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V.N. Popok,[1,]* A.V. Gromov,[2] M. Jönsson,[3] A. Taninaka,[4] H. Shinohara[4]

and E.E.B. Campbell[1,2]

[1]Department of Physics, University of Gothenburg, 41296 Göteborg, Sweden.

[2]EaStCHEM, School of Chemistry, Joseph Black Building, University of Edinburgh, West Mains Road, Edinburgh, EH9 3JJ, UK.

[3]Institute of Physical Chemistry, Polish Academy of Sciences, ul. Kasprzaka 44/52, 01-224 Warsaw, Poland.

[4]Department of Chemistry, Nagoya University, 464-8602 Nagoya, Japan.

[*]Corresponding author; e-mail: popok@physics.gu.se

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Abstract

La@C$_{82}$ and Li@C$_{60}$ thin films obtained by sublimation in vacuum are studied using four-probe current-voltage measurements and atomic force microscopy. *In situ* electrical measurements show semiconducting behaviour of both films with room-temperature resistivity of 21±8 and 1230±50 Ωcm for the La@C$_{82}$ and Li@C$_{60}$, respectively. A variable range hopping mechanism of conducyance is suggested from the temperature dependences of resistance. The activation energies for electron transport are calculated for both metallofullerenes. Irreversible changes to the Li@C$_{60}$ film structure increasing the film resistivity to the values typical for C$_{60}$ are found at elevated temperatures. The effect of exposure to ambient atmosphere on the conductance of the films is discussed.

Introduction

Electronic properties of fullerenes have been of increasing interest for practical applications in recent years. For example, C$_{60}$ has shown high field effect mobility as an n-type material [1] that makes fullerene films interesting for organic-based transistors [2, 3] and for relatively high-speed organic diodes [4]. Fullerene-based compounds are also used for photovoltaic devices and solar cells [5, 6]. By encapsulating atoms inside the fullerene cage – producing endofullerenes – the electronic properties of the molecules can be significantly changed and controlled depending on the inserted chemical elements. Thus, endofullerenes, especially those encapsulating metal atoms, become functional materials with potential applications in nanotechnologies. Endohedral metallofullerene research has been reviewed in a few papers [7, 8, 9]. However, temperature dependent four-probe investigations of metallofullerenes that can provide information on the transport mechanisms have not been extensively studied so far.

In this paper we compare the electronic properties and structure of thin films deposited by sublimation of La@C$_{82}$ and Li@C$_{60}$ in vacuum.

Experimental

La@C$_{82}$ fullerene was produced by the arc discharge method [7]. The purity of La@C$_{82}$ used in the experiments was greater than 95%. Li@C$_{60}$ was synthesised using low-energy (30 eV) Li$^+$ ion implantation into a fullerene film [10]. Fractions of Li@C$_{60}$ were chromatographically isolated as described earlier [11]. For the present study, the E2 fraction, consisting of fullerene trimers, with about 80% content of Li@C$_{60}$ was used.

The starting material for thin film production was prepared by introducing toluene solutions of the endohedral fullerenes into small quartz vials and then carefully evaporating the solvent. The thin films were then prepared

by sublimation of the endohedral fullerenes from the quartz vials at 825 K (La@C_{82}) or 850 K (Li@C_{60}) and deposition on silicon chips with four cross-configured gold electrodes in a vacuum of ca. 5×10^{-8} Torr. More details of the set up can be found elsewhere [12]. Before deposition, the vials with endofullerenes were preheated at about 400 K (La@C_{82}) or 350 K (Li@C_{60}) for 20-24 hours in vacuum to remove any remaining solvent impurities. La@C_{82} is a relatively stable endohedral fullerene and can be easily sublimed under such conditions without destruction of the material. Li@C_{60} is much less stable and will readily undergo polymerisation and/or cage destruction under heating, in particular in the presence of solvent impurities [13]. The sublimation conditions were chosen to minimise the time of thin film deposition to avoid impurity contamination in the films and to reduce the likelihood of material destruction. The thickness of the films was measured using a profilometer and a scanning probe microscope (Ntegra). This microscope was also used for the atomic force microscopy (AFM) measurements in tapping mode. The thickness was found to vary between 50 and 90 nm for La@C_{82} and between 10 and 50 nm for Li@C_{60}, differing from sample to sample because of a difference in the amount of material used for each sublimation. The standard 4-probe Van-der-Pauw method was applied for *I-V* measurements *in situ* and in an air environment using a Hewlett Packard 4156B precision analyser. The measurements were performed in the temperature range of 300-480 K. More details on the measurement procedure can be found elsewhere [14].

