFM instrument and can be isolated from the preparation chamber via a gate valve. Clean Si(1 1 1)-(7 × 7) surfaces with low defect densities are routinely prepared by sample degassing at 600 °C for 8–12 h, followed by a number of short flash anneal cycles at 1200 °C for 15–30 s using direct current resistive heating. The quality of the Si(1 1 1)-(7 × 7) surface reconstruction was examined using STM prior to any C_{60} deposition. C_{60} molecules (purity 99.9%) were sublimed, 1.00,0.00,0.00 at a rate of between 0.05 and 0.07 monolayers per minute, from a resistively heated Ta envelope onto the Si surface at room temperature. During evaporation the chamber pressure was kept below 1×10^{-9} mbar. The He-I resonance line (21.2 eV) was used to measure the valence band photoemission spectra of clean and C_{60}-adsorbed Si(1 1 1)-(7 × 7). The C_{60} coverage was directly measured using STM, by counting the number of adsorbed C_{60} molecules at sub-monolayer coverage on the Si(1 1 1)-(7 × 7) surface. All STM images shown in this paper were taken at 77 K in constant current mode using an electrochemically etched tungsten tip.

In addition to the combined photoemission and STM experiments in the home laboratory (Nottingham) we also carried out synchrotron radiation (SR) valence band photoemission spectroscopy and normal incidence X-ray standing wave (NIXSW) spectroscopy measurements of the positions of silicon atoms at the C_{60}/Si(1 1 1)-(7 × 7) interface. These measurements took place at the Daresbury synchrotron radiation source (SRS). The SR valence band photoemission measurements presented here were carried out at beamline 5U1 of the SRS. A 120 mm hemispherical analyser (PSP) was used and the spectra were acquired at 60 eV, the lower photon-energy limit of the beamline, with an energy resolution of 140 meV.

The C_{60}/Si(1 1 1) NIXSW data were taken during the final beamtime run at Station 6.3 of the SRS (before it was decommissioned). A Physical Electronics cylindrical mirror analyser was used to acquire photoelectron spectra on BL6.3. The UHV chamber had a high precision manipulator which incorporated an electron beam (e-beam) heater. C_{60} was initially deposited as a multilayer on the clean Si(1 1 1)-(7 × 7) surface after which the sample was annealed at 300 °C for 1 min to remove the physisorbed multilayer, leaving a monolayer of adsorbed C_{60} on the Si(1 1 1)-(7 × 7) surface (corresponding to 9.7×10^{13} molecules/cm^{-2}). The ratio of the C 1s and Si 1*s* peaks was taken to calibrate the deposition rate of the C_{60} source so that subsequent deposition of C_{60} could be controlled to produce an un-annealed monolayer.

NIXSW spectra were acquired by varying the photon energy using a double crystal monochromator with an InSb(1 1 1) crystal pair. The substrate was first oriented so that the reflectivity was maximised at the Si(1 1 1) Bragg backreflection energy (1977 eV). (Reflectivity curves were also acquired in parallel with the NIXSW spectra). The subsequent (1 1 1) standing wave spectra were obtained on by scanning the photon energy incrementally through the Bragg energy (while running the analyser in the constant initial state (CIS) mode) and measuring both the Si 1*s* core-level peak intensity at ~130 eV kinetic energy and the background, i.e. bulk, signal (at ~5 eV higher energy).

