

Analytical Model of Electrodiffusion of Metals in Fullerene Thin Films

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(Received September 17, 2004; accepted December 1, 2004; published April 21, 2005)

This paper presents a theoretical model of doping of C₆₀ thin films by the diffusion of ions from metal electrodes under the action of external electric bias. In the case of Au diffusion, the final nonlinear parabolic partial differential equation for the concentration of mobile metal ions was solved numerically by the finite difference method for a given electric current (galvanostatic operation). This yields the time evolution of ionic concentration profiles for different currents. A significant increase in the rate of Au ion penetration into C₆₀ films with increasing electric current is predicted by these calculations in agreement with the published experimental observations. [DOI: 10.1143/JJAP.44.2803]

KEYWORDS: fullerenes, diffusion, thin films, explicit finite difference method

1. Introduction

Fullerene-based solids have recently been demonstrated to be prospective semiconductor materials for electronic and optoelectronic applications and extensive experimental and theoretical research activities have focused on the understanding of the optical and electronic properties of novel semiconductors.^{1,2)}

At room temperature, solid C₆₀ is a molecular crystal with all C₆₀ molecules occupying the lattice sites of a face-centered cubic (FCC) structure with $a = 14.17 \text{ \AA}$.¹⁾ Closely packed, they leave large holes around four octahedral and eight tetrahedral interstitial sites of the unit cell. The radii of voids $r_{\text{octahedral}} = 3.06 \text{ \AA}$ and $r_{\text{tetrahedral}} = 1.12 \text{ \AA}$, are such that the solid C₆₀ can accommodate almost all elements from the periodic table and even small molecules, conserving the regular crystal structure.³⁾ Crystals and thin films of pristine C₆₀ are found to exhibit a semiconductor-like behavior in their optical and electronic properties by doping these materials in an appropriate manner, their electronic properties can be “tuned” to coincide with those of semiconductors and conductors and superconductivity may result.¹⁾

The most commonly practiced type of doping is *intercalation* whereby dopants are situated between the C₆₀ molecules in the interstitial positions. Intercalation may occur as a spontaneous process or it can be induced by an external stimulus, such as the vapor pressure of intercalating species or an electric field applied to the sample.³⁾ There has been a considerable research effort to study intercalated M₃C₆₀ (where M is an alkali or alkaline-earth metal) since the discovery of superconductivity in these compounds.^{4,5)}

C₆₀-metal interactions can be classified according to whether they form compounds (such as alkali- or alkali-earth fullerenes) with charge transfer from the metal donor to the C₆₀ electron acceptor, or phase-separated solids.⁶⁾ For the latter, no solid solution is formed with metals (other than alkali or alkaline-earth metals), owing to their usually high cohesive energy. A limited charge transfer between most metals and C₆₀ is still possible.⁷⁾ Recently, metal diffusion into C₆₀ films under the action of an external electric field and the corresponding formation of quasi-stable M_xC₆₀ compounds (where M is Au, Ag or In) have been experimentally demonstrated.^{3,8)} Nevertheless, there is a

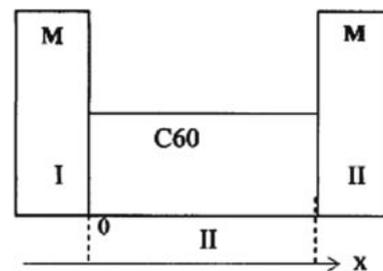


Fig. 1. Schematic diagram of electrodiffusion system where the C₆₀ film is situated in between the two metal electrodes.

serious lack of knowledge on physical mechanisms governing such as an electrodiffusion process. Our research is focused on the development of an analytical model of the metal diffusion into C₆₀ films under the action of electric bias and numerical analysis of the model for the diffusion of Au.

2. Analytical Model

We have evidenced elsewhere⁹⁾ that for our electrodiffusion system (Fig. 1) the Debye length is much smaller than the C₆₀ specimen and it is reasonable to use the local electroneutrality approximation

$$\bar{e} = \bar{p} + \bar{P} + \bar{N} \quad (1)$$

Here, $\bar{e} = 10^{12} - 10^{14} \text{ cm}^{-3}$ and \bar{P} and \bar{p} are the concentrations of free electrons and bound and mobile metal ions in C₆₀ films, respectively; $\bar{N} = \bar{e}$ is the concentration of all intrinsic fixed positive charges in per unit area (concentration of hole in the valence band is equal to concentration of electron in the conduction band) in a pristine C₆₀ film.

