Electro-diffusion phenomena in C₆₀ thin films


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As part of our ongoing research program to produce semiconductor devices based on the C₆₀ thin films, we report here on our first attempts at the intercalative doping of C₆₀ thin films by diffusion of metals. Two techniques were employed: (a) chemically-induced counter electro-diffusion of Cu and I₂ into a C₆₀ matrix; (b) diffusion of Au under the action of an external electric field.

This work was funded partly by the Israel Ministry of National Infrastructures. E.A.K. also thanks financial support by the Israel Ministry of Immigrant Absorption. S.M.T. wishes to thank the Albert Katz School for Desert Studies and the Bonna Terra Foundation.

The most commonly practiced kind of doping of a C₆₀ solid is intercalation whereby dopants are located between the C₆₀ molecules in the interstitial positions of the host crystal structure [1]. Intercalated fullerenes may be produced by the simultaneous vacuum evaporation of C₆₀ molecules and dopant atoms or by diffusion of dopant atoms into pristine C₆₀ crystal. Such diffusion 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. Study of an impurity diffusion in C₆₀ crystals and thin films has recently become one of the important subjects in fullerene research [2].

This paper presents the results of an experimental study of two diffusion phenomena in C₆₀ thin films (with emphasis on the possibility of semiconductor doping of the material): (a) chemically-induced counter electro-diffusion (CICED) of Cu and I₂ into a C₆₀ matrix, (b) diffusion of Au under the action of an external electric field. The resulting samples were characterized by X-ray diffraction, Auger Electron Spectroscopy (AES), and conductivity measurements.

1. Experimental

C₆₀ films of 100 nm thickness were grown, using a vacuum deposition technique, on glass and mica substrates as well as on glass substrates predeposited with a Cu sublayer [3,4].

The crystalline structure of these C₆₀ 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.

Elemental composition at the surface and in-depth concentration distributions ("sputter depth-profiling") for C₆₀ films were studied by AES combined with controlled Ar ion bombardment. The details of the AES measurements are given elsewhere [5]. Conductivity of the C₆₀ films was measured in two- and four-probe configurations of electrodes (Fig. 1), using a Hewlett Packard 4140B pico-meter/dc voltage source.

The other experimental details will be given below.

2. Results and discussion

2.1. CICED of Cu and I₂ into the C₆₀ matrix. Recently [5] we developed a new technique for doping (intercalation) of C₆₀ thin films, so-called CICED. The technique involves the vacuum deposition of highly crystalline C₆₀ thin film onto a metal (Cu or Au, or Ag) sub-layer [3] and subsequent exposure of the samples to a reactive gas atmosphere.

If oxygen is employed as the reactive gas atmosphere, a diffusion of oxygen atoms through the front surface of the fullerene film is observed and a corresponding slow counter diffusion of metal from the sub-layer occurs (with a characteristic time measured in months). Analysis of the resulting doped material after 10 months of air-exposure of the Cu-supported C₆₀ films, at room-temperature, revealed the presence of Cu and O atoms at all depths over the samples and the formation of a complex which we referred to as Cu₂O₆C₆₀. We have published elsewhere [5] the detailed results of the oxygen-induced doping experiment together with a suggestion that the following CICED multi-step process takes place under the experimental conditions. 1) Well-known diffusion of molecular oxygen (O₂) from air into the C₆₀ film. 2) Emission of free electrons from the Cu sub-layer to oxygen molecules in the C₆₀ matrix. 3) Generation of an internal electric field between (O₂−C₆₀)− complexes and the Cu⁺ sub-layer. 4) Drift of Cu⁺ from the sub-layer to the (O₂−C₆₀)− complexes. 5) Formation of the CuO₆C₆₀ complex.

In the case of an iodine atmosphere, the metal diffusion was observed to occur on a time scale which is orders of magnitude faster. Indeed, even 10 minutes of exposure in
Figure 1. Depth distribution of Cu, I, O and C atomic fractions (in units corresponding to the time of sputtering by Ar ions), measured by AES, after 10 minutes of exposure in an I₂ atmosphere of a Cu-supported C₆₀ film.

Figure 2. Temperature dependence of two-probe coplanar conductivity, before and after treatment of the C₆₀ films for 1 hour under an electric field of 500 V/cm at 150°C: (a) a highly dispersed film, (b) a film of intermediate-crystallinity, (c) a highly crystalline film.
Correlation between the grain sizes in C₆₀ films and their value of activation energy of conductivity, after treatment for 1 hour under an electric field of 500 V/cm at 150°C

<table>
<thead>
<tr>
<th>C₆₀ films Structure</th>
<th>Grain Size, nm</th>
<th>Activation energy, eV</th>
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</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 Textured</td>
<td>500–1500</td>
<td>1.06</td>
</tr>
</tbody>
</table>

(grain size of 80–100 nm, no texture), (c) highly crystalline films (grain size of 500–1500 nm, (111)-texture).

The conductivity measurements were performed in situ while pumping the quartz tube with sample up to a dynamic vacuum of 10⁻⁶ Torr and heating of the samples up to elevated temperatures. 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. [2,10]. 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 the temperature dependence of the two-probe coplanar conductivity of C₆₀ films with various degrees of crystallinity, before and after treatment by a 500 V/cm electric field for 1 hour 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 4 orders of magnitude (Fig. 2, a). Conversely, the maximum activation energy (i.e. the minimum doping effect) was observed for the highly crystalline sample (Fig. 2, c). Both decrease in activation energy and increase of conductivity values, after treatment, with decrease in grain sizes are in evidence.

The electrodiffusion experiment using a four-probe configuration of electrodes demonstrated similar results. AES and X-ray Photoelectron Spectroscopy (XPS) characterization of the doped samples as well as photoconductivity measurements are in progress.

In general, a diffusion rate of an impurity atom is known to be higher along grain boundaries than within a crystal grain [11]. We interpret the observed doping behavior as the electrodiffusion of Au from an electrode, dominantly along grain boundary, and the subsequent intercalation of the C₆₀ lattice by Au atoms.

1) Structural and chemical changes in Cu-supported C₆₀ thin films during their room–temperature–exposure to I₂ atmosphere were studied by XRD, AES, XPS and conductivity measurements. A C₆₀–CuI composite material was found to be produced during the exposure of Cu-supported C₆₀ film to an I₂ atmosphere. Even 10 minutes of exposure resulted in complete disappearance of the Cu sub-layer and the formation of a CuI phase over the whole thickness of the C₆₀ film. The room temperature dark conductivity of the CuI-doped samples was observed to have increased by several orders of magnitude but the semiconductor behavior was not in evidence.

2) We report the effect of an external electric field of the in situ measured conductivity of C₆₀ films with different degrees of crystallinity. Semiconductor behavior with increased conductivity values (by orders of magnitude) and decreased conductivity activation energy has been demonstrated for the doped samples. The results are explained by electrodiffusion of Au from an electrode, dominantly along grain boundaries, and the subsequent intercalation of C₆₀ lattice by Au atoms.

References