PHYSICAL REVIEW B VOLUME 57, NUMBER 19 15 MAY 1998-I

Charge transfer and doping-dependent hybridization of C_{60} on noble metals

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(Received 14 November 1997)

K-doped C_{60} monolayers on polycrystalline Cu, Ag, and Au are studied by means of ultraviolet photoelectron spectroscopy. The polycrystalline character of the substrate allows an accurate subtraction procedure to isolate the photoemission signal of the monolayer. Charge transfers of 1.0–1.8 electrons per molecule are found for the undoped monolayer. On high K doping the hybridization with the substrate is shown to practically disappear, and the overlayer almost totally suppresses the substrate signal. [S0163-1829(98)02120-1]

I. INTRODUCTION

Since what was the first paper to our knowledge on C_{60} clusters on Au(111)[1] in 1990, increasing attention has been paid to C_{60} overlayers on various crystal surfaces.[2] The interaction of the C_{60} with the substrate has been subject of research,[3–19] and in several studies the charge state of the C_{60} film was changed by doping with alkali metals.[20–23] The interaction between the alkali metals and C_{60} in bulk material has been understood in terms of complete charge transfer from the alkali atoms to the C_{60} molecules,[24] the interaction of alkali doped thin films of C_{60} with metal substrates, however, is more complicated.

Already in an undoped thin film of C_{60} the lowest unoccupied molecular orbital (LUMO) is slightly filled by charge transfer from the substrate metal to the C_{60}. The charge transfer is influenced by screening effects in the metal,[11,23] possible covalent interactions and the work function of the metal,[18,25] although some experiments using electron energy loss spectroscopy suggest that the charge transfer is strongly dependent on the type of metal, but rather independent of its work function.[11,13] Unfortunately the uncertainty in the charge transfers determined on the basis of these experiments is relatively large (±1 electron).

Both for the determination of the charge transfer in undoped C_{60} films, as for a more general investigation of the interaction of doped C_{60} films with metal substrates, it is to be preferred to measure on one single adsorbed monolayer of C_{60}, for the following reasons. First, only the first layer of C_{60} displays significant changes in electronic structure due to interaction with the metal substrate.[22] Second, a single monolayer of C_{60} on a metal substrate provides one with a quite well-defined system, compared to thicker layers or even bulk doped C_{60}, since the latter are very sensitive to mixed phase formation.[26] It is important that the monolayer *completely* covers the substrate, since this results in a high suppression of the substrate signal in photoemission experiments,[23] which will leave a much larger signal when one tries to isolate the overlayer photoemission signal from that of the substrate. In addition, island growth of C_{60} could cause inaccurate values for the charge transfer, since not all C_{60} molecules would necessarily be in contact with the substrate.

Much of the research quoted above has been done on C_{60} overlayers on single crystals, for the epitaxial growth of C_{60} on single crystals is well studied and documented. However, if one wants to distinguish a photoemission signal of an overlayer from that of the substrate, growth on polycrystalline metals is to be preferred. To obtain the net photoemission signal of the overlayer, a certain fraction of the clean substrate spectrum has to be subtracted from the photoemission spectrum of the entire overlayer system. In cases in which single crystals have been used, however, the angle resolved difference spectra show also strong features that look as if they originated from a polycrystalline substrate, even in cases where the overlayer is known to be ordered.[27] Apparently an overlayer is quite effective in destroying the angular information of the substrate photoemission signal. This finding can also be confirmed for C_{60} overlayers grown on Ag(111) single crystal surfaces.[23] Here we find that more consistent results for the overlayer partial spectral weight can be obtained if we subtract a fraction of a polycrystalline Ag rather than the original clean Ag(111) photoemission spectrum from the as-measured photoemission spectra of the overlayer system.

We present a study on K-doped monolayers of C_{60} on polycrystalline Cu, Ag, and Au surfaces using ultraviolet photoemission spectroscopy (UPS). From our measurements we can accurately determine the charge transfer from different noble metal surfaces to the C_{60} molecules, investigate the influence of the substrate on the overlayer, and witness changes in the electronic structure on doping with K.

