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The deposition of silver on a C_{60} monolayer chemisorbed on Si(111) leads to the formation of nanoscale clusters which, as determined from valence band photoemission measurements, donate minimal charge to the adsorbed fullerene molecules. The low doping level of the C_{60} monolayer leads to a slow rate of Ag cluster neutralization following the emission of a photoelectron, resulting in a significant shift of the cluster Fermi level and valence band features to higher binding energy. © *2000 American Institute of Physics.* [S0003-6951(00)04434-X]

Fullerenes and related systems such as carbon nanotubes play a central role in current nanoscale physics research. This is largely due to the wide and fascinating variety of electronic behavior displayed by these systems—ranging from, for example, phase coherent transport in nanotubes[1] to superconductivity in *K*-doped fullerite crystals.[2] In addition, scanning tunneling microscope (STM)-based manipulation of both C_{60}[3] and fullerene derivatives such as $C_{59}N$ and La@C_{82},[4] has recently enabled the molecule-by-molecule construction of experimental fullerene nanostructures on solid surfaces. Alternative ''self-assembly'' routes to fullerene nanostructure formation have also been demonstrated.[5]

The possibility of tuning the electronic properties of fullerene nanostructures in a similar manner to those of the bulk fullerite crystal has important implications for the synthesis and study of low dimensional molecular conductors. A fundamental question to address, however, is to what extent the fullerene-surface bond modifies or limits the interaction of noble or alkali metals with C_{60}. More specifically, is the same wide range of doping behavior (insulating/metallic/superconducting) that is observed for bulk C_{60} possible for a chemisorbed monolayer?

In this letter we show that the interaction of Ag with a covalently bound C_{60} monolayer differs dramatically from both the Ag-bulk C_{60} (fullerite) interaction[6] and the interaction of C_{60} with polycrystalline[6,7] and single crystal[8] Ag surfaces. Silver deposition on fullerite[6] and C_{60} adsorption on Ag surfaces[7,8] both lead to significant occupation of the fullerene lowest unoccupied molecular orbital (LUMO)-derived band producing a high density of states at the Fermi level. However, we find that charge transfer is *inhibited* for adsorption of Ag on a covalently bound C_{60} monolayer [C_{60}/Si(111)], resulting in a very low level of fullerene doping. STM measurements clearly show that the deposited Ag forms nanoscale clusters. The lack of appreciable charge transfer from Ag to the C_{60} monolayer results in poor screening of the positive charge created on a silver cluster during

the photoemission process. This, and the nanometer scale dimensions of the Ag clusters, leads to significant binding energy shifts of the valence band features and Fermi edge of the clusters.

The photoemission measurements were carried out on beamline 4.1 of the Synchrotron Radiation Source (SRS), Daresbury, UK. A Scienta SES200 hemispherical electron energy analyzer with an angular acceptance of ±5° was used to acquire the photoemission data. The synchrotron light was incident at an angle of 45° to the sample surface and the photoelectrons were collected in a normal emission geometry. All binding energies were referenced to the Fermi edge of the Mo sample holder. Photon energies of 21.2 and 55 eV were used. At 21.2 eV the C_{60} molecular orbitals are preferentially probed whereas the much higher photoionization cross section for the Ag $4d$ and $5s$ levels at a photon energy of 55 eV accentuates the Ag valence band features.

Si(111)-(7×7) surfaces were produced by flash annealing B doped (10^{16} cm^{-3}) samples at temperatures of 1200 °C (as monitored by an infra red pyrometer). A C_{60} monolayer was prepared via the deposition of sufficient C_{60} to completely attenuate the Si substrate core level followed by annealing at 300 °C. Ag was deposited from a Knudsen cell onto the C_{60} monolayer at a rate of 4(±1) ×10^{14} atoms/cm²/s, as calculated from the Ag vapor pressure and the experimental geometry and verified by *ex situ* atomic force microscope (AFM) measurements. Although, as discussed below, the growth mode of Ag on the C_{60} monolayer is not layer-by-layer, this deposition rate corresponds to 0.1 (±0.025) monolayers (ML) of Ag per second, where the ML unit is defined as a complete close packed layer of Ag atoms.

