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## Study of the conductance and structure characteristics of C<sub>60</sub>/Sb bilayers

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### Abstract

The electrical and structural properties of C<sub>60</sub>/Sb bilayers were investigated. *In situ* direct-current conductivity measurement results indicate that the doping of Sb into C<sub>60</sub> induces the C<sub>60</sub> order–disorder phase transition temperature to increase to ~278 K. According to the results of a transmission electron microscope and atomic force microscope study, such a transition (near 278 K) implies the formation of an interfacial structure of Sb-doped C<sub>60</sub>. Annealing and the absorption of gases destroy the interfacial structure of Sb-doped C<sub>60</sub>. A possible mechanism for such a phase transition is discussed.

### 1. Introduction

The unique structure and characteristics of C<sub>60</sub> and C<sub>60</sub> derivatives have attracted much scientific attention [1–6]. Below and above 260 K, C<sub>60</sub> can be fabricated in the simple cubic (sc) and face-centred-cubic (fcc) structural forms, respectively. C<sub>60</sub> crystal undergoes an orientational order–disorder (fcc–sc) phase transition between the sc and fcc forms at 260 K, as demonstrated by many experiments [1, 7–9]. Differential scanning calorimetry (DSC) results showed that the width of the fcc–sc transition for C<sub>60</sub> crystal is ~0.4 K [8], while dc conductance measurement results indicated a transition width of ~2–3 K [10]. The reasons for the different widths were explored by previous research [10]; the authors of [10] asserted that the electrical properties are more sensitive to structure change than the heat capacity. However, Mort *et al* studied the dc conductivity of C<sub>60</sub>/C<sub>70</sub> films and found that the fcc–sc transition occurred in the range 270 K–300 K [11], and they asserted that the large width is a consequence of significant lattice distortion of the C<sub>60</sub> crystal. It is reported that some fullerenes exhibit a phase transition similar to that of pristine C<sub>60</sub>. For example, structure transitions occur near 299 K and 305 K

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in  $\text{Na}_2\text{CsC}_{60}$  and  $\text{Na}_2\text{KC}_{60}$ , respectively [4]. Doping with  $\text{O}_2$  leads to the formation of  $\text{C}_{60}\text{O}$ , which undergoes a  $\text{C}_{60}$ -like phase transition at 270 K [12, 13]. Furthermore, research on Ar-doped  $\text{C}_{60}$  single crystal indicated that doping with Ar causes a drop of the  $\text{C}_{60}$  fcc–sc transition temperature [14].

In this paper, results from an investigation of the  $\text{C}_{60}$ –Sb interaction are presented. Sb is reported to be an effective surfactant in the growth of high-quality and larger-scale  $\text{C}_{60}$  single-crystal films at the surfaces of NaCl single crystal and mica. In the literature it is reported that the  $\text{C}_{60}$ –Sb interaction is complex. The effect of such an interaction on the electrical properties of Sb-doped  $\text{C}_{60}$  crystal films is of interest and is a question that remains open. The effect of Sb incorporation in  $\text{C}_{60}$  is crucial for the application of such  $\text{C}_{60}$  films and is well worth studying. The paper is organized as follows. Section 2 describes the experiments, section 3 gives the results, section 4 is a discussion, and section 5 gives our conclusions.

