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Charge transfer at aluminum-C_{60} interfaces in thin-film multilayer structures

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Thin-film multilayer structures with up to 20 repeat layers have been grown in a high-vacuum chamber by sequential deposition of aluminum (Al) and fullerene (C_{60}) onto room-temperature substrates. The periodicity of the layers is confirmed by x-ray-diffraction and *in situ* resistance measurements. The presence of underlying layers of C_{60} reduces the critical thickness at which Al becomes conducting from ~ 35 to ~ 20 Å. In addition, there is a sudden increase in resistance that occurs when each Al layer is covered by a monolayer of C_{60}. These observations, together with the measurement of a downward shift in frequency of a considerably broadened Raman-active $A_g(2)$ pentagonal-pinch mode, imply that up to six electrons per C_{60} are transferred from the Al to the C_{60} layer. This demonstration of charge transfer across planar metal-C_{60} interfaces suggests that multilayers may be a useful vehicle for forming fullerene interface compounds in two-dimensional structures.

The discoveries of conductivity[1] and superconductivity[2] in the alkali-metal-doped fullerenes have focused attention on the ability of the fullerenes, particularly C_{60}, to act as electron acceptors. The low ionization potential of the alkali metals and the high electron affinity of C_{60} greatly facilitate charge transfer in the alkali-metal-doped compounds, leading to transport properties that are isotropic, since the alkali metals diffuse into and occupy the interstitial sites of the fcc host lattice without significantly perturbing the lattice. Expectations that similar compounds might be made with nonalkali metals are reasonable since, on theoretical grounds, the work functions of most metals are sufficiently low to favor charge transfer across metal-fullerene interfaces.[3] Evidence for such charge transfer for C_{60} coatings on a variety of metals has been found in photoemission,[4-6] Raman-scattering,[6] electron-energy-loss spectroscopy,[7] and scanning-tunneling-microscopy studies.[8] However, attempts to make bulk C_{60} compounds with metals other than the alkalis or the alkaline earths have been unsuccessful, not because of the absence of charge transfer, but rather because of high cohesion energies that lead to precipitation of metal clusters.[4,9] Phase-separated materials with agglomerated and granular morphologies are the unwanted result.

In this paper we explore the possibility of making fullerene "compounds" by sequentially depositing C_{60} and metal ($M=$ Al) in alternating layers. This method is particularly suited to metals that have a moderately large cohesive energy and which therefore remain intact when covered with C_{60}. The central idea of this approach is to achieve a two-dimensional (2D) structured multilayer having smooth interfaces across which charge transfer occurs. If a sufficient amount of charge is transferred and if the individual layers are thin enough, then in-plane electrical transport in the multilayer can be significantly perturbed since the Al is now electron depleted and the adjacent monolayers of C_{60} are conducting or insulating, depending on the extent to which the t_{1u}-derived valence bands of the C_{60} host solid are filled. One complication arises from the possibility of unequal surface energies associated with two different interfaces. Thus for metal M as a substrate for C_{60} (denoted by C_{60}/M) the metal layer likely remains intact with negligible intermixing, whereas in the reverse situation (M/C_{60}), the metal atoms initially arriving at the surface might readily diffuse into the bulk, donate charge, and possibly coalesce.

The Al-C_{60} multilayers discussed here are grown by vapor-phase deposition (5×10^{-8} Torr base pressure) and studied by x-ray diffraction, *in situ* resistivity, Raman scattering, and optical reflectivity. Aluminum was chosen because it can be deposited smoothly as a thin film, it has a first-stage ionization energy (6.0 eV) only slightly larger than a typical alkali metal, and it has a moderate but not overly large work function (4.2 eV). X-ray diffraction shows peaks below $2\theta=3°$, corresponding to multiple harmonics of the superlattice period. Our characterization of multilayers grown with a variety of different Al and C_{60} thicknesses gives strong evidence for charge transfer at planar Al-C_{60} interfaces. The perturbations on the conductivity become sufficiently pronounced for thin Al layers (<40 Å) to be consistent with a decreased carrier density (low plasma frequency) and a change from the metallic sheen of Al to a deep black hue of a new composite 2D metal-fullerene insulator.

