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C_{60} on Al(111): Covalent bonding and surface reconstruction

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We present photoemission and C 1*s* photoabsorption data for an annealed monolayer C_{60}/Al(111), which show that a strong covalent bond is formed between the C_{60} molecules and the substrate. Low-energy electron-diffraction and scanning tunneling microscopy data reveal a highly symmetric overlayer structure commensurate with the substrate. Al 2*p* photoelectron spectra show that the chemical environment at the surface is greatly modified compared to clean Al(111), and indicate that a significant fraction of the surface atoms have moved, consistent with a picture of covalent bonding to the overlayer. The strength of the interaction is such that the fullerenes are distorted more than on other metal surfaces or in compounds with alkali metals.

The study of interactions between fullerenes and surfaces has become a central area for research into the properties of this new form of carbon. Much of the previous work has concentrated on quantifying the charge transfer to the C_{60} molecules known to accompany chemisorption on many metal surfaces.[1] However, C_{60} is known to bond covalently, on[2] Si(100), with itself in polymers,[3] and to other atoms and molecules.[4] We have previously shown that hybridization effects occur between the unoccupied valence orbitals of C_{60} and the Au(110) surface,[5] showing that more than a charge-transfer model is needed to fully describe fullerene-metal surface interactions. Extensive studies of ultrathin fullerene overlayers have been carried out using scanning tunneling microscopy (STM), many of which have revealed highly ordered C_{60} monolayer structures. In several cases, such as[6] C_{60}/Au(111) and Au(110),[7] the overlayer is seen to produce a reconstruction of the substrate, or to lift an existing reconstruction.

Our low-energy electron-diffraction (LEED) and STM results indicate that an annealed C_{60} monolayer has a $(2\sqrt{3}\times 2\sqrt{3})R30°$ structure, and the symmetry is reduced to (6×6) as a result of a reconstruction. Broadening observed in the Al 2*p* photoelectron-spectroscopy (PES) results show that the C_{60} molecules are chemisorbed. Our PES and C 1*s* x-ray-absorption (XAS) data differ significantly from results obtained for typical charge-transfer systems. Changes in the XAS spectra with respect to solid C_{60} show that the bond between C_{60} and the Al atoms is strong enough to cause significant distortions of the fullerene structure. A new Al 2*p* component can be interpreted in terms of a fraction of the surface atoms being pulled out of the substrate to bond covalently with the C_{60} layer, forming the lowest energy structure.

PES and XAS data were taken at Beamline 22 of MAX-lab, using a modified SX700 monochromator and a high-efficiency electron spectrometer.[8] Films were evaporated onto a clean Al(111) substrate with pressures in the low 10^{-10} mbar range, as previously described for Au(110).[5] Ordered monolayers for analysis in the electron spectrometer were produced by evaporating C_{60} while the Al(111) surface was held at a temperature of 620 K. Confirmation that a monolayer was produced was obtained from C 1*s* PES, which shows new components for multilayer growth as on Au(110).[5] XAS was measured by recording the partial electron yield as a function of photon energy above the carbon *K* edge, with a resolution of 0.16 eV.

The STM data were obtained at room temperature using a commercial microscope[9] operating in a separate UHV system with a base pressure below 2×10^{-11} mbar. For the STM experiment, C_{60} multilayers deposited at room temperature were annealed at 670 K for 15 min. After cooling to room temperature this surface gave a (6×6) LEED pattern iden-