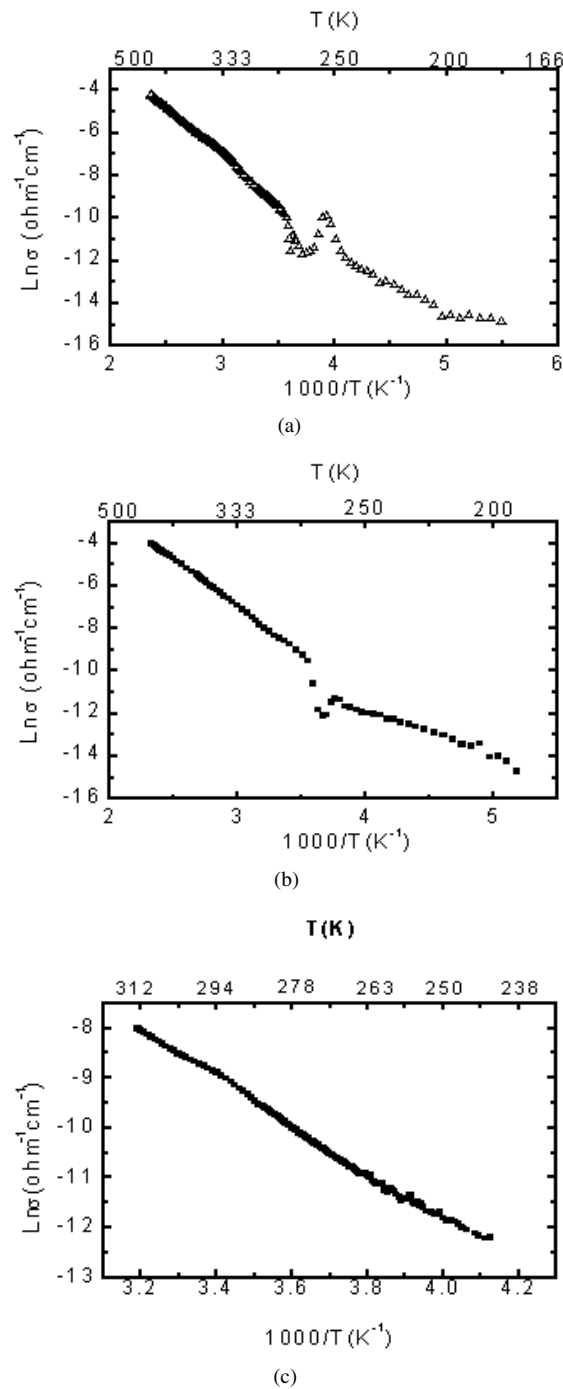
## 2. Experiments

The films were prepared by the two-source thermal co-evaporation method under a vacuum of  $3.0 \times 10^{-6}$  Torr. The purities of the Sb and  $\text{C}_{60}$  were 99.999% and 99.9% respectively. The substrate was freshly cleaved mica and was kept at 450 K during evaporation. Four pre-deposited gold pads were deposited upon the mica substrate as electrodes for conductance measurement. A quartz oscillation monitor was used to calibrate the deposition rates and thicknesses of the films. The resolution of the monitor is 0.1 nm. First a layer of Sb was deposited with the thickness of 3–10 nm, and a few minutes later a layer of  $\text{C}_{60}$  film was deposited at a rate of  $1 \text{ nm min}^{-1}$ . The thickness of the  $\text{C}_{60}$  film was in the range 10–20 nm. The resulting sample was kept at 450 K for 30 minutes before being cooled down to 130 K. The dc conductance measurement was performed using a standard four-wire configuration with computer-controlled Keithley 2400 and Keithley 6517A meters. The morphology of the films was analysed under ambient conditions using an atomic force microscope (AFM), Autoprobe CP (Park Instruments), in contact mode, with a scanning frequency of 1.2 Hz. A Hitachi H-800 TEM was used for structure characterization.

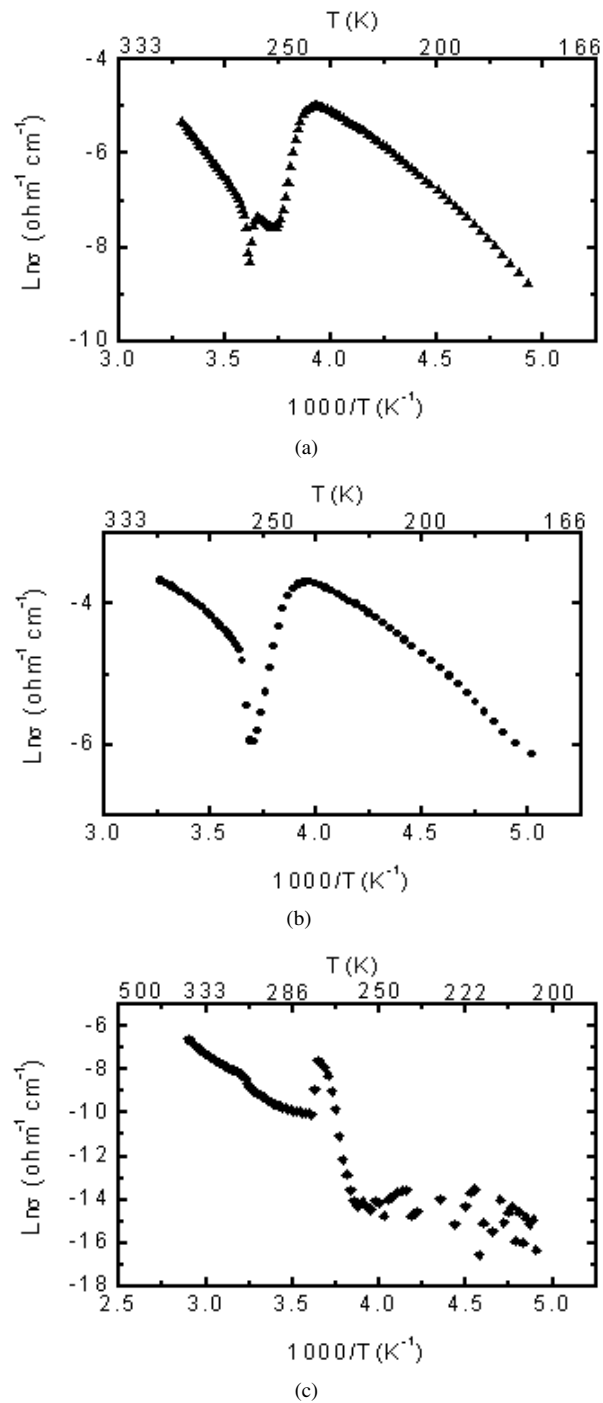
## 3. Results

### 3.1. Conductance investigation

Figure 1 shows the logarithm of the electrical conductance ( $\ln \sigma$ ) versus the reciprocal temperature ( $1/T$ ) for  $\text{C}_{60}(10 \text{ nm})/\text{Sb}(3 \text{ nm})$ . Figure 1(a) shows the results from the first measurement process. After the first measurement process, the sample was annealed at 450 K for five hours; then the second measurement cycle was performed and the results are shown in figure 1(b). The results in figures 1(a) and 1(b) were all measured *in situ*. When the second measurement cycle was finished, the sample was exposed to air, then degassed in a vacuum, and then measurements were made; the results are presented in figure 1(c). In figure 1(a), the fcc–sc phase transition of  $\text{C}_{60}$  is observed clearly near 260 K—it leads to a conductance anomaly—and the temperature width of this transition is  $\sim 15$  K, much larger than that for single-crystalline  $\text{C}_{60}$ . The large width of the transition presumably results from the poor quality of the  $\text{C}_{60}$  film. From figure 1(a), the activation energies are, below and above 263 K, 0.172 eV and 0.379 eV, respectively—considerably smaller than those of pristine  $\text{C}_{60}$  [10]. The small activation energies of the film also indicate that some Sb may be incorporated in the  $\text{C}_{60}$  crystal. The most interesting feature of figure 1(a) is the observation of the jump near 278 K. Comparing figure 1(a) with figure 1(b), we see that annealing increases the conductance