From mass conservation for the metal ions, the gradient of the flux \bar{j}_x is given by

$$\bar{P}_x + \bar{p}_x = -\bar{j}_x \quad (2)$$

Assuming a linear equilibrium relation between \bar{P} and \bar{p} , these variables can be related through the binding coefficient Γ_2 .

$$\bar{P}(\bar{x}, \bar{t}) = \Gamma_2 \cdot \bar{p}(\bar{x}, \bar{t}) \quad (3)$$

Now, the fluxes of metal ions $\bar{j}(\bar{x})$ are controlled by diffusion and drift components:

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$$\tilde{j}(\tilde{x}) = -\tilde{D} \cdot \tilde{p}_{\tilde{x}} - \frac{\tilde{D} \cdot z \cdot F \cdot \tilde{p}_{\tilde{x}} \cdot \tilde{\varphi}_{\tilde{x}}}{R \cdot T} \quad (4)$$

Similarly, mass conservation for electrons implies

$$\tilde{e}_{\tilde{t}} = \tilde{D}_e \left(\tilde{e}_{\tilde{x}} - \frac{z \cdot F \cdot \tilde{e} \cdot \tilde{\varphi}_{\tilde{x}}}{RT} \right)_{\tilde{x}} \quad (5)$$

where \tilde{D}_e is the diffusivity of electrons.

When an external electric field is applied, the electric potential on both metal side of both electrode/C₆₀ interfaces is

$$\tilde{\varphi}(0) = 0, \quad \tilde{\varphi}(1) = -\tilde{V}, \quad (6)$$

where \tilde{V} is the voltage drop between the electrodes.

At equilibrium, the electrochemical potentials of ions and electrons are continuous across the electrode/C₆₀ interfaces implying $x = 0$ and $x = 1$

$$(RT \cdot \ln(\tilde{p}_k) + zF\tilde{\varphi}_k) = (RT \cdot \ln(\tilde{p}) + zF\tilde{\varphi}) \quad (12a)$$

$$(RT \cdot \ln(\tilde{e}_k) - zF\tilde{\varphi}_k) = (RT \cdot \ln(\tilde{e}) - zF\tilde{\varphi}). \quad (12b)$$

On the other hand, the electric current continuity condition is

$$\tilde{D}_m \left(\tilde{p}_{\tilde{x}} + \frac{z \cdot F \cdot \tilde{p} \cdot \tilde{\varphi}_{\tilde{x}}}{RT} \right)_{\tilde{x}} - \tilde{D}_e \left(\tilde{e}_{\tilde{x}} - \frac{z \cdot F \cdot \tilde{e} \cdot \tilde{\varphi}_{\tilde{x}}}{RT} \right)_{\tilde{x}} = 0. \quad (13)$$

The integration of eq. (13) yields

$$\tilde{D}_m \left(\tilde{p}_{\tilde{x}} + \frac{z \cdot F \cdot \tilde{p} \cdot \tilde{\varphi}_{\tilde{x}}}{RT} \right) - \tilde{D}_e \left(\tilde{e}_{\tilde{x}} - \frac{z \cdot F \cdot \tilde{e} \cdot \tilde{\varphi}_{\tilde{x}}}{RT} \right) = -\frac{\tilde{I}(\tilde{t})}{F}, \quad (14)$$

where the electric current density $\tilde{I}(\tilde{t})$ corresponds to the galvanostatic regime of operation. The mathematical procedure of derivation of the final equation of our analytical model based on eqs. (1)–(14) is described in detail elsewhere.⁹⁾ Furthermore, the total number of metal ions $\tilde{p}(\tilde{t}, \tilde{I})$ penetrating into the film during the time \tilde{t} is

$$\tilde{p}(\tilde{t}, \tilde{I}) = \left(\left(\left(D_2 + \frac{\tilde{N}^* \left(1 - \frac{\tilde{D}_e}{\tilde{D}_m} (1 + \Gamma_2) \right)}{\tilde{p} \left(1 + \frac{\tilde{D}_e}{\tilde{D}_m} (1 + \Gamma_2) \right) + \tilde{N} \frac{\tilde{D}_e}{\tilde{D}_m}} \right) \times \tilde{p}_{\tilde{x}} + \frac{\tilde{N}^* \tilde{I}}{F \cdot \tilde{D}_m \left(\tilde{p} \left(1 + \frac{\tilde{D}_e}{\tilde{D}_m} (1 + \Gamma_2) \right) + \tilde{N} \frac{\tilde{D}_e}{\tilde{D}_m} \right)} \right)_{\tilde{x}} \right). \quad (15)$$

