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Adsorption of C_{60} on Ta(110): Photoemission and C K-edge studies

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Photoelectron and near-edge spectroscopies are used to characterize a C_{60} film on a Ta(110) surface. Like similar studies of C_{60} on a variety of metal surfaces, the valence band, C 1s core level, and photoelectron-derived work-function measurements show that C_{60} molecular states are aligned with the Fermi level and the charge is transferred from the metal to the fullerene. The photoelectron and near-edge spectra of the C_{60} peaks closest to the Fermi level show significant changes in intensity identifying those π-like states as interacting with the substrate. A careful examination of the C 1s and Ta 4f core levels suggests that some fraction of the fullerene overlayer decomposes on the clean metal surface leading to or resulting in, a thin layer of carbon between the assembled film and the metal substrate.

The electronic structures of fullerene-metal compounds and thin fullerene films on a variety of surfaces have been studied with the goal of understanding the fundamental physics of this interesting class of carbon-based materials.[1] The nature of bonding between fullerenes and metals is an important issue, given that the physical properties of fullerenes can be changed by metal doping.[2] This interaction can be studied by isolating metal atoms in C_{60} matrices or by depositing C_{60} on metal surfaces. Ohno *et al.*[3] studied the interaction of C_{60} with a series of metals including Bi, Au, Ag, Cr, and Mg. Ohno *et al.* concluded that the unoccupied C_{60} states were near the Fermi level and that the LUMO hybridized with the metal states near the Fermi level (E_F) to produce a new state with π^* character which extended below E_F.

This paper expands on the earlier work of Ohno *et al.* by using several electron spectroscopic techniques to probe the interaction between C_{60} and a Ta(110) substrate. We have also obtained surface work function information which can be used to detect changes in the magnitude of the interface dipole formed between C_{60} and Ta(110), or to detect charge transfer from the metal to C_{60}. Last, we investigated the C K edge of both a C_{60} monolayer and a thick film on the metal to show how the pre-edge feature connected to the π^* level changes when C_{60} interacts with tantalum. The data suggest that some of the C_{60} decomposes to form an atomically thin carbon layer between the fullerenes and the metal.

The photoelectron measurements were done on the *U7a* (near-edge and C 1s) and *U7b* (valence and core-level photoelectron spectroscopy) beam lines at the National Synchrotron Light Source (NSLS). Hemispherical analyzers were used to measure the photoelectron emission along the surface normal direction. The valence-band spectra were taken with a pass energy of 15 eV and the resolution is estimated to be 0.4 eV, based on the width of the Ta Fermi edge. The spectra are referenced to the Fermi edge of the tantalum support. The work functions were measured by floating the sample on a 6-V DC bias to reveal the low energy cutoff. The work-function change ($\Delta\Phi$) can be deduced from the shift of the low energy photoelectron threshold or mid point of the low-energy photoelectron cutoff. The C 1s core-level spectra were taken at a pass energy of 22 eV and ΔE is estimated to be at least an electron volt using the Fermi edge of the Ta support. It should be noted that the performance of the *U7a* monochromator is the principal factor limiting resolution of the C 1s and C K-edge features. The C K-edge measurement was taken in the total yield mode using an electrometer to measure the sample-to-ground current.

The Ta surface was cleaned by pulse heating to incandescence to remove all traces of surface oxides. The fullerenes were deposited onto the Ta foil using an effusion source filled with a commercial C_{60} powder, which contained 80% C_{60} and 20% other fullerenes. The temperature of the C_{60} source, operated at approximately 540 K, was monitored by a K-type thermocouple. It is known that C_{60} can be distilled from a mixture of C_{60} and C_{70}. The fullerene films produced for these measurements compare well with those published by other groups using pure C_{60} as a starting material. However, the resolution of the data is insufficient to rule out the admixture of other fullerenes (e.g., C_{70}) with the C_{60}.

