Reports

Electrical Resistivity and Stoichiometry of K_xC_{60} Films

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Electrical resistances of polycrystalline fullerene (C_{60}) films were monitored while the films were being doped in ultrahigh vacuum with potassium from a molecular-beam effusion source. Temperature- and concentration-dependent resistivities of K_xC_{60} films in equilibrium near room temperature were measured. The resistance changes smoothly from metallic at $x \approx 3$ to activated as $x \rightarrow 0$ or $x \rightarrow 6$. The minimum resistivity for K_3C_{60} films is 2.2 microohm-centimeters, near the Mott limit. The resistivities are interpreted in terms of a granular microstructure where K_3C_{60} regions form nonpercolating grains, except perhaps at $x \approx 3$. Stoichiometries at the resistivity extrema were determined by ex situ Rutherford backscattering spectrometry to be $x = 3 \pm 0.05$ at the resistance minimum and $x = 6 \pm 0.05$ at the fully doped resistance maximum.

THE OCCURRENCE OF CONDUCTIVITY in alkali fulleride compounds (*1*) and superconductivity at 18 K in K_xC_{60} (*2*) has stimulated many investigations of the superconducting properties but little work on transport in the normal state. There has also been considerable effort to determine whether the doped system forms continuous or discrete phases. X-ray scattering shows distinct crystal structures for phases at $x = 0$, 3, 4, and 6 (*3–6*), which suggests that there are miscibility gaps that separate the phases. Carbon-13 nuclear magnetic resonance (NMR) shows only two well-defined lines in the range $0 < x < 3$ (7), and photoemission spectra are consistent with linear combinations of $x = 0$, 3, and 6 phases (*8, 9*). Shielding diamagnetism curves with a peak near $x = 3$ are interpreted as a single superconducting phase (*10*). This evidence for discrete phases in K_xC_{60} must be incorporated into any realistic model of the transport properties.

In this report, we present resistivity measurements of K_xC_{60} as a function of temperature and doping. We used ultrahigh-vacuum (UHV) molecular beam deposition to dope polycrystalline C_{60} films with controlled quantities of K while continuously monitoring the time-dependent film resistance near room temperature. The method gives the time, temperature, and concentration dependence of the resistance as well as an estimate for the diffusivity of the K dopant. The stoichiometry of the superconducting phase, which corresponds to a minimum in the resistivity at room temperature, has a K concentration given by $x = 3.00 \pm 0.05$, as determined by ex situ Rutherford backscattering (RBS) analyses. We find that the resistivity has a maximum at $x = 6.00 \pm 0.05$. These stoichiometries agree with Raman scattering (*1*) and photoemission (*8, 9*) findings.

The results are consistent with a simple model involving a granular microstructure and a miscibility gap between the phases. The conductivity is an activated process with an activation energy derived from the charging energies of individual K_3C_{60} grains. Close to $x = 3$, the grains coalesce, the charging energies become negligible, and the coupled grains give rise to a metallic state with conductivity close to the Mott limit.

The undoped films were grown (*1*) by vacuum sublimation of C_{60} refined by liquid chromatography from material produced in an electric-arc furnace (*11*). The amount of deposited C_{60} was monitored with a quartz microbalance calibrated by RBS measurement of the C deposited on clean Si. The thickness was calibrated by an optical interferometric gauge. Potassium areal atomic densities, N_K, were determined by analysis of the RBS K peaks after the film was removed from the UHV chamber. X-ray diffraction and transmission electron microscopy show random polycrystallinity with grain sizes of about 60 Å (*12*). For electrical measurements, four contact wires were attached with Ag paste to Ag pads that were evaporated at the corners of the 1-cm-square glass or thermally oxidized Si substrate. The C_{60} films were then deposited at ambient temperature. The substrates were mounted by the contact wires on a UHV feedthrough containing a small scanning Auger electron spectroscopy molecular-beam oven (SAES Getters/USA Inc.) and, if necessary, epoxy was used to attach a thermocouple to the back of the substrate.

