Structural and chemical modifications in Cu-supported C_{60} thin films exposed to an atmosphere of air or iodine

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Received 5 February 2001

Abstract

Structural and chemical changes in C_{60} thin films, grown on a Cu substrate and exposed to air or I\textsubscript{2} atmosphere, at room temperature, were monitored by X-ray diffraction, Auger electron and X-ray photoelectron spectroscopy. Exposure to air is demonstrated to result not only in oxygen diffusion but also in a counter diffusion of the metal from the substrate into the C_{60} matrix. In particular, 10 months of air-exposure led to the presence of Cu and O atoms at all depths over the sample and the formation of a complex which we refer to as Cu\textsubscript{x}O\textsubscript{y}C_{60}. The new phase is quasi-stable at room temperature, but a relatively short thermal annealing at 150°C destroys it and restores the initial C_{60} FCC lattice.

After 10 min of exposure of the Cu-supported C_{60} films to an I\textsubscript{2} atmosphere the Cu sub-layer disappears completely and macroscopic amounts of a stable CuI phase are formed over the entire thickness of the C_{60} film. To explain the results a model of chemically-induced counter electro-diffusion is proposed. We propose the possible usefulness of this counter diffusion approach for tailoring C_{60} -based materials doped with various compounds in the form of both phase-separated composites and solid solutions (intercalated fullerides). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Fullerene; Thin films; Crystal structure; Diffusion; Phase transition

1. Introduction

The discovery of C_{60} [1], a third allotrope of carbon in addition to the more familiar diamond and graphite, together with an easy method to produce macroscopic quantities of the material [2]
have generated enormous interest in many areas of physics, chemistry and material science.

At room temperature, solid C$_{60}$ is a molecular crystal with entire C$_{60}$ molecules occupying the lattice sites of a face-centered cubic (FCC) structure [3]. Crystals and thin films of pristine C$_{60}$ are found to exhibit semiconductor-like behavior in their optical and electronic properties, while the electronic properties of doped fullerenes can be "tuned" to produce semiconductors, conductors and even superconductors [4].

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 [5]. There has been a considerable research effort to study M$_3$C$_{60}$ compounds (where M is an alkali or alkali-earth metal) since the discovery of superconductivity in these compounds [6]. C$_{60}$-metal interactions can be classified according to whether they form compounds (like alkali- or alkali-earth fullerides) with charge transfer from the metal-donor to the C$_{60}$-electron-acceptor, or phase-separated solids [7]. For the latter, no solid solution is formed with metals (other than alkali- or alkali-earth metals), owing to their usually high cohesive energy. However, limited charge transfer between most metals and C$_{60}$ is still possible, since their work functions have low values [8]. The C$_{60}$-metal interaction, with emphasis on the possibility of tailoring new C$_{60}$-metal compounds or composites, is one of the main subjects in fullerene research today [5].

Given the large size of the interstitial sites in the C$_{60}$ crystal (the corresponding voids are more than 4 Å in diameter) molecular oxygen from air readily diffuses into this solid even at room temperature [9]. The perturbing effect of such spontaneous intercalation on the electronic properties of C$_{60}$ single crystals and thin films (in particular, a drastic reduction of both dark and photo-conductivity) has been reported by many research teams [10–16]. However, some positive effects due to the spontaneous intercalation of C$_{60}$ thin films with oxygen have been reported too. Wen et al. [17] revealed that C$_{60}$ films exposed to air, at room temperature, for 1 day or longer start to emit broad, intense white light under laser irradiation. Recently [18], we demonstrated that lengthy exposure to air at room temperature of Cu-supported C$_{60}$ thin films results not only in oxygen diffusion but also in a counter diffusion of metal from the substrate into the C$_{60}$ matrix. We referred to this multi-step process as “chemically-induced counter electro-diffusion” (CICED) and suggested to use the counter diffusion approach to produce new C$_{60}$-based materials. In the present paper, motivated by this interest, we report on a detailed study of the structural and chemical transformations in Cu-supported C$_{60}$ films, as promoted by their room-temperature-exposure to air or I$_2$ atmospheres.

2. Experimental

Highly crystalline C$_{60}$ films with strong ⟨1 1 1⟩-texture were grown on glass and mica substrates as well as on glass substrates predeposited with a Cu sublayer [19,20].

The crystalline structure of these C$_{60}$ films was studied by X-ray diffraction (XRD) in Cu K$_\alpha$ radiation at room temperature and by a temperature-resolved XRD experiment in the temperature range 15–300 K. Details of the latter are given elsewhere [20].