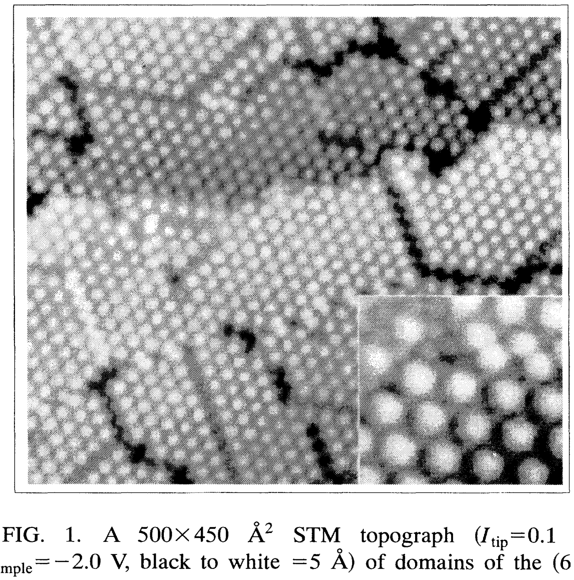

FIG. 1. A 500×450 Å^2 STM topograph ($I_{\text{tip}}=0.1$ nA, $V_{\text{sample}}=-2.0$ V, black to white $=5$ Å) of domains of the (6×6) reconstruction and an atomic step in the underlying Al. The inset shows a 70×70 Å^2 detailed view taken at the same bias and current. The bright ordered features are C_{60} molecules in a (6×6) arrangement. Between them, and along domain boundaries, can be seen a second set of molecules in a $(2\sqrt{3}\times 2\sqrt{3})R30°$ pattern.

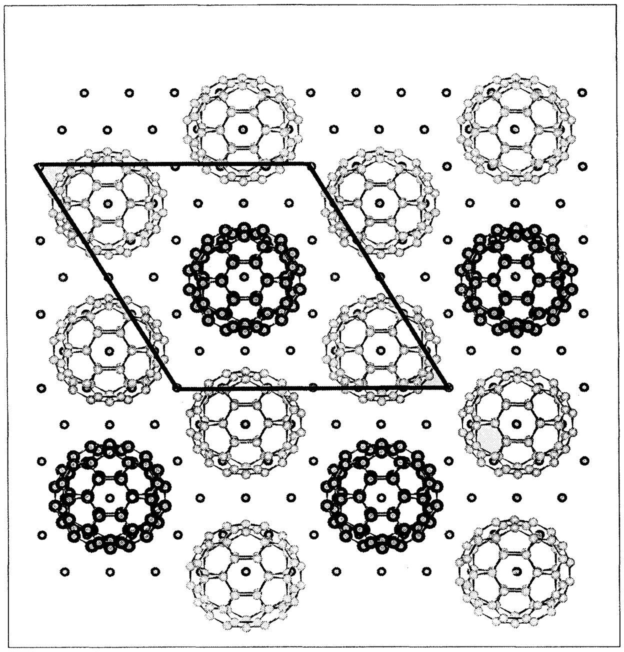

FIG. 2. A model of the $(2\sqrt{3}\times2\sqrt{3})R30°$ structure with a symmetry-reducing reconstruction where one C_{60} molecule per unit cell (shown in a darker color) is raised above the level of the other two. The boundaries of a (6×6) unit cell are indicated in the figure. The overlayer-substrate registry shown is arbitrary.

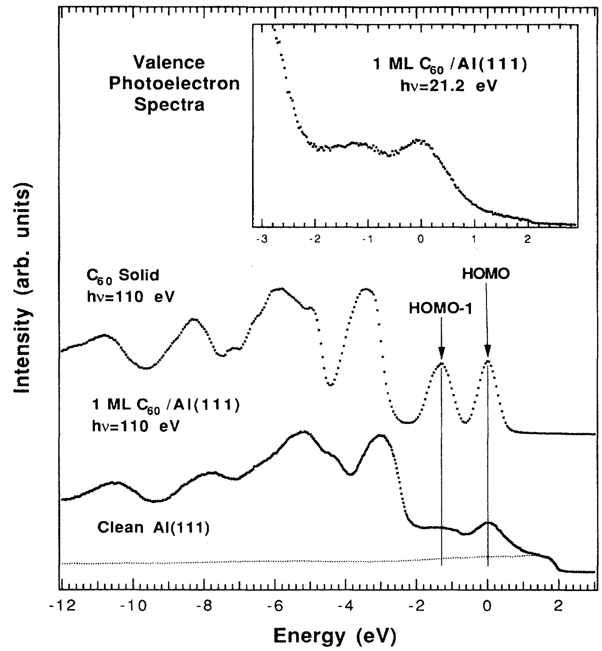

FIG. 3. PES spectra for 1 ML C_{60}/Al(111) and solid C_{60}, with energy origin arbitarily aligned to the HOMO and total resolution ~0.16 eV. The Al(111) background intensity was calibrated using second-order light as described elsewhere (Refs. 17 and 18).

tical to that obtained from samples used in the photoemission studies, and we therefore assume that the two sample preparation methods are equivalent.