Figure 1 shows photoelectron spectra from the valence-band region at the Γ point (i.e., along the surface normal) and that surface covered with increasing amounts of C_{60}. The topmost curve shows a thick layer of C_{60} whose thickness is sufficient to cause the extinction of the Ta 5d band. Photoelectron emission from solid C_{60} has been analyzed and discussed by others. For our purpose, the main features of the C_{60} valence electronic structure will be discussed. The occupied levels consist of states with π_p, σ_p, and σ_s character that are derived from the C 2s and 2p atomic states.[4] The states labeled 1 and 2 (Fig. 1, topmost curve) are π states while the deeper states (peaks 3–7) have increasing σ character and are localized on the carbon-carbon bonds.[5] The intensities and binding energies of the peaks labeled 1–7 match those published for fullerene layers deposited from pure C_{60} source material.[5]

The valence-band spectrum for the thinnest layer [0.1

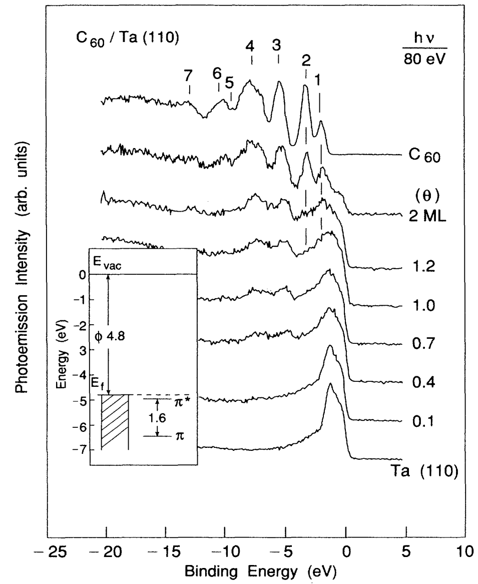

FIG. 1. Valence-band spectra for C_{60} deposited on a Ta(110) substrate and the C_{60} coverages are estimated from the attenuation of the Ta $4f$ core levels. The spectra are referenced to the E_F of Ta(110). The inset shows the alignment of the C_{60} π and π^* levels.

ML; Note: A close-packed fullerene (C_{60}) monolayer will have 1.15×10^{14} molecules/cm^2 and be 8-Å thick.] of C_{60} on Ta(110) (Fig. 1) shows the Ta $5d$ states at the Γ point of the surface Brillouin zone but no peaks identifiable with the fullerene. The presence of a carbon containing species on the surface was, however, demonstrated by the observation of the C $1s$ peak. Additional deposits (0.4–1.2 ML) of C_{60} were required to produce peaks identified with the fullerenes (peaks 3&4). For C_{60} coverages of 0.1–1.2 ML, the sharp π-like states (peaks 1&2) are weak and relatively indistinct against the background of the Ta $5d$ and $5s$ bands. It is also observed that the relatively sharp Ta $5d$ state at -1.3 eV below E_F broadens with the assembly of the C_{60} layer on top and appears to merge into the leading edge of peak 1 as the second and succeeding C_{60} layers are deposited. Peaks 3 and 4 can be seen for submonolayer coverages, but are broadened when compared to those seen for the thick fullerene film. Within the limits of the spectra, the peaks show little or no shift in position in going from submonolayer to multilayer films.

Variation in the position of the fullerene π states referenced to the Ta Fermi level provides an indication of the direction of charge transfer between the metal and the C_{60} molecules as the fullerene evolves from a chemisorbed monolayer to the thickest film (assumed to resemble the solid). The solid fullerene is a van der Waals solid and an obvious question is whether the fullerene molecule behaves like solid Kr (Ref. 6) or whether the fullerene behaves like a chemisorbed molecular species. Ta(110) has a work function of 4.8 eV and the insert in Fig. 1 shows the locations of the ground state levels of C_{60} relative to the Fermi level. If we assume our thick fullerene layer is representative of material not chemisorbed by the metal, peak 1 lies 1.72 eV below the Fermi level. This places the occupied π-like level 6.5 eV below E_{vac}. The lowest unoccupied level (π^*-like) is 1.6 eV above the peak 1 which places it just below E_f. It is known that the ionization potential of gas phase C_{60} is 7.6 eV, and our result for the thick film which should have little interaction with the substrate shows a large change in what should be the ionization potential. Peaks 1 and 2 are first observed near monolayer coverage. It is interesting that the fullerene peaks are at or near the same binding energy for the monolayer thick films as the thick fullerene film. As will be discussed later, there is evidence that some of the fullerenes decompose into a thin layer of carbon which lies between the fullerene and the metal. This film probably modifies the metal-fullerene interaction and could account for the similarity in the binding energy of the thick and thin fullerene layers.

