

Competing interactions of noble metals and fullerenes with the Si(111)7×7 surface

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Synchrotron-based photoelectron spectroscopy (PES) has been used to investigate the interaction of atomic gold and silver with a covalently bound C₆₀-monolayer adsorbed on Si(111)7×7. In contrast to the relatively benign interaction of silver with the C₆₀/Si(111)7×7 surface, core-level photoemission data reveal a strong interaction of gold with the underlying silicon despite the presence of a chemisorbed fullerene monolayer. The Si 2*p* PES data exhibit dramatic changes consistent with the formation of a gold silicide, which is also evident from the corresponding Au 4*f* spectra. Valence band photoemission also reveals the absence of any density of states at the Fermi level following the adsorption of either metal, indicating a negligible transfer of electrons from the adsorbed metal to the C₆₀ cage. © 2003 American Institute of Physics. [DOI: 10.1063/1.1628225]

I. INTRODUCTION

As a route to novel molecular electronic devices, tuning the electronic properties of fullerenes through doping offers tremendous opportunities for nanotechnology. Doped bulk fullerenes demonstrate a full range of electronic properties from insulator to superconductor.^{1,2} Fullerene molecules (C₆₀, C₅₉N, La@C₈₂) can be manipulated on surfaces^{3–6} using scanning tunneling microscopy or chemically functionalized for self-assembly into nanostructures.⁷ The interaction of supported fullerenes with the surface is crucial when considering the possibility for doping. We have previously shown that the C₆₀-Si(111)7×7 interaction is sufficiently strong as to inhibit significant charge transfer from adsorbed silver atoms to the fullerene cage,⁸ in stark contrast to the adsorption of C₆₀ on the Ag(111)⁹ surface. In this paper we compare the interaction of silver and gold with a C₆₀ monolayer chemisorbed on Si(111)7×7. In terms of electron donation to the fullerene cage we find both systems to be very similar. However, while Ag atoms adsorbed on the C₆₀ monolayer aggregate to form nanometer-sized clusters, the analogous deposition of Au atoms on the C₆₀ monolayer leads to a reaction with the underlying silicon substrate.

II. EXPERIMENTAL DETAILS

The photoemission experiments discussed in Secs. III A and III B were performed on beamline 4.1 of the SRS Synchrotron, Daresbury, UK.¹⁰ Photon energies in the range 21.2–55 eV were used for valence band spectra and 140 eV for the Si 2*p* and Au 4*f* regions. Photoelectrons were measured at normal and grazing emission angles using a Scienta

SES-200 hemispherical analyzer with an acceptance angle of ±5°. Binding energy scales were calibrated to the Fermi edge of the tantalum sample holder and an overall resolution of around 250 meV was achieved. For coverage calibration purposes a fixed x-ray anode (Al Kα) was used to measure the C 1*s* core levels as these energies fall outside the energy range of the beamline. The experiments discussed in Sec. III C were performed on Beamline MPW6.1 of the SRS using a VG-ARUPS10 analyzer with a slightly better resolution of around 180 meV.

Atomically clean reconstructed Si(111)7×7 surfaces were obtained first by extensive degassing of a B-doped sample (10¹⁶ cm⁻³) at 600 °C followed by repeated flash annealing to 1200 °C for 1 min (<1×10⁻⁹ Torr) until the characteristic surface states of the reconstructed surface were observed in the valence and Si 2*p* spectra (see Sec. III A). C₆₀ molecules (commercial source) were evaporated from a resistively heated tantalum envelope at a temperature of 425 °C, giving an evaporation rate of 0.10±0.02 ML min⁻¹, where 1 ML is defined as the number of molecules in a complete single layer on the Si(111)7×7 surface, 1.1×10¹⁴ cm⁻². C₆₀ monolayers were obtained both by building up the surface coverage in submonolayer steps and by annealing an evaporated thick film to 300 °C by electron-beam and direct resistive heating. The C 1*s*-Si 2*p* core-level photoelectron spectroscopy ratio of the annealed monolayers was then measured to provide a reliable calibration for the room temperature monolayer preparation. Atomic Ag and Au were evaporated from Knudsen cells at temperatures of 860 and 1065 °C, respectively. This resulted in Ag deposition rates of 6.0±1.8 ML min⁻¹ (Sec. III A) and 0.10±0.03 ML min⁻¹ (Sec. III C), and Au deposition rates of 1.0±0.3 ML min⁻¹ (Sec. III B) and 0.3±0.1 ML min⁻¹ (Sec. III C).

