

# Resistance measurements of conducting C<sub>60</sub> monolayers formed on Au and Cu films

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The resistances of conducting C<sub>60</sub> monolayers formed on Au and Cu films were found to be  $0.9 \pm 0.2$  and  $2.4 \pm 0.4$  k $\Omega$ , respectively, by *in situ* resistance measurements. Although the amount of charge transferred to each C<sub>60</sub> molecule from the Cu film was greater than that from the Au film, the conducting C<sub>60</sub> monolayer formed on the Cu film had higher resistance than that formed on the Au film. This result is consistent with resistance data for alkali fullerenes. © 2003 American Institute of Physics. [DOI: 10.1063/1.1598299]

## I. INTRODUCTION

The discovery of a mass production method for C<sub>60</sub> (Ref. 1) has stimulated widespread research into this type of material, referred to as a fullerene. The most significant discovery has been the superconductivity in alkali fullerenes.<sup>2</sup> This property of fullerene-based compounds is caused by the low work function of alkali metals and the high electron affinity of C<sub>60</sub> molecules which favor charge transfer across C<sub>60</sub>-metal interfaces. This charge transfer effect is not restricted to alkali or alkali-earth metals. Electrons are transferred from noble metals to C<sub>60</sub> molecules, although the work functions of noble metals are higher than those of alkali metals. The evidence of such a charge transfer effect has been observed in various experiments such as photoemission,<sup>3-8</sup> Raman scattering,<sup>3</sup> electron energy loss spectroscopy,<sup>9</sup> scanning tunneling spectroscopy,<sup>10</sup> luminescence,<sup>11</sup> second-harmonic generation studies,<sup>11</sup> and *in situ* resistance measurements.<sup>12-18</sup> Among them, *in situ* resistance measurements enable us to observe the charge transfer by the change in sheet resistance while depositing C<sub>60</sub> on thin noble metal films or vice versa.

In alkali fullerenes, alkali metals occupy the interstitial sites of the C<sub>60</sub> lattice, since the cohesive energy of alkali metals is sufficiently low. Noble metals, however, have higher cohesive energies, and cannot intercalated into the C<sub>60</sub> lattice and form a three-dimensional solid solution. For the case of C<sub>60</sub> deposited on thin noble metal films, therefore, a bilayer structure is formed as illustrated in Fig. 1. Electrons transfer to the adjacent monolayer of C<sub>60</sub> (Refs. 13-17) from metal atoms and make a *conducting* C<sub>60</sub> monolayer. Hebard *et al.*<sup>17</sup> performed *in situ* resistance measurements of the C<sub>60</sub>/Cu bilayer structure and reported that the resistance of a conducting C<sub>60</sub> monolayer on a Cu underlayer was approximately 8 k $\Omega$ . In this article, we report on the influence of the work functions of underlayer metals on the resistances of conducting C<sub>60</sub> monolayers formed on Au and Cu underlayers.

## II. CHANGE IN RESISTANCE BY DEPOSITING C<sub>60</sub>

The deposition of C<sub>60</sub> molecules on a thin noble metal film dramatically changes the sheet resistance compared to depositing metal atoms successively. Both increases and decreases can occur.

An increase in resistance is typical for films whose resistivities are close to that of the bulk metal. There are two main mechanisms for the resistance increase. First, a decrease of carrier density in the metal film: the charge transfer from metal atoms to C<sub>60</sub> molecules causes a lack of carrier electrons in the metal film. Second, enhancement of surface scattering: the charge transfer gives rise to charge separation, and this separation contributes to an increase in the scattering potential of electrons at the interface between C<sub>60</sub> and the metal layer.

