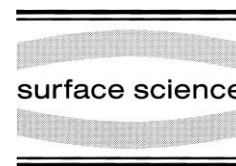




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Reconstruction dependent adsorption of C_{60} on GaAs(111)B

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Abstract

The interaction of C_{60} with the (2×2) and $(1 \times 1)_{LT}$ reconstructions of the GaAs(111)B surface has been studied using synchrotron radiation core-level and valence band photoemission. For the (2×2) phase, C_{60} adsorption produces no change in either the line-shape or the energy position of the Ga 3d and As 3d core-levels. In contrast, the As 3d photoelectron spectrum of the $(1 \times 1)_{LT}$ surface is considerably altered following the deposition of C_{60} . Our results indicate that the character of C_{60} adsorption may be changed from physisorption to chemisorption via variations in surface reconstruction and stoichiometry. © 1998 Elsevier Science B.V. All rights reserved.

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The adsorption, bonding and ordering of C_{60} on a solid substrate are strongly dependent on the nature of the electronic states at the surface. A number of experimental studies have shown that for a wide range of metal surfaces, the mechanism of C_{60} adsorption is a charge transfer from states at, or near, the Fermi level to the fullerene lowest unoccupied molecular orbital (LUMO) [1–3]. A strong chemisorption of the molecules therefore occurs. Analyses of scanning tunneling microscope (STM) images of submonolayer coverages of C_{60} on the Si(111)-(7 × 7) surface [4, 5] have suggested that a similar substrate–molecule charge transfer occurs. Recent photoelectron spectroscopy (PES) measurements have provided direct chemical infor-

mation on C_{60} -Si surface bonding, showing that for all low index Si surfaces, C_{60} adsorption induces distinct changes in the Si 2p core-level emission [6–8]. The PES data therefore corroborate the results of STM imaging [4, 9] and manipulation [7] experiments, indicating that C_{60} is chemisorbed on both the Si(111)-(7 × 7) and Si(100)-(2 × 1) surfaces. In contrast, C_{60} adsorption on GaAs(110)-(1 × 1), while leading to a shift of 300 meV in the energies of the substrate core-levels, produced no change in the Ga 3d or As 3d line-shapes [1]. The lack of modification of the core-level spectral shape implied that there was a very weak, predominantly van der Waals, interaction between C_{60} and the GaAs(110) surface [1].

In this paper, we discuss synchrotron radiation (SR) photoelectron spectroscopy (PES) spectra of GaAs(111)B surfaces before and after the adsorp-

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tion of C_{60} . Our results show that C_{60} is essentially physisorbed on the As-rich (2×2) reconstructed surface. Annealing of the clean (2×2) surface at 550°C results in the desorption of arsenic and the formation of Ga, in addition to As, dangling bonds. These changes in stoichiometry and reconstruction lead to a strong chemical interaction between adsorbed C_{60} and the GaAs(111)B surface.

The photoemission experiments were carried out on beam line 6.1 at the synchrotron radiation source (RS), Daresbury, UK. The synchrotron radiation was monochromatised using a blazed $1200 \text{ lines mm}^{-1}$ grating and the photoelectron spectra recorded with a hemispherical analyser. Photon energies of 80 and 100 eV were chosen for core-level and valence band spectroscopy. The latter photon energy provides maximum surface sensitivity with nearly identical cross-sections for the As 3d and Ga 3d core-levels. A non-linear least-squares fitting program was used to decompose the core-level spectra into their bulk and surface-related features assuming the Voigt profile (i.e. a Gaussian convolved with a Lorentzian line shape).

Arsenic-capped GaAs(111)B samples (with a 2° miscut) were used. Details on the growth and capping procedures may be found in Ref. [10]. The samples were indium-bonded to Mo plates, introduced to the ultra-high vacuum (UHV) chamber and then degassed at 200°C for 5–6 h. Increasing the temperature to 350°C caused the desorption of the As cap with a subsequent anneal at 400°C removing excess remnant amorphous As. Following the 400°C anneal, a (2×2) low-energy electron diffraction (LEED) pattern was visible. C_{60} was sublimed for a resistively heated Ta envelope on to the GaAs surface (which was held at room temperature). A chromel–alumel thermocouple, spot-welded directly to the envelope, provided a measure of the C_{60} source temperature.