The UHV chamber was baked at 175°C to outgas the C_{60} film. We deposited K at a base pressure of 10^{-9} torr and monitored the film resistance by a four-wire resistance bridge, using Van der Pauw's method. The two Van der Pauw resistance readings are typically equal within 30%, and the ratio is typically constant to 10% during the exposure, which shows that the K doping is laterally uniform.

We investigated the equilibration of the K in our films several ways. First, the resistivity changes by less than 1% in an hour if deposition is interrupted. Second, in all but the thickest films, changes in film resistance respond promptly to exposure to K. For a film 4450 Å thick, the equilibration time is slow enough to be measured: 400 s for $x < 3$. If this is interpreted as simple Fickian diffusion, then the K diffusivity is on the order of 10^{-12} cm^2 s^{-1}. The ionic conductivity is therefore not important. Third, preliminary thermopower measurements show slow responses, on the order of 3 μV/K over time scales of minutes, which we interpret as a thermally driven redistribution of K. Consequently, we expect the K distribution in

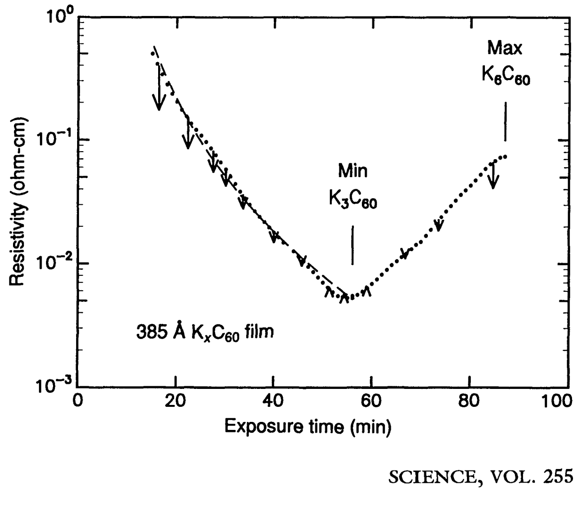

Fig. 1. Time dependence of the resistivity of K_xC_{60} film during exposure to a K molecular beam in UHV at ambient temperature near 74°C. The end point stoichiometry was determined for this particular sample; stoichiometry at the minimum was determined from other samples. The arrows show changes in the resistivity of a similar sample as it was heated from 60° to 134°C (see Fig. 2). The dashed curve is a fit to Eq. 2.

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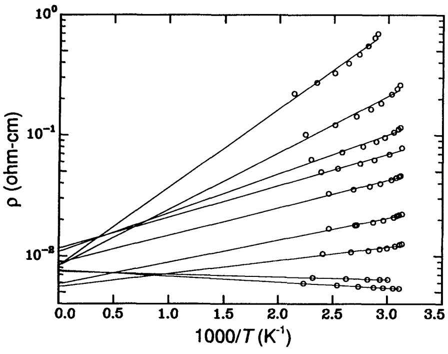

Fig. 2. Plots of the logarithm of resistivity versus inverse temperature for a film with doping in the range $1 < x \leq 3$. These data correspond to the arrows in Fig. 1. The lines are linear least-squares fits to the data and are extrapolated to $T^{-1} = 0$, to show the activated behavior of the resistivity. The doping progresses from top to bottom with the lowest curve corresponding to $x = 3$.

the film to be fully equilibrated on submicrometer length scales.

Figure 1 shows the dependence of resistivity on exposure time to K for a typical film, with arrows denoting the changes for a fixed temperature increment. The stoichiometry $x = 3$ corresponds to the minimum resistance (R_{min}) and $x = 6$ to the final maximum resistance (R_{max}). We established these x values by stopping the K exposure at either a minimum or maximum point, and then measuring the deposited K by RBS. Although the time to reach K_3C_{60} is greater than the interval from K_3C_{60} to K_6C_{60}, we cannot distinguish a stoichiometry-dependent sticking coefficient from possible systematic variations in the K flux. There is no obvious signature for the $x = 4$ phase. Film resistance decreases beyond $x = 6$, possibly because of unreacted metallic K on the surface (*1*). Data near $x = 0$ were not available for films on oxidized Si substrates because of the nonzero substrate conductivity. In our model, we assume a miscibility gap between the phases, in agreement with the aforementioned NMR, photoemission, and diamagnetism results. The resistivity is approximately activated, with a gap that is nearly symmetrical about $x = 3$, is approximately proportional to $|x - 3|$, and reaches values as high as 0.12 eV near $x = 1$.