**Figure 1.**  $\ln \sigma - 1/T$  results for  $C_{60}(10 \text{ nm})/Sb(3 \text{ nm})$  bilayers. (a) The first *in situ* measurement cycle. The conductance anomaly jumps are in the ranges 255–269 K and 275–277 K. (b) The sample annealed at 450 K before the measurements were made *in situ*; the anomalous conductance jump is in the range 266–273 K. (c) The sample exposed to air and degassed in vacuum before the measurements were made. The anomalous jump of the conductance near 260 K is blurred.  $T_s = 450 \text{ K}$ .



**Figure 2.**  $\ln \sigma - 1/T$  for  $C_{60}(20 \text{ nm})/\text{Sb}(10 \text{ nm})$  bilayers. (a) The first *in situ* measurement cycle. The conductance anomaly jumps are in the ranges 255–268 K and 273–277 K. (b) The sample annealed at 450 K before the measurements were made *in situ*; the anomalous conductance jump is in the range 255–270 K and much enhanced. (c) The results for the sample exposed to air and degassed in vacuum before the measurements were made.  $T_s = 450 \text{ K}$ .

slightly and reduces the conductance jump near 278 K. Moreover, the transition in the range 266 K–272 K is very much compressed and widened, and the activation energies are increased a little. From figure 1(c), we see that the conductance jump near 260 K is suppressed and its value decreases by about four orders of magnitude, while the activation energy is 0.420 eV, much larger than those for figures 1(a) and 1(b). These results indicate that the adsorption of air significantly affects the phase transition of C<sub>60</sub>.

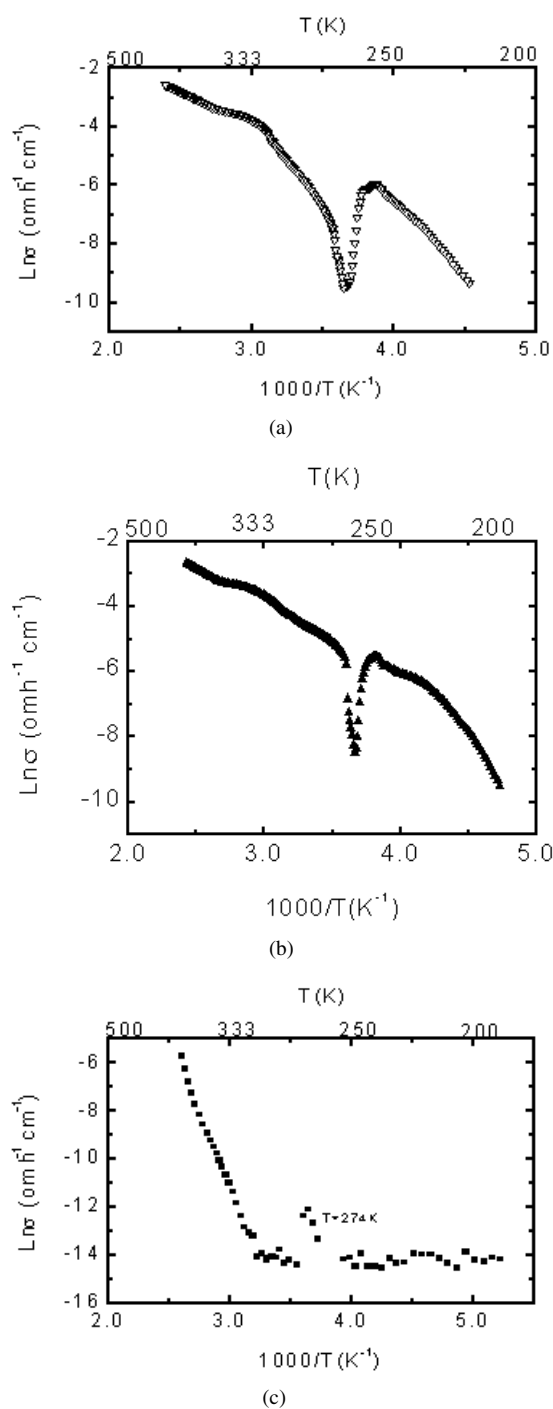
Figure 2 shows  $\ln \sigma - 1/T$  results for C<sub>60</sub>(20 nm)/Sb(10 nm). Figure 2(a) shows the results from the first measurement cycle. Figure 2(b) shows the results for the sample annealed at 450 K for five hours before the measurements. Figure 2(c) shows the results for the sample exposed to air then degassed in vacuum before the measurements. From figure 2(a), it is obvious that the two conductance jumps appeared and were enhanced compared with those in figure 1(a). Compare figure 2(a) with figure 2(b): annealing causes the jump near 260 K to be enhanced and sharpened while the jump near 275 K disappears, and annealing also increases the conductance of the film a little. Figure 2(c) indicates that the conductance dropped by about five orders when the films were exposed to air. Below and above 300 K, the activation energies are several meV and about 1 eV, respectively.

