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Thin Films of C_{60} doped with Pb

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In the present work we report the synthesis of thin films of C_{60} doped with Pb. By means of electrical characterization we found that small quantities of Pb increases the electrical conductivity, giving as a result a semiconducting-like behavior in the range of temperatures from 2 K to 470 K. At higher content of Pb, the system tends to form particles of Pb. In this case, the electrical resistance shows a metallic-like transition below 7 K, but we did not observe zero resistance up to 2 K. We also found that the films readily reacts upon exposure to the laboratory atmosphere.

KEYWORDS: C_{60} thin films, metal doping, conductivity, semiconductor

1. Introduction

Since the discovery of superconductivity in the alkali doped fullerenes,[1)] great effort has been devoted to the study of the microscopic mechanisms involved in the superconductivity of these materials, and to the discovery of new superconducting compounds related to the C_{60}.[2,3)] To date, apart of the superconductive compounds obtained with alkaline and alkaline earth ions, only a few new superconducting compounds have been synthesized using other elements; such as Sm[4)] and Yb.[5)] Other compounds based on Sn,[6)] and Cu[7)] have been claimed to be superconductors, but until today there are not conclusive evidences for these assertions. In addition, other elements such as In and Sb have been combined with C_{60} giving a semiconductor like behavior with electrical conductivities several orders of magnitude greater than pristine C_{60}.[8)] In this work we present our attempts to synthesize thin films of the compound Pb_xC_{60} ($x \sim 6$). The films were formed by thermal evaporation of mixtures of Pb and C_{60} powders on substrates held at 473 K.

2. Experimental Details

Thin films of Pb_xC_{60} were synthesized starting with mixtures of powders of Pb (6N purity) and C_{60} (99.5% purity from MER Corporation), weighted to give the desired stoichiometry. The powders were placed in a tungsten crucible and thermally evaporated on sapphire substrates, held at 473 K, and pressures better than 5×10^{-6} Torr. The thickness of the films were monitored using a quartz microbalance, and the evaporation process was interrupted until the material placed into the crucible was totally evaporated. The thickness of those films were also measured using a profilometer. The thickness measured with the quartz microbalance and the profilometer were similar within experimental error, typical values were around 3000 Å.

Although we can not assure a constant Pb/C_{60} flux ratio during the evaporation process, we can argue that the resulting Pb_xC_{60} may have a uniform composition through the film; because: (i) In vacuum C_{60} powders sublime at temperatures from $\sim 400°C$[9)] to $\sim 550°C$.[10)] On the other hand, Pb begins to evaporate at $\sim 427°C$ at $\sim 10^{-6}$ Torr. This means that both C_{60} and Pb evaporate in a similar way. (ii) For the films with $x \sim 6$, we noted that during the first minutes immediately after interruption of the evaporation process, the electrical conductivity decreased in approximately 20%; but after $\sim$ 30 min we did not observe more changes. This may be due to the existence of a thin layer of Pb on the total film, this excess of Pb readily diffuses into the film in a similar manner as, for example, aluminum does even at room temperature.[11)] Taking into account this observation, all the films reported in the present work were kept at $\sim 200°C$ during a period of time of about $\sim$ 30 min. After this time we made the corresponding measurements.

In order to perform the electrical measurements, good Ohmic electrical contacts were glued to the substrates using conductive silver paste prior to the deposition of the films. Due to the observation that the films rapidly reacted when they were exposed to the atmosphere, prior to the exposure to the ambient they were covered with evaporated layer of silicon oxide for the electrical characterizations. With this layer we reduced notably the rate of degradation, but nevertheless it persists probably due to the existence of pinholes in the protective layer. These films were introduced as soon as possible into a liquid helium cryostat to measure the electrical resistance versus the temperature using four contacts technique. Other films were characterized *in situ*, by measuring the resistance versus the temperature from room temperature to about 470 K. These measurements were performed in films in the as-deposited state, after exposure to pure oxygen at pressures of about 3 Torr and to the laboratory ambient, in a period of time of 1 h.

3. Results

Electrical resistance measurements in films with stoichiometries of Pb_xC_{60}, with $x < 6$, show semiconducting like behavior in the range of temperatures from 2 K to 470 K. Figure 1 (dashed curve) shows a typical behavior for the composition $x = 4$, it seems that the electrical resistance is continuing increasing from high temperature to below. However, as we can observe in the same figure, films with content of Pb around $x \sim 6$ present a dramatic change in the electrical resistance at about 7 K. Here, we observe that below this temperature a metallic like transition appears, the resistance shows a steep decrease in a very short interval of temperature, in only