Hence, the annealed C_{60} monolayer produces a structure with a unit cell containing 36 surface Al atoms. In contrast to the clean substrate, the surface was found to be impervious to oxidation over many hours, in agreement with previous work on polycrystalline Al.[10] This indicates a virtually gap-free overlayer lattice, thus the 6×6 unit cell must contain at least three molecules. One structure which retains a C_{60}-C_{60} separation very close to the 10 Å observed for solid C_{60} is a $(2\sqrt{3}\times2\sqrt{3})R30°$ overlayer, such as observed on the virtually isostructural Au(111) surface,[6] combined with a surface and/or overlayer reconstruction in order to break the higher symmetry.

Our STM data strongly support this model. The STM work will be discussed in detail elsewhere,[11] and here we present only a summary. Figure 1 shows STM topographs in which two inequivalent C_{60} molecules can be discerned. The spacing and orientation of the molecular overlayer can be compared to atomically resolved topographs taken on the clean Al surface, and indicate that the C_{60} molecules are indeed arranged in a close-packed $(2\sqrt{3}\times2\sqrt{3})R30°$ layer with a nearest-neighbor distance of 10 Å. However, the tops of one-third of the C_{60} molecules appear to be raised 1.7 Å above the others, with the raised molecules having the (6×6) periodicity seen in LEED. Defects in the overlayer structure agree well with the proposed model, and can be of two types: defects of the $(2\sqrt{3}\times2\sqrt{3})$ structure, of which the wider domain boundaries in Fig. 1 are an example; or defects in the (6×6) superlattice, such as the thin domain boundaries in which an intact $(2\sqrt{3}\times2\sqrt{3})$ close-packed layer can still be seen. We performed STM measurements on several different parts of the sample without observing any different structures. Figure 2 is a model of the basic structure, where the raised molecules are indicated with the darker color.

Having deduced the overlayer's fundamental physical characteristics, we now turn to its electronic structure. In Fig. 3, valence PES results for 1 ML C_{60}/Al(111) are compared to our data for solid C_{60}. There is clearly a dramatic increase in the width of all valence levels for 1 ML C_{60}/Al(111) compared to the solid; in fact, the full width at half maximum (FWHM) of the highest occupied molecular orbitals (HOMO's) is 1.2 eV for 1 ML C_{60}/Al(111), greater than any previously measured FWHM of the HOMO band for C_{60} ML systems. Compared to 0.5 eV for solid C_{60}, FWHM values for other ML systems are 0.5 eV for C_{60}/Rh(111),[12] 0.6 eV for C_{60}/Au(110),[5] and 0.8±0.1 eV for C_{60}/Sn.[13] We know that the widths of valence states are a measure of the combined substrate C_{60} and C_{60}-C_{60} bonding, together with vibrational effects. With the C_{60}-C_{60} separation within the monolayer being so close to the van der Waals distance of solid C_{60}, as discussed above, and vibrational effects not expected to be important,[14] we can state that the extra broadening in the valence band is due to a strong substrate-C_{60} interaction. Surprisingly, based on the fact that Al has a lower work function than Ag and Cu, we see no new feature at the Fermi level in Fig. 3, such as that observed[15] for C_{60}/Ag and C_{60}/Cu due to charge transfer into the lowest unoccupied molecular orbital (LUMO). We therefore interpret our PES results for 1 ML C_{60}/Al(111) as strong evidence of covalent bonding between substrate and adsorbate.