An estimate of the exact C_{60} coverage resulting from an exposure period is problematic as the value of the sticking coefficient for C_{60} on GaAs(111)B is not known. We have calibrated the source for deposition rates on Si(111)-(7 \times 7) and Si(100)-(2 \times 1) surfaces [6], where, for coverages up to 1 monolayer (ML), the fullerene molecules interact strongly with the Si surface and form a complete chemisorbed monolayer. As discussed

below, our PES data suggest a much weaker C_{60} –GaAs(111)B interaction, and the determination of absolute C_{60} coverages is not possible from photoemission data alone. Exposure times, and not C_{60} coverages, are therefore quoted.

The structure of the (2×2) reconstruction of the GaAs(111)B surface is illustrated schematically in Fig. 1. A noteworthy feature of this reconstruction is the lack of Ga dangling bonds due to the presence of two layers of As at the surface [11]. The uppermost layer consists of As trimers arranged in a (2×2) periodicity and chemisorbed on an underlying complete layer of arsenic. The Ga 3d core-level spectrum (Fig. 2a) consists of only a single (bulk) component – there is no evidence of Ga-related surface core-level shifted (SCLS) components [12–14]. However, SCLS components are clearly resolved in the As 3d spectrum shown in Fig. 3a and are labelled S_1 , S_2 and S_3 .

While the S_1 and S_2 components visible in the spectra shown in Fig. 3 have been observed by a number of groups in core-level spectra from GaAs(111)B-(2×2) [12–14], we found it essential to include a third surface component (labelled S_3 in Fig. 3a) to fit the experimental data. Andersson et al. [15] have similarly decomposed the group V core-level from InAs(111)B-(2×2) and InSb(111)B-(2×2) surfaces into four components (the bulk and three surface core-level shifted peaks). They argued that the three core-level surface components arose from the three types of surface atom in the trimer model of the (2×2) reconstruction: the trimer atoms (giving rise to component S_1), the rest atoms (component S_2) and the second layer atoms directly beneath the trimers (component S_3). Our results are in general agreement with the analysis of Andersson et al. [15], although we note that in earlier work [13] with a very similar instrumental resolution, we did not require the presence of the S_3 component to provide a good fit to core-level data from the decapped GaAs(111)B surface. However, the GaAs(111)B samples investigated in that work were nominally on-axis. In the present study, samples with a 2° miscut were used.

Figs. 2b and 3b are the Ga 3d and As 3d core-level spectra from the GaAs(111)B-(2×2) surface