3. Results and discussion

3.1. Coverage-dependent valence band photoemission spectra

We show in Fig. 1 SR valence band spectra acquired with a photon energy of 60 eV for both a bulk-like fullerite film and a C_{60} monolayer on Si(1 1 1). The valence band spectrum for the 1 ML C_{60}:Si(1 1 1) sample is in good agreement with those published by, for example, Çepek et al. [6] and features the signature broadening of the highest occupied molecular orbital-derived peak (the lowest binding energy peak in the spectrum). Also shown are sim-

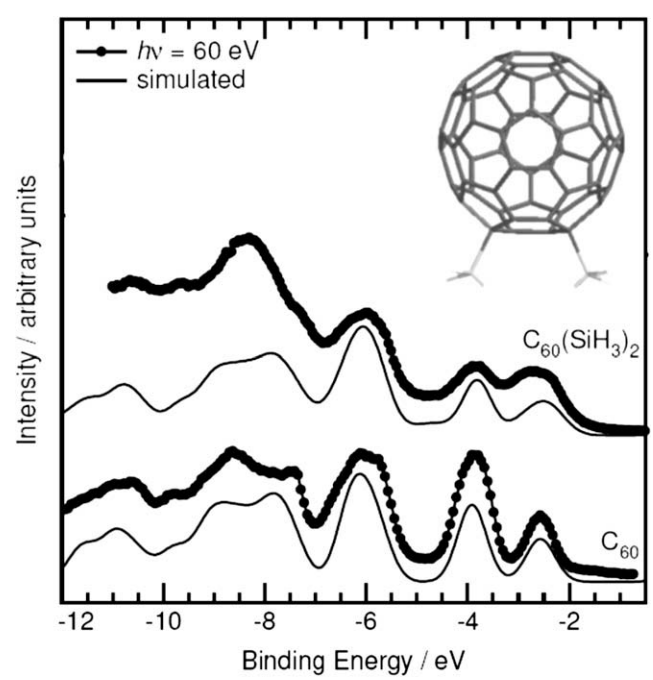

Fig. 1. Measured (closed filled circles) and simulated (solid line) valence band spectra for (lower spectra) a bulk C_{60} film and an isolated C_{60} molecule and (upper spectra) a 1 ML C_{60}:Si(1 1 1) sample and a simple cluster model of the C_{60}:Si interaction (see inset).

ulated spectra from a density functional theory (DFT) calculation (B3LYP with a 6-31G* basis set) which are the result of convolving the computed energy eigenvalue data with a Gaussian function of width 0.4 eV. Good agreement between the experimental and theoretical data is observed for a remarkably simple model of the C_{60}:Si system involving the attachment of two SiH_3 moieties to the fullerene cage (by breaking a single double bond – see inset to Fig. 1). The broadening of the HOMO peak for C_{60} adsorbed on Si(1 1 1), as first discussed by Sakamoto et al. [7], is reproduced remarkably well by the C_{60}:$(SiH_3)_2$ cluster, highlighting the key role that localised Si–C covalent bonds play in the adsorption process [12]. (We also observe good agreement between the relative intensities of the various features in the experimental valence band spectra and those in the calculated spectra. This is entirely fortuitous and largely arises from our choice of a photon energy of 60 eV for the acquisition of the experimental photoemission spectra shown in Fig. 1.)

For a direct comparison with earlier work, however, it is necessary to use He-I radiation for photoemission spectroscopy. Fig. 2 shows a set of valence band spectra for a Si(1 1 1)-(7 × 7) sample with progressively higher C_{60} coverage taken in the home laboratory with He-I radiation. Similar measurements have been reported elsewhere (e.g. [6,17]), to which we refer the reader. Nevertheless, a brief summary is useful. The spectrum of the clean Si(1 1 1)-(7 × 7) surface (Fig. 1a) is associated with three spectral features which originate from the adatoms, rest atoms and backbonds of the dimer-adatom-stacking fault (DAS) structure at ~0.2 eV (i.e. close to the Fermi level), 0.8 eV, and 1.7 eV, respectively [22]. At very low C_{60} coverages (~0.08 ML), the spectrum looks very similar to that of the clean surface but additional peaks attributed to the highest occupied molecular orbital (HOMO) and the second highest occupied molecular orbital (HOMO-1) of the C_{60} molecules start to appear around 1.8–2.5 eV and 3.2–3.4 eV, respectively, superimposed on the Si-related peaks (Fig. 2b). As the C_{60} coverage increases towards 1 ML, the fullerene-derived molecular orbital peaks progressively dominate over the Si-related peaks (Fig. 2c and d). For a coverage of 0.9 ML, the Si valence band features cannot be discerned.