Near-edge features in XAS reflect the density of unoccupied states modified by the core hole, while the σ^* reso-

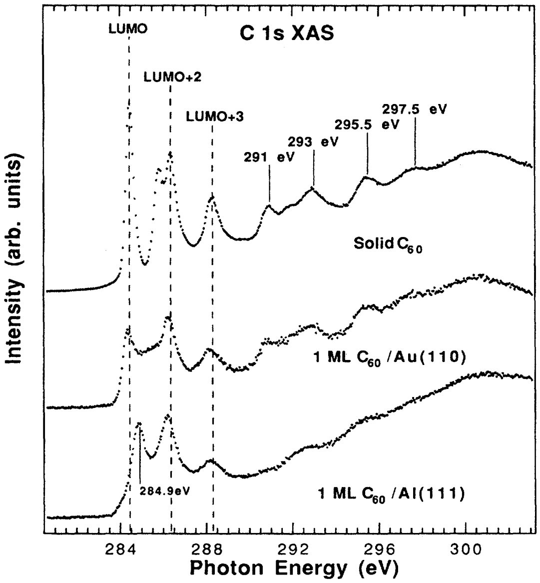

FIG. 4. C 1*s* XAS data for the indicated samples. The C 1*s* binding energy of 284.0±0.1 eV for C_{60}/Al(111) marks the first shoulder in the XAS spectrum, indicating E_F in the spectrum.

nances (above 290 eV) are well described in terms of resonant scattering of the photoexcited electron from nearby atoms.[16] XAS is atomic site specific, unlike PES, and thus derives minimal contributions from the substrate, and for C_{60}/Al(111) indicates changes in both electronic and physical structure unlike anything observed previously in C_{60}-metal surface systems. Data for solid C_{60},[17] 1 ML C_{60}/Au(110),[18] and C_{60}/Al(111) are compared in Fig. 4. The FWHM of the C 1*s*-to-LUMO resonance (hereafter called LUMO resonance) is 0.45, 0.55, and 1.0 eV, respectively, mirroring the broadening observed in PES. Coupled with the fact that XAS directly produces a neutral excited state, the similar trend confirms that vibrational effects do not explain the greater broadening for C_{60}/Al(111), but rather it is induced by substrate-adsorbate bonding, as observed for small adsorbates.[19] The LUMO resonance energy is identical for solid,[17,20–23] gas,[23] and Xe-matrix-isolated phases,[17] while a small shift of the order of 0.1 eV to lower energy is observed for C_{60}/Au(110),[5] C_{60}/Mo(110),[24] and C_{60}/Cu(001).[25] Even larger downward shifts are observed for "charge-transfer" systems.[20,21] In stark contrast, the present monolayer configuration entails a shift of 0.45 eV to higher energy of the LUMO resonance, bringing it closer to LUMO+2 and LUMO+3. This phenomenon is reminiscent of polymerized C_{60}, where an upward shift in energy of the LUMO is seen for photopolymerized films,[22] and an increase in the energy of the HOMO-LUMO absorption energy is observed in RbC_{60},[26] which is believed to be polymerized. This gives further support to a model involving covalent bonding.

Clearly defined σ^* resonances are observed in the thick film spectrum at 291, 293, 295.5, and 297.5 eV and change very little when comparing gas phase,[23] solid, and matrix isolated C_{60},[24] and K-doped C_{60}.[20] The sharp features described above are due to the fact that every C atom has a virtually identical set of surrounding C atoms from which the excited electron is scattered. We see in Fig. 4 that for 1 ML C_{60}/Au(110) these features are only weakly perturbed, in contrast to C_{60}/Al(111) for which they are greatly modified. Thus we have assembled unambiguous evidence for significant changes in the physical structure of the C_{60} molecules on Al(111), far in excess of anything previously observed in the systems mentioned above. Again similarities with XAS results for photopolymerized C_{60} occur.[22] The breaking of the symmetry induced by these distortions will lower the high degeneracy of the C_{60} electronic states, and is presumably responsible for part of the broadening observed in both PES and XAS.