Here,

$$\tilde{D}_2 = \frac{1 + \Gamma_2}{\tilde{D}_m} + \frac{1}{\tilde{D}_e}$$

and

$$\tilde{N}^* = \frac{\tilde{N} \cdot \tilde{D}_m}{(1 + \Gamma_2) \left(1 + \Gamma_2 + \frac{\tilde{D}_m}{\tilde{D}_e} \right)}.$$

Equation (15) is the final differential equation of our model to be solved with the initial and boundary conditions:

$$\tilde{p}(\tilde{x}, 0) = 0 \quad \text{and} \quad \tilde{p}(0, \tilde{t}) = \tilde{p}(1, \tilde{t}) = \tilde{p}_0 \quad (16)$$

where \tilde{p}_0 is the concentration of metal ions on the C₆₀ side of the electrode/C₆₀ interface.

3. Results and Discussion

Figures 2 and 3 show the results of numerical solution of eqs. (15) and (16) obtained by an explicit finite difference method. The dimensionless concentration p is defined as the ratio of the concentration of metal ions on C₆₀ films at any given time to the concentration of metal ions on the C₆₀ side of the electrode/C₆₀ interface. Correspondingly, the dimensionless distance x is defined as the ratio of the distance from

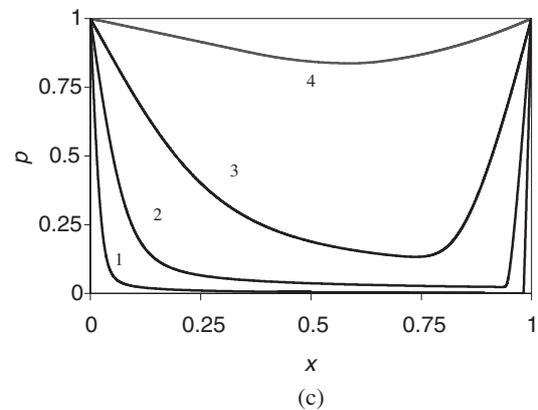
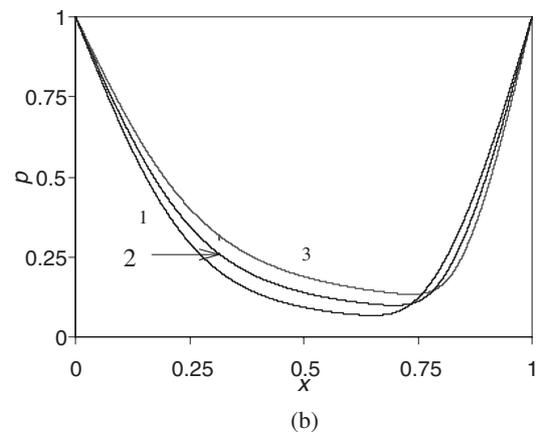
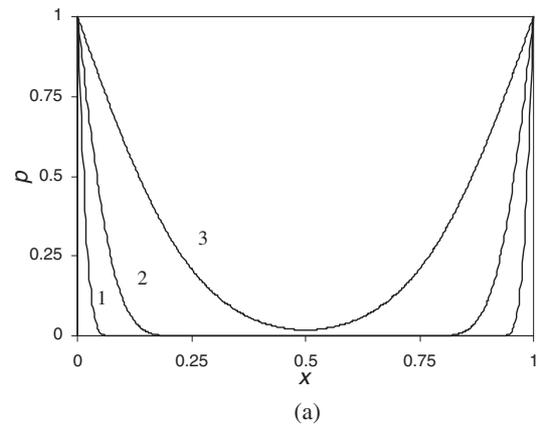


Fig. 2. Diffusion profiles of metal ions in C₆₀ at 150°C: (a) $t = 0.0001$ (1), 0.001 (2) and 0.01 (3), without any electric field between the electrodes; (b) $t = 0.01$ and the electric currents between the electrodes of ~ 5 mA (1), 23 mA (2) and 47 mA (3) (c) the electric current of 47 mA and $t = 0.0001$ (1), 0.001 (2), 0.01 (3) and 0.1 (4).

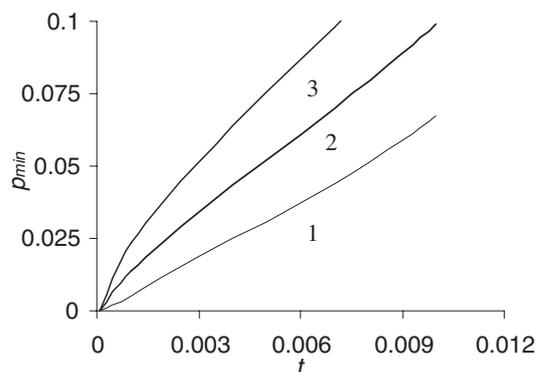


Fig. 3. Time dependence of the minimum concentration of metal ions in C_{60} films (p_{\min}) after the diffusion at 150°C and electric currents of $\sim 5\text{ mA}$ (1), 23 mA (2) and 47 mA (3).

the given point in the C_{60} films to the nearest electrode to the distance between two electrodes (Fig. 1). Finally, the dimensionless time t is normalized by the typical time of diffusion, which is equal to the squared distance between the electrodes divided by the metal diffusivity value.