The evolution of the spectral lineshape as a function of coverage is very much in line with the data published by Çepek et al. [6] but there are significant differences when one compares the measurements of Fig. 2 with the spectra reported by Sakamoto et al. [16–19]. These differences are most pronounced for the higher coverages. In particular, we do not see the pronounced dip between the HOMO and HOMO-1 features that is observed in, for example, Fig. 1 of Ref. [16]. In our case there is a very small error bar associated with measurement of the coverage of C_{60} as we simply count up the number of molecules observed in the STM images: a key advantage of a combined photoemission-STM study. We note that the 1 ML valence band spectrum reported in Refs. [7,16,18,19] is similar to that one would expect if the coverage of C_{60} were significantly greater than 1 ML. Our results therefore appear to confirm the suggestion, first put forward by Pesci et al. [20], that an improper coverage calibration explains the discrepancy between the valence band photoemission data published in Refs. [7,16,18,19] (and elsewhere) and that reported by other groups. We also note that a similar assertion regarding a mixture of physisorbed and chemisorbed molecules has been made for C_{60} adsorption on Si(1 0 0)-(2 × 1) [7], calling into question the mixed physisorption-chemisorption model also put forward for that surface.

For a C_{60} coverage of approximately 3.0 ML, the HOMO peak is located at 2.2 eV and is symmetric with a full-width-at-half-maximum of 0.5 eV. The HOMO-1 peak is located at a binding energy of 3.5 eV. For sub-monolayer and monolayer C_{60} coverages, and as observed in both Figs. 1 and 2, a significant broadening of the HOMO peak due to Si–C bond formation occurs as compared to that for the multilayer sample. In order to quantify the broadening and, thus, ascertain the contribution of the Si–C bonding-derived peak as a function of coverage, we have fitted the HOMO and HOMO-1 regions of the valence band spectra (following subtraction of a Tougaard background) for a 0.25 ML and a 0.9 ML C_{60} coverage (Fig. 3). Best fits are achieved for a separation between the

