

Linear electronic and optical processes in Fullerene thin films

J. Moghal*, N. Brant, S.B. Phelan, H.J. Byrne, G. Chambers
Focas Institute/School of Physics, Dublin Institute of Technology, Kevin Street, Dublin 8,
Ireland.

ABSTRACT

The electrical properties of C_{60} have been extensively studied in both the solid and solution phases. The vibrational spectroscopy of C_{60} is predominantly molecular in character. However electronic spectroscopy reveals features, which are specific to the solid. These features have been attributed to intermolecular charge transfer states. The relative importance of these inter – and intramolecular processes in terms of their contribution to the electronic transport is discussed. Cyclic voltammetry is employed to generate charged molecular species, which also contribute to the conduction process and comparisons to optical excited states species are drawn. The cyclic voltammetry was monitored in situ with vibrational spectroscopy so as to observe any shifts in the C_{60} spectrum due to charging. The current voltage characteristics of thin film sandwich structures fabricated by vacuum are then presented and discussed. A strongly non-linear behaviour is observed, a sharp increase in the device conductance being observed at relatively low voltages at both room temperature and at 20K. The room temperature IV curves confirm a lattice collapse upon charging. The high conductivity state is however observed to be stable at low temperature.

Keywords: C_{60} , Electronic Properties, Cyclic Voltammetry, Raman, IV characteristics

1.INTRODUCTION

Fullerene science has been proposed to hold great promise for nanotechnology. Indeed the potential of C_{60} is well renowned. In the past few years fullerenes, namely C_{60} , and its derivatives have been subjected to intense research for a wide range of potential applications in the science industry. The discovery of Buckminsterfullerene (C_{60}) [1] triggered an explosion of research in the early 90's, which gave birth to fullerene science.

This work primarily focuses on the arch-type fullerene, which is C_{60} . C_{60} is electron rich, and yet can be six fold reduced, taking on up to six additional electrons [2]. Interest in electrical properties of the solid were intensified when it was observed that they could be chemically doped with alkali metals, producing a metallic state A_1C_{60} , and even a superconducting state A_3C_{60} [2]. This corresponds to a transfer of 1 and 3 electrons to the LUMO state of each C_{60} molecule respectively. The LUMO of the A_6C_{60} salt is completely full, and the material is electrically insulating. It has been shown that a similar partial occupation of the LUMO band can be achieved by optical pumping of the C_{60} solid, and at a critical excitation density, an insulator to metal transition is observed [3]. A reversible insulator to metal transition has great potential for device applications, however the requirement for optical pumping is impractical. As a result of this a number of groups have concentrated their studies towards electronically inducing the reversible insulator to metal transition, the most high profile being the controversial work reported by Jan Hendrik Schön [4]. Schön and his colleagues at Bell Labs wondered whether instead of converting insulating C_{60} into a superconductor by doping it with potassium atoms, they could use the electric fields produced by an FET geometry to induce a conducting channel in C_{60} . If the density of charges were high enough, perhaps the material would resemble a metal like copper, or maybe even a superconductor. This was not a simple condition to achieve; the density of free electrons in a metal is at least 1000 times greater than that of a semiconductor and if a high electron concentration is required a very high field must be applied to the gate electrode. This was virtually impossible as the FET would be turned to ash but somehow over his experiments, Schön proclaimed that he had succeeded in getting this to work. Unfortunately though no one else was able to reproduce the work of Schön [5].

Other groups have reported changes in the conductivity of single crystals of C_{60} and of fullerene thin films [6] where it was noted that the conductivity of the films jumps by an order of six in magnitude and was also seen to be stable at low temperatures.

Indeed Smie and Heinz reported that the point that the C₆₀ film was most conducting was equivalent to the first reduction peak obtained for a film using cyclic voltammetry. They showed that solid-state measurements of C₆₀ at room temperature showed that the C₆₀ could be charged up to its di-ionic state in two separated potential steps [7]. In this paper the electrical generation of ionic species, which could potentially contribute to the electronic transport in solid-state C₆₀, is examined using cyclic voltammetry techniques. The current voltage characteristics of thin film sandwich structures fabricated by vacuum deposition of C₆₀ on ITO with an aluminum top electrode are also presented in terms of solid-state voltammetric processes. Both are monitored in situ with vibrational spectroscopy.

