Interfacial reaction of C_{60} with silver

G. K. Wertheim and D. N. E. Buchanan
AT&T Bell Laboratories, Murray Hill, New Jersey 07974

(Received 14 July 1994)

When C_{60} is in contact with Ag the metal donates electronic charge into the lowest unoccupied molecular orbital of the C_{60} molecules at the interface, resulting in a monomolecular metallic layer of C_{60}. We find no evidence for the formation of a bulk Ag_xC_{60} compound.

It is well established that C_{60} forms interstitial, metallic compounds with the alkali metals.[1] In these compounds the metal atoms donate their outer electron into the lowest unoccupied molecular orbital (LUMO) of C_{60}, which becomes the conduction band. Earlier investigations have shown that C_{60} layers in contact with Cu (Ref. 2) or Au (Refs. 3 and 4) are modified by charge transfer, but no bulk metallic noble-metal compounds have been reported. We report here an investigation of the reaction of C_{60} with metallic silver.

EXPERIMENTAL DETAILS

Two different methods were employed to investigate the nature of the interaction of C_{60} with silver. In the first Ag was deposited on top of layers of C_{60} supported by an inert substrate; in the second C_{60} was directly deposited on a single-crystal Ag(111) surface. The depositions were made at room temperature. Data were taken at room temperature after annealing at temperatures up to 400 °C.

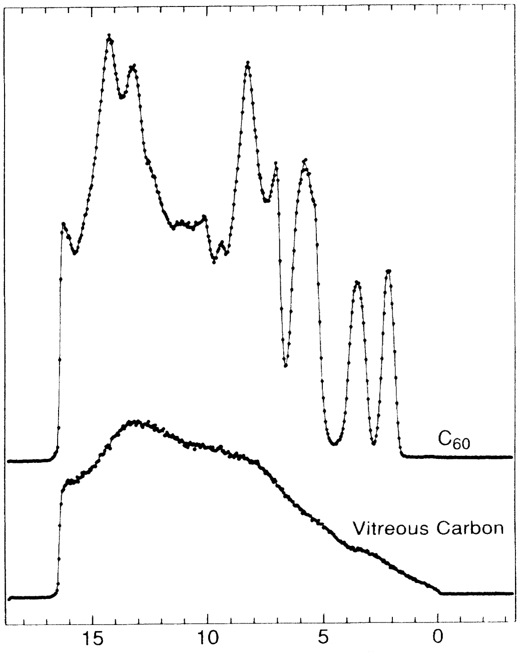

FIG. 1. Comparison of the valence-band spectra of C_{60} and vitreous carbon. The data were taken with He I radiation. The work-function cutoff is at the same energy in the two materials.

Vitreous carbon (VC) was used as the inert substrate. Although made of carbon, this material is actually quite favorable for studies of the valence band of C_{60}, because it does not react chemically with C_{60} and has no sharp features between 15 eV and the Fermi level (see Fig. 1). Since the loss of C_{60} by sublimation may interfere with the annealing experiments, some experiments were initially performed with only C_{60} on VC to assess this problem. This was necessary because the published vapor pressure data for C_{60} (Ref. 5) do not extend down to the annealing temperatures used here. In subsequent experiments Ag was deposited on top of the supported C_{60} and the annealing experiments repeated. It was found that the Ag causes the C_{60} to be retained on the surface at temperatures where C_{60} alone would desorb. This provides the first indication of a chemical reaction between these two materials.

The Ag substrate was first cleaned by etching with a 1:1 mixture of Superoxol (H_2O_2) and ammonium hydroxide and immediately inserted into the UHV chamber of the photoemission spectrometer. There the surface was prepared by repeated sputtering and annealing and characterized by photoemission. When a clean surface had been obtained, C_{60} was evaporated onto it from a Knudsen cell operated at 425 °C. The deposition rate was ~2 ML per minute. Layers of C_{60} with thickness ranging from 0.5 to 30 monolayer (ML) were deposited onto the substrate at room temperature. (1 ML denotes close-packed coverage with one layer of C_{60}.) Data were taken for the layer as deposited and after annealing at temperatures up to 400 °C. The photoemission data were taken with He I resonance radiation using a Vacuum Science Workshop 50-mm analyzer operated at a resolution of 100 meV. A 4.0-V negative bias was applied to the substrate in order to shift the work-function cutoff well above that of the spectrometer.