A decrease in resistance is typical for films with very high sheet resistance. There are two main mechanisms for the resistance decrease. First, enhancement of the conduction between metal islands: such island (nucleus) formation is seen in the early stage of growth of noble metal films on insulating substrates. Many conduction models for noncontinuous films with metal islands have been reported. For example, thermal emission conductivity<sup>19</sup> in the low-field regime can be written as

$$\sigma \propto \exp\left\{-\left(C/k_B T\right)^{1/2}\right\},$$

where  $k_B$  is the Boltzmann constant,  $T$  is the temperature, and the value of  $C$  depends on the relative dielectric constant of the conduction medium ( $C \propto 1/\epsilon$ ). For C<sub>60</sub>,  $\epsilon$  is greater than 4,<sup>20</sup> which is much larger than for the vacuum. Thus, the involvement of C<sub>60</sub> as a tunneling medium decreases the sheet resistance of *noncontinuous* metal films. Second, the formation of a conducting C<sub>60</sub> monolayer: the charge transfer effect causes adjacent C<sub>60</sub> molecules to conduct. It is not possible for the C<sub>60</sub> film on the bare substrate between metal islands to contain conducting electrons. Therefore, the decrease in resistance by the formation of the conducting C<sub>60</sub> monolayer occurs when the metal underlayer is *continuous*.

In order to measure the resistance of the conducting C<sub>60</sub> monolayer, it is necessary to perform *in situ* resistance measurements for the case of the resistance decrease.

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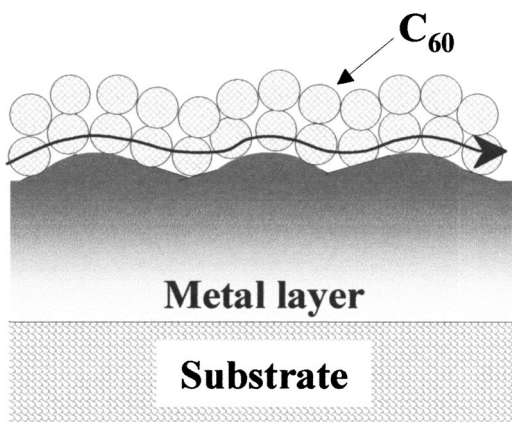


FIG. 1. Separated structure of the  $C_{60}$ /noble metal bilayer. The curved arrow is a schematic drawing of the conduction path brought about by the conducting  $C_{60}$  layer.

### III. EXPERIMENTAL DETAILS

All deposition and resistance measurements were performed at room temperature in a vacuum chamber which could be pumped to a base pressure of  $8 \times 10^{-7}$  Torr. This vacuum chamber had two heat sources for the evaporation of noble metals and  $C_{60}$  molecules, a shutter, and a quartz oscillation device. To eliminate any possible residual solvent in  $C_{60}$  powder, the powder was heated for several hours at a temperature of about  $200^\circ\text{C}$  in the vacuum chamber (below  $10^{-5}$  Torr) before deposition. A quartz glass with dimensions of  $1\text{ cm} \times 1\text{ cm}$  was used as the substrate. On the quartz substrate, four parallel electrodes made of Au ( $1\text{ mm} \times 8\text{ mm} \times 30\text{ nm}$ ) were fabricated with  $1\text{ mm}$  distances between them for the four-probe method. A thin Au or Cu film was deposited onto the electrodes by thermal heating of a W boat. After this process,  $C_{60}$  was deposited onto the noble metal underlayer by thermal heating of a Mo boat. During  $C_{60}$  deposition, *in situ* resistance measurements were performed by the four-probe method. We monitored the average film thickness and the deposition rate using a quartz oscillation device.

During the deposition of  $C_{60}$  molecules onto the noble metal underlayer, the heat radiation from the evaporation source affected the sheet resistance. This temperature dependence of the resistance disturbed accurate measurement of the resistance of the conducting  $C_{60}$  monolayer. To compensate for the heat difference in heat before and after opening the shutter of the evaporation source for  $C_{60}$ , another heat source was turned on until the shutter was opened. We employed the W boat, which was not used during the deposition of  $C_{60}$ , as the compensating heat source. The current of the compensating heat source was adjusted so as to yield no change in the sheet resistance after opening the shutter of the Mo boat without  $C_{60}$  powder.