Results and Discussion

AFM images of the deposited films are shown in Figure 1. The La@C_{82} films have a granular structure with a mean lateral grain size of 20-40 nm which is comparable to that found earlier for C_{60} films [14]. The film structure and the grain sizes are also very similar to those observed elsewhere for deposited C_{82} films [15] where it was found, using x-ray diffraction, that the grains have a polycrystalline nature. The surface morphology of the films deposited by sublimation of Li@C_{60} is more inhomogeneous (Figure 1b) and amorphous in nature [16].

In situ measurements of the La@C_{82} films directly after the deposition in vacuum give a mean value of resistivity of 21 ± 8 Ω.cm. In the case of Li@C_{60} the resistivity is higher at 1.23 ± 0.05 kΩ.cm and in agreement with earlier measurements [12]. These values are obtained from the measured *I-V* dependences which are found to be linear for both fullerenes in the interval from -5 to +5 V. Typical *I-V* dependences for La@C_{82} are presented in Figure 2. The linear voltage dependence is characteristic of ohmic behaviour, i.e. no Schottky barriers are formed at the fullerene interfaces with the gold electrodes. Both mean values of resistivity are much lower compared to that of pure C_{60} films (ca. 33 MΩ.cm) deposited under similar conditions [14] and also lower than 4-probe measurements reported for a single crystal of Dy@C_{82} that yielded a room temperature resistivity on the order of 6 kΩ.cm [17]. The earlier modelling of La@C_{82} endohedral fullerenes supported by electron paramagnetic resonance and photoelectron spectroscopy studies suggested that the most

probable electronic state is $La^{3+}@C_{82}^{3-}$ [18-20]. Later photoelectron spectroscopy data provided evidence that about 1/3 of an electron charge is left in the La-valence orbitals [21]. In the case of Li, simulations suggest a positive charge of less that $1e$ on the encapsulated atom and formation of a partly covalent bond between Li and C_{60} [22, 23]. Thus, 2-3e charges can be transferred from the La atom and less than 1e charge from the Li atom to the fullerene cage. A recent theoretical study of $Gd@C_{82}$, that has a similar electronic structure to $La@C_{82}$, predicted the *I-V* dependence for a single endohedral molecule placed between gold electrodes [24]. The results suggested that charge carrier transport occurs through the cage without involving the encapsulated metal atoms, i.e. via the electrons donated to the fullerene molecules. Such considerations provide one explanation for the higher resistivity of the $Li@C_{60}$ film compared to the $La@C_{82}$. Another contribution can be attributed to the quality of the films. One can see from the AFM images (Figure 1) that in the case of $La@C_{82}$ the film is compact and consists of small grains that are uniform in size while in the case of $Li@C_{60}$ the film is more inhomogeneous and contains cavities. This film morphology will affect the mechanism and efficiency of the charge transport in the $Li@C_{60}$ case, thus reducing the conductance.

