Electrical Properties of Pure and Oxygen-Intercalated Fullerene Films

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The conductivity of polycrystalline fullerene films as a function of oxygen concentration was investigated and found to be affected significantly by changes in oxygen partial pressure. The conductivity of the film was fitted to an Arrhenius curve. Analysis of the data indicated that a change of 0.11eV in activation energy occurred as the oxygen pressure was varied over two orders of magnitude.

1. Introduction

In recent years it has been shown that the electrical characteristics of fullerene films are sensitive to environmental factors. Another notable feature of solid fullerene structures is the intercalation of molecular gases into the interstitial sites of these structures. Previous studies have shown influence of oxygen gas and temperature changes on the electrical, optical and structural properties of fullerene materials as determined by electron paramagnetic resonance (EPR) intensity changes and x-ray diffraction patterns [1], as well as more conventional electrical measurements [2-4]. The aim of this work is to investigate the effects of oxygen partial pressures on the conductivity of fullerene thin films. We were able to determine a relationship between the oxygen pressure and the electrical conductivity of the film and to provide insight into the electronic structure of oxygen-intercalated C_{60} film.

While previous work has been performed on the reactions between fullerene films and oxygen gas, such work focussed primarily on the impact of oxygen saturation on the fullerene material [3, 5-7], or the extent of oxygen photopolymerisation of the fullerene chains [8,9]. By contrast, the work reported here considers the use of vacuum chambers in conjunction with evaporation methods and heat stages in order to control the oxygen partial pressures in the sample chamber. This in turn allows us to obtain a conductivity/temperature plot for the oxygen partial pressures in order to determine a relationship between activation energies and oxygen partial pressures.

2. Experimental

Films of C_{60} were prepared by sublimation onto a clean glass substrate in a vacuum chamber operating at better than 10^{-7} Torr, which contain pre-deposited gold electrodes. The starting material C_{60} (Sigma-Aldrich Company, USA) was over 99% pure. A quartz-crystal microbalance was used to monitor the rate of deposition and final film thickness. Film thickness and uniformity in depth were also characterised by carrying out a series of image scans across scratches cut through the film using an Atomic Force Microscope tip scratch method described previously [10]. Conductivity measurements were performed using a Keithley Two Probe Electrometer in the dark vacuum chamber (pressure less than 10^{-7} Torr), and in oxygen atmospheres with pressures of 10^{-3} and 10^{-5} Torr. The temperature of the sample was controlled using an electric heater and measured with a thermocouple attached to the rear of the sample.

3. Results

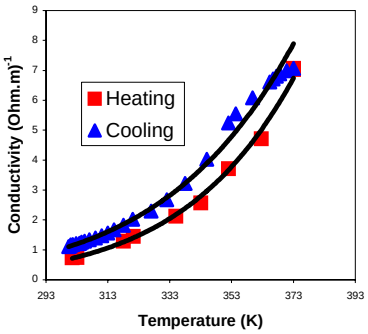

Figure 1. Temperature dependence of conductivity of a C_{60} film in vacuum 10^{-7} Torr after one heating/cooling cycle.

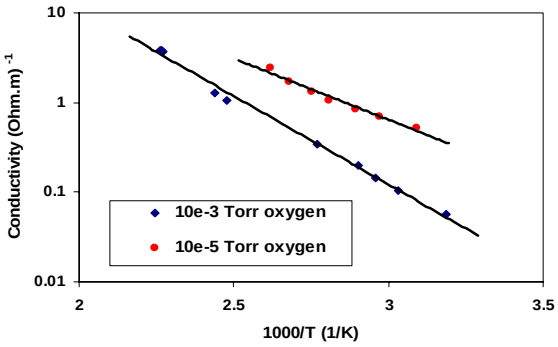

Figure 2. Arrhenius plot of conductivity showing its clear dependence of the conductivity on the oxygen pressure.