In situ resistivity measurements were found to be especially useful in monitoring the layer-by-layer growth and in determining the electronic behavior of our multilayers. This was accomplished by preevaporating four equally spaced and radially symmetric conducting leads onto epipolished (100) single crystal yttrium-stabilized zirconia (YSZ) substrates and then masking the substrate to obtain a four-terminal Van der Pauw configuration. Multiple shutters were used in combination with two film-thickness monitors to ensure that the C_{60} and Al fluxes could be independently measured while separately directed at the substrate. The final film thicknesses for a sequence of depositions were measured by optical interferometry, and calibration constants for the C_{60} and Al sources were then calculated from a two-parameter fitting algorithm. Quartz, silicon, and glass slides, which were used for separate optical and structural characterizations, were mounted in close proximity.

Shown in Fig. 1 is a comparison of the dependence of the sheet resistance of Al on thickness when evaporated directly

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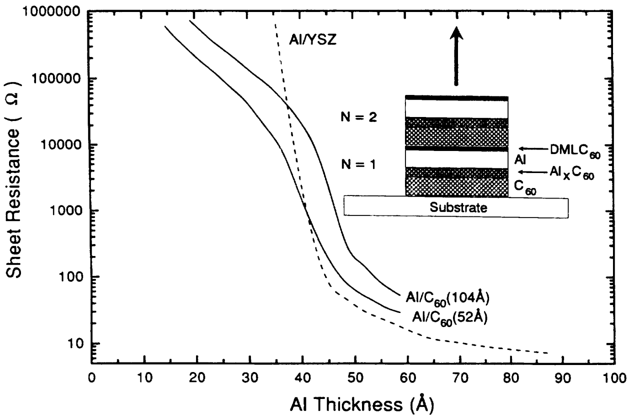

FIG. 1. Dependence of the sheet resistance on Al thickness for Al deposited directly on yttrium-stabilized zirconia (YSZ, dashed line) and on underlying layers of C_{60} (solid lines). The inset shows schematically the doped monolayer (DML) and Al_xC_{60} interface phases discussed in the text.

onto YSZ (dashed line) and onto C_{60}-coated YSZ (solid lines). The Al films with C_{60} as an underlayer begin to conduct on the 10^5-Ω scale at about half the thickness (15–20 Å) as does the Al film directly deposited on the YSZ substrate. There are two possible explanations for this behavior: (1) the initial Al atoms arriving at the C_{60} surface either diffuse into the C_{60} or remain at the interface, but nevertheless donate charge and give rise to conductivity in the C_{60} layer, thus providing electrical pathways between the percolating but still isolated islands of the growing Al film, and (2) tunneling barriers between the Al islands deposited on a C_{60} substrate are lower than those between Al islands deposited on a YSZ substrate. Both scenarios, donated electrons and lowered substrate tunnel barriers, will give rise to an onset of conductivity for thinner films. Interestingly, however, there is a crossover near the Al film thickness, $d_{\mathrm{Al}} = \sim 40$ Å, beyond which the resistance of the Al/YSZ sample plummets below that of the Al/C_{60}/YSZ samples towards a final value (where the shutter has been closed) at 88 Å, corresponding to a resistivity $\rho = 6.3$ $\mu\Omega$ cm. This is reasonably close to the bulk value of 2.5 $\mu\Omega$ cm for pure Al. Scenario (1) above is thus favored, since the consistently observed higher resistance values of the Al/C_{60} samples for $d_{\mathrm{Al}} \geq 40$ Å shown in Fig. 1 would be expected for Al films that have donated charge and/or Al atoms into the underlying C_{60}. If substrate tunneling or different interfacial energies cause the Al/C_{60} samples to percolate at smaller coverage, one would expect the resistance of the subsequently grown films to be less than (not greater than, as observed) the resistance of a similar Al/YSZ film at all thicknesses.

Evidence for growth of multilayers comprising distinct and separate layers is revealed in the time dependence of the resistance of a six-period multilayer structure shown in Fig. 2. At a time of 280 sec (leftmost dotted line) the deposition is initiated by opening the C_{60} source shutter, depositing 52 Å, closing the shutter (not shown), opening the Al source shutter (leftmost dashed line), depositing 58 Å, closing the Al shutter (not shown), and repeating this procedure for six layers. The alternating sequence of a rapidly decreasing resistance when the Al shutter is open and a relatively constant resistance when the C_{60} shutter is open is consistent with a parallel resistance model in which highly conducting Al layers are shunted by significantly less conducting C_{60} layers. The uniformity and reproducibility of these layers is demonstrated by noting that the resistance R_N of the Nth plateau obeys the parallel resistance formula $R_N^{-1} = R_0^{-1} N$, where the resistance of each layer, R_0, is assumed to be the same for all layers. When the order of the layer is reversed, however, and Al with $d_{\mathrm{Al}} > 40$ Å is deposited first (YSZ underlayer), we find by analysis of the resistance plateaus of six separate samples that R_1 is *always* less than R_0 $(N \geq 2)$, as would be expected from the behavior shown in Fig. 1 and discussed in the preceding paragraph.