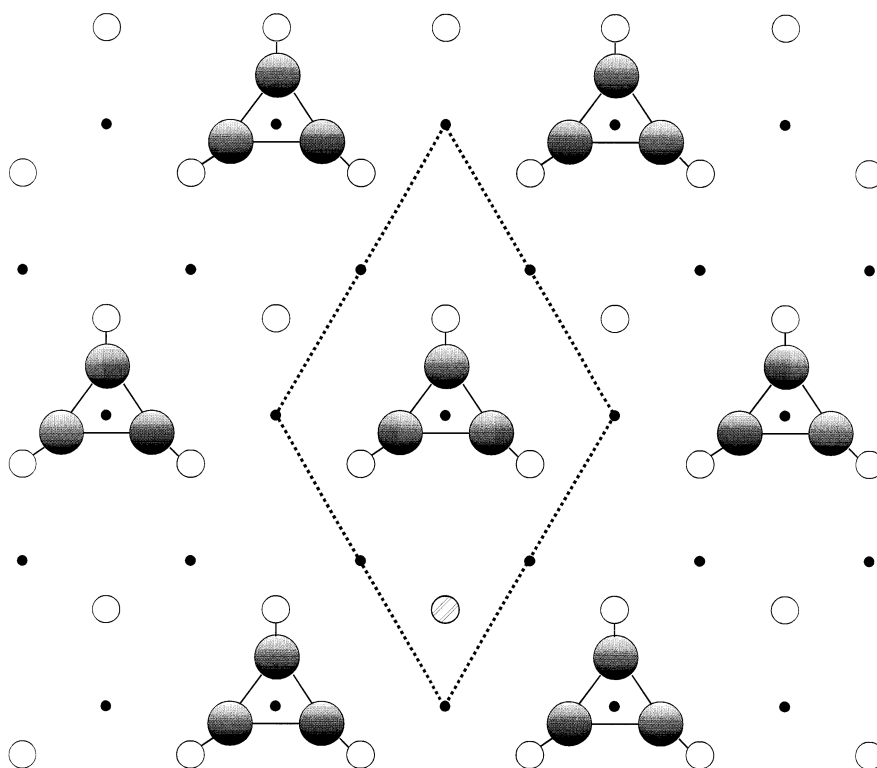


Fig. 1. A schematic illustration of the (2×2) reconstruction of the GaAs(111)B surface. Large shaded circles represent the As trimer atoms, open circles the second layer As atoms and small filled circles the Ga atoms. The dashed lines enclose a (2×2) unit cell. The As rest atom in the unit cell is shown as a “hatched” circle.

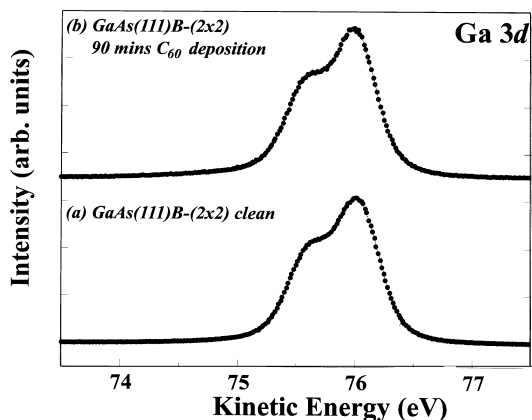


Fig. 2. (a) Ga 3d core-level spectrum from the clean GaAs(111)B- (2×2) surface; (b) the Ga 3d spectrum following deposition of C_{60} for 90 min. Both spectra were acquired with a photon energy of 100 eV.

following exposure to the C_{60} source for 90 min. It is clear from a comparison of Figs. 2a and 3a with Figs. 2b and 3b respectively, that C_{60} adsorption induces no change in the core-level spectra. However, the valence band spectrum of the (2×2) surface following 90 min of C_{60} deposition differs considerably from that of the clean surface. As shown in Fig. 4b, the spectral features relating to the fullerene π - and σ -derived molecular orbitals are clearly resolved.

Our PES data on the interaction of C_{60} with GaAs(111)B- (2×2) are similar to the results of Ohno et al. [1] for fullerene adsorption on GaAs(110)- (1×1) . For both surfaces, C_{60} induces no change in the core-level line-shapes, indicating that there is no redistribution of valence electronic charge and, thus, no new bonding configurations are formed. The molecules are therefore essentially physisorbed.