Figure 1 illustrates the changes in the C_{60} monolayer valence band that occur following the deposition of various amounts of Ag. The lowest curve is from the C_{60} monolayer in the absence of Ag. A detailed analysis of the valence band spectrum for a C_{60} monolayer on Si(111)[9] clearly reveals that the monolayer is covalently bound to the Si(111) substrate. Deposition of 0.5 ML of silver leads to a shift of the peaks in the valence band spectrum by 0.4 eV to higher binding energy (BE). The C_{60} molecular orbital-related features also
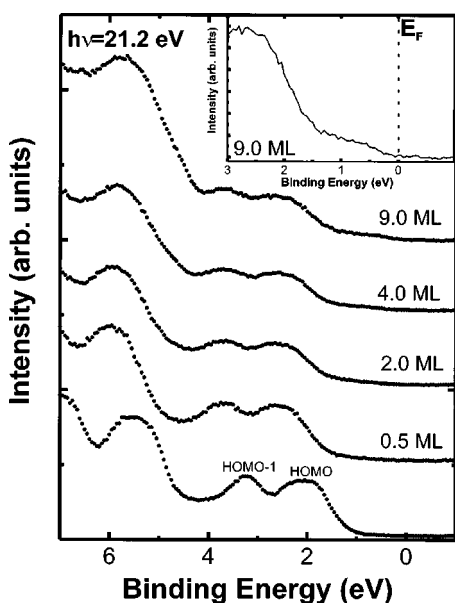
FIG. 1. Valence band spectra of the Ag/1 MLC$_{60}$/Si(111) system as a function of Ag coverage. The inset is an expansion of the near Fermi edge region of the uppermost spectrum illustrating that there is no appreciable density of states at the Fermi level. The photon energy for all spectra is 21.2 eV. Note that the error in the quoted coverages in this figure and throughout the letter is ±25%.

become less distinct with increasing Ag coverage. Note that there is no further shift of the highest occupied molecular orbital (HOMO) and HOMO-1 features following the first Ag deposition. In addition, and most importantly, even for the highest Ag coverages we do not observe any density of states at the Fermi level—see inset to Fig. 1. This is clear evidence that there is a very low level of electronic occupation of the fullerene LUMO, in strong contrast with the 1.7 and 0.75 electrons per molecule which are transferred to adsorbed fullerenes from polycrsytalline and Ag(111) surfaces, respectively.[7,8]

The gradual loss of well defined C$_{60}$-related features and the growth in spectral intensity between the HOMO-derived feature and E_F are due to the increasing contribution of the Ag valence band states. These states have a low photoionization cross section at a photon energy of 21.2 eV. The shift of the spectrum by 0.4 eV to higher BE is of more significance and is due to Fermi level movement arising from the

donation of electrons from Ag into the LUMO-derived (conduction) band of the C$_{60}$ monolayer. As discussed by Owens *et al.*[10] for the Al/bulk C$_{60}$ system, the BE shift due to Fermi level movement will be offset by a negative BE shift due to enhanced screening by the electrons donated by the metal atoms. For Ag/1 MLC$_{60}$/Si(111), there is much less efficient screening than for the Al/fullerite case—a point that is discussed in further detail below with regard to the Ag valence band results—and the net BE shift is positive.

The morphologies of Ag films deposited on the C$_{60}$ monolayer were investigated using STM. Figure 2(a) is an STM image of a C$_{60}$ monolayer with a 0.37 ML Ag coverage. It is clear that the deposited silver forms nanometer scale clusters with, as shown in Fig. 2(b), a mean diameter of 1.5 nm. In a very recent STM study, Wang *et al.*[11] suggest that Ag clusters on C$_{60}$/Si(111) nucleate at defect sites in the fullerene monolayer where Si dangling bonds are exposed. However, following adsorption of Ag on the C$_{60}$ monolayer we observed no change in the Si 2p core-level line shape, strongly suggesting that Si dangling bonds do not play a major role in the Ag cluster nucleation process.