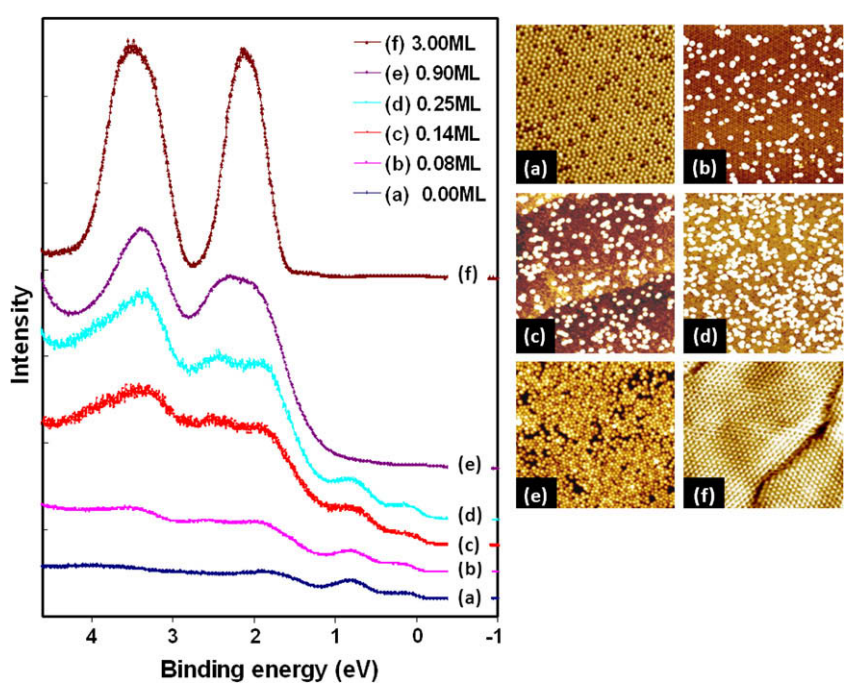

Fig. 2. UPS spectra and corresponding STM images for (a) 0; (b) 0.08 ML; (c) 0.14 ML; (d) 0.25 ML; (e) 0.90 ML; and (f) 3.0 ML coverage of C_{60} on Si(1 1 1)-(7 × 7). The UPS and STM data are taken from the same sample in each case.

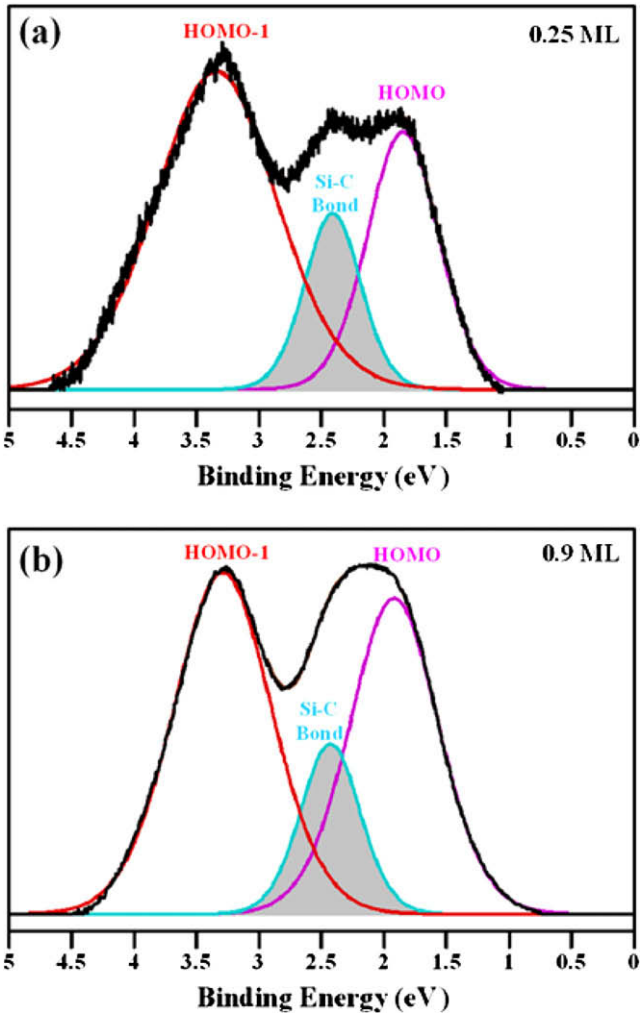

Fig. 3. The HOMO and HOMO-1 regions of the valence band spectra for C_{60}/Si(1 1 1)-7 × 7 for a coverage of (a) 0.25 ML and (b) 0.90 ML. The spectra have been decomposed, via non-linear least squares fitting, into three Gaussian peaks (following the subtraction of a Tougaard background) labelled HOMO, HOMO-1, and Si–C, arising from the highest occupied molecular orbital, the next highest occupied molecular orbital, and silicon–carbon bonds respectively.

HOMO peak and the Si–C related spectral feature of 0.5 ± 0.05 eV, in good agreement with the results of Çepek et al. [6].

Although detailed quantitative analysis of the contribution of the Si–C component for the 0.25 ML spectrum is somewhat problematic due to the contribution of the silicon valence band – specifically, back-bond related – photoelectrons, this is a relatively small effect. The key result arising from fitting the 0.25 ML and 0.9 ML coverage spectra is that the contribution of the Si–C derived peak to the valence band spectrum remains roughly constant as the C_{60} coverage increases from 0.25 ML to 0.9 ML. The integrated Si–C peak intensity at 0.25 ML comprises 14% of the integrated valence band spectral intensity; at 0.9 ML the integrated Si–C peak intensity is 15%. Notwithstanding the uncertainties due to the contribution of photoelectrons from the silicon substrate, the lack of significant change in the relative spectral weight of the Si–C component as a function of coverage is a clear indication that the adsorption character of C_{60} on Si(1 1 1)-(7 × 7) does not change with coverage. We certainly do not see the dramatic reduction in the contribution of the Si–C related spectral component expected if the majority of C_{60} molecules were physisorbed at 1 ML coverage.