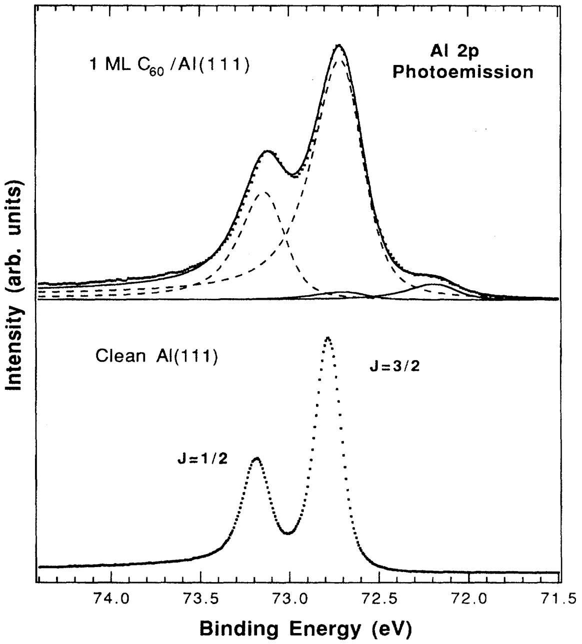

FIG. 5. Al 2*p* PES spectra for the indicated samples. The structure observed at a binding energy 550 meV below the substrate $2p_{3/2}$ peak is the $2p_{3/2}$ component due to atoms that have moved significantly from their positions in the clean substrate.

Al 2*p* XPS data for clean Al(111) and 1 ML C_{60}/Al(111) are displayed in Fig. 5. There is a considerable broadening of the main line in the 1 ML C_{60}/Al(111) spectrum, as well as the formation of a new peak situated 0.55 eV lower in binding energy. These changes are further proof that a chemical bond is formed between substrate and adsorbate. The shift to lower binding energy of the new peak is of a magnitude normally associated with a reconstruction of the Al(111) substrate and/or mixing of substrate and adsorbate atoms.[27] In fact, the changes in the Al 2*p* PES spectrum between clean Al(111) and 1 ML C_{60}/Al(111) show that the forces induced by the C_{60}-Al(111) interaction are sufficient to move substrate Al atoms, and are consistent with covalent bonding. In contrast to our results larger shifts, and to higher binding energy, have been observed for the ionically bonded oxidized Al(111) surface.[28] From an analysis based on the mean free path at this kinetic energy, we estimate that the low binding energy peak observed is a result of about one in six Al interface atoms being strongly affected. This represents an upper limit on the number of Al atoms involved in mixing between the C_{60} ML and Al(111) substrate, and the binding energy shift is consistent with Al atoms still in contact with the Al substrate.[27]

The apparent presence of two C_{60} sites in the STM data leads one to question whether the spectra can, in fact, be understood as the sum of two spectra due to molecules with different bonding, e.g., differing amounts of charge transfer. However, this does not explain the changes observed in the σ^*-derived features, which do not shift with charge transfer.[20] In addition, curve fitting can successfully model the HOMO and HOMO-1 in the valence data with two Voigt functions with relative areas very similar to solid C_{60}. The fact that the C 1s binding energy coincides with the XAS threshold shows[29] that part of the LUMO is occupied, which is similar to C_{60}/Au(110).[5] It is clear, however, that for 1 ML C_{60}/Al(111) most of the LUMO is still above E_F. The occupied LUMO-substrate hybrid band formed on Al(111) is broad, and/or located well below E_F, indicating that the LUMO has split into bonding and antibonding states as expected for a covalently bonded system. The high temperature required to form the present phase may lead one to consider whether Al-catalyzed decomposition of the fullerenes may occur. However, the lack of structure in the C 1s XPS and XAS spectra at lower binding/photon energy, as normally associated with atomic C, excludes this interpretation.[30]

Thus Al plays a special role among elements studied so far in its binding to C_{60}: there is no evidence for significant charge transfer, and covalent bonding with the sp-hybrid levels of the substrate takes place. Alkali-metal surfaces, with their low work functions and cohesive energies, reconstruct extensively to accommodate transfer of significantly more than six electrons to a deposited C_{60} molecule,[31] forming a highly ionic system. On other metals with a larger substrate cohesion, it may not be energetically possible for metal atoms to move close enough to the C_{60} molecules to form this type of covalent bond. A previous study of Al-C_{60} multilayers reported transfer of up to six electrons from Al to C_{60};[32] however more recent results appear to contradict this.[33] All our films were prepared at high temperature, and we make no predictions concerning possible low-temperature phases.

In conclusion, for the lowest-energy structure of C_{60}/Al(111), a chemisorptive bond with dominantly covalent character is present between substrate and adsorbate, strong enough to cause distortions of the fullerene molecules that are not observed for "charge-transfer" systems. Al 2p PES data show that the forces involved in the bond are sufficient to cause movement of substrate Al atoms. The C_{60} overlayer is a $(2\sqrt{3}\times 2\sqrt{3})R30°$ with respect to the substrate, where the symmetry is reduced to (6×6), as a result of a reconstruction involving both the substrate and the overlayer.