2.EXPERIMENTAL

For the cyclic voltammetry of C₆₀ films, C₆₀ was deposited onto the surface of a 2mm diameter Platinum electrode. Initially the electrode surface was polished, rinsed with relevant solvent and dried. The C₆₀ in toluene was drop cast onto the electrode surface. The toluene was allowed to evaporate, and a C₆₀ film was formed at the centre of the electrode. The electrolyte that was used was acetonitrile and the supporting electrolyte was 0.1M of Tetrabutylammonium Perchlorate (TBABF₄). The electrochemical cell was then used in situ with Raman spectroscopy, so as to obtain Raman spectra at the reduction peaks of the C₆₀ films.

C₆₀ thin films were produced through vacuum sublimation of C₆₀ powder onto glass predeposited with an indium tin oxide (ITO) layer. A small part of the ITO was etched away using boiling HCL exposing the glass. The substrates were then mounted into an Edwards Auto-305 evaporator, which was pumped down to a pressure of 10⁻⁶mbar. The C₆₀ was sublimed onto the ITO by resistively heating a molybdenum boat containing C₆₀ powder. A layer of aluminum was deposited on top of the C₆₀ to form the top electrode. The sandwich structures were electrically contacted in a cryostat and the current voltage measurements were recorded with a Keithley 237 programmable electrometer where the voltage was varied while measuring the current.

3.RESULTS

Figure 1 shows the low voltage region of the current-voltage (IV) characteristic of a C₆₀ film at room temperature. The IV is initially Ohmic with a conductivity of $\sim 6.0 \times 10^{-8} \text{Scm}^{-1}$, determined from the slope from the beginning of the graph of $2.9 \times 10^{-4} \text{A/V}$, film thickness of $1.0 \times 10^{-4} \text{cm}$, and film area of 0.48cm^2 . As the voltage is increased the conductivity decreases to $3.5 \times 10^{-8} \text{Scm}^{-1}$ determined from the second half of the graph with a slope of $1.7 \times 10^{-4} \text{A/V}$. The change in conductivity is potentially due to space charge limited transport. Values for conductivity measurements of 10^{-10}Scm^{-1} for pristine C₆₀ films have been previously reported [8]. The lower conductivity of these films may be due to fact that they were measured in a planar geometry where conductivity is limited by polycrystalline domain boundaries. The sandwich geometry C₆₀ film shows an insulating behaviour of low conductivity at low voltages and a temperature dependence study was carried out to investigate this behaviour. The results of this study are shown in figure 2.

The temperature dependence of conductivity was performed by subjecting the C₆₀ sample to 1V, holding it at this voltage and noting the current as the temperature was decreased from 293K to 78K. If the samples were in an insulating state it would be expected that the current would decrease as the temperature was decreased, at these low voltages. Normal behaviour of a molecular insulator is thermally activated hopping. Figure 2 shows a decrease in current as the temperature is decreased as expected, however interestingly the rate of decrease of the current changes abruptly as it goes through the phase transition temperature. The activation energy above the transition temperature is very much higher than below. This implies that the intermolecular hopping energy is significantly increased above the transition temperature. This is consistent with decreased intermolecular mobility due to rotational motion [8].

The electrochemistry behavior of a C₆₀ solution is totally different to that of a C₆₀ film. The electrochemistry of C₆₀ in solution has up to six reversible one-electron reduction steps. Solid fullerenes, attached to an electrode via spin coating or drop cast (drop cast usually with toluene) exhibits significantly different electrochemical behavior from that observed when C₆₀ is dissolved in solution. For the electrochemistry of C₆₀ films an electrolyte has to be used. The most common is Acetonitrile (MeCN) and the support electrolyte is TBAPF₆ (0.1M). Early voltammetric studies of C₆₀ films on platinum electrodes in Acetonitrile (MeCN) and ammonium salts such as TBAPF₆ reported four reduction peaks with E_{1/2} potentials of -1.17V , 1.39V , -1.88V and -2.24V Vs Fc/ Fc⁺. The first three peaks closely resemble the first three reduction peaks seen for the solution of C₆₀. However, reported with these E_{1/2}