Figure 2 shows the shift of the low-energy photoelectron threshold, identical to the work-function change, $\Delta\phi$, when a Ta(110) surface is covered by a monolayer of C_{60}. The work function increases by 0.6 eV. If the fullerene were aligned to the vacuum level, the C_{60} valence peaks should move an additional 0.6 eV towards the Fermi level. A quick examination of Fig. 1 shows that the C_{60} peaks remain more or less fixed in position relative to E_f and do not shift to smaller binding energy for any of the coverages studied. This argues that the C_{60} levels align with the Fermi level for C_{60} coverages of a few monolayers and shift in lock step with the work function.

The changes in the valence fullerene π-like levels are mirrored in the modification of the unoccupied π^* levels that can be probed by soft x-ray absorption. In the near-edge spectrum, the fullerene features are no longer obscured by the Ta $5d$ states. For the pure fullerene, the sharpest pre-edge features at 287.5- and 289.5-eV photon energy are peaks due to transitions from the C $1s$ to π^* levels.[7,8] A series of weaker peaks from 291 to 305 eV result from $1s$ to σ^* transitions, and a large shape resonance is seen at about 310 eV. The spectra for the C_{60}

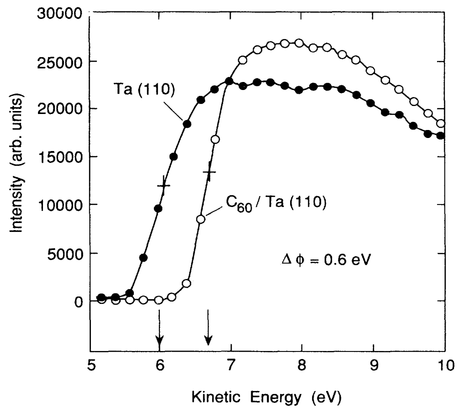

FIG. 2. A plot of the low-energy cutoff for Ta(110) (black circles) and the same surface covered by a single close-packed layer of C_{60}. The energy scale has not been shifted to account for the 6-V bias applied to the sample to reveal the low-energy photoelectron cutoff. The shift of the midpoints indicates the work function increases by 0.6 eV.

monolayer on Ta(110) show that the π^* peaks lose a substantial fraction of their intensity relative to the σ^* peaks and shift about an electron volt to lower photon energy. The broad shape resonance near 310 eV photon energy is also greatly reduced.

The weakening of the π^* transitions is consistent with charge transfer from the metal to the fullerene π^* level and can be compared to the changes seen in the K edge of molecular oxygen in superoxides.[9] In the case of the superoxides, where an O_2^- species is formed, charge is transferred from the alkali-metal atom which ionizes to the oxygen π^* level. This type of interaction is more likely in alkali-metal-fullerene systems, given the relative positions of the fullerene π^* levels and the occupied alkali-metal state. The modification of the C_{60} π^* levels could also be explained by the hybridization of the π and π^* levels with the occupied and unoccupied parts of the Ta 5d band. Figure 1 (inset) showed that the lowest energy π^* level was initially located below the Fermi level. The near-edge spectrum shows that the same π^* level is located above the Fermi edge. This could be explained by the hybridization of this molecular level with the occupied part of the valence band. The interaction broadens or splits the π^* level into bonding and anti-bonding components and part of the antibonding-bonding component lies above the Fermi level. In a similar fashion, the changes in the intensity of the second π^* peak can be explained by an interaction with the unoccupied valence states. At this point, it should be emphasized that the presence of a thin layer of carbon between the fullerenes and the metal could have a significant impact on the metal-fullerene interaction.