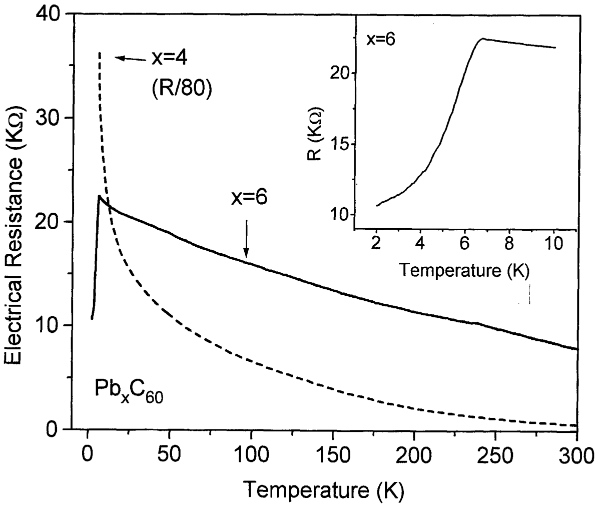

Fig. 1. Electrical resistance against temperature for two Pb$_x$C$_{60}$ films with $x = 4$ and $x = 6$ from the original stoichiometry of the starting powders. In the inset appears an amplification around the semiconductor-metallic like transition for the sample with $x = 6$.

2 or 3 K it changes to half the value at 7 K. The inset of Fig. 1 shows more clearly this variation. In spite of this dramatic change in resistance, we never observe zero resistance when we measured the films down to 2 K.

An important experimental observation in our films is that the Pb$_x$C$_{60}$ films show clear signs of degradation upon exposure to the laboratory atmosphere. To observe carefully and in more detail the process of degradation, we prepared two films with stoichiometries close to $x \sim 6$. One sample was exposed to dry pure oxygen (99.6% purity), and the other sample was exposed to the laboratory atmosphere immediately after deposition. In both cases the exposure was at room temperature by a period of one hour. In Fig. 2 we present the evolution of the electrical conductivity as a function of the exposure time, for the two films. In this figure we can observe that the ambient exposure has a stronger effect in the conductivity of the film, than the exposure to pure dry oxygen. The strong effect can be easily explained by assuming that the ambient air contents some percent of humidity which acts as a catalyst, increasing therefore, the speed of the chemical reaction that degrade the films.

After one hour of exposure, the vacuum chamber was again evacuated at a pressure of $\sim 5 \times 10^{-6}$ Torr. The temperature of the samples was raised to about 470 K and maintained in this condition for about 30 min. We monitored continuously the conductivity of the film, and we did not observe any significative change during this period of time. If some desorption of the gases took place, this had to be during the heating process. After this procedure, the conductivity as a function of the temperature was measured during the cooling cycle from 470 K to room temperature with a cooling rate of $\sim$ 2 K/min. In Fig. 3 we show the electrical conductivity as a function of the temperature for an as-deposited film, and the other two films; one after exposure to oxygen, and the other after exposure to the laboratory atmosphere. Note that the conductivity decreases dramatically after the exposure to the laboratory atmosphere. The activation energy of the samples increases notably and take values ranging from 46 meV, for the as-deposited film without exposition to any gas, to 84 meV for the film exposed to dry oxygen, and to 220 meV for the film exposed to the laboratory ambient. It is worth mention that similar observations in the degradation process has been found in compounds of C$_{60}$ with In and Sb.[12]

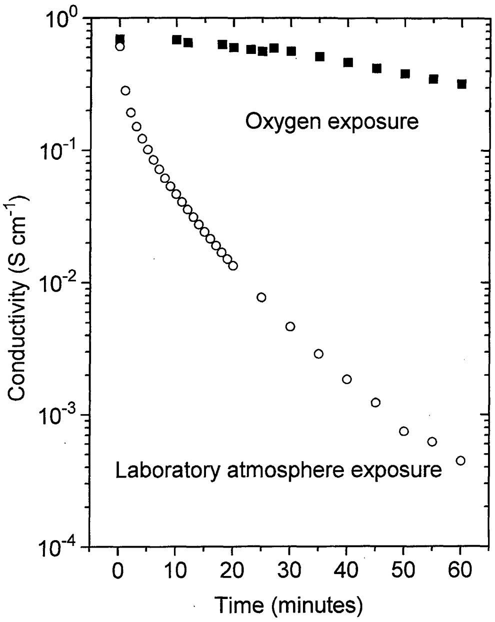

Fig. 2. Variation of the electrical conductivity as a function of the exposure time for different gases in two films with $x = 6$. One film was exposed to pure dry oxygen (full squares) and the other one was exposed to the laboratory atmosphere (open circles).