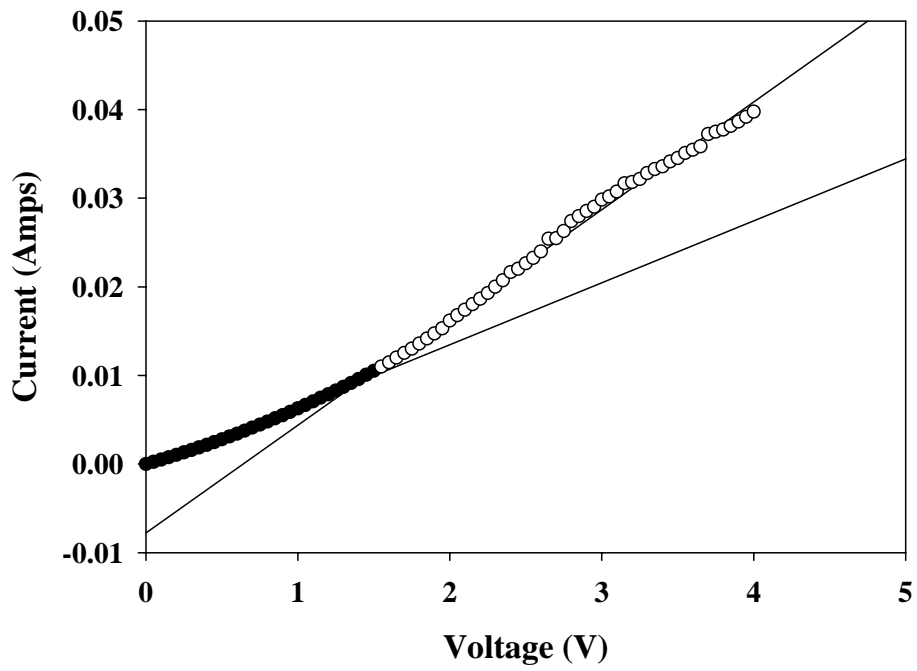


Figure 1 Current-voltage characteristics observed in low voltage region of pristine C₆₀ Film at room temperature