RESULTS AND DISCUSSION

A. Vitreous carbon substrate

The preparation of C_{60} compounds by annealing C_{60} layers deposited on metal substrates depends critically on the competition between the rate of diffusion of substrate metal atoms into the C_{60} and the rate sublimation of the pure C_{60}. Since C_{60} compounds generally have a much lower vapor pressure than the pure material, they can be separated from unreacted material by annealing above 300 °C. The C_{60}-derived material that remains after such an anneal is not necessarily a bulk compound but may amount to no more than the monolayer of C_{60} in direct contact with the metal substrate. Because the electron mean free path in C_{60} is no larger than the thickness of one molecular layer,[6] photoemission spectra of bulk compounds and adsorbed monolayers are not necessarily very different. Some effort is required to distinguish between the two cases.

We begin with a determination of the rate of sublimation of pure C_{60} from a bulk layer supported on a VC substrate. This information is useful in the interpretation of data taken with metal substrates. The desorption of C_{60} resulting from annealing for 4 min at the temperatures indicated is shown in Fig. 2. The data are all plotted with the same vertical sensitivity, so that they accurately reflect the strength of the C_{60} signal. We note that there is a decrease in the C_{60} signal even after the 175 °C anneal, suggesting that some clustering has taken place, since desorption should be quite slow at this temperature. After higher temperature anneals, the VC spectrum emerges as the C_{60} signal decreases. A 4-min anneal at 275 °C suffices to remove almost all of the C_{60}. This is in good accord with an estimate of desorption obtained from an extrapolation of the vapor pressure data,[5] which yield a rate of 0.5 ML/min at 275 °C. It is interesting to note that there is no change in the binding energy of the highest occupied molecular orbital (HOMO) with coverage in Fig. 2, confirming that there is no chemical interaction, no pinning of the LUMO at the Fermi level E_F, and no band bending for C_{60} on VC. As a result, good C_{60} spectra are readily obtained, even for quite thin coverages, from a VC substrate.

When silver is evaporated onto a thick C_{60} film supported on VC, the valence-band spectrum undergoes significant changes [see Figs. 3(a) and 3(b)]. A new component appears next to the HOMO at smaller binding energy, broadening the spectrum and giving it an apparent negative shift. The deep valley between 4 and 5 eV shows the presence of an additional component and a small step appears at E_F. Annealing this composite layer at 225 °C removes most of the unreacted C_{60}, yielding the spectrum shown in Fig. 3(c). Annealing also increases the amplitude of the step at E_F.

The first question is whether the effect at E_F is due to photoemission from the Ag itself or due to its effects on the C_{60}. Comparison with the spectrum obtained after an anneal at 400 °C [Fig. 3(d)], which removes all of the C_{60} but leaves the Ag, shows that the step at the E_F due to the Ag (and VC) is too weak to account for the step observed when both Ag and C_{60} are present. We conclude that the response at the Fermi level is due to charge donation into the LUMO of C_{60}. [The data in Fig. 3(d) also show that the Ag 4*d* band is responsible for the sig-

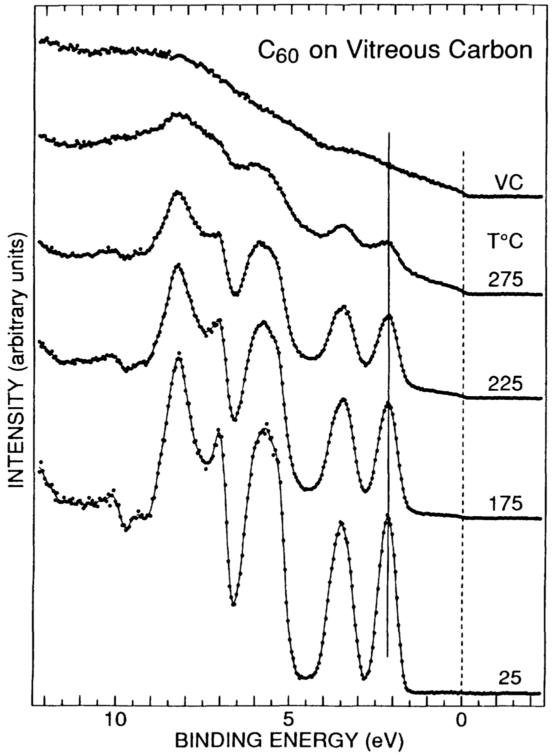

FIG. 2. Sublimation of C_{60} from a vitreous carbon substrate. The data were taken at room temperature after annealing for 4 min at the temperatures shown. The data labeled VC are those of the clean substrate, prior to the deposition of C_{60}.