Figure 3 shows  $\ln \sigma - 1/T$  for C<sub>60</sub>(20 nm)/Sb(15 nm). Figure 3(a) shows the results from the first measurement process, and figure 3(b) shows the results for the sample annealed *in situ* for nine hours before the measurements. Figure 3(c) shows the results for the sample exposed to air then degassed in vacuum before the measurements. In figure 3(a), two conductance jumps appear in the ranges 258 K–262 K and 262 K–274 K. Following annealing, the jumps observed in figure 3(b) can no longer be clearly distinguished and are moved to the range 263 K–273 K. In figure 3(c), the activation energies below and above 300 K are ~45 meV and ~1.06 eV, respectively.

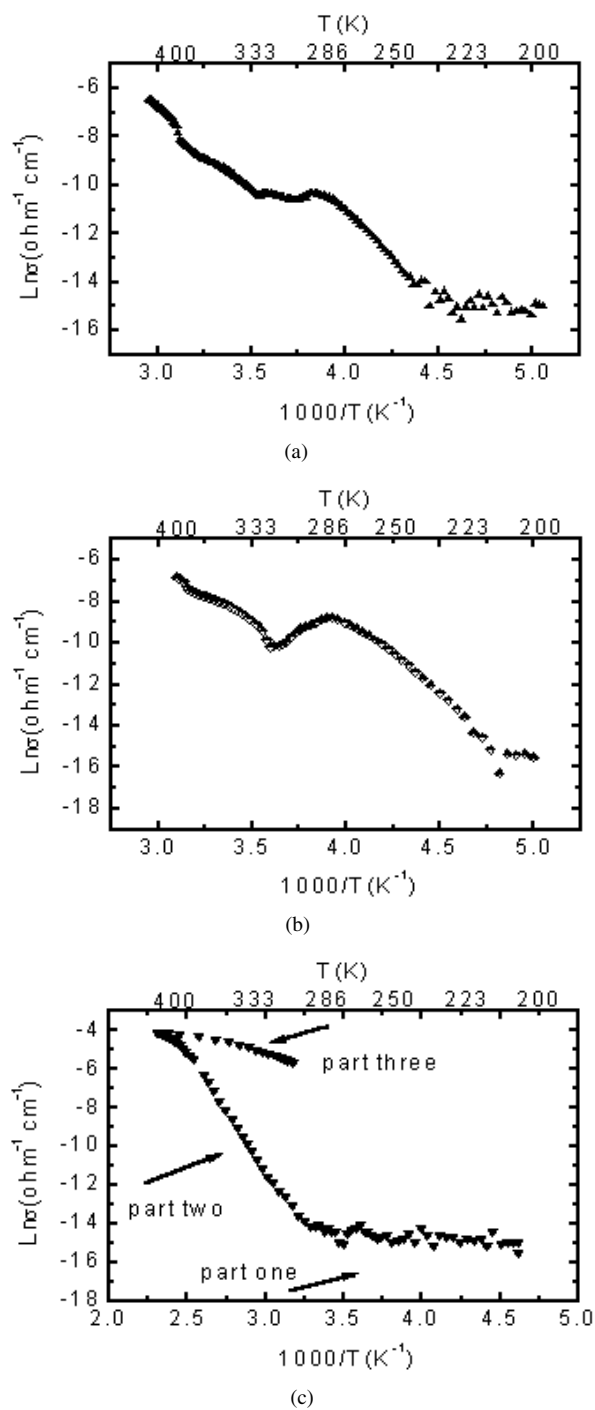
Figure 4 shows  $\ln \sigma - 1/T$  for C<sub>60</sub>(60 nm)/Sb(1.5 nm). Figures 4(a)–4(c) show results from measurement processes similar to those of figure 3. In figure 4(a), two conductance jumps are observed in the ranges 263 K–269 K and 280 K–283 K. The linearity of  $\ln \sigma - 1/T$  is very poor compared with that in figure 1. In figure 4(b), only one jump is observed, in the range 256 K–279 K. In figure 4(c), the activation energies below and above 300 K are ~45 meV and 1.1 eV, respectively. After the sample was heated to 450 K and then the temperature dropped, the slope of the graph was smaller than that for the increasing-temperature process. The temperature-drop process in figure 4(c) indicates that the absorbed air can be partly caused to desorb by annealing. The desorption of air from the film increases its conductance and decreases its activation energy.

### 3.2. Microstructure and surface morphology

Figure 5 shows AFM images of C<sub>60</sub>/Sb. Figures 5(a), 5(b), 5(c) are images of C<sub>60</sub>(20 nm)/Sb(1.0 nm), C<sub>60</sub>(20 nm)/Sb(3.5 nm), C<sub>60</sub>(20 nm)/Sb(5.0 nm), respectively. The images indicate that C<sub>60</sub> film grown upon 1.0 nm Sb has a size of  $270 \pm 30$  nm; C<sub>60</sub> film grown upon 3.5 nm Sb has a size of  $470 \pm 30$  nm—larger than that in figure 5(a); and in the case of C<sub>60</sub> film grown upon 5.0 nm Sb the size is  $133 \pm 30$  nm—much smaller than that of figures 5(a) and 5(b). AFM images reveal that in figure 5(a) the morphology of the film has the typical characteristics of an island growth mode, while in figure 5(b) the surface of the film is more planar and smooth compared with that in figure 5(a), showing pronounced characteristics of a layer-by-layer growth mode. Furthermore, in figure 5(c) the grain size of C<sub>60</sub> in the film is much smaller than those in figures 5(a) and 5(b), and its microstructure has the characteristic of high uniformity. Xu *et al* have discussed the different growth behaviours of C<sub>60</sub> on the different Sb films in detail [15, 17, 18]. Our results are consistent with the previous reports. Comparing figures 5(a)–5(c),