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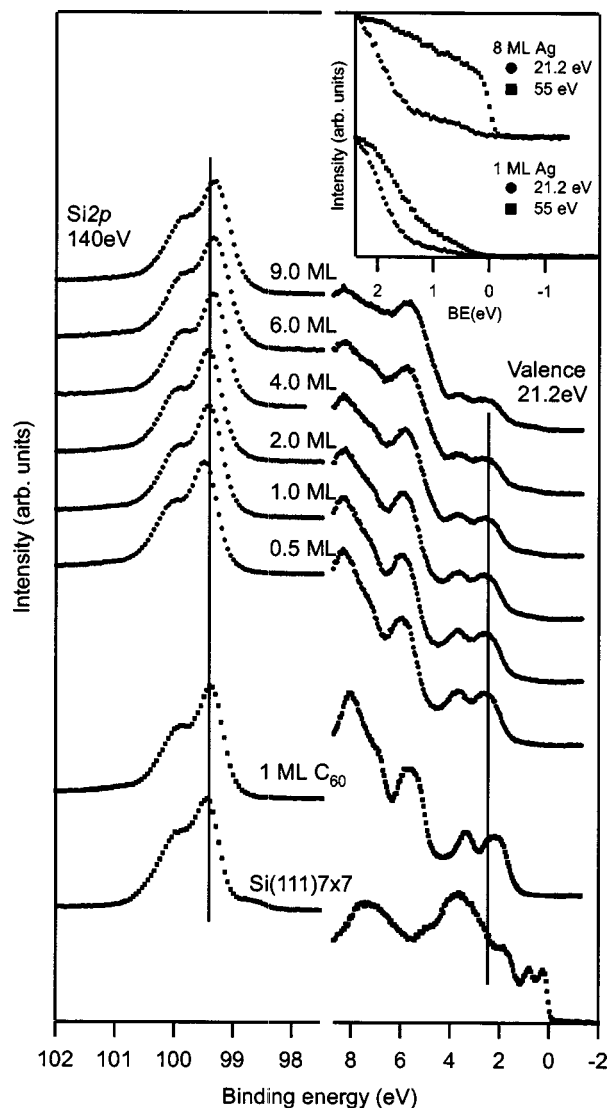


FIG. 1. Si $2p$ ($h\nu=140$ eV) and valence band ($h\nu=21.2$ eV) photoemission for the deposition of silver on the 1 ML $C_{60}/Si(111)7\times 7$ surface. The monolayer in this case was obtained by annealing a thick film of C_{60} by electron beam heating to 300°C . The Si $2p$ spectra (normalized to the intensity of the main peak) exhibit no significant change in line shape or binding energy during the deposition (see the text). The inset shows a comparison of the region near the Fermi level measured at photon energies of 21.2 and 55 eV to show that any intensity in this region is due to the Ag valence states which have a greater cross section at the higher photon energy.

Here a monolayer is defined as the number of metal atoms in a close packed layer and the deposition rates are calculated from the parameters of the Knudsen cells and the geometry of the experiment (and verified by *ex situ* atomic force microscopy). Substrate temperatures were monitored *via* an infrared pyrometer.

III. RESULTS AND DISCUSSION

A. Ag/ C_{60} -Si(111)7 \times 7

Figure 1 shows the changes that occur in the valence band and Si $2p$ regions when silver is progressively deposited onto a C_{60} monolayer adsorbed on a Si(111)7 \times 7 surface produced by annealing a thick C_{60} film (5 ML) to 300°C by

e-beam heating. The starting point for the preparation (and for all others discussed in this paper) is the Si(111)7 \times 7 reconstructed surface whose cleanliness was verified by the presence of characteristic features in the Si $2p$ and valence band spectra:¹¹ the “rest atom” Si $2p$ peak shifted by -0.73 eV binding energy from the bulk component (99.48 eV), and the three surface states at the top of the valence band (0.27, 0.82, and 1.82 eV).