### IV. RESULTS AND DISCUSSION

In order to say that the observed resistance decrease originates from the conducting  $C_{60}$  layer, it is necessary to know whether the metal underlayer is noncontinuous or continuous. The formation of islands is seen in the early stage of

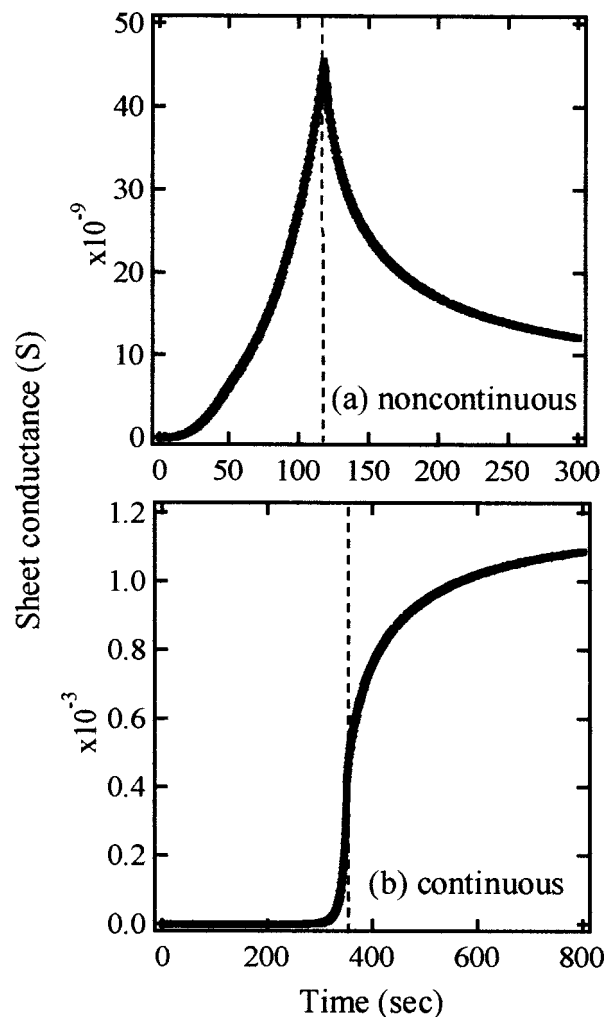


FIG. 2. Time course of the sheet conductance of thin Cu films from the start of deposition. (a) Noncontinuous Cu film with a final average thickness of  $3.2\text{ nm}$ . (b) Continuous Cu film with a final average thickness of  $6.4\text{ nm}$ . The dotted lines indicate the time at which the shutter of the evaporation source was closed.

noble metal growth, as described above. If the supply of metal atoms to the substrate is stopped at this stage, the sheet conductance of the film decreases rapidly as adatoms move and coalesce to increase the distance between metal islands.<sup>21</sup> As the metal film grows further, metal islands become connected to each other and the film becomes continuous. If the supply of metal atoms is stopped in this regime, the sheet conductance of the film increases as adatoms move to smoothen the film. Shown in Fig. 2 are the changes in sheet conductance during and after the deposition of Cu on the quartz glass substrate. The conductance decrease [Fig. 2(a)] and increase [Fig. 2(b)] after stopping deposition confirm that the thin Cu films are noncontinuous and continuous, respectively.

Figure 3 illustrates the decrease in sheet resistance by depositing  $C_{60}$  on a thin Cu film. The vertical axis indicates the sheet resistance normalized to the value of the resistance of the Cu film before  $C_{60}$  deposition,  $R(0)$ . The average thickness and resistance of the Cu underlayer are  $5.5\text{ nm}$  and