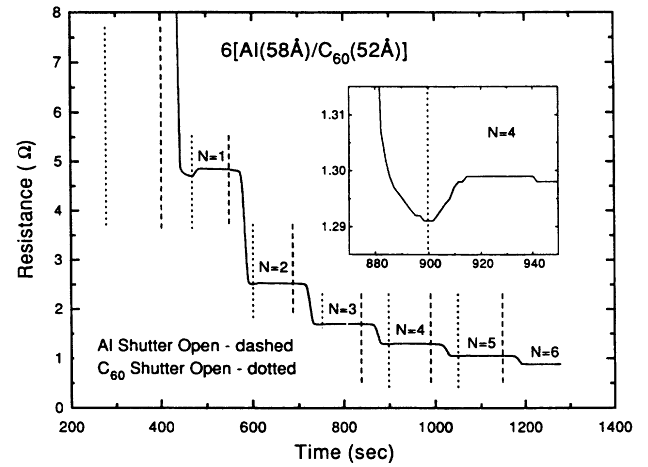

FIG. 2. Dependence of resistance on deposition time for a six-layer sample comprising an alternating sequence of 52 Å of C_{60} followed by 58 Å of Al. The vertical dashed (dotted) lines delineate the Al (C_{60}) shutter openings. The expanded data of the inset shows the increase in resistance at the beginning of the $N = 4$ plateau when C_{60} is deposited after the C_{60} shutter is opened.

The most intriguing aspect of the data in Fig. 2 is the sudden increase in resistance, δR_N, that occurs simultaneously with the opening of the C_{60} shutter (vertical dotted lines) at the beginning of each plateau. This increase is readily apparent in the main figure for the first plateau ($N = 1$) and has been expanded in the inset for the fourth plateau ($N = 4$). It is especially important to note that these changes in resistance occur in a ramplike fashion and are completed in a time interval sufficient for the deposition of just *one monolayer* of C_{60}. If the average change in resistance, δR_0, for each C_{60}/Al interface is the same, then it is straightforward to show that the observed change obeys the relation $\delta R_N = \delta R_0 / N^2$. This relation is indeed found, and we therefore conclude that not only is the resistance of each layer the same but also that each layer undergoes the same change when coated by a monolayer of C_{60}. The increase in resistance cannot be due to a thinning of the metal resulting from outdiffusion of Al atoms, since not enough Al atoms can diffuse into a monolayer of C_{60} to cause a significant thinning of the Al; nor can the effect be due to interfacial stress of the C_{60} overlayer, since the resistance starts to increase immediately after the shutter is opened and stress effects would not begin to be felt until a large fraction of the surface is covered.

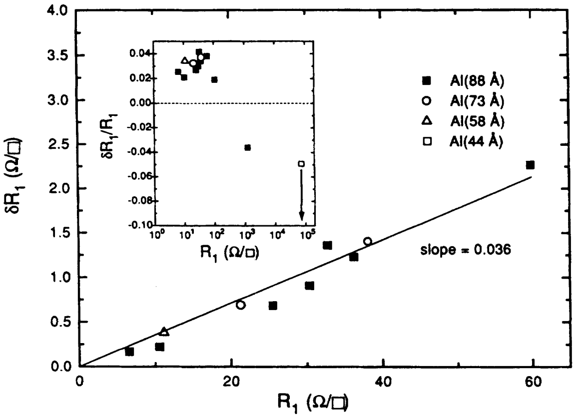

FIG. 3. Plot of δR_1 versus R_1 for ten different samples with thicknesses indicated in the legend. The inset plot of $\delta R_1/R_1$ versus R_1 includes data at higher resistances and shows a change in sign of δR_1 from positive to negative as R_1 increases.