Ohno et al. [1] observed a 0.3-eV shift of the

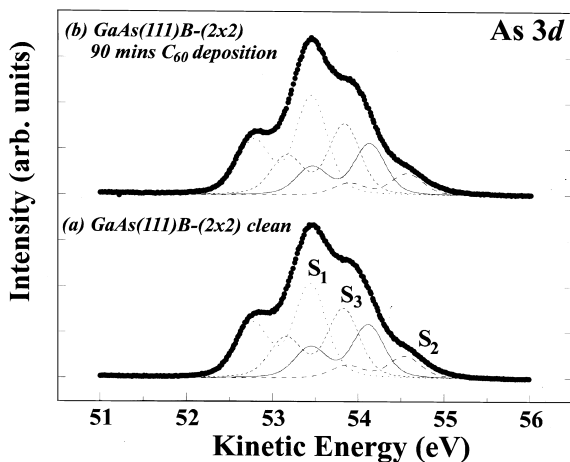


Fig. 3. (a) As 3d core-level spectrum from the clean (2×2) surface. Three surface core-level shifted (SCLS) components were necessary to fit the experimental data. These have binding energies (relative to the bulk peak) of: S_1 , $+0.65$ eV; S_2 , -0.5 eV; and S_3 , $+0.27$ eV. The SCLS components have been shown as dashed lines for clarity. (b) GaAs(111)B- (2×2) As 3d spectrum following 90-min C_{60} deposition.

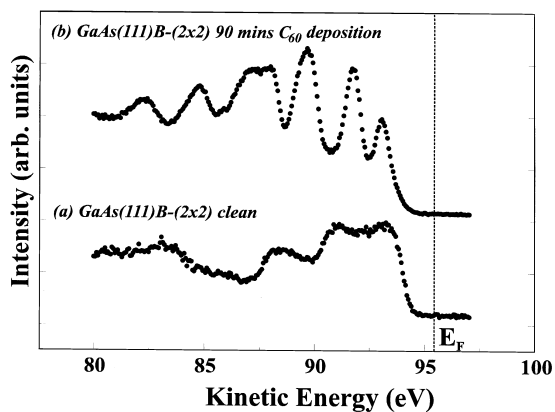


Fig. 4. Valence band spectra from (a) the clean and (b) C_{60} -covered GaAs(111)B- (2×2) surface. The photon energy was 100 eV.

core-levels towards a higher binding energy (BE) that they attributed to band bending arising from the transfer of a very small amount of electronic charge from the GaAs surface to the fullerene molecules. An important difference between the GaAs(110)- (1×1) and GaAs(111)B- (2×2) surfaces is that for the former, there are no mid-gap electronic states and, correspondingly, no band

bending associated with the clean surface relaxation. From measurements of the valence band maximum (VBM) (referenced to the Fermi level of the Mo sample holder), we find that for the GaAs(111)B- (2×2) surface, the Fermi level is pinned at 0.6 ± 0.1 eV above the VBM. As found from previous STM and tunneling spectroscopy measurements [16,17], the clean surface band bending arises from defect states associated with stacking faults between different domains of the (2×2) reconstruction. The lack of any shift in the core-level positions following C_{60} adsorption can be attributed to the stacking fault induced Fermi level pinning.

Annealing of the clean (2×2) surface at a temperature of 550°C led to the removal of the half-order spots in the LEED pattern, resulting in a (1×1) pattern. As 3d, Ga 3d and valence band spectra from the (1×1) surface are shown in Figs. 5a, 6a, and 7a respectively. Unlike the Ga 3d spectra from the (2×2) surface, the inclusion of SCLS components (at -0.3 and $+0.35$ eV BE) was necessary to provide a good fit to the experimental data shown in Fig. 6a. In addition, the As 3d spectrum differs considerably from that of the (2×2) surface. Most noticeably, the As-trimer related component (S_1 in Fig. 3a) has been removed.

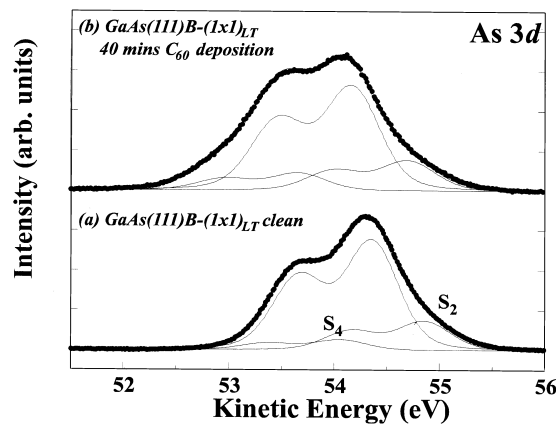


Fig. 5. As 3d core-level spectra from (a) the clean and (b) the C_{60} -covered $(1 \times 1)_{LT}$ surface. Although there is a difference in the position of the bulk components of the core-level spectra before and after C_{60} deposition, this energy shift was not rigid and most likely arises from a charging effect due to the presence of a relatively thick C_{60} film.