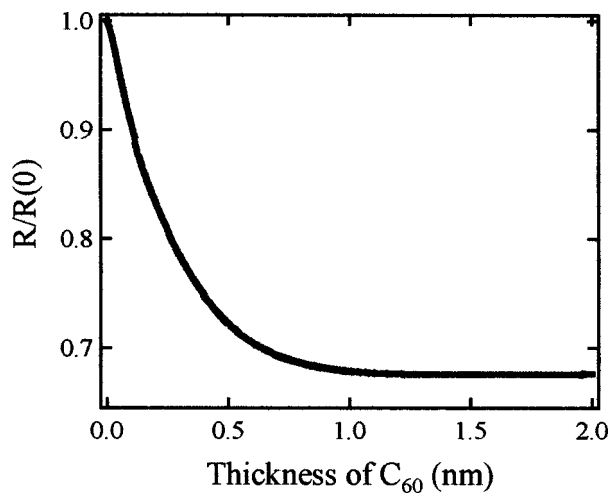


FIG. 3. Change in the normalized sheet resistance by depositing  $C_{60}$  on a 5.5 nm thick Cu film.

1.43 k $\Omega$ , respectively. A drastic change (32% decrease) in the sheet resistance is observed. This change is due to the conducting  $C_{60}$  layer brought about by charge transfer from Cu atoms to  $C_{60}$  molecules because the Cu underlayer is continuous according to the criterion described above. The most important fact is that the sheet resistance does not change when the average thickness of the  $C_{60}$  overlayer is over 1 nm, which is approximately equal to a thickness of one monolayer. This indicates that the charge transfer is limited to one monolayer and makes a conducting  $C_{60}$  monolayer.<sup>17</sup>

Shown in Fig. 4 are the resistances of conducting  $C_{60}$  monolayers formed on thin Au and Cu films with various conductances. These values are simply calculated with experimental data by assuming that the resistances of the  $C_{60}$  monolayer and of the metal underlayer make a parallel connection. The values of the horizontal axis show the conductances of the metal underlayers. Employing the criterion for the continuity of metal films (Fig. 2), all the data in Fig. 4 correspond to continuous metal underlayers. Therefore, enhancement of conduction between metal islands by depositing  $C_{60}$ , which occurs when the metal underlayer is noncontinuous, has no effect on the resistances of the  $C_{60}$  monolayers. The resistance of the conducting  $C_{60}$  monolayer decreases as the conductance of a metal underlayer increases, i.e., as the underlayer grows. In the initial stage of the continuous regime of noble metal growth, metal islands begin to become connected to each other and form a mesh structure. Then, metal atoms cover the whole surface of the substrate and the metal film becomes completely continuous. The growth of the metal underlayer implies enlargement of the  $C_{60}$ -metal interfacial area. Thus, the more the underlayer grows, the more  $C_{60}$  molecules receive electrons from the metal film.

The values in the observed plateau of the resistance curves (Fig. 4) can be attributed to the resistance of a conducting  $C_{60}$  monolayer. As averages of the values in the plateaus (above 1 mS for both data),  $0.9 \pm 0.2$  and  $2.4 \pm 0.4$  k $\Omega$  are obtained for the resistances of the conducting  $C_{60}$  monolayers formed on the Au and Cu underlayers, respectively.  $C_{60}$  molecules on a Cu film receive more elec-