II. EXPERIMENT

The measurements were carried out in a combined UPS/XPS (where XPS is x-ray photoemission spectroscopy) setup of Surface Science Instruments. UPS spectra are taken with He-I radiation ($h\nu = 21.2$ eV). The resolution is set to 0.15 eV. A standard procedure was applied to correct the spectra for the contribution (1.3%) of the He-I satellite. All spectra presented are effectively normalized to the photon flux, since the spectra were taken with the same gas pressure in the He lamp. The work functions of the overlayer systems were determined from the positions of the secondary cutoffs of the photoemission spectra with respect to the Fermi level.

For the *in situ* preparation of a monolayer C_{60} on a noble

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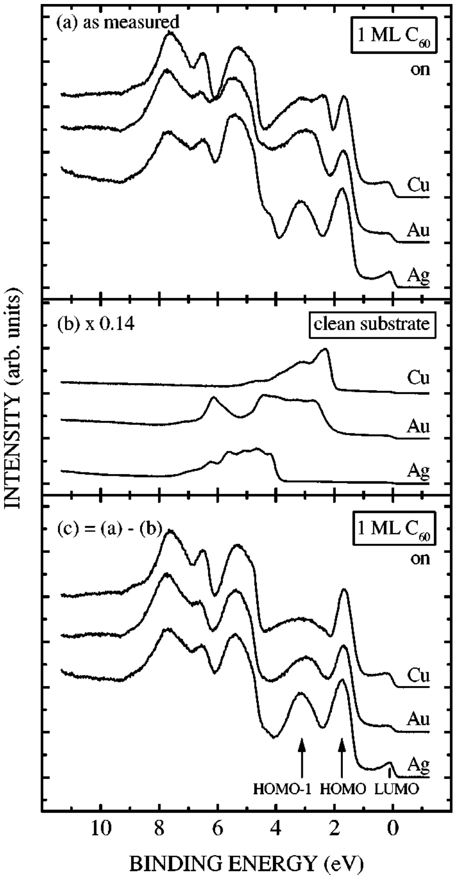

FIG. 1. Undoped C_{60} monolayer on noble metals: (a) as measured photoemission spectra of the overlayer on polycrystalline Cu, Au, and Ag; (b) photoemission spectra of clean polycrystalline Cu, Au, and Ag multiplied by 0.14; and (c) net photoemission spectra of the overlayer on polycrystalline Cu, Au, and Ag, taken as the difference between (a) and (b).

metal surface we followed a distillation procedure that was previously used on a Ag(111) substrate and is described in detail elsewhere.[23] K-doped spectra were collected by repeatedly evaporating K (at room temperature) for a fixed period (20–60 s), and recording the spectrum after each evaporation period. The period was taken such that it took approximately eight periods to reach a state in which no changes occured in the spectrum anymore on further doping, and such that the entire acquisition time is less than 2 h to minimize aging of the rather reactive overlayer. The fully doped films were then annealed for 10 min at 240-260 °C in order to obtain a K_3C_{60}-like monolayer. This annealing procedure gives very reproducible K_3C_{60}-like overlayers, and provides better defined results than can be obtained by gradual doping, as was done in previous experiments.[23] The base pressure in the UPS chamber was 3×10^{-11} mbar. The base pressure in the preparation chamber was 4×10^{-11} mbar, and rose to 7×10^{-10} mbar during C_{60} evaporation, and to 2×10^{-10} mbar during K evaporation.

III. RESULTS AND DISCUSSION

Figure 1(a) shows the photoemission spectra of an undoped C_{60} monolayer on polycrystalline Cu, Au, and Ag surfaces. To isolate the pure overlayer spectra from those of the substrate, we have also measured the clean noble metal surfaces as depicted in Fig. 1(b). Using a trial and error method, we find that subtracting $14\%\pm2\%$ of the clean substrate signal from the as-measured spectra of the overlayer systems gives the most consistent results for the net partial spectral weight of the overlayer itself. The results are shown in Fig. 1(c). Subtracting too much or too little will result in extra dips or peaks in the difference spectra appearing at energies where the clean substrate photoemission spectra also have sharp high-intensity features.