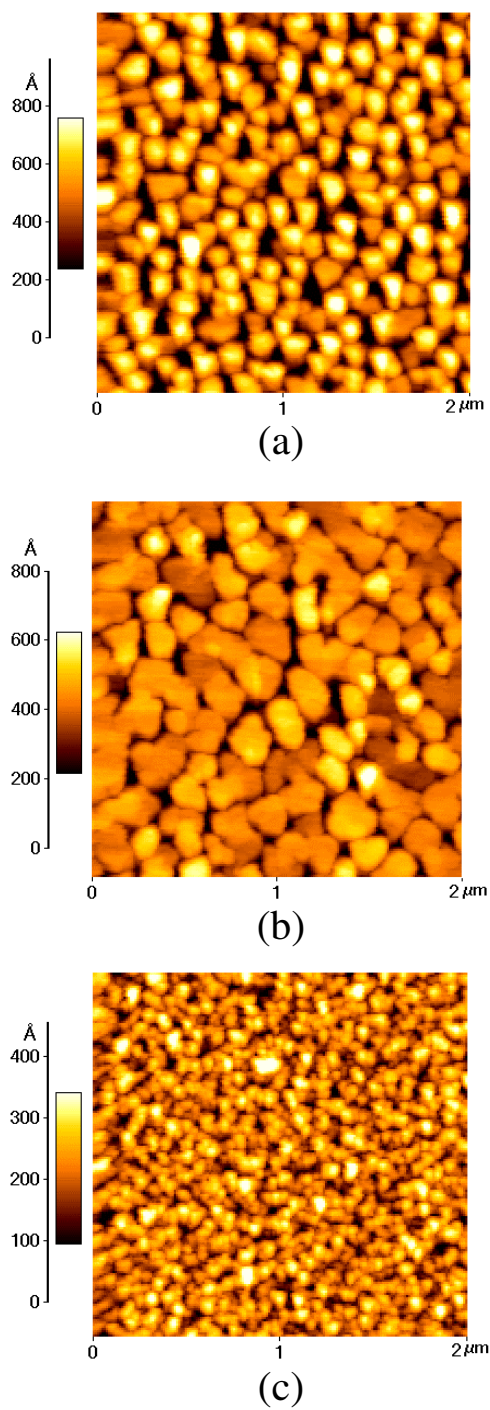


**Figure 3.**  $\ln \sigma - 1/T$  results for  $C_{60}(20 \text{ nm})/Sb(15 \text{ nm})$  bilayers. (a) The first *in situ* measurement cycle. The conductance anomaly jumps are in the ranges 258–262 K and 262–274 K. (b) The sample annealed at 450 K before the measurements were made *in situ*; the anomalous conductance jump is in the range 263–273 K. (c) The results for the sample exposed to air and degassed in vacuum before the measurements were made.  $T_s = 450 \text{ K}$ .



**Figure 4.**  $\ln \sigma - 1/T$  results for  $C_{60}(60 \text{ nm})/Sb(1.5 \text{ nm})$  bilayers. (a) The first *in situ* measurement cycle. The conductance anomaly jumps are in the ranges 263–268 K and 280–283 K. (b) The sample annealed at 450 K before the measurements were made *in situ*; the anomalous conductance jump is in the range 256–270 K. (c) The results for the sample exposed to air and degassed in vacuum before the measurements were made.  $T_s = 450$  K.