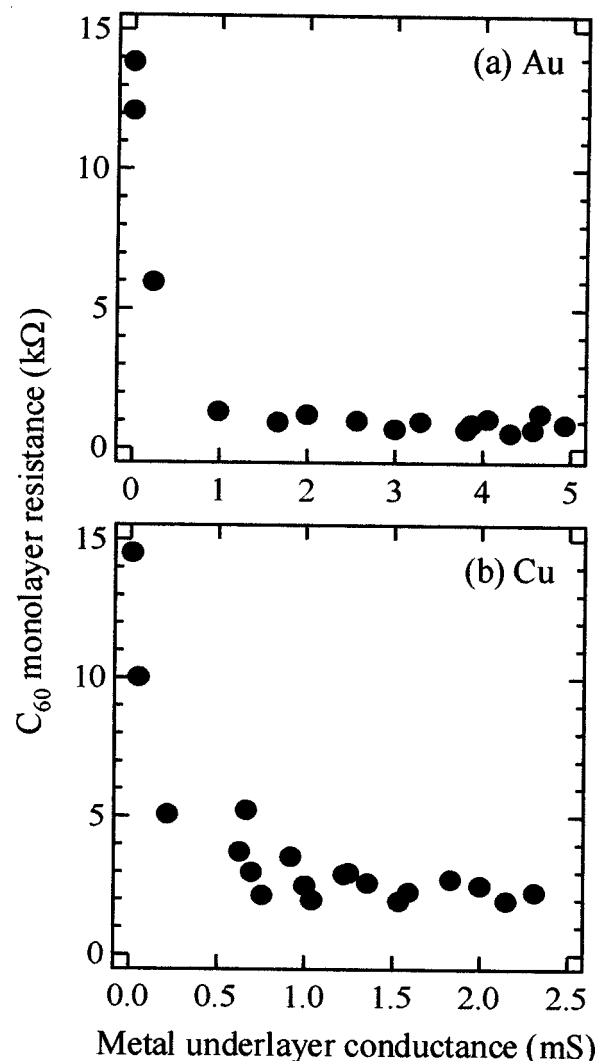


FIG. 4. Change in resistance of a conducting  $C_{60}$  monolayer as a function of the conductance of thin (a) Au and (b) Cu underlayers. The values are simply calculated with experimental data assuming that the resistances of a  $C_{60}$  layer and a metal underlayer make a parallel connection.

trons than those on a Au film because the work function of Au is higher than that of Cu (5.1 and 4.65 eV for bulk Au and Cu, respectively). The conducting  $C_{60}$  monolayer on the Cu film, however, has higher resistance than that on the Au film.

It is well known that  $A_3C_{60}$ -type alkali fullerides ( $A = K, Rb$ ) have the smallest resistance. This corresponds to half filling of the lowest unoccupied molecular orbital (LUMO)-derived  $t_{1u}$  band, which is equivalent to the transfer of three electrons. The concentration of alkali metal atoms ( $x$  in  $A_xC_{60}$ ) thus indicates the number of transferred electrons per  $C_{60}$  molecule. Meanwhile, the results of surface-enhanced Raman scattering experiments<sup>3</sup> showed that the shifts of the charge sensitive  $A_g(2)$  pentagonal breathing mode of  $C_{60}$  molecules on the Au and Cu substrates are  $-15.4$  and  $-23.2$   $cm^{-1}$ , respectively. Using a calibration of  $-6.1$   $cm^{-1}$  shifts per electron transferred to each molecule,<sup>22</sup> these shifts correspond to the transfer of 2.5 and 3.8 electrons. In terms of the resistance of alkali fullerides,  $K_{3.8}C_{60}$  has about 10 times higher resistance than  $K_{2.5}C_{60}$ , and

$\text{Rb}_{3.8}\text{C}_{60}$  has about 3 times higher resistance than  $\text{Rb}_{2.5}\text{C}_{60}$ .<sup>23,24</sup>

It is impossible to make a quantitative comparison between resistances of alkali fullerides and conducting  $\text{C}_{60}$  monolayers because alkali fullerides have interstitial atoms whereas  $\text{C}_{60}$  monolayers do not have such interstitials and thus have different lattice constants. Interstitials and the associated different lattice constant have a large effect on the resistance. However, a qualitative comparison is still valid. Our result of higher resistance of the conducting  $\text{C}_{60}$  monolayer formed on a Cu film than that formed on a Au film is consistent with these resistance data of alkali fullerides.

## V. CONCLUSIONS

The conducting  $\text{C}_{60}$  monolayer is formed on a noble metal film by charge transfer from metal atoms adjacent to  $\text{C}_{60}$  molecules. In order to determine the resistance of this  $\text{C}_{60}$  monolayer, we performed *in situ* resistance measurements for the case of depositing  $\text{C}_{60}$  on noble metal underlayers. Resistances of  $0.9 \pm 0.2$  and  $2.4 \pm 0.4$  k $\Omega$  for the ones formed on the Au and Cu underlayers, respectively, were obtained. Although the amount of charge transferred to each  $\text{C}_{60}$  molecule from Cu films is greater than that from Au films, the conducting  $\text{C}_{60}$  monolayer formed on Cu films had higher resistance than that formed on Au films. This is consistent with resistance data of alkali fullerides.

