Diffusion processes for doping of C\textsubscript{60} (fullerene) thin films

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Abstract

As part of our ongoing research program to produce a high-efficiency, low-cost, photovoltaic cell based on the fullerene C\textsubscript{60}, we report here on our first attempts at the intercalative doping of C\textsubscript{60} thin films by the electrodiffusion of metals. Semiconductor behavior with decreased values of conductivity activation energy has been demonstrated for the doped samples. The results are explained by electrodiffusion of Au from an electrode, dominated by grain boundary diffusion. © 2002 Published by Elsevier Science B.V.

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1. Introduction

C\textsubscript{60} (fullerene)-based solids have recently been discussed as prospective materials for photovoltaic cells [1]. Various types of C\textsubscript{60}-based solar cells have been reported (such as fullerene thin film/inorganic semiconductor heterojunctions and Schottky barriers [2], networks of internal fullerene/conjugated polymer heterojunctions [3]).
Doping of solid C$_{60}$ to increase its conductivity is one of the central challenges for high efficiency fullerene-based solar cell production.

The most commonly practiced kind of doping is intercalation: whereby dopants are located between the C$_{60}$ molecules in the interstitial positions of the host crystal structure. Intercalation may occur as a spontaneous process or it can be induced by an external stimulus, like vapor pressure or an electric field applied to the sample [4]. Recently, we developed a new technique for doping (intercalation) of C$_{60}$ thin films, so-called “chemically induced counter electro-diffusion” (CICED) [5]. The technique involves the vacuum deposition of highly crystalline C$_{60}$ thin film onto a metal (Cu or Au, or Ag) sub-layer [6] and subsequent exposure of the samples to a reactive gas atmosphere. In the case of an iodine atmosphere, the metal diffusion was demonstrated to occur very rapidly: even 10 min of exposure of a Cu-supported C$_{60}$ film to an I$_2$ atmosphere, at room temperature, led to a complete disappearance of the Cu sub-layer. Analysis revealed that the Cu had diffused into the C$_{60}$ film with the corresponding formation of CuI at all depths throughout the C$_{60}$ film (the most surprising result being that Cu was present even at the front surface of the film!).

Such extremely fast metal diffusion into the C$_{60}$ film under the action of an internal electric field suggested that we should attempt the diffusion of metals into C$_{60}$ films under the action of an external electric bias. This paper summarizes our first results in this direction: the diffusion of Au from the electrodes into C$_{60}$ films under the action of an external electric field.

2. Experimental

C$_{60}$ films with thickness of 100 nm and various crystallinity were grown, using a vacuum deposition technique, on glass and mica substrates [6,7].

The crystalline structure of these C$_{60}$ films was studied by X-ray diffraction (XRD). The morphology of the front surface of the films, in particular grain sizes at the front surface was studied by atomic force microscopy.

Three types of C$_{60}$ films grown on an insulator substrate were used in these experiments:

- highly dispersed films (grain size of ~20 nm, no texture);
- films of intermediate crystallinity (grain size of 80–100 nm, no texture);
- highly crystalline films (grain size of 500–1500 nm, (1 1 1)-texture).

Conductivity of the C$_{60}$ films was measured in two- and four-probe configurations of gold electrodes (Fig. 1). For example, for two-probe measurements, two electrodes with length and gap width of 10 and 1 mm, respectively, were deposited on the front surface of the films. All of the conductivity measurements were performed using a Hewlett Packard 4140B pico-meter/dc voltage source, while pumping the quartz tube with sample up to a dynamic vacuum of $10^{-6}$ Torr and applying heat to the sample.
3. Results and discussion

After the sample temperature had reached a value of 150°C, we applied a series of external electric fields, with strengths of 150, 300 and 500 V/cm between the Au-electrodes. We observed an increase in time of the measured value of current (i.e. film conductivity) the longer the field was applied. The rate of increase was observed to be intensified as the electric field strength was increased. These results are in agreement with those of a similar experiment performed by Firlej et al. [4,8]. However, in addition, we revealed a strong correlation between the rate of conductivity increase and the crystalline structure of the films: for an increase of the film grain sizes, the rate of conductivity increase was observed to diminish.

Fig. 2 shows (on an Arrenius plot) the temperature dependence of the two-probe coplanar conductivity of C$_{60}$ films with various degrees of crystallinity, before and after treatment by a 500 V/cm electric field for 1 h at a temperature of 150°C. All temperature-dependent results show a semiconductor-like activated behavior. Furthermore, we can certainly conclude that the values of activation energy decrease as a result of treatment in all three cases. This is direct evidence that semiconductor doping was occurring during the treatment.

The other interesting feature of these results is an observed relationship between the decrease in activation energy and the crystalline structure of the samples (Table 1). Specifically, the minimum value of activation energy after the treatment (or in the other words, the maximum doping effect) was observed for those samples with the smallest grains. In this case, room-temperature conductivity was found to increase by more than 50 times (Fig. 2a). Conversely, the maximum activation energy (i.e., the minimum doping effect) was observed for the highly crystalline sample. Both decrease in activation energy and increase of conductivity values, after treatment, with decrease in grain sizes are in evidence (Fig. 2, Table 1).

In general, a diffusion rate of an impurity atom is known to be higher along grain boundaries than that within a crystal grain [9]. It is possible to explain all of
the reported results by the electrodiffusion of Au from an electrode, dominantly along grain boundary, and the subsequent intercalation of the C₆₀ lattice by Au atoms.

Fig. 2. Temperature dependences of two-probe coplanar conductivity, before and after treatment of the C₆₀ films for 1 h under an electric field of 500 V/cm at 150°C: (a) a highly dispersed film, (b) an intermediate-crystallinity film, and (c) a highly crystalline film.
The electrodiffusion experiment using a four-probe configuration of electrodes demonstrated similar results. Auger electron and X-ray photoelectron spectroscopy characterization of the doped samples as well as photoconductivity measurements are in progress.

4. Conclusions

We report the effect of an external electric field on the in situ measured conductivity of C$_{60}$ films with different degrees of crystallinity. Semiconductor behavior with increased conductivity values and decreased conductivity activation energy has been demonstrated for the doped samples. The results are explained by electrodiffusion of Au from an electrode, dominated by grain boundary diffusion, and the subsequent intercalation of C$_{60}$ lattice by Au atoms.

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References


Table 1
Correlation between the grain sizes in C$_{60}$ films and their value of activation energy of conductivity, after treatment for 1 h under an electric field of 500 V/cm at 150°C

<table>
<thead>
<tr>
<th>C$_{60}$ films structure</th>
<th>Grain size (nm)</th>
<th>Activation energy after treatment (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highly dispersed</td>
<td>~20</td>
<td>0.5</td>
</tr>
<tr>
<td>Intermediate crystalline</td>
<td>80–100</td>
<td>0.78</td>
</tr>
<tr>
<td>Highly crystalline textured</td>
<td>500–1500</td>
<td>1.06</td>
</tr>
</tbody>
</table>