(a)

(b)
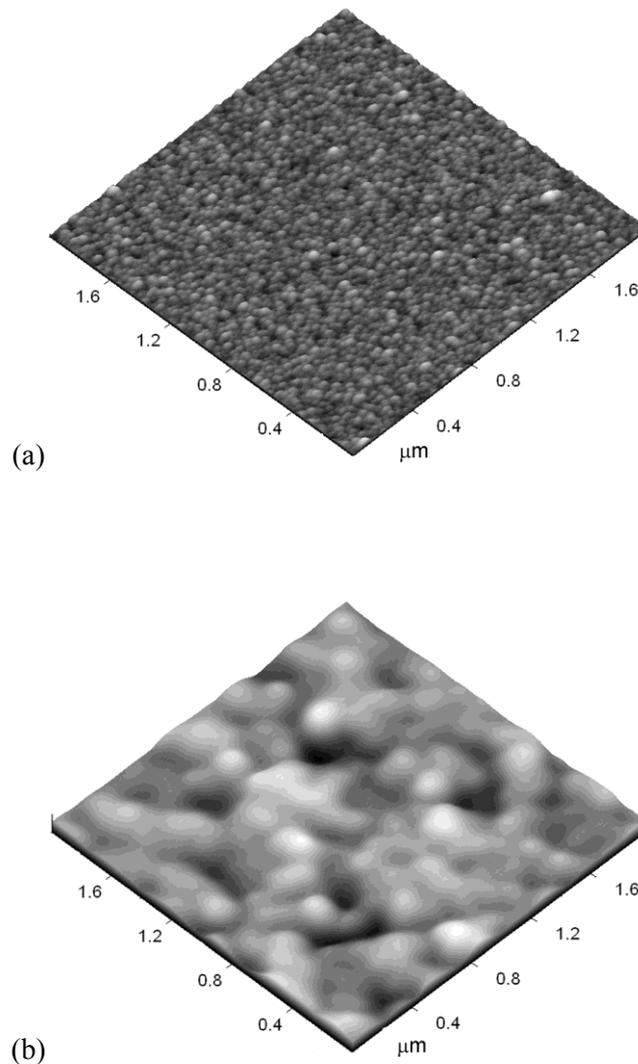
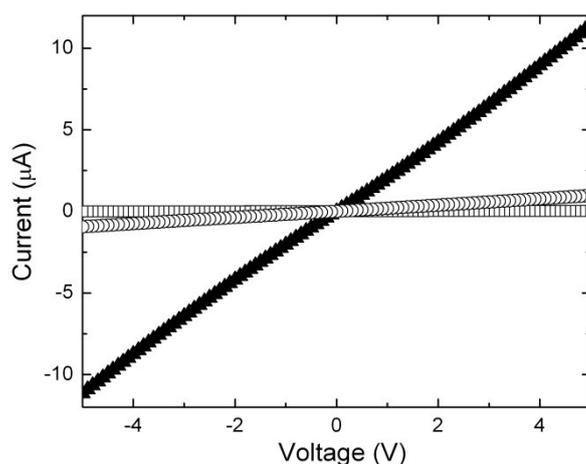*Figure 1.* AFM images of films obtained by sublimation of (a) $La@C_{82}$ and (b) $Li@C_{60}$.

Figure 2. *In situ I-V* dependences for the La@C$_{82}$ film: as deposited in vacuum, $\rho = 13$ Ωcm (▲), after 5 days in air, $\rho = 6.8$ kΩcm (□) and after 50 h of annealing at 420 K in vacuum, $\rho = 150$ Ωcm (○).

After exposure to air at ambient pressure and temperature the resistivity of the as-deposited films increases. It is a slow and gradual process for the La@C$_{82}$ (Figure 2). The resistivity increases by about 30 % after 1 hour in air. However, it increases by a further 3 orders of magnitude after 5 days. A similar but more rapid increase in resistivity on air exposure (one order of magnitude after 5 minutes exposure at ambient temperature and pressure) was observed for C$_{60}$ films and attributed to oxygen diffusion [14]. Oxygen penetrating into boundary gaps can attach to the fullerenes generating a disorder potential and acting as a trap for hopping electrons. These mechanisms are discussed in more detail, for instance in refs. 25 and 26. For C$_{60}$ films the original resistivity can be restored by annealing the films in vacuum [25,27]. The La@C$_{82}$ films were annealed at 420 K in a vacuum of 5×10^{-8} Torr for 50 h. As one can see from Figure 2, the conductance is only partially restored. It was shown earlier using laser desorption mass spectrometry that La@C$_{82}$ complexes react with oxygen when exposed to air over a period of days to produce oxides [28]. Thus, one can assume that the irreversible oxidation reaction will significantly reduce the conductivity of the films. Exposure to ambient atmosphere of the films obtained from Li@C$_{60}$ affects the conductance in a much more rapid manner. After 2 minutes exposure the resistivity increases by 3 orders of magnitude and after 1 hour it reaches a value comparable to that of pure C$_{60}$.