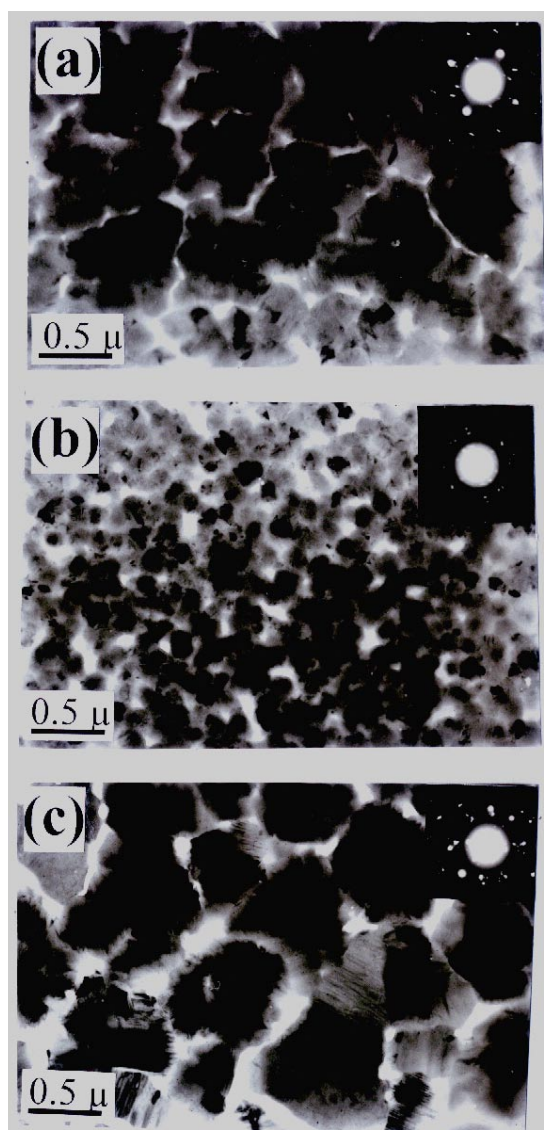




**Figure 5.** AFM images of  $C_{60}/Sb$  deposited at the substrate temperature of 450 K. (a), (b), (c) Images of  $C_{60}(20\text{ nm})/Sb(1.0\text{ nm})$ ,  $C_{60}(20\text{ nm})/Sb(3.5\text{ nm})$ ,  $C_{60}(20\text{ nm})/Sb(5.0\text{ nm})$ , respectively;  $T_s = 450\text{ K}$ . With increasing thickness of the Sb layer, the  $C_{60}$  film changed from rough to planar and smooth, then to rough again; the grain size becomes smaller and smaller. (This figure is in colour only in the electronic version, see [www.iop.org](http://www.iop.org))

we see that the presence of a moderate amount of Sb mediator significantly reduces the contact barrier of C<sub>60</sub> and mica, and improves the transport of adsorbed C<sub>60</sub> clusters on the surface of the substrate. On the other hand, a thick (more than 5 nm) Sb mediator increases the density of the aggregation nuclei and also induces an additional barrier to the diffusion of deposited C<sub>60</sub>, which in the end reduces the average scale of the C<sub>60</sub> films.

Figure 6 shows the TEM images of samples with different Sb layers. Figures 6(a)–6(c) are images of C<sub>60</sub>(60 nm)/Sb(1.5 nm), C<sub>60</sub>(20 nm)/Sb(3 nm), and C<sub>60</sub>(20 nm)/Sb(10 nm), respectively. The SED pattern indicates that no Sb diffraction pattern can be clearly observed,



**Figure 6.** TEM images of (a) C<sub>60</sub>(60 nm)/Sb(1.5 nm), (b) C<sub>60</sub>(10 nm)/Sb(3 nm), (c) C<sub>60</sub>(20 nm)/Sb(10 nm);  $T_s = 450$  K. With increasing thickness of the Sb layer, the growth mode of the C<sub>60</sub> changed from island to layer-by-layer then to island growth again.

which implies that Sb is uniformly dispersed in the matrix of  $C_{60}$ . The TEM images indicate that, with increase of the thickness of the Sb layer, the grain size of the film changes: first there are large islands; these give way to very smooth and planar layers, then to grains of very small sizes for the thickest Sb layer. In figure 6(a), the crystal size of  $C_{60}$  is  $\sim 1.5 \mu\text{m}$  and the SED pattern demonstrated that the lattice structure of  $C_{60}$  has some distortion. In figure 6(b) the grain size of the crystalline  $C_{60}$  is about  $1.3 \mu\text{m}$ ; the SED pattern indicates that the  $C_{60}$  crystalline lattice is perfect. In figure 6(c), the grain size of the  $C_{60}$  crystal is  $\sim 0.15 \mu\text{m}$ , and the density of the interface is very much higher than those for figures 6(a) and 6(b); the SED pattern shows that the  $C_{60}$  is polycrystalline. These results are in agreement with those from the AFM study. The structural differences between the samples before and after the annealing were also characterized by means of TEM and SED. The results showed that the annealing enhances the growth of  $C_{60}$  grains, but no significant change of the SED pattern was observed.

## 4. Discussion

### 4.1. The effect of Sb doping

Comparing figures 1–4, we see that the increase in the thickness of Sb causes the electrical conductivity of the bilayer to increase, and the magnitude of the jump near 278 K is significantly enhanced. Moreover, increasing Sb thickness increases the linear deviation of  $\ln \sigma - 1/T$  for the film and decreases its activation. The parameters of the conductance jumps, derived from figures 1–4, are listed in table 1.

**Table 1.** The parameters of the conductance jumps during the transition for different samples.

Sample	Pristine- $C_{60}$ -related transition		Novel transition	
	$T_1-T_2$	$(\sigma_1 - \sigma_2)/\sigma_2$	$T_3-T_4$	$(\sigma_3 - \sigma_4)/\sigma_4$
$C_{60}(60 \text{ nm})/\text{Sb}(1.5 \text{ nm})$	263 K–268 K	34%	280 K–283 K	10.5%
$C_{60}(10 \text{ nm})/\text{Sb}(3 \text{ nm})$	255 K–269 K	516%	275 K–277 K	104%
$C_{60}(20 \text{ nm})/\text{Sb}(10 \text{ nm})$	255 K–268 K	1250%	273 K–277 K	162%
$C_{60}(20 \text{ nm})/\text{Sb}(15 \text{ nm})$	258 K–263 K	20%	263 K–273 K	2814%

The parameters in table 1 are as follows:  $T_1$ ,  $T_2$ ,  $T_3$ , and  $T_4$  are the temperatures at which the sample conductance reaches its maxima and minima;  $\sigma_1$ ,  $\sigma_2$ ,  $\sigma_3$ , and  $\sigma_4$  are the conductances corresponding to  $T_1$ ,  $T_2$ ,  $T_3$ , and  $T_4$  respectively.