Specifically, we demonstrate a symmetric characteristic of the diffusion concentration profiles without applying an electric field between the electrodes [Fig. 2(a)]. The application of an electric field manifested in the asymmetrical diffusion profiles. Moreover, an increase in electric current between the electrodes results in a significant increase in the rate of metal ion penetration into C_{60} films [Fig. 2(b)]. A monotonic increase of metal ion concentration with time at any position in the C_{60} films for the constant electric current [Fig. 2(c)] as well as that of the minimum metal ion concentration (p_{\min}) in the films (Fig. 3) are also shown. The rate of the latter is shown to increase with the magnitude of the electric current (Fig. 3). Our results are consistent with the experimental findings^{3,8} and can be considered as lines of analytical evidence of the metal electrodiffusion in C_{60} films.

The diffusivity value of O_2 in C_{60} films at 150°C is reported to be $10^{-12}\text{ cm}^2/\text{s}$.¹⁰ Since the radius of the Au atom is nearly equal to that of the O_2 molecule, we have assumed that the diffusivity of these species should be of the same order of magnitude. In contrast to this assumption, our calculation revealed that, in order to reproduce the equilibrium distribution of the Au ions in the C_{60} film shown by curve 4 in Fig. 2(c), the Au diffusivity should be of $\sim 10^{-7}\text{ cm}^2/\text{s}$. This finding together with the experimental

observation of the Au electrodiffusion into C_{60} films⁸) indicates a certain enhanced diffusion mechanism in the films. We may suggest that a grain boundary diffusion may control this phenomenon in the polycrystalline C_{60} films. This is consistent with the experimental finding that the rate of Au electrodiffusion into C_{60} films increases with the decrease in the grain size of the C_{60} films.⁸⁾

4. Conclusions

1. An analytical model for doping of fullerene thin films by the electrodiffusion of ions driven by an electric current from metal electrodes is proposed. The diffusion profiles of metal ions are numerically calculated and traced as a function of time and electric current.
2. A significant increase in the rate of the metal ion penetration into C_{60} by the electric current is predicted.
3. Electric-field-induced diffusion can constitute an alternative electrochemical method for the doping of fullerene solids.
4. The possibility of the electrode metal diffusion even at relatively small applied electric fields should be considered for the analysis of conductivity measurements of C_{60} solids.

Acknowledgement

B. P. K. thanks the Albert Katz International School for Desert Research and the Bonna Terra Foundation for financial support. E.A.K. acknowledges the Israel Ministry of Immigrant Absorption and the Daichmann Foundation for financial support.

- 1) M. S. Dresselhaus, G. Dresselhaus and P. C. Eklund: *Science of Fullerenes and Carbon Nanotubes* (Academic press, San Diego, 1996) p. 224.
- 2) E. A. Katz: *Solid State Phenom.* **67–68** (1999) 435.
- 3) L. Firlej, A. Zahab, F. Brocard and N. Kirova: *Phys. Rev. B* **59** (1999) 16028 and references therein.
- 4) L. Forro and L. Mihaly: *Rep. Prog. Phys.* **64** (2001) 649.
- 5) A. Hebard, M. Rosseinsky R. C. Haddon, D. W. Murphy, S. H. Glarum, T. T. M. Palstra, A. P. Ramirez and A. R. Kortan: *Nature* **350** (1991) 600.
- 6) J. H. Weaver and D. M. Poirier: *Solid State Phys.* **48** (1994) 1.
- 7) J. G. Hou, X. Li and B. Wang: *J. Phys. Chem. Solids* **61** (2000) 995.
- 8) E. A. Katz, D. Faiman, S. Tuladhar, S. Stutina, N. Froumin, M. Polak and Y. Strzhemenchny: *Sol. Energy Mater. Sol. Cells* **75** (2003) 421.
- 9) B. Kafle: MSc. Thesis, Department of Solar Energy and Environmental Physics, Ben-Gurion University of the Negev, Beer-Sheva, 2004.
- 10) E. Halac, E. Burgos and H. Bonadeo: *Phys. Rev. B* **52** (1995) 4764.