The temperature dependence of the resistance of the films was measured to obtain insight into the charge transport mechanism. Typical obtained curves are presented in Figure 3. One can see that the dependence for La@C$_{82}$ is consistent with a linear *lnR-T$^{-1/4}$* plot for the whole temperature range excepting a short interval

between 345-360 K. This deviation from the dependence can be related to restructuring of the film at elevated temperatures. Since AFM does not show any change in the grain size, we can suggest that the nanocrystallites are undergoing re-ordering inside the grains. Note that the data presented in Figure 3 do not cover a sufficiently large temperature range to clearly distinguish between different exponent values but the least squares fit is marginally better for a 1/4 exponent compared to 1/2 or 1/3. It was also shown earlier [14] that a 1/4 exponent gives the best fit for the C_{60} films. Thus, one can suggest that the most probable mechanism of charge carrier transport is a 3D variable range hopping (VRH) [29]. However, we cannot exclude the possible contribution of a 2D VRH (especially because the films are thin) giving a 1/3 exponent or a charged energy limited tunnelling giving a 1/2 exponent [30]. A 3D VRH in the presence of a Coulomb gap, that also gives a 1/2 exponent, is of low probability in our case because this mechanism prevails at low temperatures [31]. Assuming the 3D VRH to be the dominant mechanism, from Mott's theory we found the activation energy to be in the range 0.12-0.14 eV that gives a mean value for the band gap E_g of 0.26 eV. The photoemission spectra of thin (~15 nm) La@C_{82} films presented elsewhere [32] gives E_g of 0.35 eV, which is consistent with the recently observed optical gap of 0.3 eV [33]. Slightly higher value of a HOMO-LUMO gap, ca. 0.5 eV, was measured using scanning tunnelling microscopy that can be explained by very low thickness of the film (just a few layers of La@C_{82} deposited on Si). [34] Close data for the band gap (0.2 eV) was obtained for Dy@C_{82}, which has very similar electronic structure [17]. It was also suggested that depending on the packing, the films can change their conductance behaviour from semiconducting to semi-metallic by further decreasing the gap.[35] In our case the films demonstrate semiconductor-like behaviour and the obtained gap value is in agreement with the above-mentioned data.
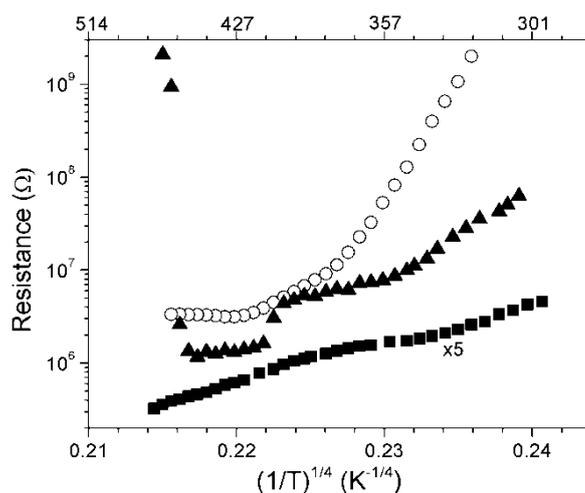

Figure 3. *In situ* temperature dependences of resistance for the films deposited in vacuum from La@C_{82} (■), Li@C_{60} (▲) and for comparison from C_{60} (○) according to ref. 14.