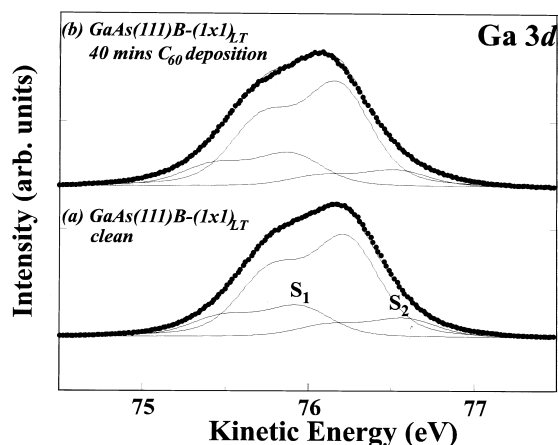


Fig. 6. (a) The Ga 3d spectrum from the clean $(1 \times 1)_{LT}$ surface. Two surface core-level shifted components, S_1 and S_2 , are observed. (b) the $(1 \times 1)_{LT}$ Ga 3d spectrum following 40-min C_{60} deposition.

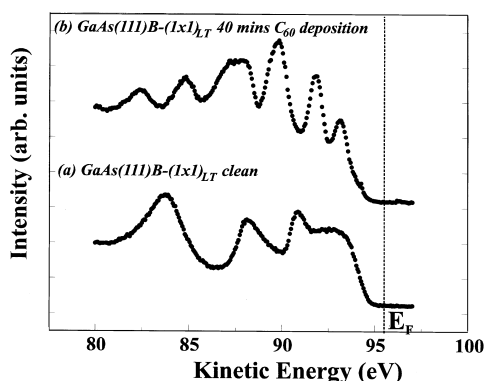


Fig. 7. Valence band spectra from (a) the clean and (b) C_{60} -covered $(1 \times 1)_{LT}$ surface. Note that the energy position of the C_{60} HOMO peak differs to that from the C_{60} -covered (2×2) surface by ~ 0.4 eV. While this may be related to a difference in coverage [the C_{60} sticking coefficient is likely to be very different for the (2×2) and $(1 \times 1)_{LT}$ surfaces] or the nature of the C_{60} adsorption on both surfaces, charging effects (as noted for Fig. 4) due to the presence of a relatively thick C_{60} film may not be discounted.

In a recent STM study of phase transitions on GaAs(111)B, Thornton et al. [18] found that following a 540°C anneal, while there were small areas of ordered $(\sqrt{19} \times \sqrt{19}) R23.4^\circ$ structure, the surface exhibited a high degree of disorder. This disorder accounts for the difficulty experienced in obtaining a $(\sqrt{19} \times \sqrt{19}) R23.4^\circ$ LEED pattern in

our, and previous, [18] work. The $(\sqrt{19})$ structure has been studied by Bieglesen et al. [11] using STM and found to arise from the ordering of ring-like structures consisting of six As atoms back-bonded to underlying Ga. For the GaAs(111)B surface annealed at 540°C , which gives rise to a (1×1) pattern [18], As trimers [in a (2×2) arrangement] and $(\sqrt{19})$ rings coexist. (This transitional (1×1) phase has been labelled $(1 \times 1)_{LT}$ to distinguish it from the $(1 \times 1)_{HT}$ structure that forms at a higher annealing temperature [19]).