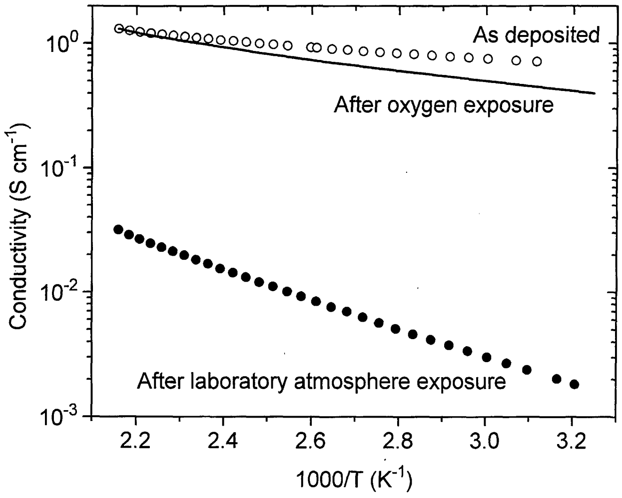

Fig. 3. Arrhenius plots for three films with $x = 6$ measured *in situ*. The open circles correspond to the conductivity measured in the as-deposited condition, the other two curves correspond to the samples measured after the exposure to pure oxygen (continuous line), and after the exposure to the laboratory atmosphere (full circles). The samples exposed to the gases corresponds to those shown in Fig. 2.

4. Discussion

For the interpretation of the experimental results, we performed X-ray diffraction analysis of the samples after deposition (without the protective layer). The results indicate the existence of pure lead and lead oxide, which means that the degradation of the electrical conductivity in principle might be due to oxidation of Pb. We performed optical microscopy observations in one of the films after deposition, this reveals the existence of small Pb particles, which in a rough estimation have dimensions of less than tenths of a micron. It is important to mention that also we noted a change of color in the films: immediately after deposition and exposed to the air of the laboratory, the films show a metallic bluish color, which after a period of several hours disappears and turns into a transparent yellowish coloration.

Related to the as deposited film with high Pb content ($x \sim 6$, from the original stoichiometry of the starting powders), we obtained an activation energy of ~ 46 meV, and conductivities of the order of 1.0 $(\Omega\cdot\text{cm})^{-1}$. If we compare these values to those obtained in pristine C_{60} films, having an activation energy of ~ 500 meV, and dark conductivities of the order of 10^{-10} $(\Omega\cdot\text{cm})^{-1}$ at room temperature,13) thus, we can conclude that the introduction of Pb shift the Fermi level to near to the LUMO band of C_{60}, in a similar way as Hoshimono *et al.* proposed when C_{60} is doped with In and Sb.8)

On the other hand, the metallic-like transition observed in the Pb_xC_{60} film with $x \sim 6$ below ~ 7 K might be explained by assuming Josephson coupling between different superconducting Pb particles;14) in this manner the effective conductivity of the film increases due to the Josephson coupling below the superconducting critical temperature of Pb ($T_C \sim 7.2$ K). For temperatures above T_C there is not Josephson coupling and the behavior of the conductivity of the film is of semiconductor type, as clearly is observed in Fig. 3. It is important to mention that granular Pb films have been studied by Barber *et al.* They find that when the superconducting Pb particles are poorly coupled, a long resistive tail exists below the superconducting transition temperature of Pb.15,16) Our curve with $x \sim 6$ in the inset of Fig. 1 closely resembles the results of Barber *et al.*, and offers additional evidence of the existence of Pb particles into the film.

Now, we can make a crude explanation for the change of color of the films after exposure to the laboratory ambient. We can see our films as a composite system; consisting of metallic particles embedded into a semiconducting matrix. In the fresh film, absorption bands exists within the energy gap due to the metallic particles and the appearance of the film looks metallic if the volume fraction of the particles is large.17) When the film is exposed to the laboratory atmosphere, the metallic particles oxidizes and the absorption bands due to the particles shifts to the infrared region, leaving the optical appearance in the visible region mainly controlled by the semiconducting matrix; which is transparent in this region. In our model, the position in energy of the absorption bands is basically controlled by the bulk plasmon energy of Pb, and when it oxidizes, the plasmon energy shifts to lower energies.

Generally speaking, the interaction of fullerenes with other elements can be classified according to whether they form compounds (as in the A_xC_{60} compounds, where A is an alkaline or alkaline-earth element), or form different phases in which one of the phases may be segregated of the host element.11,18) In our case we might conclude that small quantities of Pb into solid C_{60} form a system with impurity levels, introduced by Pb. However, when Pb is in excess, it tends to form particles of Pb.

5. Conclusion

In conclusion, we have studied the effect of introduction of Pb into C_{60}. Small quantities of Pb might introduce impurity levels close to the LUMO band of C_{60}. The electrical conductivity of the films increases by several orders of magnitude and the activation energy decreases notably. However, in the films with excess of Pb, this tends to form particles embedded into solid C_{60}. The prepared films readily react with the exposure to the laboratory ambient, forming Pb oxide.

Acknowledgements

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