3.2. NIXSW spectroscopy of the C_{60}/Si(1 1 1) interface

Sànchez-Portal et al. [12] have found, via DFT calculations, that the strong covalent interaction of C_{60} with the Si(1 1 1) substrate can promote substantial motion of the silicon atoms. Indeed, they note that, with regard to fullerene adsorption, the Si(1 1 1)-(7 × 7) substrate "appears quite soft". Similar behaviour was found in molecular dynamics simulations of C_{60} adsorption on Si(1 1 1) [23]. Comprehensive surface X-ray diffraction measurements by Hong et al. [10] have, however, also shown that the (7 × 7) reconstruction is largely preserved under the fullerene monolayer. Given that the combined photoemission and STM data in the previous section show that all (or the vast majority) of C_{60} molecules in a monolayer on Si(1 1 1)-(7 × 7) are chemisorbed, an interesting question relates to the extent to which this relatively strong interaction can perturb the positions of the (near) surface atoms. Our NIXSW experiments therefore focussed on attempting to observe the displacement of the near-surface silicon substrate atoms following C_{60} adsorption.

NIXSW, although a relatively new surface science tool, is a widely applied method for the determination of atomic and molecular positions [24–27] and can be applied both to adsorbates at surfaces and to atoms at buried interfaces. The technique exploits the backscattered wavefield which occurs at the Bragg condition for X-rays normally incident on a crystalline substrate. The illuminating and reflected X-rays interfere to produce a standing wave having a periodicity (in intensity) equal to that of the scattering planes. By varying the incident photon energy across a narrow range about the Bragg diffraction condition, the positions of the nodes of the standing wave can be adjusted with respect to the crystal lattice planes. Woodruff [27] provides a detailed review of the theory underlying the technique.

NIXSW has previously been applied to the investigation of the structure of both the clean Si(1 1 1)-(7 × 7) surface and its very many adsorbate-induced reconstructions [27]. In early NIXSW studies of the clean (7 × 7) surface, Durbin et al. [28] used a novel method of comparing the Si *LVV* and *KLL* Auger signals where, because of the different mean free paths, they could determine the difference in position of the surface and subsurface planes. They estimated a surface contraction of 0.5 Å. Their work pre-dates the discovery of Auger signal contamination from secondary electrons [29], however, and is generally discounted. Work by Patel et al. [30] used Ge as a "marker" for an investigation of the surface structure.

The only NIXSW study to date of the Si(1 1 1)-(7 × 7) surface that does not use a marker and in principle does not suffer from the effects of Auger contamination is that of Woicik et al. [35]. They used a method involving the separation of the total signal, T, into its surface, S, and bulk, B, components, $T = S + \alpha B$. By considering the total signal "ratioed" to the bulk signal, they argue that the division reduces the unknown bulk contribution to the measured NIXSW spectrum to a constant offset, α. This then means that any remaining surface signal will be devoid of bulk-like characteristics. Woicik et al. interpreted this residual signal as the adatom position of the 7 × 7 surface. They make the key and quite large assumption that the NIXSW Si 1*s* signal is dominated by the adatom contribution. Moreover, the quantitative reliability of the ratio-ing technique they put forward is questionable [33]. Here we shall not attempt to extract quantitative data via the ratio-ing technique but instead use it as a useful data manipulation tool to highlight differences between the clean Si(1 1 1)-(7 × 7) surface NIXSW spectrum and that for the 1 ML C_{60}/Si(1 1 1) sample.