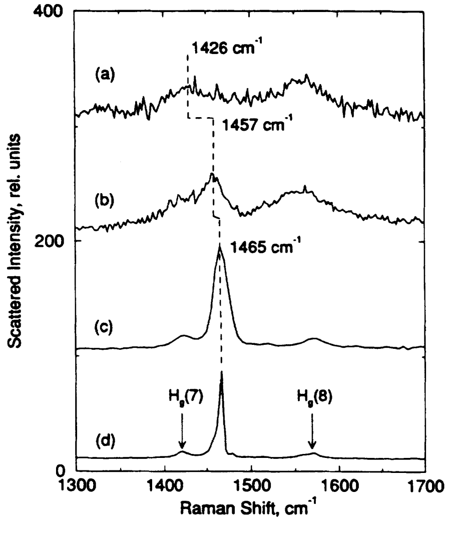

FIG. 4. Raman-backscattering (hh) spectra of three Al/C_{60} heterostructures (a)–(c) and a pure C_{60} film (d). The structures (thicknesses in Å) are (a) 6[Al(88)/C_{60}(52)], (b) 6[Al(88)/C_{60}(104)], (c) 6[Al(88)/C_{60}(208)], and (d) C_{60}(800). Trace (b) is multiplied ×3. Trace (d) is obtained on a scanning spectrometer, and is presented for comparison of line positions only, but its gain can be estimated to be about ×0.1 that of the other traces. There is a large fluorescence background subtracted from trace (a) which is not present in (b) and (c). Roughly corrected for the amount of C_{60} present in the scattering volume, then, the relative gains of the traces presented, as (a):(b):(c):(d), are 0.25:1.5:1.0:0.1, with trace (c) defined as unity. There is therefore a large increase in the scattered intensity for the H_g modes which accompanies the fluorescence in sample (a).

There are, however, two other explanations that require close examination. In the first of these, there is a transfer of electronic charge, δN_e (areal charge density), from the Al into a monolayer of close-packed C_{60} having an areal density of 1.2×10^{14} molecules/cm^2. If, as in the A_6C_{60} (A = K,Rb) compounds, each C_{60} molecule accepts six electrons, then δN_e can be as high as 7.2×10^{14} cm^{-2}. For an aluminum film with volume electron density n and thickness d_{Al}, a simple charge-transfer model[10] gives the result $\delta R_1/R_1 = \delta N_e/nd_{\mathrm{Al}}$. Alternatively, the increase in resistance could also arise from a change in scattering of electrons at the film surface, δP_s, from specular (vacuum interface) to diffuse (C_{60} interface). The scattering probability P, which is proportional to the reciprocal of the electron mobility, μ, may be written as the sum of bulk and surface scattering terms, i.e., $P = P_{\mathrm{bulk}} + \delta P_s$. Then, to a first approximation the correction, derived from the Drude relation $R_1 = 1/ne\mu d_{\mathrm{Al}}$, can be written as $\delta R_1 \propto \delta P_s/ned_{\mathrm{Al}}$. This Fuchs-Sondheimer[11] size-effect correction to the resistance of a thin film becomes significant when the mean free path l is large compared to the thickness.

The dependence of δR_1 on R_1 (Fig. 3) provides a ready means of distinguishing between these two mechanisms. The data shown are clearly inconsistent with the surface scattering mechanism (δR_1 = const) and consistent with charge transfer ($\delta R_1 \propto R_1$). The regression fit to these data (solid line) reveals that the average fractional charge in resistance, $\delta R_1/R_1$, is 3.6%. We attribute the large variation in resistance for the same film thicknesses to a combination of factors, including the ordering of the layers (see Fig. 1), and run-to-run variations in the thicknesses of the underlying C_{60} layer, the film deposition rate, the temperature, and pressure. Using the literature value $\rho l = 1.6\times10^{-11}$ Ω cm^2 pertaining to Al,[11] we can estimate the mean free paths for the data in Fig. 3 and confirm using detailed Fuchs-Sondheimer theory[11] that for the range of resistivities shown in Fig. 3, δR_1 is indeed nearly constant. On the other hand, $n = 2.2\times10^{22}$ cm^{-3} can be calculated directly from ρl, and with this number the charge-transfer scenario with six elements transferred per C_{60} molecule gives a value for $\delta R_1/R_1$ of 3.7% for the 88-Å films. This good agreement with the slope in Fig. 1 may be somewhat fortuitous because of uncertainty in the value of ρl. The uncertainty is further compounded by the fact that if the free-electron density for Al of 1.8×10^{23} cm^{-3} rather than the resistivity value of 2.2×10^{22} cm^{-3} is used to calculate δN_e, then an unphysical result is obtained.