Elemental composition at the surface and in-depth concentration distributions (“sputter depth-profiling”) for C$_{60}$ films were studied by Auger Electron Spectroscopy (AES) combined with controlled Ar ion bombardment. A PHI 549 SAM/AES/XPS apparatus with a base pressure of 2 × 10$^{-9}$ Torr in the chamber and a cylindrical mirror analyzer were used. Sputtering was done using a differentially pumped, small-spot (0.5 mm diameter beam) ion gun (IQE 12/38) with an Ar pressure of 10$^{-7}$ Torr and a power supply of 3 kV, giving a sputtering rate of ~100 Å/min. Quantitative analysis of the AES spectra, was based on atomic sensitivity factors [21].

The X-ray Photoelectron Spectroscopy (XPS) data were collected with a Kratos ES300 X-ray photoelectron spectrometer, employing a
non-monochromatic Mg Kα X-ray source (1253.6 eV) and a hemispherical analyzer operated in the fixed retardation ratio mode. The samples were mounted on a sample-holder with double-sided adhesive tape. The main analysis chamber was maintained at a pressure of about $10^{-8}$ Torr during the experiments. The measurements were performed for electrons having a $15°$ off-normal escape angle.

3. Results and discussion

3.1. XRD, AES and XPS study of samples exposed in air

Figs. 1–3 illustrate changes in the x-ray diffraction pattern of a Cu-supported, (1 1 1)-textured C₆₀ film during exposure of the sample to air, at room temperature, for 10 months. For the as-grown film (Fig. 1) the X-ray diffraction revealed an intense reflection from the Cu sub-layer, an intense (1 1 1) - reflection from C₆₀ and its weak second-order line (2 2 2).

We remark that after 2 months of sample exposure we visually observed that the Cu sub-layer had started to disappear. After 10 months it had disappeared almost entirely. At the same time the X-ray diffraction pattern for the 2 months-exposed sample (Fig. 2) exhibited a reduction in intensity of the C₆₀-peaks accompanied by the appearance of four new peaks with inter-planar spacing $d = 9.35$, 6.68, 3.34 and 2.46 Å. We cannot identify these new reflections as belonging to any peak of the known oxides, carbides or carbonates of copper. This points to the formation of some new phase.

Finally, after 10 months of exposure (Fig. 3) a progressive increase in the intensities of the new peaks and a concomitant reduction of the Cu-peak were observed. The latter indicates a decrease in the Cu sub-layer thickness due to Cu diffusion from the sub-layer into the C₆₀ film: a quantitative confirmation of our visual observation.

The depth distribution of Cu, O and C atomic fractions are shown in Fig. 4 (in units corresponding to the time of sputtering by Ar ions). These curves are based on AES measurements for the
same sample after 10 months of exposure. The distance/time scale in Fig. 4 is such that, for the as-grown sample, the original C$_{60}$ layer would have occupied approximately 0–20 min, the Cu sub-layer would have extended from approximately 20 to 30 min and the glass substrate—from approximately 30 min onwards.

The following trends can be noted:

1. Cu and O atoms are present at all depths in the sample (the most surprising result being that Cu is present even at the front surface of the film);
2. depth-distributions of the Cu and O atomic fractions have qualitatively similar trends over the whole thickness of the initial C$_{60}$ film;
3. qualitatively, the Cu depth-distribution from 20 to 0 min shows a diffusive character;
4. there is a co-accumulation of Cu and O atoms near the exposed C$_{60}$ film surface.

While the lateral Cu distribution at any given depth is found to be very inhomogeneous, one can observe a clear linear correlation between the Cu and O atomic fractions (Fig. 5). All of the above-mentioned results motivate us to identify the new X-ray diffraction peaks with a compound or, more generally, a complex of Cu$_x$O$_y$C$_{60}$.

The observed Cu diffusion from the substrate into the C$_{60}$ film at room temperature is an unexpected result. Furthermore, there are many papers (for review see [22]) which discuss the thermodynamic instability of metal fullerides and predict that only alkali and alkaline-earth metals should form stable compounds with C$_{60}$. Most authors agree that the fundamental limitation for the intercalation of C$_{60}$ by non-alkali and -alkaline-earth metals lies in their high cohesive energy. This means that the formation of the two-phase system Me(s) + C$_{60}$(s) is thermodynamically more favorable than the formation of a Me$_x$C$_{60}$ compound. On the other hand, metal diffusion and formation of quasi-stable Me$_x$C$_{60}$ compounds (where Me is Au, Ag or In) is possible under the action of an external electric field [5,23].