Our measurements show clearly that the C_{60} molecular orbital structure remains intact, suggesting strongly that the C_{60} molecule does not disintegrate upon adsorption on the metallic surface. The high stability of the C_{60} molecule has also been reported on a wide variety of surfaces.[3–23]

We see that for an undoped overlayer the LUMO is already slightly filled by charge transfer from the metal substrate, although not by the same amount for the different substrates. With the noble metal *d* and *sp* band background signal already subtracted out, the entire structure between 0 and 1.5 eV must be ascribed to the LUMO. Integrating the area beneath this structure, normalized to the areas beneath the occupied molecular orbital structures at higher binding energies (HOMO, HOMO-1, etc.), and comparing it to the corresponding areas in K_6C_{60}-like overlayers (see Fig. 3) where the LUMO is completely filled and contains six electrons, we estimate that the amount of charge transferred is about 1.8 electrons per C_{60} molecule on a Cu substrate, 1.7 on Ag, and 1.0 on Au, with an uncertainty of about 0.2 electrons.

Our values are considerably larger than those estimated from Raman data.[5,13] However, as the Raman measurements were performed before the distillation procedure was known that produces a monolayer that completely covers the substrate,[23] comparison with those data may not be valid. More interesting is to compare the present results with those from previous work on Ag(111),[23] on which surface the charge transfer to the C_{60} molecule is found to be much lower, i.e., about 0.75 electrons. This is quite remarkable since the experimental conditions were comparable. This difference can probably be related to the difference in the work function,[18] which is about 0.5 eV higher for Ag(111) than for the polycrystalline Ag.[28] The work functions determined for the polycrystalline substrates were: $\phi_{\mathrm{Cu}}=4.5$ eV, $\phi_{\mathrm{Ag}}=4.3$ eV, and $\phi_{\mathrm{Au}}=5.2$ eV. The accuracy is estimated at about 0.1 eV. These values correspond reasonably well with the generally accepted values of $\phi_{\mathrm{Cu}}=4.65$ eV, $\phi_{\mathrm{Ag}}=4.26$ eV, and $\phi_{\mathrm{Au}}=5.1$ eV.[28]

The charge transfer on the Au surface, with the largest work function, is the smallest, as can be expected intuitively.[18] Interestingly, the difference in the amount of charge transferred on the Au surface as compared to that on the Cu and Ag surfaces shows that the filling of the LUMO cannot be understood in terms of a one-electron model: although the work functions of Cu and Ag surfaces are smaller than that of Au by an amount of similar magnitude ($\gtrsim$0.7 eV) as the bandwidth of the LUMO ($\sim$0.7 eV, see Fig. 3), the LUMO is not completely filled. This can be attributed to the presence of an on-site Coulomb interaction, which, with a reduced value of $U=0.6$ eV for a C_{60} monolayer,[19] prevents the charge transfer from exceeding two electrons.

