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Title	Resistance measurements of conducting C[60] monolayers formed on Au and Cu films
Author(s)	Nouchi, R; Kanno, I
Citation	JOURNAL OF APPLIED PHYSICS (2003), 94(5): 3212-3215
Issue Date	2003-09-01
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Type	Journal Article
Textversion	publisher

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Resistance measurements of conducting C_{60} monolayers formed on Au and Cu films

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(Received 11 February 2003; accepted 11 June 2003)

The resistances of conducting C_{60} monolayers formed on Au and Cu films were found to be 0.9 ± 0.2 and 2.4 ± 0.4 kΩ, respectively, by *in situ* resistance measurements. Although the amount of charge transferred to each C_{60} molecule from the Cu film was greater than that from the Au film, the conducting C_{60} 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 fullerides. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1598299]

I. INTRODUCTION

The discovery of a mass production method for C_{60} (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 fullerides.[2] This property of fullerene-based compounds is caused by the low work function of alkali metals and the high electron affinity of C_{60} molecules which favor charge transfer across C_{60}–metal interfaces. This charge transfer effect is not restricted to alkali or alkali-earth metals. Electrons are transferred from noble metals to C_{60} 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,[3–8] Raman scattering,[3] electron energy loss spectroscopy,[9] scanning tunneling spectroscopy,[10] luminescence,[11] second-harmonic generation studies,[11] and *in situ* resistance measurements.[12–18] Among them, *in situ* resistance measurements enable us to observe the charge transfer by the change in sheet resistance while depositing C_{60} on thin noble metal films or vice versa.

In alkali fullerides, alkali metals occupy the interstitial sites of the C_{60} lattice, since the cohesive energy of alkali metals is sufficiently low. Noble metals, however, have higher cohesive energies, and cannot intercalated into the C_{60} lattice and form a three-dimensional solid solution. For the case of C_{60} 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_{60} (Refs. 13–17) from metal atoms and make a *conducting* C_{60} monolayer. Hebard *et al.*[17] performed *in situ* resistance measurements of the C_{60}/Cu bilayer structure and reported that the resistance of a conducting C_{60} monolayer on a Cu underlayer was approximately 8 kΩ. In this article, we report on the influence of the work functions of underlayer metals on the resistances of conducting C_{60} monolayers formed on Au and Cu underlayers.

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II. CHANGE IN RESISTANCE BY DEPOSITING C_{60}

The deposition of C_{60} 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_{60} 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_{60} 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[19] in the low-field regime can be written as

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

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 ($C \propto 1/\varepsilon$). For C_{60}, ε is greater than 4,[20] which is much larger than for the vacuum. Thus, the involvement of C_{60} as a tunneling medium decreases the sheet resistance of *noncontinuous* metal films. Second, the formation of a conducting C_{60} monolayer: the charge transfer effect causes adjacent C_{60} molecules to conduct. It is not possible for the C_{60} film on the bare substrate between metal islands to contain conducting electrons. Therefore, the decrease in resistance by the formation of the conducting C_{60} monolayer occurs when the metal underlayer is *continuous*.

In order to measure the resistance of the conducting C_{60} monolayer, it is necessary to perform *in situ* resistance measurements for the case of the resistance decrease.

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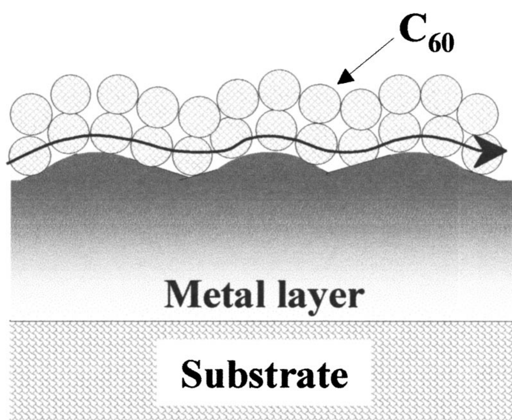

FIG. 1. Separated structure of the C_{60}/noble metal bilayer. The curved arrow is a schematic drawing of the conduction path brought about by the conducting C_{60} layer.

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 8×10^{-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 °C in the vacuum chamber (below 10^{-5} Torr) before deposition. A quartz glass with dimensions of 1 cm×1 cm was used as the substrate. On the quartz substrate, four parallel electrodes made of Au (1 mm ×8 mm×30 nm) were fabricated with 1 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 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.[21] 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.