A shift of the peaks in the valence band by 0.4 eV to higher binding energy is observed following the first adsorption of 0.5 ML Ag due to the interplay between Fermi-level movement and core-hole screening induced by charge transfer from the metal to the fullerene.^{8,12} As the surface coverage is gradually increased to 9.0 ML the increasing contribution from the Ag valence band states result in the highest occupied molecular orbitals of the fullerene becoming less defined and also cause the peak around 6 eV to appear to shift slightly in energy (-0.1 eV). There is no significant intensity observed at the Fermi edge (at a photon energy of 21.2 eV) even for the highest coverage of silver; clear evidence of the minimal electronic occupation of the C_{60} lowest unoccupied molecular orbital (LUMO). This is in stark contrast with C_{60} molecules adsorbed on polycrystalline¹³ Ag and Ag(111)⁹ where 1.7 and 0.75 electrons per molecule are transferred to the fullerene cage, respectively. That any intensity near the Fermi level in Fig. 1 is due only to the valence states of the metallic Ag is supported by a comparison of the valence band spectra measured at 21.2 and 55 eV (as shown in the inset). The relative intensity between the Fermi level and the highest occupied molecular orbital (HOMO)-derived peak is much stronger at a photon energy of 55 eV, where the cross section of the Ag states is greater.

The Si $2p$ spectra in Fig. 1 have been normalized to the intensity of the main (bulk) peak to illustrate that although a small shift (0.1 eV) is observed in the binding energy (possibly due to band-bending), absolutely no change occurs to the line shape up to a coverage of 4 ML Ag. At 9 ML there are very minor changes to the spectrum arising from a severe attenuation of the spectra due to the monolayers of adsorbed Ag on the surface resulting both in a significant reduction in the signal-to-noise ratio and a slight broadening of the spectra. The absence of any interaction with the underlying silicon is significant because it suggests that the Ag atoms are situated on top of the C_{60} monolayer and not localized at defect sites in the monolayer where Si dangling bonds might be exposed.¹⁴ Scanning tunneling microscopy (STM) data for the adsorption of 0.37 ML Ag on the C_{60} monolayer show that the Ag atoms nucleate to form clusters (with a mean diameter of 1.5 nm) on the C_{60} surface.⁸

B. Au/ C_{60} -Si(111)7 \times 7

Figure 2 shows the Si $2p$, Au $4f$, and valence band regions recorded when 5 ML gold was deposited onto a C_{60} monolayer adsorbed on the Si(111)7 \times 7 surface. In this case the monolayer was produced by annealing a thick C_{60} film (deposited at room temperature) to 300°C by direct resistive heating. The broad width and perturbation of the HOMO and HOMO-1 peaks in valence band spectra of the monolayer

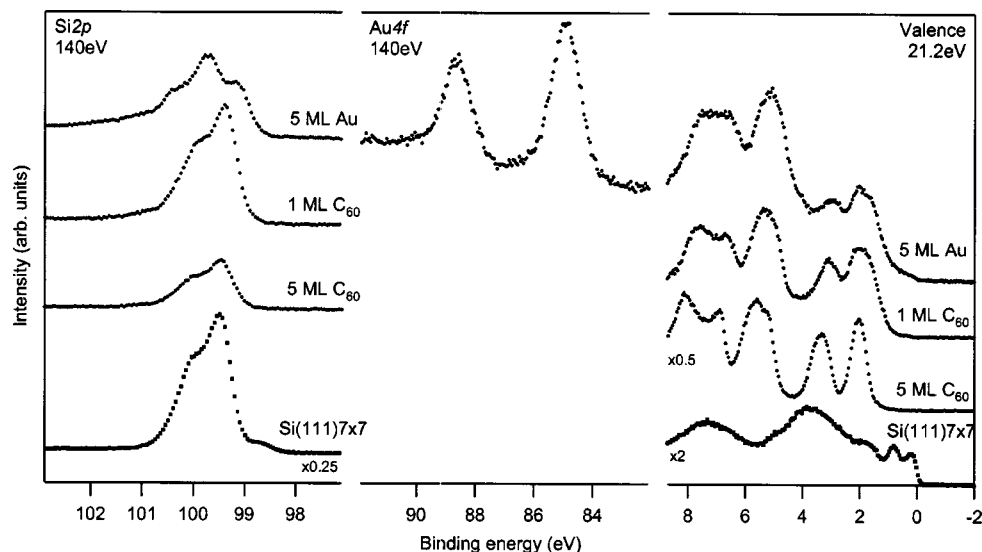


FIG. 2. Si 2*p* ($h\nu=140$ eV), Au 4*f* ($h\nu=140$ eV), and valence band ($h\nu=21.2$ eV) photoemission spectra for the interaction of 5 ML Au with the 1 ML C_{60} /Si(111)7 \times 7 surface. The monolayer was formed by annealing a thick fullerene film to 300 °C by direct heating. A substantial reaction is observed in the Si 2*p* spectra upon deposition of the gold on top of the C_{60} film. All spectra shown are the raw data normalized to the photon flux and the number of scans.