In a typical granular metal system, there is a marked change in properties at the percolation threshold. This occurs near a 50% volume fraction of the conducting phase and usually is marked by a sharp change in resistivity and a change in the sign of the temperature coefficient (*13*). Our data show no signs of dramatic change in either the resistivity or the temperature coefficient (lengths of arrows in Fig. 1) (*14*) near $x = 1.5$ or $x = 4.5$; instead, the changes occur very near $x = 3$. Thus, a random percolation model with $x = 0$ or $x = 6$ insulating phase and $x = 3$ conducting phase is inconsistent with the data. A percolation model could explain the data if there were repulsive interactions between grains or if the K_3C_{60} grains are determined by the preexisting grains in the film before doping. If the conducting regions are located in the center of grains, because K_3C_{60} is most energetically favorable there, then the percolation threshold can be pushed arbitrarily close to $x = 3$. Presumably for $x > 3$, the insulating $x = 4$ and $x = 6$ phases would grow in from the grain boundaries and form a similar structure. This explains the symmetry about $x = 3$. Because the energy differences between various phases of K_xC_{60} are not large, on the order of 0.1 eV (*5*), it is plausible that there are mixed compositions at the grain boundaries where strains are large and disorder is more important.

To explore the exponential doping dependence, we measured the temperature dependence of resistance in the range $46°C < T < 194°C$ (there are irreversible changes in the resistance slightly above 200°C). Over this temperature range, Arrhenius plots of the resistance show a slight positive curvature (Fig. 2), but least-squares fits extrapolate to a compact cluster as $T^{-1} \rightarrow 0$. This convergence is the signature of an approximately activated conductivity.

For thicknesses greater than 1000 Å, the data of Fig. 3 show a thickness-independent minimum resistivity $\rho_{min}(K_3C_{60}) = 2.2$ microohm-cm. The cause of the larger resistivity in films thinner than 1000 Å, which also have the stoichiometry $x = 3$, is not presently understood, although it might be due to the exposure of the C_{60} films to air before doping or to systematic changes in grain size with thickness.

The lattice constant of the $x = 3$ face-centered cubic unit cell is 14.28 Å (*4*). Accordingly, the carrier density is 4.1×10^{21} cm^{-3}, with four C_{60} molecules and twelve donated electrons per unit cell. This charge density corresponds to a Fermi wave vector $k_F = 0.50$ Å^{-1} which, when substituted into a Boltzmann equation description of the minimum resistivity ρ_{min}, gives $\ell = 2.3$ Å for the electronic mean free path. This unphysically small ℓ implies that, even at $x = 3$, the Boltzmann equation is inadequate for describing a system where intergranular transport may still be limiting the conductivity.

The standard treatment for conduction in granular systems has been reviewed by Abeles (*15*), who showed that the charging energy of the grains is important to the conduction process. Adding K changes the grain size and therefore the charging energy and conductivity. The simplest model of the medium consistent with our data is a constant number density of metallic grains surrounded by an insulating phase. We assume that the relation between grain spacing, L, and grain size, d, is $d = L(x/3)^{1/3}$ (*16*). The gap between grains is $s = L - d$. Following Abeles (*15*), we calculate the energy required to move an electron from one grain to another distant grain

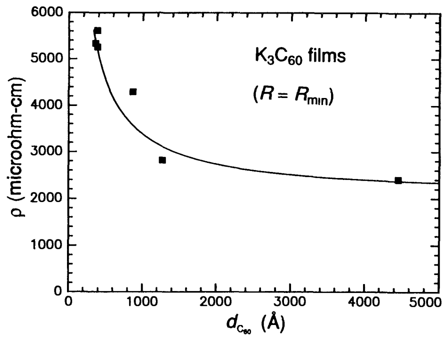

Fig. 3. Dependence of the resistivity of K_3C_{60} films on the thickness of the initial C_{60} film (curve is arbitrary).