Figure 3(a) shows the valence band spectra for various Ag coverages taken with a photon energy of 55 eV. As observed in the spectra taken with a photon energy of 21.2 eV, the C$_{60}$ HOMO and HOMO-1 features move by 0.4 eV to higher BE on deposition of 0.8 ML of Ag. The doublet feature observed between ~5 and 8 eV in the spectra shown in Fig. 3(a) arises from the Ag 4d valence band whose bandwidth increases with silver coverage from 2.21 (0.5 ML) to 2.64 eV (4 ML) to 3.1 eV (9 ML). The latter value is almost identical to the Ag 4d bandwidth in bulk Ag[12] and this observation, coupled with the appearance of a sharp well-defined Fermi edge at 0 BE leads us to conclude that the uppermost spectrum in Fig. 3(a) is representative of bulk Ag.

Figure 3(a) also clearly illustrates that the Ag 4d-derived valence band peaks shift to lower binding energy as the Ag coverage increases. Figure 3(b) shows the near-Fermi-edge region for a range of Ag coverages. It is particularly clear for both the 4 and 6 ML coverages that the Ag cluster Fermi edge, like the Ag 4d valence band, is shifted to higher binding energy compared to the bulk Ag spectrum.

Wertheim *et al.*[12] discussed the shifts to higher BE observed for the valence band and Fermi edge spectra of nanos-
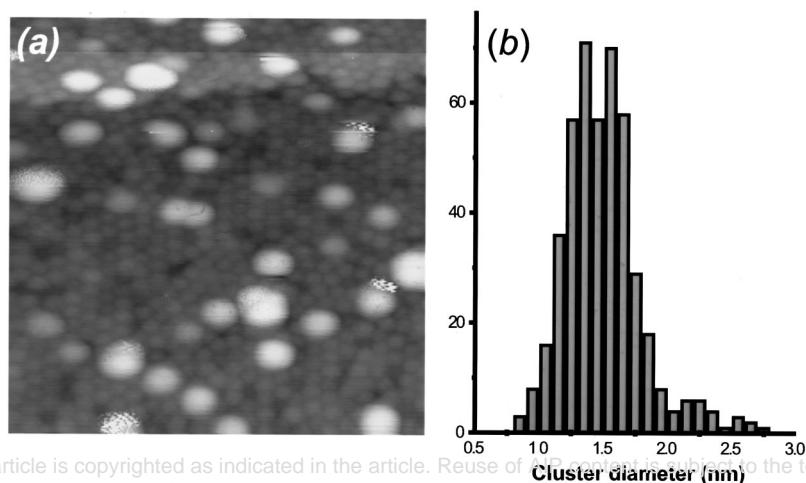