3.1 Heating and Cooling Cycles

As is apparent from Figure 1, the room temperature conductivity of the film remains almost constant after the first cycle, indicative of a more stable – but potentially polycrystalline – material, unaffected by further annealing cycles [3]. Subsequent annealing of the film does not cause significant changes to the film conductivity, allowing the temperature-dependent electrical measurements to be carried out in situ without causing further changes in the polycrystalline structure of the film.

While the thickness of the film was being determined, it was observed that the film showed signs of crystalline grains approximately 200nm in diameter on the surface of the fullerene film. This is indicative of a polycrystalline C_{60} film, confirming the polycrystalline structure of the film.

3.2 Impact of Oxygen Partial Pressures

Electrical conductivity of fullerene films was found to be highly sensitive to oxygen partial pressures in the pressure range from 10^{-3} to 10^{-5} Torr. It was noted that maintaining the film in an atmosphere of nitrogen has no significant effects on the conductivity. Exposure to oxygen at a pressure of 10^{-3} Torr induces an abrupt fall of the conductivity by two orders of magnitude. Figure 2 shows that the change in temperature at each oxygen concentration has a significant influence on the electrical conductivity. The linear relationship of lnσ against 1000/T observed for the pure and oxygen-intercalated films indicates the temperature-dependent electrical conductivity is thermally activated and can be described by the Arrhenius relation (Equation 1). This relation also indicates the nature of semiconductor conduction as it refers to the rate at which the carriers diffuse through the material as a function of temperature.Log-linear plot of conductivity σ against 1/*T*, as shown in Figure 2, allows the determination of the activation energy for the fullerene films. Table 1 shows the activation energies of our films as well as previously reported values, which show that the activation energies of oxygen-intercalated films are generally higher than pure films kept in vacuum. The fact that the activation energy of the fullerene film increases from 0.27 to 0.38 eV as the oxygen pressure increases from 10^{-5} to 10^{-3} Torr indicates that oxygen has a significant impact on the film electrical properties.

$$\sigma = \sigma_0 e^{\left(-\frac{E_a}{kT}\right)}$$

Equation 1. The Arrhenius Equation where σ_0 is the pre-exponential factor and E_a is the activation energy.

Oxygen molecules can interact with fullerene films and form a dipole moment from the C_{60} to the O_2 [4]. This creates a complex centre that can act as either an acceptor to free

electron carriers [5], or as a scattering centre that reduces carrier mobility. If the electrons are trapped by the oxygen-fullerene dipoles, it is reasonable to assume that there will be a reduction in the carrier concentration directly correlated to the concentration of oxygen gas present within the fullerene film, which in turn is related to the concentration of oxygen in the environment. The drop in carrier concentration leads to a reduction in electrical conductivity and an increase in activation energy.

	E_a (eV)
Single fullerene crystal [2]	~0.2
Fullerene film (Highly crystalline) [3]	0.26
Fullerene film – 10^{-5} Torr oxygen (this study)	0.27
Single crystal under high pressure (7.5×10^6 Torr) [11]	0.32
Fullerene film – 10^{-3} Torr oxygen (this study)	0.38
C_{60}/C_{70} film [12]	0.43

Table 1. Activation energies of pure and oxygen-intercalated fullerene films.

Our fullerene films exhibit an association between oxygen pressure and activation energy. The increase in the activation energy as oxygen pressure increases indicates that oxygen concentration within the film is directly related to the oxygen pressure surrounding the film. It was also observed during the measurements that there were no significant changes in the film conductivity after 38 min oxygen exposure so long as the oxygen pressure and sample temperature were maintained unchanged. This indicates the film has reached oxygen equilibration within the time period.

4 Conclusions

We found that oxygen intercalation into fullerene films has a considerable impact on the film electrical properties, with their conductivities dropping by several orders of magnitude in an oxygen atmosphere. Both pure and oxygen-intercalated fullerene films show the semiconductor conduction and follow the Arrhenius relationship. As the oxygen partial pressure increases from 10^{-5} to 10^{-3} Torr, the activation energy of the fullerene film decreases by 0.11 eV. It appears credible that further development into fullerene-based gas sensors could be feasible.

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