Before discussing the effects of C_{60} adsorption on the photoemission spectra from the $(1 \times 1)_{LT}$ phase, we will consider the differences in the As 3d and Ga 3d core-levels from the (2×2) and $(1 \times 1)_{LT}$ surfaces. The trimer component visible in the As 3d spectrum from the (2×2) surface is no longer observed for the $(1 \times 1)_{LT}$ phase, indicating a significant decrease in the surface As concentration. A considerable amount of As desorption was also observed in STM studies of the (2×2) to $(1 \times 1)_{LT}$ transition [18]. However, it is interesting to note that the S_2 component of the (2×2) spectrum [attributed to As rest atoms (see Fig. 1) and with a BE of -0.5 eV] is also present in the $(1 \times 1)_{LT}$ As 3d spectrum. In addition, a second SCLS component labelled S_4 in Fig. 5a (BE: $+0.33$ eV) was required to fit the data. The Ga 3d spectrum (Fig. 6) shows that, unlike the (2×2) reconstruction, surface Ga atoms are present on the $(1 \times 1)_{LT}$ phase. Two SCLS components, S_1 and S_2 , with binding energies of $+0.3$ eV and -0.35 eV, respectively, were necessary to provide a good fit to the $(1 \times 1)_{LT}$ Ga 3d core-level data. It should also be noted that, as compared to the spectra from the (2×2) surface, larger Gaussian widths were required in fitting the $(1 \times 1)_{LT}$ As 3d and Ga 3d core-levels.

A comparison of Figs 5a and 5b clearly shows that deposition of C_{60} on the $(1 \times 1)_{LT}$ surface induces a distinct change in the As 3d core-level spectrum. The S_4 component is removed, and a component at $+0.5$ eV BE appears. (For shorter C_{60} deposition times, both the S_4 and the 0.5 eV BE component were required to fit the data.) This distinct modification of the As 3d line-shape is in contrast to the lack of core-level modification

observed following deposition of C_{60} on the (2×2) surface. Our results show that C_{60} chemically interacts with the $(1 \times 1)_{LT}$ phase and, therefore, the fullerene–GaAs interaction may be changed by varying the surface structure and composition. Furthermore, the higher relative binding energy of the C_{60} -induced component suggests that (assuming an initial state model) charge is transferred from surface As atoms to the adsorbed C_{60} molecules.

While we observe a modification of the $(1 \times 1)_{LT}$ As 3d spectrum, there is no change in the Ga 3d spectral line-shape following C_{60} deposition (see Fig. 6). Furthermore, it is particularly interesting to note that C_{60} adsorption does not affect the S_2 component of the $(1 \times 1)_{LT}$ As 3d spectrum (the S_2 -to-bulk-component intensity ratio is 0.31 before, and 0.29 following, C_{60} adsorption). As suggested above, the S_2 peak from the $(1 \times 1)_{LT}$ phase most likely arises from As atoms that are chemically equivalent to the rest atoms (see Fig. 1) of the (2×2) reconstruction. Both these observations are also consistent with a charge-transfer based model of C_{60} adsorption on the $(1 \times 1)_{LT}$ surface. Within the electron counting model [20] (or simply from a consideration of the Ga and As electronegativities), we expect As atoms to be associated with a higher valence electron density than Ga atoms. Fully filled As orbitals (lone pairs) will, however, not give rise to electronic states near the Fermi level. If the chemisorption of C_{60} on the $(1 \times 1)_{LT}$ phase is driven by charge transfer from the surface state with energies near the Fermi level (analogous to C_{60} adsorption on metals [1,3] and the Si(111)-(7×7) surface [4]), it is not surprising that we observe little interaction with Ga dangling bonds and As lone pairs. In both cases, there is little, or no, density of states near the Fermi level associated with the orbitals.

In conclusion, we have studied the interaction of C_{60} with the (2×2) and $(1 \times 1)_{LT}$ phases of the GaAs(111)B surface using photoelectron spectroscopy. It is only for the latter phase that we observe a modification of the substrate core-level photoelectron emission following C_{60} adsorption. This may be explained in terms of surface–molecule charge transfer, which is possible only from

the partially filled dangling bonds that exist on the $(1 \times 1)_{LT}$ phase.

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