compared with the thick film indicate that the C_{60} monolayer is covalently chemisorbed to the surface, in agreement with previous studies.^{15–17} There is a slight increase in intensity on the high binding energy side of the Si 2*p* spectrum around 101 eV, and additional intensity in the vicinity of the valence band HOMO as compared to the previous e-beam annealed monolayer (3A). We attribute these spectral differences to the fullerene molecules “bedding down” into the surface forming additional Si–C bonds around the bottom of the cage.¹⁵ The fact that this effect is more pronounced for resistive heating may be attributed to the much higher heating rate of this method compared with e-beam. Indeed, the evolution of C_{60} molecules from an initially metastable bonding configuration to a more stable configuration on the Si(111) surface has been observed recently,¹⁸ and this process is likely to be highly sensitive to the rate at which the surface is annealed. Unlike the previous silver experiment (Sec. III A), we observe a dramatic change in the Si 2*p* spectrum due to a reaction of the deposited gold with the underlying silicon substrate. A change in the line shape of the HOMO in the valence band region is also observed. At this stage one might imagine that defects in the C_{60} monolayer caused by annealing the thick film have exposed regions of the silicon substrate with which the deposited gold can react to form a gold-silicide. For this reason we have performed the experiment again using just over 1 ML C_{60} built up in submonolayer steps to form a nonannealed monolayer.

Figure 3 shows the changes that occur in the Si 2*p*, Au 4*f*, and valence band regions when gold is gradually deposited onto a C_{60} layer formed at room temperature *via* submonolayer depositions to approximately 1.2 ML coverage. The valence band spectra for this coverage are completely consistent with those found in the literature and suggest that the nonannealed fullerene monolayer is also covalently chemisorbed.¹⁵ Here we can eliminate thermal-induced defects in the C_{60} monolayer since no annealing has

taken place. We have deliberately deposited slightly more than 1 ML in order to ensure at least one complete chemisorbed monolayer bound to the silicon. Even under these conditions we can clearly see a reaction occurring between the deposited gold and the underlying silicon. At the lowest Au coverage we observe a shift of the entire Si 2*p* spectrum by around -0.3 eV (most likely due to band-bending) and increasing to -0.5 eV with increasing gold coverage. A corresponding effect can also be observed in the valence band region as the HOMO gradually splits into two features, the lowest energy peak shifting further to lower binding energy with increasing gold coverage. Above 4 ML Au the Si 2*p* spectrum becomes dominated by a new silicide-related peak to higher binding energy. This, and additional structure in the high binding energy tail is clearly evident in the curve fitted spectra of Fig. 4, which shows the Si 2*p* spectrum for the reacted Au/ C_{60} /Si surface measured at normal and grazing emission angles.

The spectra have been fitted to a series of 5 Voigt spin-orbit doublets having a branching ratio of 0.5 and a spin-orbit splitting of 0.6 eV based on a fit of the clean Si(111)7 \times 7 surface. The lowest energy component (99.0 eV) is attributed to bulk silicon (Si^0), having a width consistent with that of the clean surface. This peak clearly diminishes at grazing emission as we probe with increasing surface sensitivity. The dominant and slightly broader component at 99.6 eV is related to gold silicide, denoted as the stoichiometric compound Au_3Si . This component is shifted by +0.6 eV with respect to bulk Si^0 and is consistent with the silicide formation observed when Au is deposited at room temperature onto the bare Si(111) surface.^{19–21} Thermodynamic calculations²² of the core-level binding energies predict a shift of +0.6 eV for AuSi, decreasing in magnitude with the concentration of Si.