A mechanism responsible for this newly observed phenomenon is not quite clear yet and requires further investigation. One possible explanation of our results assumes that the following CICED multi-step process takes place under the experimental conditions [18]:

1. well-known diffusion of molecular oxygen (O$_2$) from air into the C$_{60}$ film;
2. emission of free electrons from the Cu sub-layer to oxygen molecules in the C$_{60}$ matrix;
3. generation of an internal electric field between (O$_2$–C$_{60}$)$^-$ complexes and Cu$^+$ in the sub-layer;
4. drift of Cu$^+$ from the sub-layer to the (O$_2$–C$_{60}$)$^-$ complexes;
5. formation of the Cu$_x$O$_y$C$_{60}$ complex.
We are developing a quantitative model for the CICED process which will be published elsewhere [24]. We may note here that preliminary results do indicate an acceleration of metal diffusion under the action of the chemically-induced electric field.

The new \( \text{Cu}_x\text{O}_y\text{C}_{60} \) phase is quasi-stable at room temperature. Annealing of the samples at 150°C in vacuum for 2 h is found to suppress the XRD reflections belonging to the new phase and to restore the initial XRD pattern of highly crystalline \( \langle 111 \rangle \)-textured \( \text{C}_{60} \) film (similar to that shown in Fig. 1). This reversibility allows us to conclude that the observed structural transformation does not lead to a destruction of \( \text{C}_{60} \) molecules. It also suggests that the observed new phase is a \( \text{Cu}_x\text{O}_y\text{C}_{60} \) complex rather than a compound. Such conclusions are also supported by the temperature-resolved XRD measurements as the following discussion shows.

It is known that near the temperature \( T_c = 250–260 \text{ K} \), \( \text{C}_{60} \) crystals in general [25], and our \( \text{C}_{60} \) thin films in particular [20], undergo a first-order phase transition from FCC structure above \( T_c \) to simple cubic (SC) structure below \( T_c \). \( \text{C}_{60} \) molecules have been shown to rotate freely in the FCC phase and the rotation locks into specific orientations in the SC phase. This disorder/order transition is accompanied by a discontinuity in lattice parameter. Fig. 6 shows the results of temperature-resolved XRD measurements of the lattice parameter in the 10 months-exposed sample, before and after annealing. There is no indication of a phase transition for the 10 months-exposed sample: only a gradual decrease in the lattice parameter is observed during cooling of the sample. On the other hand, after annealing, one sees a well defined discontinuity in the lattice parameter at \( T_c = 230–250 \text{ K} \). This is strong additional evidence that annealing restores the initial high quality FCC lattice of \( \text{C}_{60} \).

Fig. 7 shows the XPS characterization of the 10 months-exposed sample before and after annealing. The results confirm the formation of a quasi-stable \( \text{Cu}_x\text{O}_y\text{C}_{60} \) complex and provide an additional information on its electronic structure. In order to see this, let us discuss the results for the carbon 1s peak. The C1s peak for the as-grown sample (not shown) is symmetric and its energy position almost coincides with that for pure C–C bonding (~285 eV).² After 10 months of sample exposure, this peak was found to have become asymmetric shifted towards higher binding energies (Fig. 7a). Furthermore, one can observe a conspicuous second peak at ~289 eV which implies a charge transfer between carbon and some electronegative element, such as oxygen, in this case. The same period of exposure to air of \( \text{C}_{60} \) film on glass and mica substrates, without a Cu sub-layer, did not lead to any substantial asymmetry and there was no indication of the second high-energy peak (Fig. 7b). These results are consistent with the concept of \( \text{Cu}_x\text{O}_y\text{C}_{60} \) complex formation in the Cu-supported \( \text{C}_{60} \) film. Moreover, a short vacuum annealing for 2 h at 150°C of the Cu-supported sample revealed an increase in intensity of the main C1s peak and a tangible reduction of the second peak (Fig. 7a). This observation is in agreement with the XRD results, demonstrating annealing-assisted remission and disappearance of the \( \text{Cu}_x\text{O}_y\text{C}_{60} \) phase.

²It is worth mentioning that overall peak shifts may occur due to either the formation of new chemical bonds or to a different degree of charging for samples deposited on conducting and insulating substrates. These shifts, however, do not overshadow the observed qualitative changes in peak shape that occur due to air-exposure and annealing of the same samples.
Fig. 7c displays the Cu3p spectrum for the 10 months-exposed Cu-supported sample, before and after annealing. In the former case, the Cu3p peak is shifted towards higher binding energies, which corresponds to electropositive behavior of Cu in the complex. The ∼1.8 eV shift and the change in peak shape might correspond to Cu⁰ → Cu⁺² transition [26]. One can also observe an increase in relative intensity of the Cu3p peak and a sufficient change in its shape after annealing. In particular, a shift towards lower binding energies is in evidence. This is further evidence for the disintegration of a Cu₃O₃C₆₀ complex and the corresponding growth of a pure copper phase upon annealing.