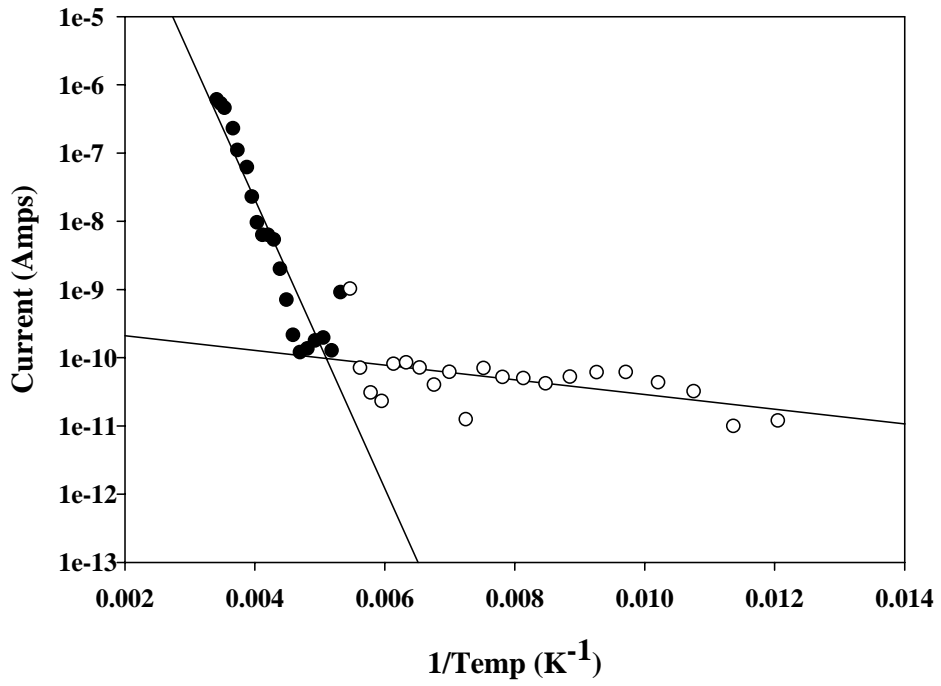


Figure 2: Temperature dependence of low conductivity of Pristine C₆₀ film

potentials was a large potential splitting between the reduction and the re-oxidation. In the solution the reduction and re-oxidation peaks are reported to occur at approximately the same potential with a peak separation ΔE_p of $\sim 59\text{mV}$. This is characteristic of a single electron transfer as can be deduced from Equation 1 [9].

$$\Delta E_p = E_{pa} - E_{pc} = \frac{0.059}{n} \text{Volts} \quad (\text{Equation 1})$$

Thus the peak separation can be used to determine the number of electrons transferred, and it can be seen that one electron process should exhibit a ΔE_p of 59mV .

Figure 3 shows a typical cyclic voltammogram obtained for a C_{60} drop cast film showing the first two reduction peaks. The cyclic voltammogram shows the first reduction peaks for C_{60} at -1.17V and -1.39V vs. Fc/Fc^+ and the corresponding re-oxidation peaks at -0.65V and -0.89V vs. Fc/Fc^+ . It can also be seen that the peak separation ΔE_p for both the reduction and the re-oxidation couples are quite large, i.e. approximately 500mV . The considerable peak separation has been attributed to large structural rearrangements of the film following the first electron transfer [9,10,11]. Initially the drop cast should consist of C_{60} crystallites, each with a fcc packing geometry and a small percentage of toluene, which was trapped in the crystallites during film preparation. Upon reduction, most of the C_{60} in the film reduces to C_{60}^{-1} . The TBA^+ counter ion must then diffuse into the lattice in order to balance the negative charges [10]. The counter ion however is comparable in size to the C_{60} molecule and physically cannot intercalate into the spaces of the fcc structure. Therefore the system rearranges into a new more stable structural configuration, which allows the TBA^+ ion to balance the changes.