The width and presence of structure in the high binding energy tail of the Si 2*p* spectrum necessitate the inclusion of

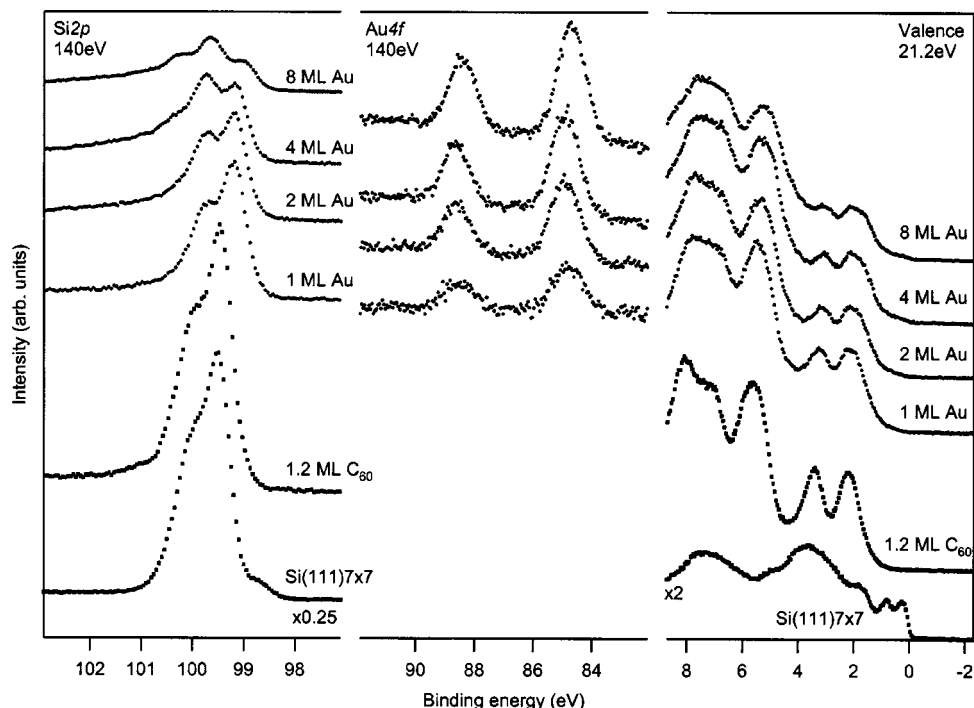


FIG. 3. Si 2*p* ($h\nu=140$ eV), Au 4*f* ($h\nu=140$ eV), and valence band ($h\nu=21.2$ eV) photoemission spectra for the interaction of gold with the 1.2 ML C₆₀/Si(111)7×7 surface. The thin fullerene film (1.2 ML) was formed through successive submonolayer depositions at room temperature. Reaction of the gold with the underlying silicon substrate is also evident even for this *unannealed* monolayer. All spectra shown are the raw data normalized to the photon flux and the number of scans.

at least three additional spin-orbit doublets into the fit as shown. We attribute the first two of these components at 100.3 and 101.1 eV to Si atoms bound to C₆₀ molecules and Au₃Si bound to C₆₀ molecules, respectively. The origin of the high-binding energy component at 102.0 eV is unclear at present. It has been suggested²³ that since gold can induce

changes in the silicon oxidation state²⁴ that the tail might consist of nonstoichiometric Au_xSi. However, the fact that we do not observe such an intense high-binding energy tail for the reaction of Au with the clean Si(111)7×7 might suggest that the origin of the high binding energy tail is related to C₆₀. A plethora of complex C₆₀/Au/Si combinations can be imagined, but these would be mere speculation in the context of the current data. A detailed high-resolution C 1*s* core-level study may yield further insight into the bonding of the C₆₀ on the reacted surface.