Fig. 4 shows the NIXSW profile of the clean Si(1 1 1)-(7 × 7) surface derived from the Si 1*s* photoelectron signal. The bulk NIXSW signal, derived from measuring the background photoemission signal approximately 5 eV above the Si 1*s* core level emission peak, is

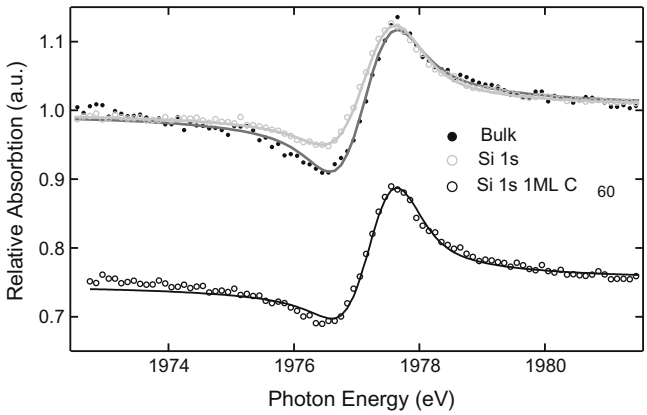

Fig. 4. Top: NIXSW profile of the clean Si(1 1 1)-(7 × 7) surface derived from Si 1*s* photoelectrons (open circles) with bulk signal (filled circles) overlaid. Bottom: Si 1*s*-derived NIXSW signal from a Si(1 1 1)-(7 × 7) surface with an adsorbed C_{60} monolayer (displaced by 0.25 for clarity).

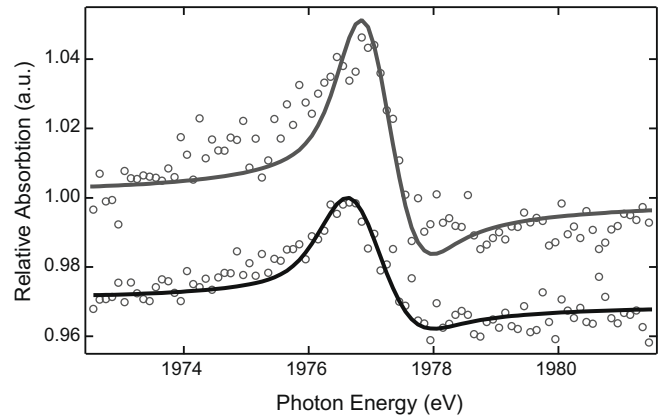

Fig. 5. Ratio-ed Si 1*s* NIXSW spectra for **top:** the clean Si(1 1 1)-(7 × 7) surface, and **bottom:** the 1 ML C_{60}/Si(1 1 1)-(7 × 7) surface (displaced for clarity). The solid line in each case represents the best fit to theory but is for illustrative purposes only (see text).

also shown in Fig. 4. The best fit for the bulk profile was obtained with $D = 0.97 \pm 0.04$ and $f_{co} = 0.68 \pm 0.05$ which are in agreement with the expected bulk values of 1 and 0.71, respectively. As described by Woicik et al. [34,35], the background photoemission signal is due to inelastically scattered electrons and hence contains information pertinent to the bulk crystal structure. The Si 1*s* electrons, however, contain information related to the near-surface region or, to be more precise, related to atoms within a distance comparable to the inelastic mean free path of the Si 1*s* electrons. Analysis of the Si 1*s* NIXSW signal reveals that the coherent distance and fraction are 1.04 ± 0.05 and 0.48 ± 0.05, respectively. These values are within experimental error of previous measurements made for Si(1 1 1)-(7 × 7) by Woicik et al. [35]. They are also in close agreement with Patel et al.'s [30] analysis of the top double layer and adatom co-ordinates which yielded values of $D = 0.96$ and $f_{co} = 0.42$. The work by Woicik et al. [35] pre-dates the general acceptance of non-dipolar effects on NIXSW measurements [36]. Systematic errors presented by the non-dipolar effects have been estimated by Lee et al. [37]. Their measurements and theoretical calculations suggest an asymmetry parameter, *Q*, of 0.1 for the Si 1*s* photoemission derived signal and that the error corrections for the structural parameters are $\Delta D = 0.04$ and $\Delta f_{co} = 0.02$, if non-dipolar corrections are omitted. These errors are below our experimental uncertainties.