From the different behaviours of the anomalous conductance jumps in figures 1(a)–4(a) and the parameters presented in table 1, one can see that a thin Sb layer corresponds to a sharp conductance jump while thick-Sb-layer films correspond to large temperature widths of the transition. Meanwhile, in the thin-Sb-layer samples the dominant jump is of  $\sim 260$  K and in thick-Sb-layer samples the dominant jump is of  $\sim 270$  K. Considering the small grain size and the high density of the interface for  $C_{60}$  films, it is reasonable to assume that the jump in the higher-temperature range (263 K–273 K) is related to the doping of Sb into crystalline  $C_{60}$ .

Early work reports that noble metal aggregates at the surface of  $C_{60}$  [18]. We believe that a similar process happens which induces the disappearance of Sb from Sb/ $C_{60}$ . When noble gas is doped into  $C_{60}$  crystal, the temperature of the  $C_{60}$  fcc–sc transition drops [14]. When noble metal and  $O_2$  are doped into  $C_{60}$  crystal,  $C_{60}$ -derived compounds form that have  $C_{60}$ -like order–disorder phase transitions, and the resulting compounds have phase transition temperatures higher than those of pristine  $C_{60}$  [3, 4, 12, 13]. Sb is used as a surfactant for

the growth of high-quantity and large-scale C<sub>60</sub> single-crystal film [15, 16]. Some researchers believe that Sb efficiently enhances the interlayer diffusion in C<sub>60</sub> [15–18], which favours the exchange of C<sub>60</sub> and Sb in different layers. In Sb/C<sub>60</sub>, some Sb remains doped into the C<sub>60</sub> grains; the density of the Sb remaining is reciprocally proportional to the distance from the boundaries of the C<sub>60</sub> grains. The Sb atoms remaining in the C<sub>60</sub> act as defects or intercalate, distorting the C<sub>60</sub> crystal lattice. Due to the small diameter of the Sb atom, the Sb doped into C<sub>60</sub> crystal most probably locates at the tetrahedral or octahedral sites, just like Na, K, Cs in Na<sub>2</sub>CsC<sub>60</sub> and Na<sub>2</sub>KC<sub>60</sub> [4]. The presence of Sb intercalates in crystalline C<sub>60</sub> may also induce a ‘negative expansion’ of its lattice, and result in a smaller C<sub>60</sub>–C<sub>60</sub> separation compared with that in the pristine C<sub>60</sub> crystal. The C<sub>60</sub> phase transition partially results from the lattice parameter changing with temperature (the lattice of fcc C<sub>60</sub> is a little larger than that of sc C<sub>60</sub>). The lattice expansion is one of the main reasons for the fcc–sc phase transition occurring in C<sub>60</sub> [19]. Accordingly, in Sb-intercalated C<sub>60</sub> crystal a higher temperature is needed to produce sufficient lattice expansion to induce a C<sub>60</sub>-like phase transition, just as in the case of a high-pressure-compressed C<sub>60</sub> crystal [19, 20]. There is also very probably a weak charge interaction between Sb and C<sub>60</sub>. Such an interaction will hinder the rotation of C<sub>60</sub> just as in the alkali–C<sub>60</sub> fullerenes [4] and C<sub>60</sub>O [12, 13], which might also be a reason for the increase of the phase transition temperature for the Sb-doped crystalline C<sub>60</sub>. Consequently, the jump near 278 K in Sb/C<sub>60</sub> results from incorporation of Sb in crystalline C<sub>60</sub>.

Considering the results presented above, we see that the smaller the scale of the C<sub>60</sub> grains, the more enhanced the jump at ~278 K. Such results give explicit evidence that Sb is incorporated in the C<sub>60</sub> crystalline lattice. In thick-Sb-layer samples, the interfacial structure of Sb-doped C<sub>60</sub> dominates the properties due to the small grain size.

#### 4.2. The effect of annealing

Compare the results in figures 1(a)–4(a) with those in figures 1(b)–4(b); annealing results in the suppression and disappearance of the jump in the high-temperature ranges (figure 1(a): 275–283 K; figure 2(a): 273–277 K; figure 3(a): 263–273 K; figure 4(a): 280–283 K). Annealing also sharpens the jump near 260 K (except in figure 1(b)). This may be because the annealing promotes the diffusion of Sb and C<sub>60</sub>, and results in the separation of Sb and C<sub>60</sub>, finally increasing the size of the C<sub>60</sub> crystal, and improving the structure of the crystalline C<sub>60</sub>.

The annealing effects for different Sb films are different. For thin-Sb-layer samples, in figure 1 the jump in the range 255 K–277 K changed to a jump in the range 266 K–272 K, indicating that annealing compresses and widens the conductance jump (in the range 255–269 K in figure 1(a)). In figure 4, in the first measurement cycle, the two conductance jumps are in the ranges 263 K–260 K and 280 K–282 K, showing that the temperature width of the jump is narrower than those in figures 2 and 3, and demonstrating that the lattices of both pristine C<sub>60</sub> and Sb-doped C<sub>60</sub> are perfect. Annealing blurs the difference between the two jumps in figure 4(a) and results in the jump being in the range 256 K–278 K. These results imply that annealing destroys the structure of Sb-doped C<sub>60</sub> formed in the preparation of the sample and increases its conductance significantly.

For a thick-Sb-layer sample, the interface effects dominate its characteristics. For small C<sub>60</sub> grains, the crystal lattice is distorted and unstable. In the Sb-doped C<sub>60</sub> crystal, the high stress and plentiful defects as well as the high aggregation energy of Sb reduce the stability of the interface structure.