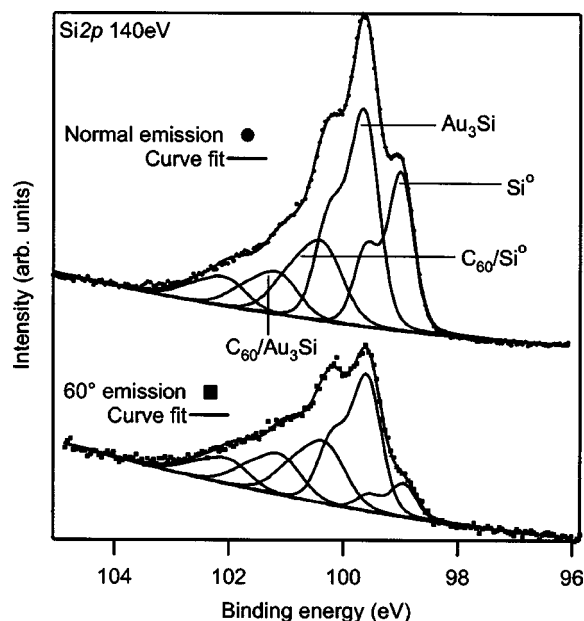


FIG. 4. Si 2*p* ($h\nu=140$ eV) photoemission spectra recorded at normal and grazing (60°) emission angles. The spectra have been fitted to a series of Voigt spin-orbit doublets as indicated. The parameters and origins of the individual components are discussed in the text.

In Fig. 5 we compare the Au 4*f* spectrum of the reacted surface (8 ML Au) with the adsorption of Au on a clean Si(111)7×7 surface. The spectrum for a thick Au film is accurately described by a single asymmetric Voigt spin-orbit doublet with a branching ratio of 0.66 and a spin-orbit splitting of 3.73 eV. The spectrum for a thin Au film adsorbed on Si(111)7×7, on the other hand consists of two chemical states due to the formation of the gold silicide and to the presence of unreacted metallic gold. The chemical shift in this case is 0.68 eV, again consistent with data from the literature.²¹ Applying the same fitting procedure to the Au/C₆₀/Si(111) spectrum in Fig. 5 shows that the vast majority of the 8 ML of Au is present in the reacted Au₃Si state. A small metallic Au contribution is evident on the low binding energy side of the peak which represents gold atoms that have accumulated at the silicon interface below the silicide layer. That metallic Au can diffuse to the interface below the silicide layer has been shown previously²¹ for the adsorption of Au on clean Si(111)7×7 but additional experiments at higher Au coverages are required to confirm that this is indeed occurring in the present case.

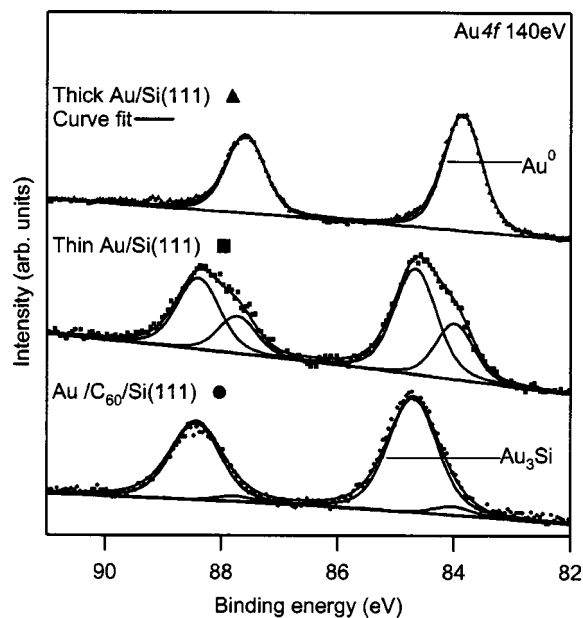


FIG. 5. Au 4f ($h\nu=140$ eV) photoemission spectra recorded at normal emission angle for the reacted Au/C₆₀/Si(111)7×7 surface, a thin film of Au/Si(111)7×7, and a thick film of Au/Si(111)7×7. The spectra have been normalized to unit height and fitted to asymmetric Voigt components as discussed in the text. Note that the asymmetry is not shown in the individual components but is included in the sum of the fit.

The strength of the Au–Si interaction is demonstrated here by the fact that silicide formation occurs even in the presence of a chemisorbed C₆₀ monolayer. Encapsulating sensitive surfaces, including Si(111), with C₆₀ has previously been shown to inhibit surface reactions such as oxidation.²⁵ We would not, therefore, expect gold to react with silicon in this “encapsulated” state.