In addition, non-trivial annealing-promoted changes were observed for the O1s peak of the same sample (Fig. 7d). After annealing, the peak appears somewhat broadened and with reduced total intensity. This serves as another confirmation for the depletion of the Cu₃O₃C₆₀ phase.

Fitting the carbon, copper and oxygen signals with multi-Gaussian curves confirms the present picture (the results of such a quantitative analysis of the XPS spectra will be published elsewhere).
3.2. Exposure of samples in an I₂ atmosphere

To further check our model of the CICED process we decided to expose some Cu-supported C₆₀ films to an I₂ atmosphere. Since the chemical formation of copper iodides is known to be more favorable than that of copper oxides [27], one can expect acceleration of the CICED process. Indeed, even 10 min of exposure in an I₂ atmosphere, of a sample with the same crystalline structure and configuration (i.e. thickness of Cu and C₆₀ layers) as the sample exposed in air for 10 months led to a complete disappearance of the Cu sub-layer due to Cu diffusion into the C₆₀ film. X-ray diffraction (Fig. 8) revealed an absence of any Cu peaks. At the same time, together with the (1 1 1) - peak of C₆₀ and its higher harmonics (2 2 2) and (3 3 3), four intense new peaks appeared. These new peaks completely coincide with the known (1 1 1), (2 0 0), (2 2 0) and (3 1 1) peaks for CuI. This points to the formation of CuI as a result of the counter diffusion of Cu and I₂ into the C₆₀ matrix. AES depth profiling measurements of this sample (Fig. 9) revealed a clear correlation between the Cu and I atomic fractions at all depths throughout the C₆₀ film. This indicates the existence of CuI over the entire thickness of the C₆₀ film. XPS measurements (not shown) also support the conclusion that it is the CuI phase, rather than any fulleride, that is formed.

In other words, we may conclude that the exposure of a C₆₀ film on a Cu sub-layer in an I₂ atmosphere leads to counter diffusion of Cu and I₂ into the C₆₀ matrix resulting in the formation of a C₆₀–CuI composite material.

Annealing of the samples at 150°C in vacuum for 2 h and longer does not lead to any significant change in the XRD and XPS signals from the CuI phase. This suggests that the CuI phase in the C₆₀ matrix is a stable compound.

4. Conclusion and prospects

Structural and chemical changes in Cu-supported C₆₀ thin films during their room-temperature-exposure to air or I₂ atmosphere were studied by XRD, AES and XPS techniques.

After 10 months of exposure to air, Cu and O atoms were found to be present at all depths in the film, and reliable experimental evidence was gathered that a CuₓOᵧC₆₀ complex had been formed during the exposure. The new CuₓOᵧC₆₀ phase was quasi-stable at room temperature. XPS and XRD measurements revealed that thermal annealing of the samples in vacuum, at 150°C, for 2 h leads to a disappearance of the CuₓOᵧC₆₀ phase and restores the initial high quality C₆₀ FCC lattice.

A C₆₀–CuI composite material was found to be produced during the exposure of Cu-supported C₆₀ film to an I₂ atmosphere. Even 10 min 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 results of CuI formation suggest that by using this “counter diffusion” approach and optimizing the process conditions one might be able to produce C₆₀-based materials doped with various compounds in the form of both phase-separated composites and solid solutions (intercalated fullerides). Intercalation of C₆₀ with compounds is now becoming a research direction of vital importance because of the following findings published very recently. Schon et al. [28] discovered superconductivity with a transition temperature $T_\text{c} = 52$ K in a single crystal of C₆₀ doped by holes using the technique of gate-induced doping in a field-effect transistor. This value of $T_\text{c}$ is the highest ever observed in a C₆₀-based material. Furthermore, the authors believe that $T_\text{c}$’s up to 100 K should be achievable in a suitably expanded, acceptor-intercalated C₆₀ lattice. On the other hand, to the best of our knowledge, the only successful examples of the doping of C₆₀ by acceptors is intercalation by compounds such as InCl₃, AsF₅, SbF₅, SbCl₅ [29–35].

The present approach furnishes a promising, versatile route for the controlled fabrication of such intercalated materials.

Acknowledgements

This work was funded partly by the Israel Ministry of National Infrastructures. E.A.K. also acknowledges the financial support by the Israel Ministry of Emigrant Absorption and Gensseler Foundation.

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