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[14] Large contribution to the broadening from low-energy vibrational modes (e.g., corresponding to the fullerene cage vibrating against the surface) would lead to a temperature dependence which we have not observed in spectra taken between 200 and 300 K. To explain the extra broadening as due to coupling to higher-energy vibrations would only be reasonable if symmetry changes due to the observed molecular distortions (described below) resulted in modified selection rules compared to solid C_{60}. Such an effect cannot be ruled out, but would anyway not change our interpretation of the observed broadening as a result of the substrate-adsorbate bond, as the distortions require strong bonding effects.

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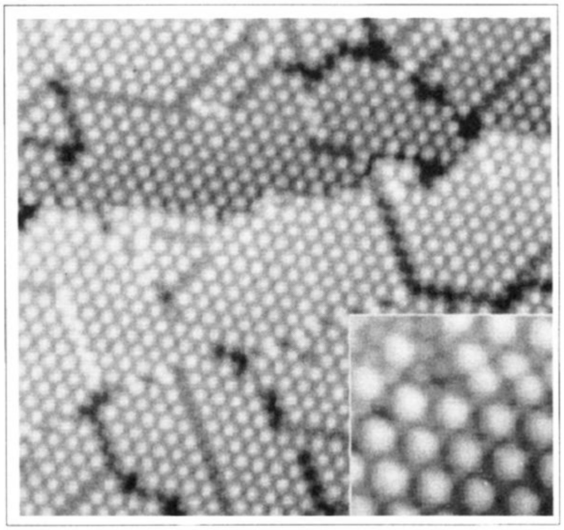

FIG. 1. A 500×450 Å^2 STM topograph (I_{tip}=0.1 nA, $V_{\mathrm{sample}}=-2.0$ V, black to white =5 Å) of domains of the (6×6) reconstruction and an atomic step in the underlying Al. The inset shows a 70×70 Å^2 detailed view taken at the same bias and current. The bright ordered features are C_{60} molecules in a (6×6) arrangement. Between them, and along domain boundaries, can be seen a second set of molecules in a $(2\sqrt{3}\times2\sqrt{3})R30°$ pattern.

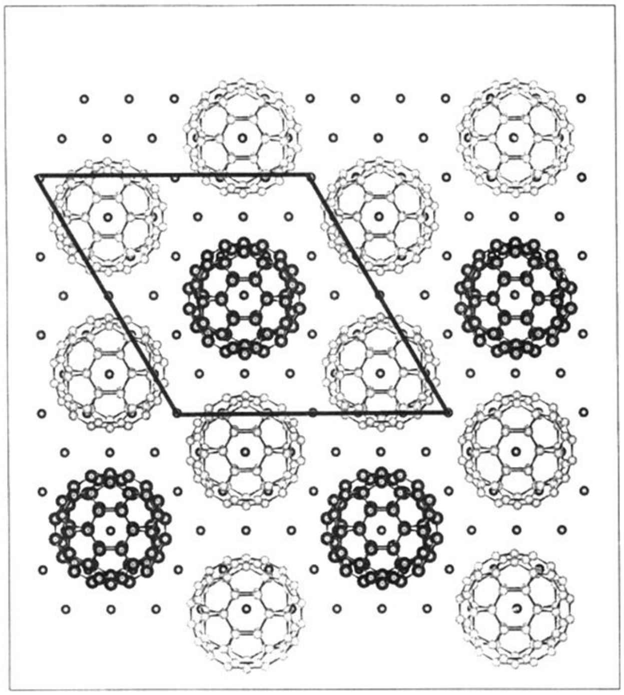

FIG. 2. A model of the $(2\sqrt{3}\times2\sqrt{3})R30^\circ$ structure with a symmetry-reducing reconstruction where one C_{60} molecule per unit cell (shown in a darker color) is raised above the level of the other two. The boundaries of a (6×6) unit cell are indicated in the figure. The overlayer-substrate registry shown is arbitrary.