While the Si–C₆₀ bond is covalent^{15,17} in character with little or no charge transfer to the fullerene cage, the Ag–C₆₀ and Au–C₆₀ interactions are ionic and characterized by a strong charge transfer.^{26,27} However, using valence band spectroscopy we have observed negligible charge transfer to the cage under the conditions studied here, with both metals exhibiting very similar behavior. This is evident for silver from the comparison of the valence band near the Fermi level at different photon energies as shown in the inset of Fig. 1. A similar treatment of the interaction with gold is presented in Fig. 6 in which the valence band measured at a photon energy of 55 eV is shown. There is approximately a factor of 5 difference between the cross sections at 21.2 eV (Fig. 3) and 55 eV (Fig. 6) of the C 2s and 2p states. This contrasts with a much smaller change in the Au 6s cross section at these two energies. The fact that the relative intensity between the Fermi level and the HOMO-derived peak is stronger for a photon energy of 55 eV as compared with 21.2 eV (inset of Fig. 6) further suggests that the weak intensity near the Fermi edge is not derived from the partial filling of the LUMO and that negligible charge-transfer occurs.

The metal–fullerene interaction therefore cannot explain why the two metals behave very differently on the C₆₀/Si surface or how the noble metal can penetrate the covalently bound fullerene monolayer to interact with the silicon sub-

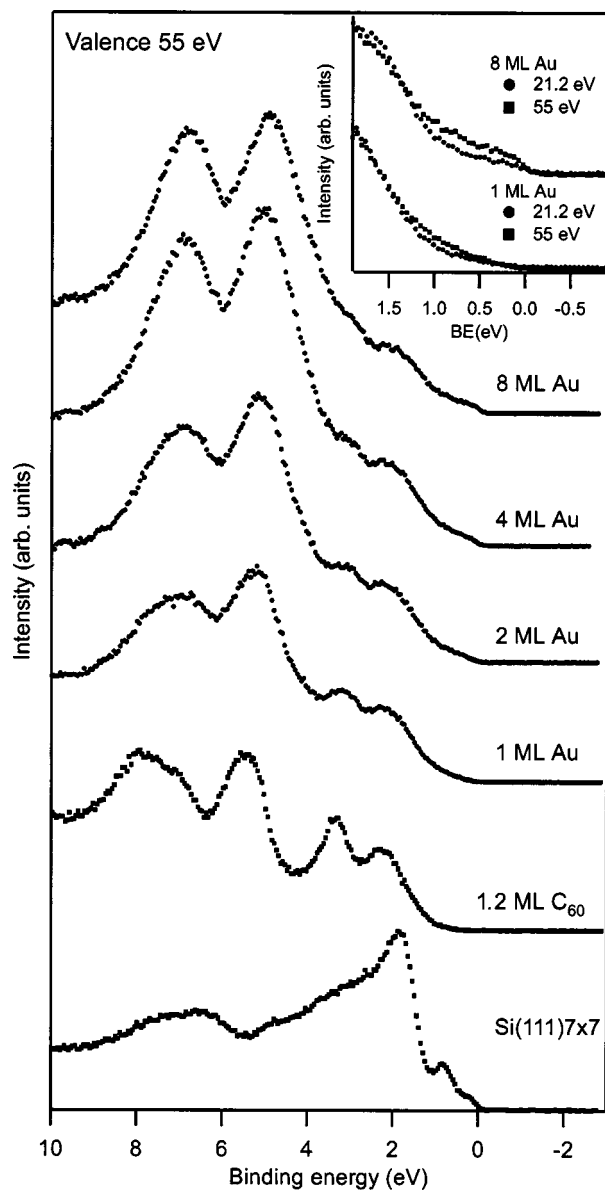


FIG. 6. Valence band ($h\nu=55$ eV) photoemission for the deposition of Au on the 1.2 ML C₆₀/Si(111)7×7 surface. The thin fullerene film (1.2 ML) was formed through successive submonolayer depositions at room temperature. The inset shows a comparison of the region near the Fermi level measured at photon energies of 21.2 and 55 eV to show that any intensity in this region is due to the Au valence states rather than partial filling of the LUMO as discussed in the text.

strate. Instead, we propose that the reaction occurs initially at step edges and domain boundaries on the C₆₀-covered surface, where the underlying silicon atoms may already be exposed. The different reactivity of the two noble metals is then determined solely by the strength of the metal–silicon interaction which favors significantly the reaction with gold to form a silicide compound.^{19–21} Silver, on the other hand, does not react with silicon at temperatures below 500 K,^{28,29} but tends instead toward nucleation³⁰ and epitaxial growth³¹ with a number of surface reconstructions known.³² If the Au–Si interaction is comparable to the C₆₀–Si chemisorption bonds, the reaction will displace C₆₀ molecules which will then form new bonding states as suggested earlier and significantly disrupt the surface allowing more substrate at-