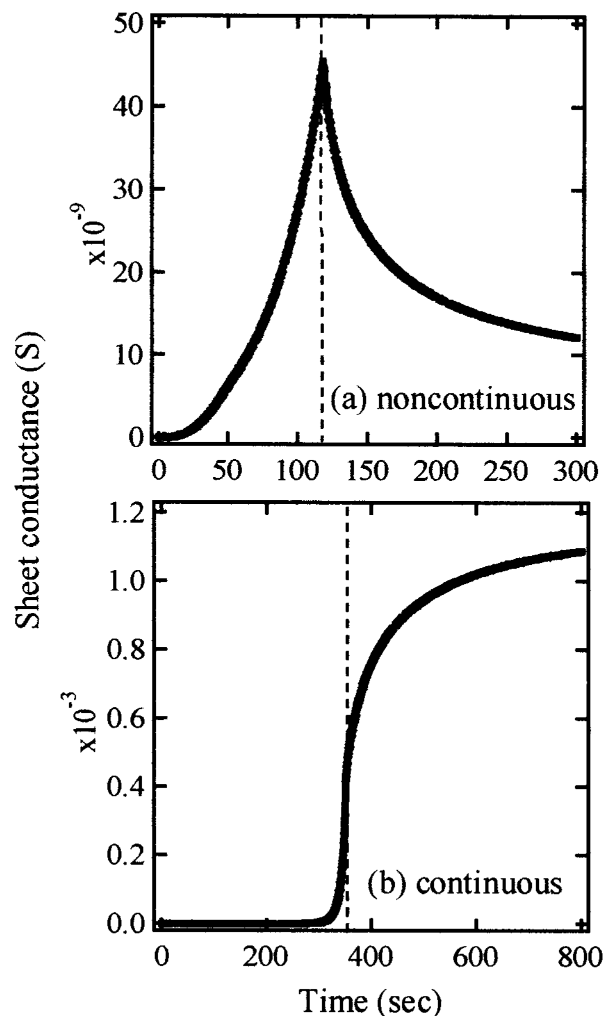

FIG. 2. Time course of the sheet conductance of thin Cu films from the start of deposition. (a) Noncontinuous Cu film with a final average thickness of 3.2 nm. (b) Continuous Cu film with a final average thickness of 6.4 nm. The dotted lines indicate the time at which the shutter of the evaporation source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

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 nm and

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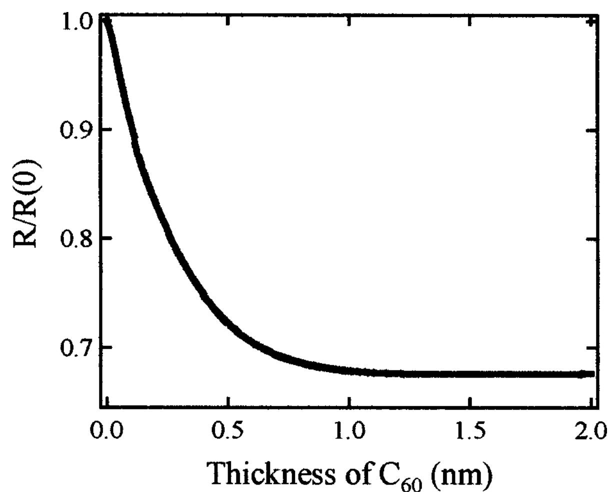

FIG. 3. Change in the normalized sheet resistance by depositing C_{60} on a 5.5 nm thick Cu film.

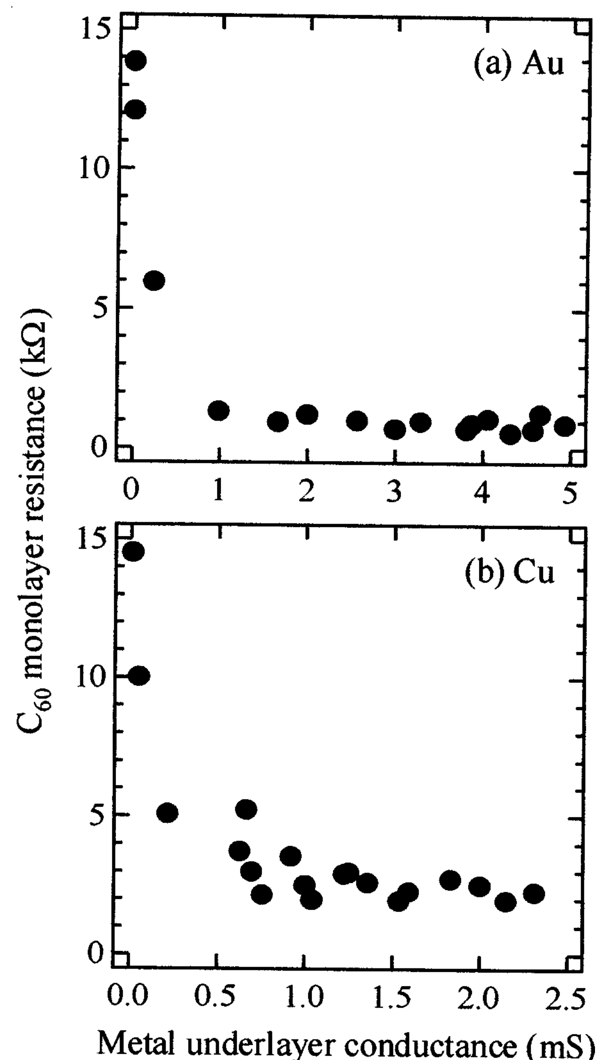

FIG. 4. Change in resistance of a conducting C_{60} monolayer as a function of the conductance of thin (a) Au and (b) Cu underlayers. The values are simply calculated with experimental data assuming that the resistances of a C_{60} layer and a metal underlayer make a parallel connection.

1.43 kΩ, 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.[17]

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 ± 0.2 and 2.4 ± 0.4 kΩ 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 electrons 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[3] 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,[22] 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

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$Rb_{3.8}C_{60}$ has about 3 times higher resistance than $Rb_{2.5}C_{60}$.[23,24]

It is impossible to make a quantitative comparison between resistances of alkali fullerides and conducting C_{60} monolayers because alkali fullerides have interstitial atoms whereas 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 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 C_{60} monolayer is formed on a noble metal film by charge transfer from metal atoms adjacent to C_{60} molecules. In order to determine the resistance of this C_{60} monolayer, we performed *in situ* resistance measurements for the case of depositing C_{60} on noble metal underlayers. Resistances of 0.9 ± 0.2 and 2.4 ± 0.4 kΩ for the ones formed on the Au and Cu underlayers, respectively, were obtained. Although the amount of charge transferred to each C_{60} molecule from Cu films is greater than that from Au films, the conducting 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.

ACKNOWLEDGMENT

The authors are grateful to Dr. M. Shiraishi of Materials Laboratories, SONY Corporation, Japan, for helpful discussions and his continuing interest in their work.

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