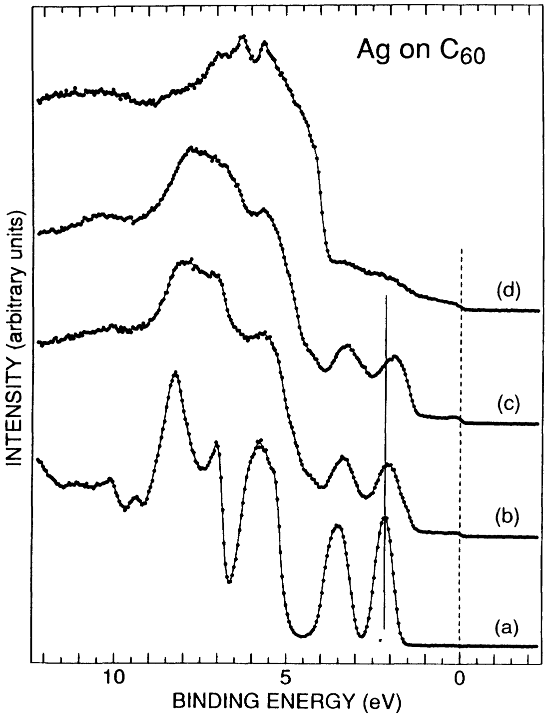

FIG. 3. Deposition of Ag on C_{60} supported by vitreous carbon and the effects of subsequent annealing: (a) Clean C_{60} (b) after Ag deposition, (c) after annealing at 225 °C, and (d) after annealing at 400 °C.

nal between 4 and 5 eV.]

The second question concerns the state of aggregation of the evaporated Ag on the C_{60}. Although Ag is known to form clusters when deposited on VC, it does not follow that it will do so on C_{60}, since we have evidence of a reaction with this material. A likely morphology for the material resulting from the deposition of Ag onto C_{60} followed by annealing is Ag clusters surrounded by adsorbed C_{60} molecules.

The spectrum after the 225 °C anneal is shown in greater detail in Fig. 4 with the region near the Fermi level vertically magnified. These data are characteristic of those obtained over a wide range of annealing temperature. Quite similar spectra were obtained after anneals ranging from 175 °C to 325 °C, a temperature where desorption from clean VC would have been complete. As mentioned above, the retention of the C_{60} indicates that the C_{60} is chemically bound to Ag. The magnified region near E_F shows a peaking that can be attributed to neither the VC substrate nor to metallic Ag clusters. The valence band of the VC substrate rises continuously from the Fermi level with only a weak cutoff (see Fig. 1). The Fermi edge of polycrystalline Ag has the form of a step and is quite weak. The peaking must then be due to the partial filling of the LUMO of C_{60} by electrons from Ag. The peak is quite narrow, ~0.5 eV, as one would expect on the basis of band-structure calculations.[7-9] However, since we have no measure of the fractional filling of the LUMO, this comparison may not be significant. Moreover, it is worth noting that there is evidence for filled states between the HOMO and LUMO peaks. This is quite similar to data for metallic compounds such as K_3C_{60}, where it has been attributed to electron-correlation effects. If this mechanism also accounts for the present observations, a detailed comparison of the width of the peak at the Fermi level with uncorrelated band structures is not appropriate. Nevertheless, the narrow feature at the Fermi level provides definitive proof of charge donation into the LUMO of C_{60} when it is in contact with metallic Ag.

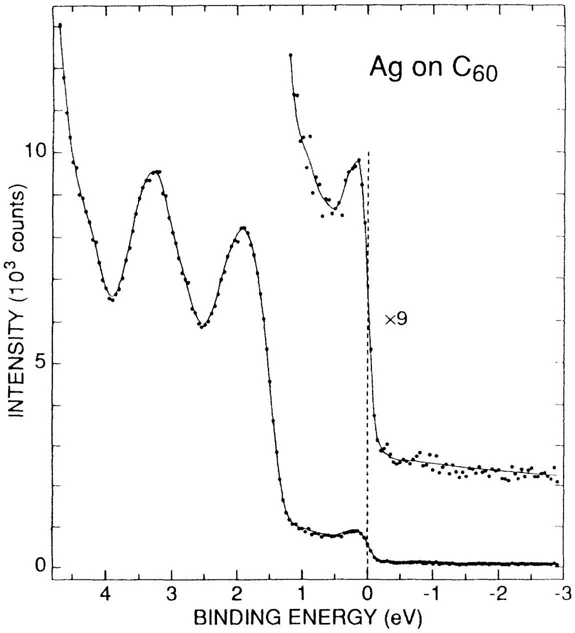

FIG. 4. Enlarged view of the region near the Fermi edge of Fig. 3(c), showing a peak due to charge donation into the LUMO.