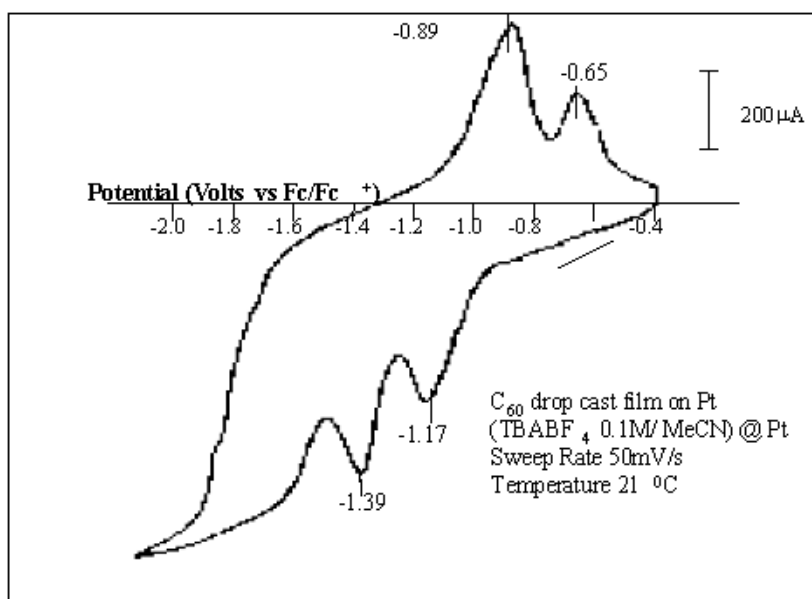


Figure 3: Cyclic Voltammetry of C_{60} drop cast film

The effect of this proposed rearrangement can be readily observed by in situ Raman spectro-electrochemistry as shown in Figure 4. Initially at OV the A_{2g} pentagonal pinch mode is positioned at 1469cm^{-1} . As the negative potential is applied the pentagonal pinch mode is seen to broaden considerably, and at potentials approaching the first reduction peak (-1.17V) a new feature emerges between 1463cm^{-1} and 1464cm^{-1} . The mode positioning of this new feature (initially at 1464cm^{-1}), is reminiscent of the $\sim 6\text{cm}^{-1}$ down shift which occurs in A_1C_{60} [12]. As this emerges at voltages in the region of the first reduction maximum in figure 3, this mode positioning is attributed to the singly charged C_{60} within the lattice. In the region of the second CV peak at -1.39V , the Raman profile is seen to further evolve developing a peak at 1459cm^{-1} . An obvious candidate for this feature is a doubly charged molecule,

but it does not conform with the generally accepted trend of 6cm^{-1} shift per charge, observed in alkali metal fullerene salts. The mode positioning does however match that of the so-called photopolymer [6].