From the NIXSW Si 1*s* signal for the 1 ML C_{60}:Si(1 1 1) sample (the lower spectrum in Fig. 4), it initially appears that there is little if any effect of fullerene adsorption on coherent fraction and distance. Thus, the surface silicon atoms apparently remain in positions identical to those of the clean Si(1 1 1)-(7 × 7) reconstruction. This apparent lack of difference is, however, due to the bulk signal swamping the rather subtle spectral changes that are occurring. If we employ the ratioing technique of Woicik et al. (i.e. we divide the total Si 1*s* NIXSW signal by the bulk signal) we remove all the signal that has bulk-like character and are left with a spectrum solely derived from non-bulk-like absorbers (with a concomitant reduction in signal-to-noise ratio due to the division of the two spectra). As shown in Fig. 5, a small, but distinct, change is observed in the ratio-ed spectrum when a monolayer of C_{60} is absorbed. This indicates that the surface silicon atoms are perturbed, but not strongly displaced, by the adsorption of the fullerene molecules. Note that if the (7 × 7) reconstruction were "lifted" by the adsorption of C_{60}, so that the silicon atoms at the interface were in bulk-like sites, we would expect the ratio-ed spectra to be constant, i.e. to exhibit no dependence on photon energy [35].

Our NIXSW results are therefore broadly in line with the surface X-ray diffraction data of Hong et al. [10]: fullerene adsorption perturbs the positions of silicon atoms at the Si(1 1 1)-(7 × 7) surface but this interaction is not sufficiently strong to remove the key structural components of the (7 × 7) reconstruction (adatoms, rest atoms, corner holes etc...). This is also clear from STM images of 1 ML C_{60}/Si(1 1 1)-(7 × 7) previously reported in the literature [3] where the relative positions of C_{60} molecules are fixed by the underlying (7 × 7) periodicity (and local (2 × 2) periodicity within each triangular sub-unit of the (7 × 7) unit cell).

4. Conclusions

A combination of STM and photoemission measurements has been used to address uncertainties remaining in the literature regarding the adsorption state of C_{60} on the Si(1 1 1)-(7 × 7) surface. We find no evidence for the 70:30 mixture of physisorbed to chemisorbed molecules which has previously been proposed for a 1 ML C_{60} coverage. Rather, our data are consistent with the chemisorption of all C_{60} molecules. Although chemisorption of C_{60} does not lift the (7 × 7) reconstruction, the adsorption of C_{60} on the Si(1 1 1)-(7 × 7) surface is sufficiently strong to cause detectable perturbation of silicon surface atoms, as measured using NIXSW spectroscopy.

Acknowledgements

We gratefully acknowledge very helpful discussions with Bruce Cowie and Christoph Stadler on the 'ratioing' method of NIXSW analysis and thank Rob Jones, University of Nottingham for providing the *XSWFIT* IGOR macro that was used as a test bed for subsequent analysis programs. We also thank the Engineering and Physical Sciences Research Council (ESPRC) for funding (under Grant GR/1880/01) and the Council for the Central Laboratories of the Research Councils (CCLRC) (now the Science and Technology Facilities Council) for the provision of beamtime at Daresbury SRS under awards 40021 and 37421. The Marie Curie Research Training Networks funding scheme (as part of Framework Programme 6) is gratefully acknowledged for funding (under Grant MRTN-005728, (PATTERNS)).

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