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- <sup>1</sup>W. Kraetschmer, L. D. Lamb, K. Fostiropoulos, and D. R. Huffman, *Nature (London)* **347**, 354 (1985).
- <sup>2</sup>A. F. Hebard, M. J. Rosseinsky, R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez, and A. R. Kortan, *Nature (London)* **350**, 600 (1991).
- <sup>3</sup>S. J. Chase, W. S. Bacsá, M. G. Mitch, L. J. Pilione, and J. S. Lannin, *Phys. Rev. B* **46**, 7873 (1992).
- <sup>4</sup>T. R. Ohno, Y. Chen, S. E. Harvey, G. H. Kroll, J. H. Weaver, R. E. Haufler, and R. E. Smalley, *Phys. Rev. B* **44**, 13747 (1991).
- <sup>5</sup>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).
- <sup>6</sup>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).
- <sup>7</sup>G. K. Wertheim and D. N. E. Buchanan, *Phys. Rev. B* **50**, 11070 (1994).
- <sup>8</sup>D. W. Owens, C. M. Aldao, D. M. Poirier, and J. H. Weaver, *Phys. Rev. B* **51**, 17068 (1995).
- <sup>9</sup>S. Modesti, S. Cerasari, and P. Rudolf, *Phys. Rev. Lett.* **71**, 2469 (1993).
- <sup>10</sup>T. Hashizume *et al.*, *Phys. Rev. Lett.* **71**, 2959 (1993).
- <sup>11</sup>W. Zhao, L.-Q. Chen, Y.-X. Li, T.-N. Zhao, Y.-Z. Huang, Z.-X. Zhang, H.-T. Wang, P.-X. Ye, and Z.-X. Zhao, *Spectrochim. Acta, Part A* **50**, 1759 (1994).
- <sup>12</sup>W. Zhao, K. Luo, J. Cheng, C. Li, D. Yin, Z. Gu, X. Zhou, and Z. Jin, *J. Phys.: Condens. Matter* **4**, L513 (1992).
- <sup>13</sup>X. D. Zhang *et al.*, *Chem. Phys. Lett.* **228**, 100 (1994).
- <sup>14</sup>W. B. Zhao, J. Chen, K. Wu, J. L. Zhang, C. Y. Li, D. L. Yin, Z. N. Gu, X. H. Zhou, and Z. X. Jin, *J. Phys.: Condens. Matter* **6**, L631 (1994).
- <sup>15</sup>J. Q. Wu *et al.*, *Phys. Rev. B* **54**, 9840 (1996).
- <sup>16</sup>A. F. Hebard *et al.*, *Phys. Rev. B* **50**, 17740 (1994).
- <sup>17</sup>A. F. Hebard, R. R. Ruel, and C. B. Eom, *Phys. Rev. B* **54**, 14052 (1996).
- <sup>18</sup>H. Wang, X. Li, B. Wang, and J. G. Hou, *J. Phys. Chem. Solids* **61**, 1185 (2000).
- <sup>19</sup>J. G. Simmons, *J. Appl. Phys.* **34**, 1793 (1963).
- <sup>20</sup>S. L. Ren *et al.*, *Appl. Phys. Lett.* **59**, 2678 (1991).
- <sup>21</sup>M. Nishiura and A. Kinbara, *Thin Solid Films* **24**, 79 (1974).
- <sup>22</sup>M. S. Dresselhaus, G. Dresselhaus, and P. C. Eklund, *Science of Fullerenes and Carbon Nanotubes* (Academic, San Diego, 1996), p. 380.
- <sup>23</sup>F. Stepniak, P. J. Benning, D. M. Poirier, and J. H. Weaver, *Phys. Rev. B* **48**, 1899 (1993).
- <sup>24</sup>R. Hesper, L. H. Tjeng, A. Heeres, and G. A. Sawatzky, *Phys. Rev. B* **62**, 16046 (2000).