The differences in the amount of charge transferred be-

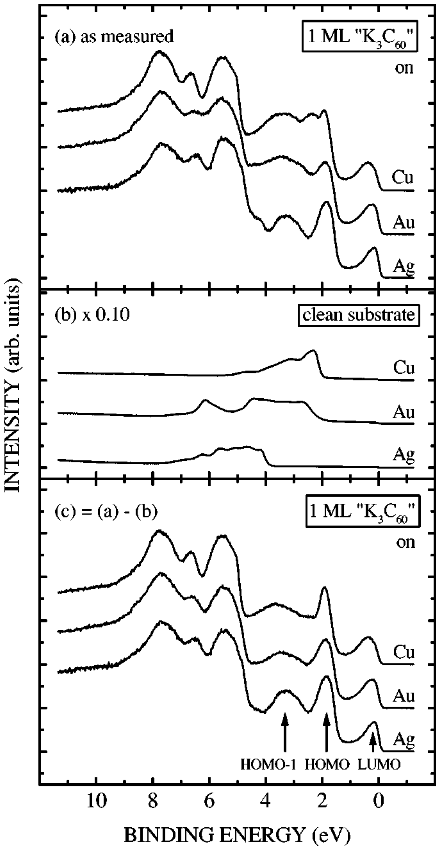

FIG. 2. K_3C_{60}-like monolayer on noble metals: (a) as measured photoemission spectra of the overlayer on polycrystalline Cu, Au, and Ag; (b) photoemission spectra of clean polycrystalline Cu, Au, and Ag multiplied by 0.10; and (c) net photoemission spectra of the overlayer on polycrystalline Cu, Au, and Ag, taken as the difference between (a) and (b).

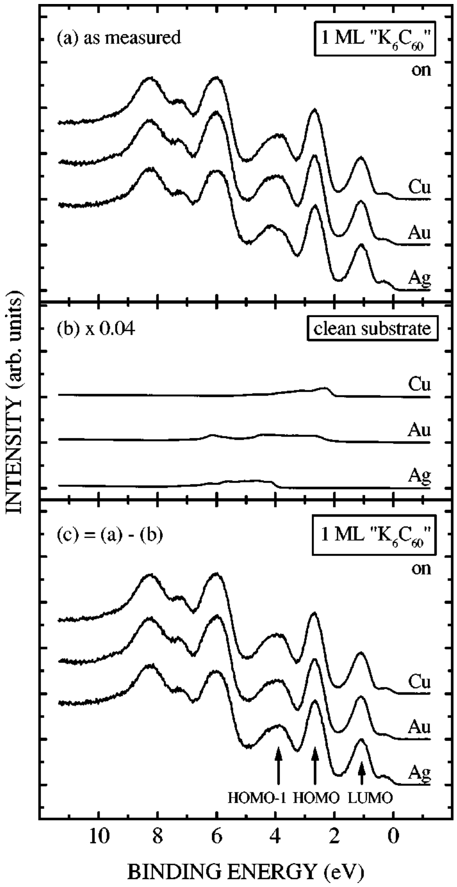

FIG. 3. K_6C_{60}-like monolayer on noble metals: (a) as measured photoemission spectra of the overlayer on polycrystalline Cu, Au, and Ag; (b) photoemission spectra of clean polycrystalline Cu, Au, and Ag multiplied by 0.04; and (c) net photoemission spectra of the overlayer on polycrystalline Cu, Au, and Ag, taken as the difference between (a) and (b).

tween the Cu and Ag surfaces are small, and probably cannot be explained solely in terms of differences in the work functions. On the basis of our measurements, one could envision that, for example, the strength of the hybridization of the LUMO with the substrate will play a role. Observing the photoemission spectra, one can also clearly see the differences in hybridization for the Cu and Au substrates on the one hand, and for the Ag substrate on the other. The HOMO-1 especially is much broader for the Cu and Au substrates than for the Ag substrate. This can be related to the position of the Ag *d* band, which lies at a higher binding energy than the Cu and Au *d* bands by about 2 eV, so that the Ag *d* band hardly overlaps with the HOMO-1, in contrast to the Cu and Au *d* bands. The low-density Ag 5*sp* bands play a negligible role in the hybridization with the HOMO-1, since their interaction with C_{60} is known to be very weak.[29] The *sp* bands, however, can be important for the hybridization with the LUMO, because of their overlapping energy levels.

The fact that the HOMO is hardly affected by hybridization might be due to its lower binding energy with respect to the *d* bands of the noble metals. However, preliminary results of experiments on C_{60} grown on polycrystalline Fe indicate that even there, in spite of the position of the Fe *d* band close to the Fermi level, the HOMO hybridizes considerably less than the HOMO-1. This suggests that other factors like the symmetry and dispersion of the HOMO and HOMO-1 bands may play an important role.[11,24] One should note here that the LUMO, HOMO, and HOMO-1 are all π-like and formed from atomic orbitals pointing in the radial direction.[24]