B. Silver substrate

Data taken as the Ag surface was progressively covered with C_{60} at room temperature are shown in Fig. 5. The HOMO binding energy increases steadily with coverage, from 1.85 eV at 0.5 ML to 2.7 eV at 30 ML. The small binding energy at low coverage is due to the pinning of the LUMO at the Fermi level, and is characteristic of the first monolayer of C_{60} in contact with the Ag substrate. Spectra at submonolayer coverage are not affected by annealing to 225 °C. The HOMO binding energy is quite similar to that obtained after annealing C_{60} with Ag on VC at 225 °C [Fig. 3(c)]. A fairly thick layer of C_{60} is required before the band bending allows the spectrum to approach that of an unperturbed layer. The work-function cutoff also shows the band-bending shift. The fact that the step at the Fermi level remains visible at 2-ML coverage, where the Ag 4*d* band has been almost completely attenuated, indicates that the Fermi cutoff is due to a metallic C_{60} band.[10] This gives an independent indication of the formation of a metallic C_{60} layer.

When a thick C_{60} film on the Ag(111) substrate was annealed for 4 min at 275 °C, the spectrum shown in Fig.

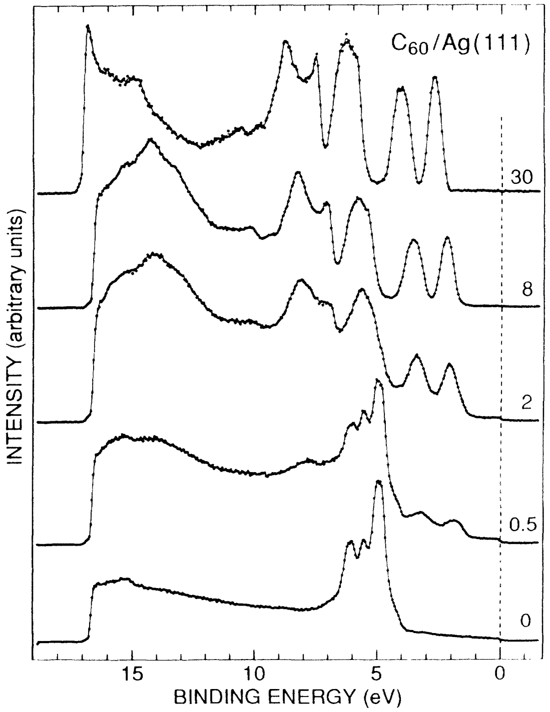

FIG. 5. Valence-band spectra of the clean Ag(111) substrate progressively covered by vapor-deposited C_{60}. The coverages are approximately 0.5, 2, 8, and 30 ML.

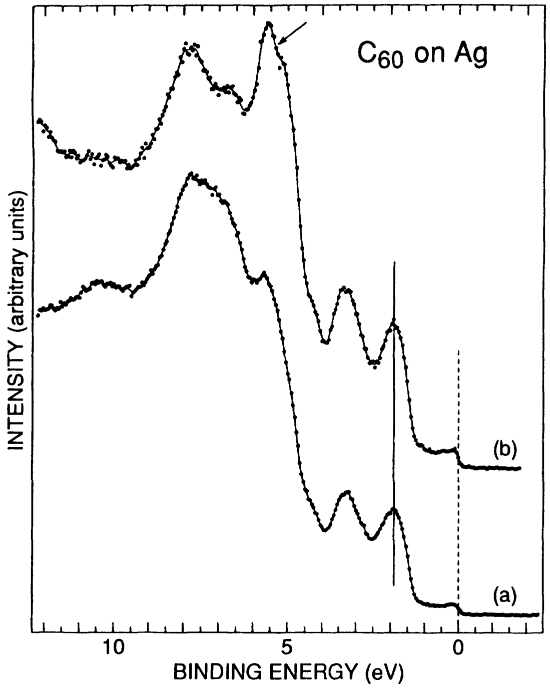

FIG. 6. Comparison of the valence-band spectra of (a) C_{60} and Ag annealed on a VC substrate at 225 °C and (b) a thick C_{60} layer annealed at 375 °C on an Ag(111) substrate.