FIG. 2. (a) A 30×30 nm^2 STM image of a 1.5×10^{15} atoms cm^{-2} (0.37 ML) coverage of Ag on the C$_{60}$ monolayer. (b) A histogram of apparent cluster diameters as measured by STM. (Note that the sample used for the STM measurements was prepared in a separate system to that in which the photoemission measurements were made.)
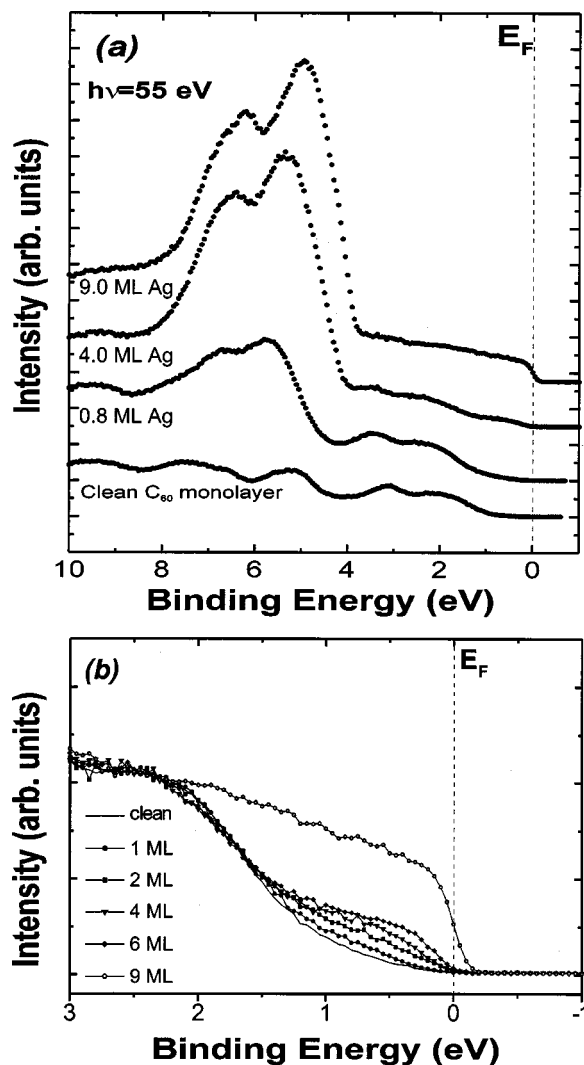
FIG. 3. (a) Valence band spectra as a function of Ag coverage taken at a photon energy of 55 eV to accentuate the Ag valence band and Fermi edge features. (b) The near Fermi edge region of the valence band spectra as a function of coverage. To facilitate comparison of the relative intensities of the Fermi edges the spectra have been normalized to the intensity of the C_{60} HOMO feature.

cale metal clusters on poorly conducting substrates. Their key result was that the positive BE shifts arise from the positive charge remaining on the cluster following ejection of a photoelectron. On a poorly conducting substrate this charge is not neutralized on the timescale of the photoemission process and this gives rise to a Coulomb potential due to the cluster charge. Classically, this potential will shift the photoelectron energies to higher BE by an amount

$$\Delta BE = e^2/8\pi\varepsilon_0 r.$$

If we take the apparent mean cluster diameter determined from the STM images for a coverage of 0.37 ML, $r = 0.75$ nm and, thus, $\Delta BE = 0.96$ eV. The BE shift observed experimentally for a 0.5 ML coverage, 0.75 ± 0.05 eV, is close to this value.

The reasonably good agreement between the measured BE shift for Ag clusters on the C_{60} monolayer and that predicted by the simple model described above is further strong evidence that the adsorption of Ag produces a fullerene monolayer on Si(111) that is only weakly conducting (due to

the absence of an appreciable level of doping). Perfect agreement between the measured binding energy shift and that estimated using the simple ''free cluster'' argument outlined above is not to be expected given: (i) the STM measurements, due to the finite radius of curvature of the tip, overestimate the cluster size; (ii) image charges in the dielectric substrate will contribute to the BE shift measured by photoemission, and (iii) the clusters may deviate from spherical symmetry.

Finally, we note that Alonso *et al.*[13] have reported somewhat similar coverage-dependent shifts in valence band features for metal overlayers on GaP. Following work by Hecht,[14] they attributed the energy shifts to the presence of strong surface photovoltages (SPVs). We can rule out SPVs as the origin of the valence band and Fermi edge shifts we observe for the following reasons. First, the Si $2p$ core-level binding energy remains fixed (at 99.3 ± 0.05 eV) regardless of Ag coverage or photon flux. Second, although the C_{60} HOMO–LUMO gap is appreciably larger than the Si band gap, there is no depletion region and hence no ''built-in'' electric field within the C_{60} monolayer in which to separate electron–hole pairs.[15]

Concluding, these results clearly demonstrate that C_{60}-surface interactions will place significant limitations on the ability to control, via doping, the electronic properties of molecular nanostructures based on adsorbed fullerenes.

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