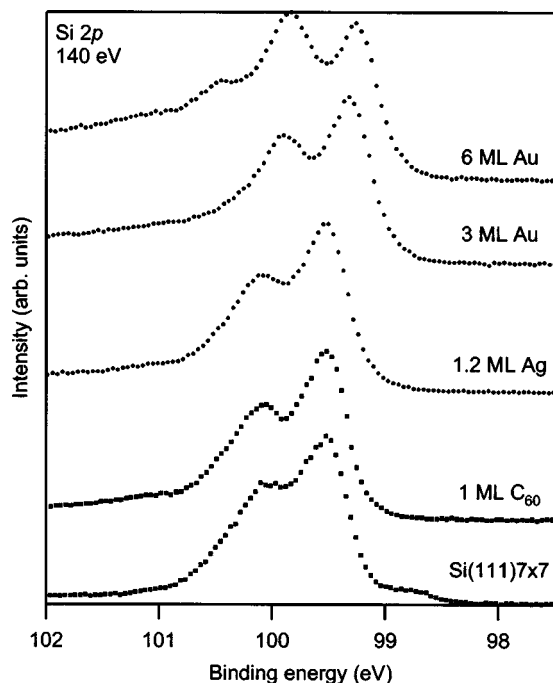


FIG. 7. Si $2p$ ($h\nu=140$ eV) photoemission spectra recorded at normal emission angle for a C_{60} monolayer on Si(111) 7×7 , onto which was deposited 1.2 ML of Ag, followed by 3 then 6 ML Au (note that these spectra were acquired with slightly higher total energy resolution than those in Figs. 1–6). Spectra have been normalized to the intensity of the main peak and clearly show that while adsorption of Ag onto the C_{60} has no effect on the underlying Si, subsequent adsorption of gold results in the silicide formation discussed in Sec. III B even in the presence of a chemisorbed C_{60} monolayer and a Ag adlayer.

oms to react. The driving force is the formation of a gold silicide, which as discussed earlier for Au/Si(111) extends several layers into the surface. Furthermore, we still observe significant intensity in the valence band from the C_{60} molecular orbitals and the C_{60} /Si interaction in the Si $2p$ region even after the equivalent of 8 ML Au deposition. This suggests that the C_{60} molecules are still localized at the surface of the reacted system, while the silicide formation occurs below the surface as the Au atoms diffuse into the substrate.

C. Au/Ag/ C_{60} -Si(111) 7×7

In order to account for variations in the quality of C_{60} monolayers prepared by different annealing methods we have repeated the experiments discussed in Secs. III A and III B using *identical* preparation conditions (in this case monolayers prepared using direct heating of Si) and have confirmed that the results are consistent with those already discussed. Furthermore, to eliminate variations in the quality of the fullerene monolayer from sample to sample as a possible cause of differences in the Au and Ag interactions, a coadsorption experiment was also carried out. Figure 7 shows the Si $2p$ spectra recorded for this experiment in which a C_{60} monolayer was prepared by annealing a C_{60} thick film to 300 °C by direct heating. Approximately 1.2 ML of Ag was then deposited onto the surface which results in no change in the Si $2p$ spectrum as shown in Fig. 7, in complete agreement with the data presented in Sec. III A for the e-beam monolayer. Au was subsequently deposited onto the

Ag-precovered C_{60} monolayer as indicated in Fig. 7, resulting in the dramatic change in the Si $2p$ spectrum indicative of silicide formation. This result is significant as it demonstrates that the different interactions observed for the two noble metals are due solely to their reactivity with silicon rather than to variations in the preparation of the C_{60} monolayer.

IV. CONCLUSIONS

The room temperature interaction of silver and gold with a chemisorbed C_{60} monolayer on a reconstructed Si(111) 7×7 surface has been investigated using synchrotron-based photoelectron spectroscopy. While Ag forms nanoclusters on top of the fullerene monolayer, Au penetrates the C_{60} monolayer to react with the underlying silicon. This reaction, proposed to initiate at domain boundaries and defects in the monolayer, leads to the formation of a Au_3Si silicide and the displacement of C_{60} molecules. These results clearly show that there are very significant constraints on the use of conventional doping methods to modify the electronic structure of covalently bound fullerene films.

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