Annealing supplies enough energy for the diffusion of Sb and C<sub>60</sub> and improves the structure of C<sub>60</sub> crystallites. The high cohesion energy of Sb also favours separation of C<sub>60</sub> and Sb, which results in aggregation of Sb. The exchange of Sb and C<sub>60</sub> in C<sub>60</sub>/Sb considerably

improves the quality of the  $C_{60}$  crystal and reduces the thickness of the layer of Sb-doped  $C_{60}$ . Such exchange finally reduces the temperature width of the  $C_{60}$  fcc–sc phase transition and results in the jump near 278 K disappearing. The annealing also reduces the density of defects and boundaries in  $C_{60}$ ; thus the scattering of the charge carriers by defects and boundaries considerably decreases. Consequently, the conductance of the film significantly increases.

In addition, there is a significant difference between figure 1(b) and figures 2(b)–4(b): the annealing compresses and widens the conductance jump in the range 255–272 K (figure 1(b)). The reason for such difference in behaviour is still not clear. A possible reason is that in figure 1, the structure of the  $C_{60}$  film becomes highly perfect and the anomalous jump near 278 K is reduced due to annealing. This leads to the result that the anomalous jumps in the ranges 263–268 K and 280–283 K can no longer be clearly distinguished, and finally results in the compression of the conductance jump and the widening of the temperature spread of the jump in figure 1(b).

#### 4.3. Effects of gas contamination

Figures 1(c)–4(c) indicate that absorption of air induces the conductivity of the samples to drop by about four orders of magnitude. The difference between the activation energies below and above the jump temperature ranges in figure 1(c) changed less than those in figures 2(c)–4(c). In figures 2(c)–4(c), the activation energies below and above the conductance jump ranges are a few meV and  $\sim 1$  eV, respectively.

The intercalation of oxygen significantly affects the electrical properties of  $C_{60}$  films [20–22]. Unlike alkali metal intercalates, which can transfer a large amount of charge (one electron per alkali metal atom) to  $C_{60}$  balls, a very low charge transfer occurs for the case of oxygen intercalation [20–22].

In particular, oxygen decreases the intrinsic conductivity of fullerites by as much as four orders of magnitude [22]. When the sample is exposed to air,  $O_2$  is absorbed into the interface of the films and some of the  $O_2$  diffuses into the lattice of the  $C_{60}$  crystal and bonds to the  $C_{60}$ , forming some impurity states and reducing the symmetry of the  $C_{60}$  ball. So  $C_{60}$  in different positions in the film faces bonds differently to the absorbed  $O_2$ , which induces the different impurity band energies. Different environments of  $C_{60}$  lead to different densities of impurity states. The absorbed  $O_2$  may act as a compensating centre and capture the carriers as well as reducing the conductance of the films. The incorporated  $O_2$  will form deep impurity states, increasing the activation energy of the films.

The adsorbed oxygen plays a remarkable role in the conductivity and activation energy processes [22, 23]. The lower conductivity for  $C_{60}$  films also tends to lead to high activation energy, and vice versa. This can be explained by observing that, when introduced interstitially into a fullerene material, molecular oxygen quenches the conductivity and creates deep electronic traps. The more oxygen present in the  $C_{60}$  matrix, the deeper these traps are, and thus the higher the activation energy is.

Below 300 K, the activation energies of the samples are very small: some of them are of a few meV; such small values of the activation energy are probably caused by the combination of Sb and absorbed  $O_2$  in crystalline  $C_{60}$ . Sb and absorbed  $O_2$  form different electronic states at the band gap of crystalline  $C_{60}$ , and also some states have subband gaps that cause some tunnelling of carriers. Alternatively, as the sample has been exposed to the air, most of the Sb is very probably oxygenated, so the surviving Sb is present in very limited amounts, which will result in a low conductivity with a small activation energy. The oxygenation process can be signalled by the lack of recovery of the conductivity after annealing treatments. Above 300 K, large activation energies may be contributed by activation effects of  $O_2$  bonded with

C<sub>60</sub>. Upon annealing, the absorbed O<sub>2</sub> will be pulled out of the C<sub>60</sub> solid. The activation energy of the expulsion adds to the activation energy of oxygenated C<sub>60</sub>, yielding a relatively high (relative to the optical absorption edge) value of  $E_a = 2.2$  eV.

Annealing increases the conductivity of the film (shown in region 3 in figure 4(c)) probably both by improving the crystallinity of the films and by driving oxygen out of the interstitial regions. The driving out of oxygen can also be inferred from the relatively small activation in the temperature-drop process shown in figure 4(c).

## 5. Conclusions

Interesting structure and conductivity properties of C<sub>60</sub>/Sb bilayers have been studied. Sb doped into C<sub>60</sub> crystal has some remarkable effects on the C<sub>60</sub> fcc–sc phase transition. For Sb-doped C<sub>60</sub> crystal, the fcc–sc transition temperature is higher than that of pristine C<sub>60</sub> crystal. The smaller grain size of C<sub>60</sub>/Sb corresponds to an Sb-doped C<sub>60</sub>-dominated phase transition, indicating that an interfacial phase of Sb-doped C<sub>60</sub> has formed. The heat treatment destroys the interfacial structure of Sb-doped C<sub>60</sub>. The absorbed O<sub>2</sub> can also destroy the structure of Sb-doped C<sub>60</sub> entirely, to the extent that it cannot be recovered after the O<sub>2</sub> desorption. Although our conclusions from the above results are qualitative, to get firm evidence for the intrinsic interaction of Sb and C<sub>60</sub>, more chemical probing and *in situ* STM study are needed, and such research is being undertaken.

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