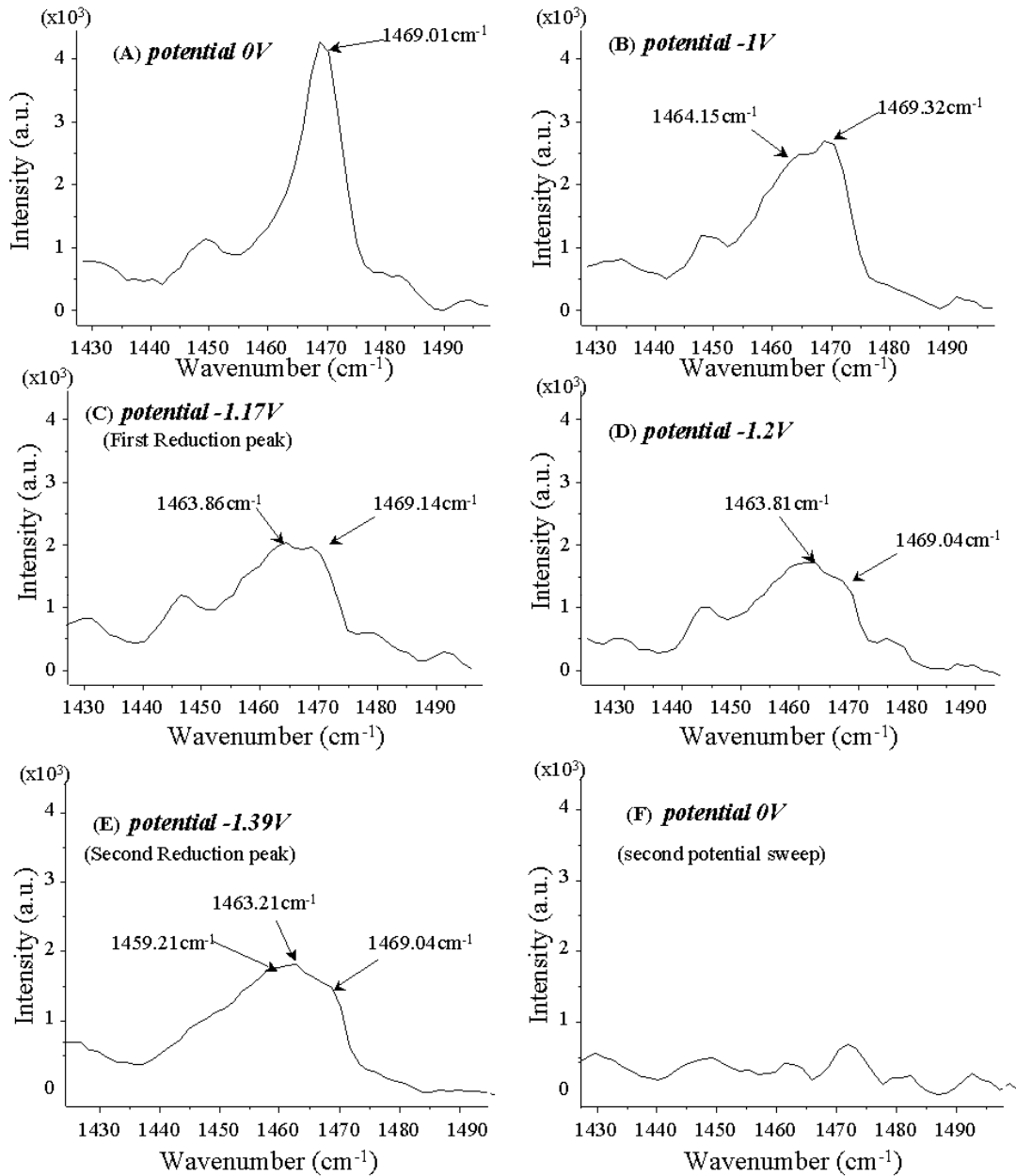


Figure 4: In situ Raman spectra of cyclic voltammetry, A-E first cycle, F is the second

Such a lattice collapse was reported by Smie and Heinze [7], for the electrochemical reduction of C_{60} films. Solid-state cyclic voltammetry measurements were combined with both in situ conductivity and ESR measurement. In their study they found that the onset of the first reduction peak coincided with a strong increase in conductivity although at the point of maximum reduction, the conductivity values were substantially reduced. This reduction in conductivity was attributed to structural rearrangements due to cationic inclusion into the lattice, and was also

strongly supported by the peak ESR signal, which corresponded to the peak in the conductivity rather than in the voltammogram. ESR indicates 50% charging at collapse.

Figure 5 shows conductivity measurements of C_{60} film at room temperature. It can be seen at low voltages ($<6V$), pristine C_{60} films show initially the sample to be at most weakly conducting, as discussed above. As the voltage was increased in the positive direction with respect to the aluminum electrode there was a sharp increase in current, at approximately 9.5V. Further increases in voltage result in little or no change in current until about 10.5V whereupon there is a sharp reduction in current observed. As the voltage was increased the characteristics were seen to be irreversible indicating a structural or chemical change in the material. However reversal of the polarity results in similar sharp features, after which the positive bias characteristics can be reproduced.

Figure 5 can be compared with the cyclic voltammetric curve of figure 3 whereby at a well-defined voltage a sharp increase in the conductance results. The relative stability for this highly conducting species may be due to the absence of any charge balancing cation in the sandwich type structure. However further increasing the voltage results in a sharp reduction with a second maximum. The cyclic voltammogram reported by Smie and Heinze also displays a second reduction maximum [7], which was attributed to the formation of dimeric dianions. The presence of a second maximum in Figure 5 may thus suggest that the C_{60} lattice is unstable to the addition of electrons and can collapse to a polymeric-like species with or without the presence of charge balancing cations.