$$E_c^0 = \frac{e^2}{2\pi\epsilon d}\,\frac{2d}{d + 2s} \qquad (1)$$

where ϵ is the dielectric constant of the insulating phase. The resistivity as a function of x and T is then given by the expression

$$\rho = \frac{h}{e^2}\,\frac{(d + s)}{\gamma}\exp\left(\frac{E_c^0}{2kT}\right)\exp(2\chi s) \qquad (2)$$

where h is Planck's constant, k is the Boltzmann constant, T is temperature, χ is the decay constant of the wave function between the grains, and γ is a factor of order unity describing the spatial distribution of the tunneling. We obtain a good fit to the data with $L = 83$ Å, $\gamma = 4.1$, and $\chi = 0$, as shown in Fig. 1.

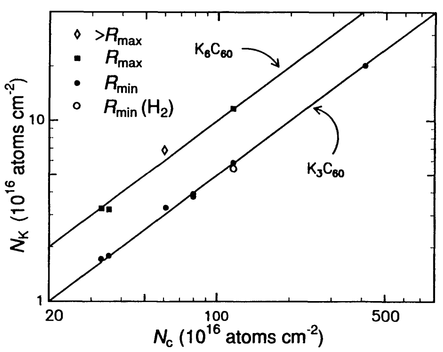

Fig. 4. Areal atomic densities in K_xC_{60} films. Filled symbols correspond to the turning points (min or max) in plots of resistance versus K doping (for example, Fig. 1). The open circle represents a film doped in the presence of 1 torr H_2. The diamond indicates a film doped beyond the R_{max} turning point.

Equation 2 is derived for weakly coupled grains, and $E_c^0 >> kT$. As $x \to 3$, these assumptions fail as the arguments of the exponentials approach zero. We cannot say how tightly coupled the grains become in the real system; it is possible that disorder on the grain boundaries may not allow the metallic regions to completely merge.

We have made an ad hoc improvement to the theory that has the proper behavior as $E_c^0 \to 0$ and can represent granular metal conductivities and percolation well:

$$\rho = \frac{2h}{e^2}\,\frac{(d+s)}{\gamma}\,\sinh\left(\frac{E_c^0}{2kT}\right)\exp(2\chi s) + \rho_g \qquad (3)$$

where ρ_g is a resistivity contribution from intragrain scattering. Our motivation for the replacement exp() → 2sinh() is that, as $E_c^0 \to 0$, the barriers to conduction vanish and $\rho \to 0$ (neglecting intragrain scattering). Fits with this modified theory are similar, with $L = 75$ Å, $\gamma = 6$, $\chi = 0$, and $\rho_g = \rho(x = 3)$. The data cannot be fit well using any reasonable effective medium model unless the conductivity of the percolating phase has a similar activated behavior.

The fitted values of L are in good agreement with the 60 Å grain size for the C_{60} film before doping. The result $\chi = 0$ implies that the energy barriers between grains are comparable to the charging energies (*17*), and about as many electrons go over the barriers as go through them. The fitted values of γ are close enough to unity to be plausible in the absence of a complete theory (*18*).

Stoichiometries of films of various thicknesses are shown in Fig. 4. The filled symbols correspond to doping at either the R_{min} or R_{max} points in plots of resistance versus K exposure. These points fall to within an error of ±0.05 on solid lines drawn respectively for the precise stoichiometries at $x = 3$ or $x = 6$. Although implied by existing work (*1*), this result demonstrates that the conductivity extrema fall exactly at half and full band filling.

In summary, the diffusion of K into C_{60} films produces a minimum resistivity phase that is barely metallic with $\rho = 2.2$ microohm-cm at composition $K_{3.00\pm0.05}C_{60}$, and a high resistivity (max) phase at composition $K_{6.00\pm0.05}C_{60}$. Intermediate compositions yield activated conduction with x-dependent activation energy, which can be explained by a simple model with immiscible phases where the metallic phase maximally avoids percolation. The recognition that the normal state has a granular microstructure will also be important in understanding superconductivity in thin films.