In Figs. 2 and 3 we show the spectra for ''K_3C_{60}'' and ''K_6C_{60},'' respectively. In the latter case the C_{60} is slightly overdoped to ensure a complete filling of the LUMO. The indices 3 and 6 refer to charge transfers to the C_{60} of about three and (slightly more than) six electrons, respectively. The quotation marks indicate that the actual K concentrations may be somewhat different from 3 and 6. To isolate the pure overlayer spectral weight from that of the substrate, we have subtracted a fraction of the clean substrate spectra from the as-measured overlayer spectra. Using the method described above, we find that the fraction is 10%±2% for the ''K_3C_{60}'' overlayer system and 4%±2% for the ''K_6C_{60}'' case. The decrease in this fraction, from 14% for the undoped C_{60} to 4% for the fully doped film, is quite large. This suggests that the scattering properties of the K_xC_{60} monolayer for electrons strongly depend on the amount of doping.

In comparison with the undoped monolayer, the HOMO-1 in ''K_3C_{60}'' still clearly exhibits more hybridization for the Cu and Au substrates than for the Ag substrate, although the spectra look more similar to each other. Upon further doping to ''K_6C_{60},'' on the other hand, all influence of the substrate in the spectra seems to have disappeared. The spectra for the

Cu, Ag, and Au substrates are surprisingly similar, even without applying the subtraction procedure. In fact, the spectra for the Cu and Au substrates have almost adopted the line shape of the undoped C_{60}/Ag spectrum, although the HOMO-1 peaks are slightly broader, and the filling of the LUMO is of course different. This trend towards more similar spectra for the different substrates on increasing K doping could also be observed for intermediate values of K doping. The largest changes in hybridization take place between doping levels that correspond to three and six electrons per C_{60} molecule.

The decrease in hybridization of the HOMO-1 for the Cu and Au substrates (as derived from the decrease in broadening) on high K doping, might be attributed to several effects. It is clear that the charge state of the C_{60} will be more negative on high K doping, and the HOMO-1, which has shown to be the most sensitive to hybridization with the substrate *d* bands, is shifted to higher binding energy by about 1 eV on going from the undoped film to ''K_6C_{60}.'' The overlap of the Cu *d* band and the HOMO-1 thereby decreases. This cannot be said for the Au *d* band, and indeed the change in hybridization on K doping is smaller than for Cu. For Ag the shift of the HOMO-1 might even lead to an increase in hybridization, but it is difficult to be conclusive about this.

Another effect to be considered is the fact that there are more K ions in the overlayer with increasing doping. To clarify the role of the K ions here, it would be worth investigating whether the K ions are *in between* the substrate and the C_{60} monolayer, thus hampering hybridization between the substrate and the C_{60}. Furthermore it would be interesting to find out if there is any relation between the increasing suppression of the substrate signal and the decreasing hybridization on high K doping.

IV. CONCLUSIONS

We have performed a UPS study on K-doped monolayers grown on polycrystalline Cu, Ag, and Au. The polycrystalline character of the substrate enables a more accurate subtraction procedure for the photoemission spectra in order to isolate the overlayer signal. Charge transfers of 1.8 electrons for Cu, 1.7 for Ag, and 1.0 for Au substrates are found. Our results are not in disagreement with the expectation that the charge transfer will be dependent on the work function of the substrate, although other factors cannot be excluded.

Upon doping with K the substrate signals are gradually suppressed from 14% to 4% of the original clean substrate spectra. A very remarkable result is the apparent strong decrease of the hybridization of the C_{60} with the substrate on high K doping. This indicates that by doping with K we are able to tune the hybridization between the C_{60} and the substrate.

ACKNOWLEDGMENTS

It is a pleasure to acknowledge P. Rudolf for stimulating discussions, and J.C. Kappenburg, A. Heeres, and H.J. Bron for their skillful technical assistance. This investigation was supported by the Netherlands Foundation for Chemical Research (SON), the Netherlands Foundation for Fundamental Research on Matter (FOM) with financial support from the Netherlands Organization for the Advancement of Pure Research (NWO). The research of L.H.T. has been made possible by support from the Royal Netherlands Academy of Arts and Sciences.

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