6(b) was obtained. The peaking just below the Fermi level is comparable to that in the spectrum obtained by annealing Ag and C_{60} on VC, as shown in Fig. 6(a). The spectrum on the Ag substrate differs from the one on the VC substrate mainly in the peak between 5 and 6 eV indicated by the arrow, which is due to the 4*d* electrons of Ag. It is much too strong to be due to Ag in a hypothetical AgC_{60} compound. A measure of the strength of the Ag 4*d* signal obtained from Ag directly associated with the C_{60} is provided by Fig. 6(a). The 4*d* peak in Fig. 6(b) must then be due to the metallic Ag substrate. This provides a clear indication that only 1 ML of C_{60} remains on the Ag surface, i.e., that there is no bulk AgC_{60} compound. (We should point out that the 4*d* contribution of the Ag does not resemble the angle-resolved spectrum obtained from the clean Ag surface shown in Fig. 5 because of the scattering by the C_{60} overlayer.) Additional 4-min anneals up to 375 °C produce little change in the spectrum, indicating that the C_{60} is strongly bound to the Ag surface. This provides a simple method for the preparation of an Ag surface covered by a single layer of C_{60}. Continued annealing at 375 °C will eventually desorb the C_{60} layer in contact with the Ag, an event that is recognized by the reemergence of the *d*-band spectrum of the clean surface. In fact, spectra essentially identical to the one shown in Fig. 5 for 0.5 ML of C_{60} deposited on the Ag substrate were obtained by annealing the thick layer for 28 min at 375 °C.

Having demonstrated that Ag is able to donate electrons into the LUMO of C_{60}, the question remains as to why no bulk compound is formed. The problem is certainly not due to ionic size, since the 1.26-Å radius of Ag^+ is actually smaller than the 1.33-Å radius of K^+, which readily intercalates into fcc C_{60} to fill both the tetrahedral and octahedral sites. The main reason appears to be the larger cohesive energy of Ag,[11] which makes it energetically more favorable for Ag to have Ag neighbors rather than C_{60} neighbors. These results and this conclusion are not at odds with the report of the formation of an AgC_{60} complex in matrix isolation[12] where the molecular units are well separated.

CONCLUSIONS

We have found that metallic Ag will donate electrons into the LUMO of adsorbed C_{60} molecules, resulting in a metallic conduction band. This reaction is confined to those C_{60} molecules in direct contact with the metal substrate. There is no evidence for the formation of a bulk Ag-C_{60} compound.

ACKNOWLEDGMENTS

We are indebted to Robert C. Haddon for the purified C_{60} used in these experiments and to E. E. Chaban and R. A. Malic for the Ag evaporating furnace.

---

[1] R. C. Haddon, A. F. Hebard, M. J. Rosseinsky, D. W. Murphy, S. J. Duclos, K. B. Lyons, B. Miller, J. M. Rosamillia, R. M. Fleming, A. R. Kortan, S. H. Glarum, A. V. Makhija, A. J. Muller, R. H. Eick, S. M. Zahurak, R. Tycko, G. Dabbagh, and F. A. Theil, Nature **350**, 320 (1991).

[2] J. E. Rowe, P. Rudolf, L. H. Tjeng, R. A. Malic, G. Meigs, C. T. Chen, J. Chen, and E. W. Plummer, Int. J. Mod. Phys. B **6**, 3909 (1992).

[3] Y. Kuk, D. K. Kim, Y. D. Suh, K. H. Park, H. P. Noh, S. J. Oh, and K. S. Kim, Phys. Rev. Lett. **70**, 1948 (1993).

[4] T. R. Ohno, Y. Chen, S. E. Harvey, G. H. Kroll, P. J. Benning, J. H. Weaver, L. P. F. Chibante, and R. E. Smalley, Phys. Rev. B **47**, 2389 (1993).

[5] J. Abrefah, D. R. Olander, M. Balooch, and W. J. Siekhaus, Appl. Phys. Lett. **60**, 1313 (1992).

[6] G. K. Wertheim, D. N. E. Buchanan, E. E. Chaban, and J. E. Rowe, Solid State Commun. **83**, 785 (1992).

[7] S. Saito and A. Oshiyama, Phys. Rev. Lett. **66**, 2637 (1991).

[8] S. C. Erwin and W. E. Pickett, Science **254**, 842 (1991).

[9] A. Oshiyama and S. Saito, Solid State Commun. **82**, 41 (1992).

[10] S. J. Chase, W. S. Bacsa, M. G. Mitch, J. Pilione, and J. S. Lanin, Phys. Rev. B **46**, 7873 (1994).

[11] G. K. Wertheim and D. N. E. Buchanan (unpublished).

[12] J. A. Howard, M. Tomietto, and D. A. Wilkinson, J. Am. Chem. Soc. **113**, 7870 (1991).