The Ta 4f and C 1s core levels (Figs. 3 and 4) were examined to see whether the core-level shifts were consistent with such charge transfer. The spectra have been processed using a Shirley-type routine to remove the inelastic background and fitted with Doniac-Sunjic functions using the standard procedures. For the Ta 4f features, the bottom panel in Fig. 3 shows the core-level components for clean Ta(110) and the fit peaks can be assigned to the bulk and surface components, respectively. The surface-to-bulk splitting for the $4f_{7/2}$ components is 0.36 eV and is in agreement with the values reported for this surface.[10] When the C_{60} is deposited, the surface Ta 4f core level components shift to higher binding energy and the surface-to-bulk or in this case interface-to-bulk splitting is 0.73 eV. A determination of the cause of the metal core-level shifts is complicated because a number of physical phenomena can be responsible for the observed behavior. In addition, the fullerene could react with the surface and decompose to coat the surface with a thin carbon or tantalum carbide layer. For the C_{60}-covered surface, the surface component (metal-fullerene interface component) is much broader for the fullerene covered surface than the clean surface and the ratio of the area of the surface component to the bulk component decreases from 1.19 to 1.08. The broadening of the Ta 4f peaks and the apparent decrease in the area of the surface (interface) peak relative to the bulk peak argue for the latter interpretation. Tantalum carbides with a range of carbon concentrations have been studied by photoemission[11] and the Ta 4f peaks shift of higher binding energy with increasing carbon concentration. Stoichiometric TaC has a reported Ta $4f_{7/2}$ binding energy of -23.6 eV and a core-level shift of -1.8 eV. Reducing the carbon concentration from $x = 1.0$ to 0.5 reduced the core-level shift to -1.0 eV. If the C_{60}-induced Ta 4f feature is identified with a tantalum carbide layer, it must be Tarich compared to the tantulum carbides studied by Gruzalski and

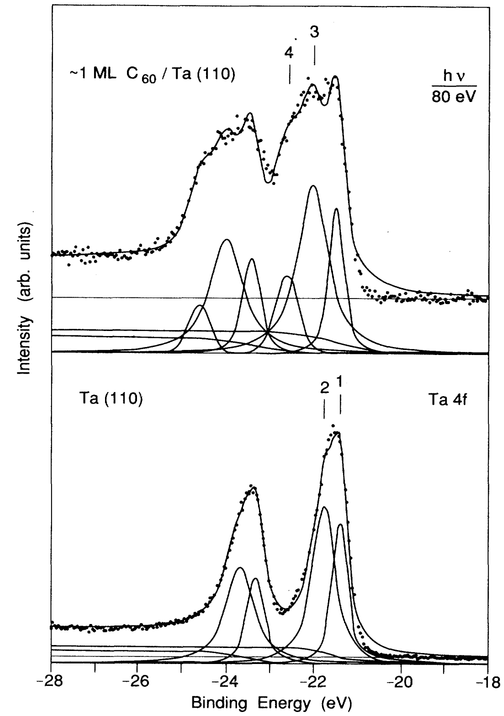

FIG. 3. The Ta 4f core levels for Ta(110) and the same surface covered by a C_{60} monolayer.

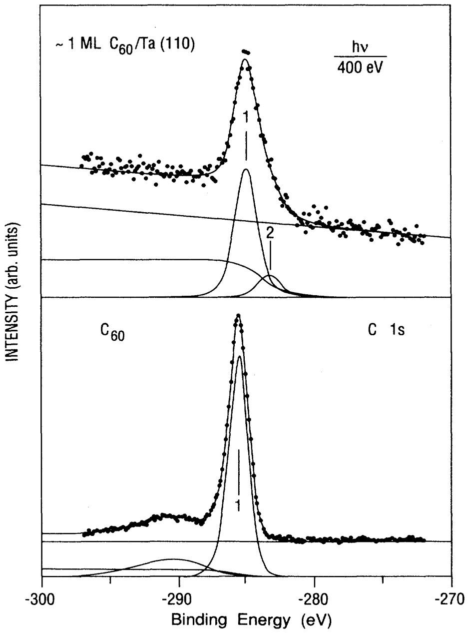

FIG. 4. C 1s core-level spectra for the pure fullerene and C_{60} on Ta(110).

Zehner.[11] The interaction of carbon films with niobium was studied by Wesner *et al.*[12] It was found that high temperatures ($T > 1000\,^\circ\mathrm{C}$) were needed to convert a graphitic carbon layer to NbC. The work of Wesner *et al.*[12] suggests the carbon film generated by the fullerene reaction with the substrate is more likely to be graphitic than carbidic.