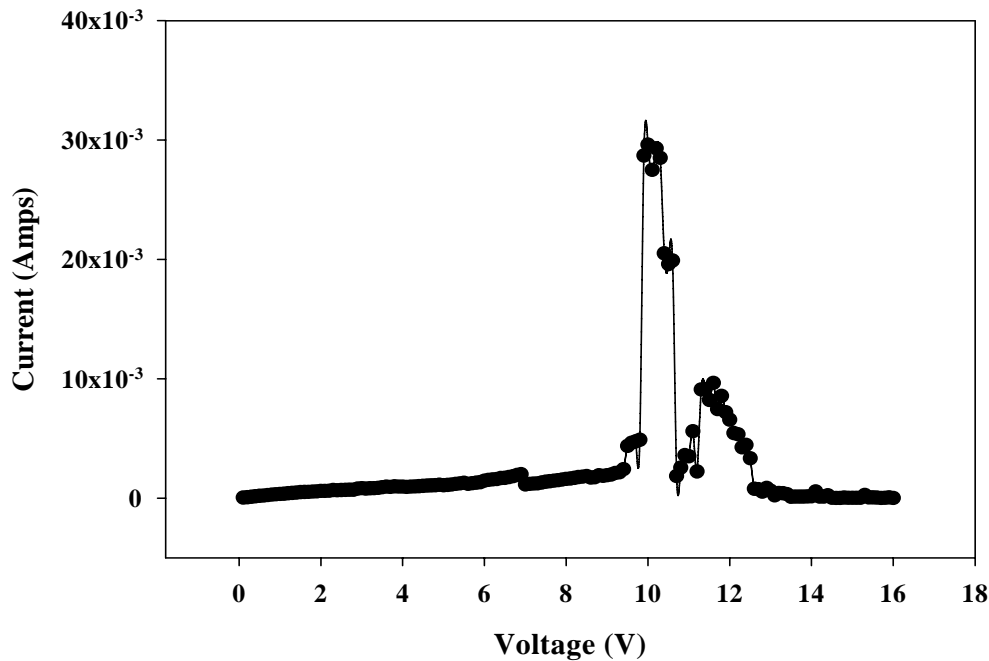


Figure5. Current-Voltage characteristics observed for Pristine ITO/ C_{60} /Al structure at 300K

In situ with Raman spectroscopy was performed on the C_{60} sandwich structures at room temperature. At low voltages, as shown in figure 6, the profile has maximum at 1469cm^{-1} , characteristic of pristine C_{60} . At 12 volts, after the proposed collapse of the C_{60} lattice, the profile has changed to that characteristic of a polymerized C_{60} lattice. When the voltage is removed, this profile remains, indicating that is not characteristic of a charged species but rather of a modified C_{60} lattice.

Optically, the polymerisation of C_{60} is well documented. Of note, the process only occurs above the orientational phase transition where the rotational freedom allows adjacent molecules to align to optimum reaction conditions.

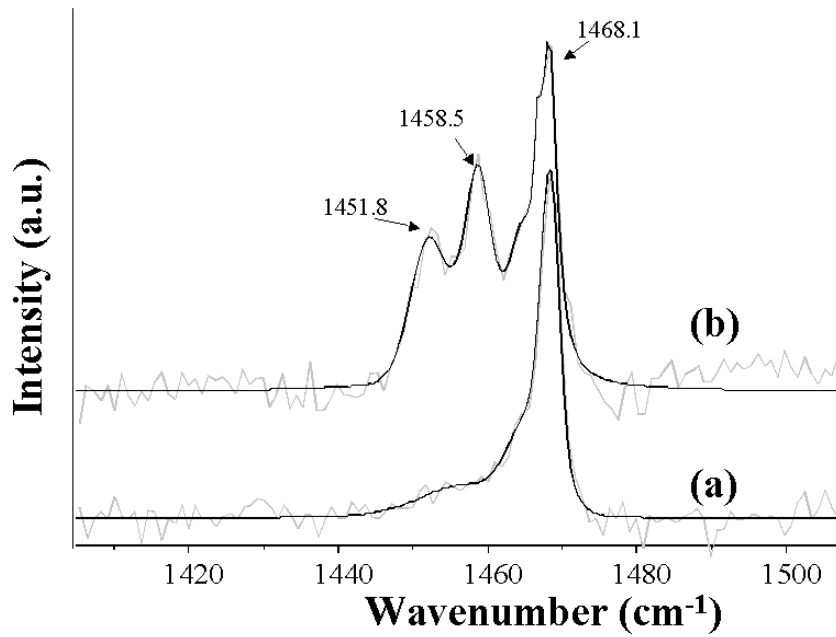


Figure 6: Raman Spectra of C₆₀ film showing the pentagonal pinch mode at 1469cm⁻¹ and after breakdown of the excited state showing two new peaks at 1458cm⁻¹ and 1452cm⁻¹.The Raman signature returns to the 1469cm⁻¹ position after electroluminescence