The results of typical measurements of the temperature-dependence of the resistance for Li@C_{60} films are also presented in Figure 3. It is consistent with a linear lnR-$T^{-1/4}$ plot only for short interval of 300-350 K. The mean activation energy calculated according Mott's theory gives a value of 0.26 eV yielding a band gap of ca. 0.52 eV. This band gap is larger than that for La@C_{82}, consistent with the higher resistivity of these films compared to La@C_{82}. With a further increase in temperature, the dependence is changed first towards the one with a lower activation energy for an interval of 360-405 K and then to a plateau-like region (ca. 415-455 K). Heating at $T > 455$ K leads to stepwise increase of the resistance by about 3 orders of magnitude. At 465 K the resistivity becomes equal to ca. 370 GΩ.cm which is very close to 340 GΩ.cm obtained earlier for the C_{60} films at the same temperature [14]. Contrary to the La@C_{82} case, a decrease in temperature does not lead to the recovery of the conductance. Thus, one can assume irreversible change of the film properties at $T \approx 455$-460 K.

We can suggest two possible scenarios for the irreversible change of the Li@C_{60} film properties. One of them is thermally induced polymerisation of the endohedral fullerenes. The weak bonds between the fullerenes in the trimers which were found to be the main structures of the material used are broken under the sublimation and they are deposited as monomers. Heating of the film leads to the reordering of the fullerene molecules in the film, the observed "kinks" in the experimental dependence can be an evidence for that. Finally, the heating at $T \approx 455$-460 K can lead to the bond formation between the neighbouring molecules.

Alternatively, one can assume a possibility of transformation of endohedral Li@C_{60} into exohedral LiC_{60} under sublimation.[36] Theoretical modelling predicts that the binding energy of endohedral complexes Li@C_{60} can vary between 1.4-1.9 eV depending on the position of the Li atom in the cage [22,37]. For comparison, the calculated binding energy of La@C_{82} complexes can be between 3.2-5.0 eV [37-39] which is much higher. Laser ionization studies have shown a much stronger tendency for Li@C_{60} to lose the encapsulated atom than for the more stable La@C_{82}.[36] The loss of the Li atom may be additionally enhanced by the breakage of the bonds between the fullerenes in the original trimer material in the oven. Both possibilities can explain the observation of a very rapid decrease of conductance when the film is exposed to ambient atmosphere. Either the intact endohdderal fullerene radicals or exohedral Li atoms sitting outside the cages may react with atmospheric oxygen. In both cases the formation of chemical bonds leads to the decrease of conductance. Returning to the second scenario, one can suggest that the stepwise irreversible increase of the resistance at 455-460 K can be related to the breakage of Li-C_{60} bonds and the loss of Li atoms thus converting the Li@C_{60} film into a C_{60} one. The theoretical modelling predicts binding energy for one of the LiC_{60} isomers (C_{3v}) to be 1.46 eV [40] that is not too high a value to allow bond breakage at such temperatures.

Conclusions

Thin films were deposited by sublimation of La@C$_{82}$ and Li@C$_{60}$ in vacuum. Both films are found to be semiconducting: metal atoms donate electrons to the fullerene molecules. Resistivity of the La-doped fullerenes ($\approx$ 21 Ω.cm) is about 2 orders of magnitude lower than that of Li-doped ($\approx$ 1.2 kΩ.cm). 3D variable range hopping is suggested to be the most probable mechanism of charge carrier transport. In the case of La@C$_{82}$ the band gap is calculated to be ca. 0.26 eV. The film conductance at ambient pressure and room temperature is affected by oxidation, thus, gradually decreasing with time. To be used in electronics, the La@C$_{82}$ films should be encapsulated or covered with a protective layer. In the case of Li@C$_{60}$ the band gap is larger, ca. 0.5 eV. Conductance of the film sublimed from LiC$_{60}$ is extremely unstable at ambient pressure and room temperature because of the rapid oxidation. It is also found that heating of the films up to 455-460 K in vacuum leads to an irreversible change of their properties, in particular, to an increase of resistance by more than 3 orders of magnitude. Two possible scenarios are suggested: polymerisation of the endohedral molecules and transformation of Li@C$_{60}$ into LiC$_{60}$ following detachment and vaporisation of Li. Further study is required for clarification of this effect.

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