Figure 4 shows the C 1*s* core levels for the pure fullerene film and the C_{60} monolayer on Ta(110). The C 1*s* core level for the thick layer was fitted with a single Doniac-Sunjic peak [Fig. 5(a)] which has a binding energy of -285.5 eV, in agreement with published data.[13] The broad nature of our spectrum is probably instrumental but could also be due to the presence of more than one type of fullerene on the surface. The lower curve in Fig. 4 also shows a broad but weak feature 8 eV above the main C 1*s* peak. It can be attributed to unresolved electron energy loss features. The C 1*s* core level for the monolayer is much broader and can be fitted with a single broad peak or two peaks as shown in Fig. 5(b). Choosing the two component fit, the spectrum shows that the largest component is at -284.8 eV and the smaller component is at -283.8 eV. The larger peak is similar to the peak recorded for the bulk fullerenes and has shifted 0.63 eV to lower binding energy when compared to the C 1*s* peak obtained for the thick fullerene film. The smaller peak at -283.8 eV is broader than the larger peak attributed to the fullerenes. The C 1*s* data shows evidence for inequivalent initial or final states at carbon atomic sites or the existence of more than one type of carbon. Gruzalski and Zehner[11] studied the C 1*s* feature by x-ray photoelectron spectroscopy and found that the C 1*s* peak is near -282.8 eV binding energy and moves about 0.2 eV to lower binding energy as the carbon concentration decreases. Our C 1*s* component attributed to Ta-C bonding is nearly an electron volt deeper in binding energy than the carbides but nearly as far from the position (-284.7 eV) reported for graphitic carbon.[14]

The Ta 4*f* and C 1*s* spectra suggest that the initial fullerene depositions (0.1 ML or less) react with the surface and probably form a thin carbon layer that acts to passivate the surface. A single fullerene molecule has 60 carbon atoms and 0.18 ML of the fullerenes would provide enough carbon to fill every site on a Ta(110) surface. The decomposition of some of the first fullerene molecules on the surface can explain the failure to see any fullerene peaks in the valence spectrum at the lowest coverage (0.1 ML). However, the fullerene itself is large enough to have inequivalent carbon sites when chemisorbed, i.e., carbon atoms bonded to the substrate and carbon atoms that are not. The smaller C 1*s* component shown in Fig. 4(b) could be interpreted as coming from carbon atoms directly bonded to the metal.

This experiment has provided data concerning the chemisorption of the fullerene to an early transition metal. Some of the conclusions have to be qualified in light of evidence that some of the fullerene molecules appear to decompose when deposited on the metal surface. In the specific case of C_{60} on Ta(110), the C_{60} states near E_f are well placed to hybridize with the states at the interface (metal or carbon-coated metal). The spectra show evidence for charge transfer between the metal and the fullerene, as well as interactions between the rest of the metal *d* band (both occupied and unoccupied parts) and the C_{60} molecular levels which lie at the same binding energies or overlap with each other above the Fermi level. Some of the interactions between the metal *d*-band and the C_{60} π states might produce resonances in the metal *d* band, whereas, others might produce new unoccupied states above the Fermi level. An open question at this point is the detailed nature of the bonding between the metal and the fullerene and how this bonding is mediated by a thin layer of carbon believed to be at the interface. We believe some charge is transfered to the fullerene from the metal because the work function varies in the way expected when this happens. If this is the case, that charge is being transferred to the fullerenes through an atomically thin layer of carbon which lies between the metal and the fullerene.

In conclusion, the photoelectron and near-edge x-ray-absorption fine-structure (NEXAFS) results for C_{60}/Ta(110) can be described by the conventional ideas of the bonding of molecules to metal surfaces. The core-level results suggest that the interaction between the clean surface and the fullerene is strong enough to cause the first molecules on the surface to decompose. Thus surface seen by subsequent fullerene molecules is covered with a thin layer of carbon. These molecules are adsorbed on what can be considered to be a passivated surface but with an interfacial layer of carbon thin enough to allow charge transfer to the fullerene layer.

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