Additional evidence that charge is transferred to the C_{60} molecules is seen in the Raman spectra of Fig. 4 for the spectral evolution of the charge-sensitive $A_g(2)$ pentagonal-pinch mode. The data are taken for three six-layer samples deposited onto quartz substrates and having a constant Al thickness (88 Å) but varying C_{60} thicknesses $d_{C_{60}}$. The laser excitation (5145 Å) is introduced through the back side of the substrate and therefore samples primarily the first deposited layer of C_{60}, which is presumably better protected by the capping layers during sample transfer from the vacuum system to the Raman apparatus, where a flowing He gas atmosphere is maintained. A cylindrical lens limited the incident power density to about 2.5 W/cm^2, far below the range where photopolymerization is found to occur.[12]

The data show clearly a broadening and shift (dashed line) of the $A_g(2)$ mode to lower frequency as $d_{C_{60}}$ decreases and a greater proportion of transformed C_{60} close to the C_{60}-Al interface is sampled. Using a calibration of ~6 cm^{-1} shift per electron transferred to each molecule,[1] the shift of 40 cm^{-1} for the topmost trace can be identified as corresponding to a filling of the t_{1u} band with ~6 additional electrons per C_{60} molecule. It is noteworthy, although not yet understood, that the H_g modes at 1420 and 1560 cm^{-1} exhibit a very large increase in intensity relative to the pentagonal-pinch mode as the C_{60} layer thickness decreases. First, we note that this behavior is inconsistent with, and in fact opposite to, the behavior observed in bulk alkali-metal-doped metallic M_xC_{60}, if we attribute the shift of the A_g mode to charge transfer. Typically the H_g modes are observed[13] to broaden and become far weaker, to the point of unobservability, when the material becomes metallic. Second, the presence of these H_g peaks, especially the one at 1420 cm^{-1}, makes it impossible to ascertain the A_g position with any degree of accuracy, due to the overlap of the peaks. Thus, although the trend in the spectra appears clear in Fig. 4, and indicates the presence of charge transfer, the detailed evolution of the spectra is difficult to interpret.

The inset of Fig. 3 reveals that for higher R_1 ($R_1 > 60\ \Omega/\square$) there is a change in sign of δR_1 from positive to negative, indicating that the Al is becoming *less* resistive when overcoated with C_{60}. It is possible that, since the Al film is islanded in this regime, electrons that transfer out of the islands might give rise to an increase in the local resistance of isolated islands which does not affect the tunnel-coupled conduction between islands. These same electrons can, however, dope the C_{60} overlayer and create a shunting path that decreases the resistance. This is precisely the same physics that explains the reduced Al thicknesses for the onset of conductivity in the data of Fig. 1 where the C_{60} is the underlying, not the overlying, layer. Similar effects have been reported for C_{60} overlays on thin films of Sn, Ba, and Ga.[14]

The inset of Fig. 1 summarizes schematically the two interface phases discussed in this paper. When Al is deposited onto C_{60}, some Al most likely diffuses into the C_{60} and donates charge (Raman data of Fig. 4) to form a conducting Al_xC_{60} phase, thereby facilitating the onset of conductivity. At the second interface, the resistivity data (Figs. 2 and 3) indicate that a doped monolayer of C_{60} ($DMLC_{60}$) is formed accompanied by a resistance change of the Al which is argued to be caused by the transfer of up to six electrons per C_{60} molecule. Similar results have also been reported for a monolayer of C_{60} deposited on a potassium surface.[7] To create such a high electron density ($\sim 7\times 10^{14}\ \mathrm{cm}^{-2}$) with a perpendicular electric field at a metal surface would require a field greater than 10^9 V/cm, which is a factor of 100 larger than the breakdown field in the best dielectrics. Accordingly, the $DMLC_{60}$ phase seems to be a true chemical or interfacial phase where charge transfer is occurring over atomic distances and there is strong chemical bonding of the molecules to the surface. Since the metal is depleted of electrons and the C_{60} can be either conducting or insulating depending on the amount of charge transferred, we anticipate that further studies of metal-fullerene multilayer structures might lead to novel materials with unusual transport properties.

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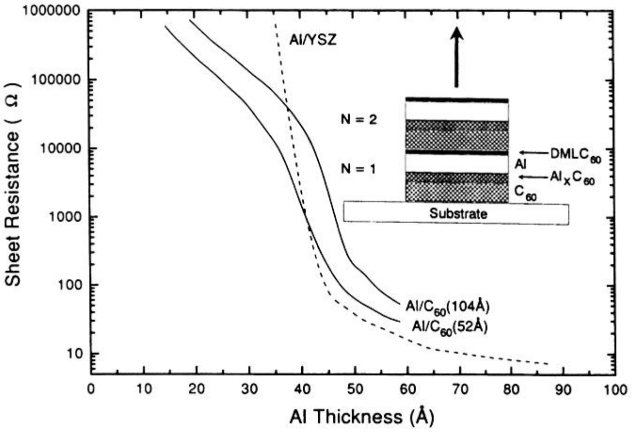

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