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14. The temperature coefficient of resistance, $R^{-1}dR/dT$ is negative for all films, except for $2.8 < x < 3.2$ where the behavior is metallic with $R^{-1}dR/dT = (7.9 \pm 0.4) \times 10^{-4}$ K^{-1} at $x = 3$. The width of the resistance minimum (and the region of positive temperature coefficient) is comparable to our estimates of doping uniformity (10%), so an ideal experiment might reveal a sharp minimum.
15. B. Abeles, *Appl. Solid State Sci.* **6**, 1 (1976).
16. If the grains were spheres on a simple cubic lattice, they would intersect at $x = \pi/6$; the intersection would correspond to a percolation threshold. Because we see no percolation until $x \approx 3$, the expression we use (corresponding to a lattice of cubes) is the simplest choice.
17. In the derivations in (*15*), the assumption is made that the barrier is large compared to the charging energies. What is referred to as the "barrier height" is more accurately the barrier height above the charging energy.
18. The calculation of γ in (*15*) is only valid in the limit $\chi(d + s) >> 1$; its derivation assumes the strong dependence of current on grain separation that is characteristic of a tunneling process.
19. We thank E. E. Chaban, D. J. Eaglesham, R. H. Eick, R. M. Fleming, A. R. Kortan, A. V. Makhija, D. W. Murphy, T. T. M. Palstra, J. C. Phillips, M. J. Rosseinsky, J. E. Rowe, F. C. Unterwald, B. E. Weir, and G. K. Wertheim for their contributions to this work.

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Hydrogen as a Probe of Semiconductor Surface Structure: The Ge(111)-c(2 × 8) Surface

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Hydrogen can be used as an effective probe of the structure of semiconductor surfaces. Such surfaces consist of bonds with varying degrees of bond strain, and hydrogen can react with each selectively depending on the reaction conditions. This selectivity is derived from a reduced barrier to reaction associated with strained bonds. In this manner, hydrogen can be used to pick apart the surface one bond type at a time, thereby revealing the structure of even complex multilayer reconstructions. This method is used to directly show that the rest-layer of the Ge(111)-c(2 × 8) surface has a bulk structure.

THE CHEMISTRY OF SEMICONDUCTOR surfaces is of great technological importance and an understanding of this chemistry requires a detailed knowledge of the surface structure. The surfaces of semiconductors typically reconstruct and form structures that differ substantially from those of the bulk (*1*). Surface reconstructions are often complex and may extend for several layers beneath the surface. This is particularly true of (111) surfaces; (100) surfaces, however, usually form simple single-layer dimer reconstructions. The structure of such complex multilayer reconstructions cannot be resolved by conventional surface scattering techniques. However, the advent of scanning tunneling microscopy (STM) offers the unprecedented capability to study surfaces at the atomic level (*2*). Although this technique can be used to determine the structure of the outermost surface layer, the structure of the underlying layers cannot be readily studied. This report describes the use of atomic hydrogen as an effective means of exposing and stabilizing these underlying layers. Once exposed, these layers may be directly probed by STM. This technique has been used to study the structure of the Ge(111)-c(2 × 8) surface and to show directly that it is a pure adatom surface, the underlying layer having a bulk (1 × 1) structure.

The Ge(111) surface consists of an outer layer of Ge adatoms that are arranged in a c(2 × 8) structure (*3*). Each adatom has three backbonds to the layer beneath, the so-called rest-layer. The remaining bonding orbital constitutes the unsaturated adatom dangling bond. The structure of this rest-layer has not been definitively established. Early STM studies of this surface clearly showed the c(2 × 8) adatom structure (*3*). However, the structure of the rest-layer had to be inferred from regions of this layer that were imaged between the gaps in the structure of the outer adatom layer. Based on this analysis, the rest-layer was suggested to have a bulk structure (*3*). This structure is consistent with the presence of bilayer-deep holes that form after the (2 × 1) to c(2 × 8) transformation on the Ge(111) surface (*4*). However, a more recent STM study has shown that there exists an asymmetry in the

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