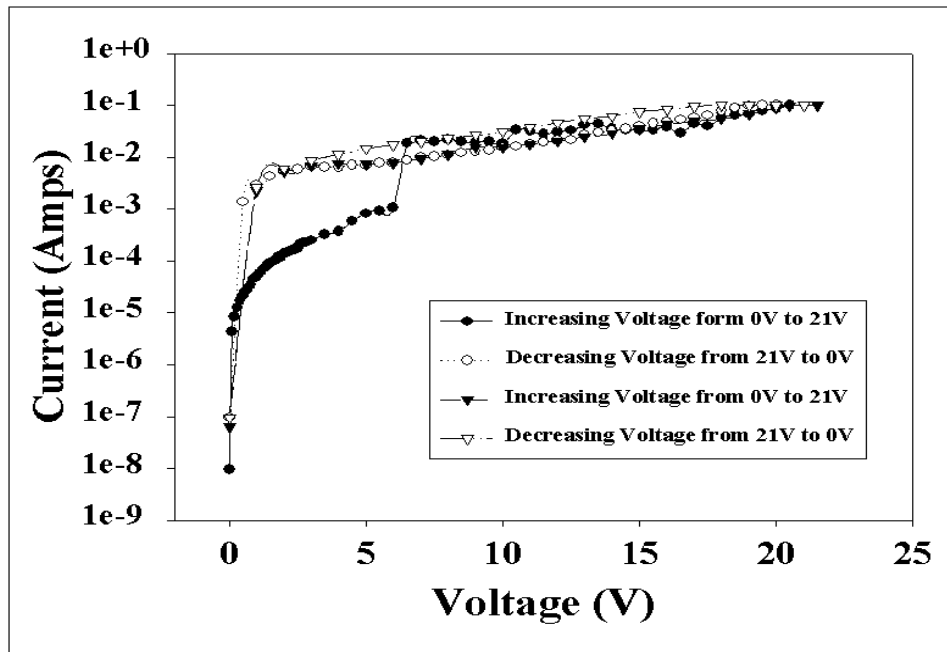


Figure 7: Current voltage characteristics observed for ITO/C₆₀/Al sandwich structure at 30K.

Below this phase transition the material is photochemically stable. Figure 7 shows IV characteristics of the C₆₀ sandwich structure at 20K. As in the room temperature measurements, a dramatic increase in the conductance of the

structure is observable at an apparent threshold voltage. At low temperatures, however, this high conducting state is stable with respect to further increase in voltage. The characteristics are fully reversible and cyclable. These results lend strength to the proposal that the C₆₀ solid state can be effectively doped to a conducting state by the electrical injection of charges.

4. CONCLUSION AND DISCUSSION

For the first part of this paper involving the conductivity, it can be suggested that a highly conducting C₆₀ film can be readily produced by application of a moderate. Further to this it is speculated that the conducting species maybe analogous to a high intensity optically excited state specific to solid-state C₆₀. The possibility of producing such an excited state at relatively low voltages would contribute greatly to then development of potential fullerene based devices in the near future.

Cyclic voltammetry of C₆₀ films results in two reduction peaks and two re-oxidation peaks. These peaks may to shift to a different voltage depending on the electrode being used and on the set up of the apparatus. When the cyclic voltammetry was used in situ with resonant Raman a mode positioning at 1463.86cm⁻¹ for the first reduction peak at 1.17eV was found, in good agreement with previously reported resonant Raman measurements of anionic C₆₀, which is, characterised the mono-anionic signature as a shift of 6cm⁻¹ from the pentagonal pinch mode at 1469cm⁻¹. These shifts are similar to those observed by Kuzmany for doped C₆₀ films [12]. The mechanism for the second reduction peak in figure 5 should be similar to that of the first reduction, however the reduction occurs in a film whose electronic configuration is significantly different to the pristine fcc structure. For this reason it has been suggested that further processes can take place in addition to the electron transfer and incorporation of counter ions. It has been proposed by [5] analogy to similar findings with electron-attracting aromatics and conjugated chain like oligimers, that after the generation of C₆₀⁻¹, dimeric dianions are immediately formed i.e. (C₆₀⁻¹)₂. Figure 4 shows a further softening of the pentagonal pinch mode towards the lower Raman frequency of 1460cm⁻¹ as the second reduction maximum is reached. The softening of this mode is indicative of increased intermolecular interactions between the π-electrons, which is consistent with the suggestion that this reduction peak is due to the production of dimeric dianions (C₆₀⁻¹)₂. In situ ESR and conductivity measurements by Smie and Heinz seem to further support this concept [4]. Moreover the conductivity measurements revealed that neither the electrochemically doped films (which are essentially doped with the counter ion, C₆₀⁻¹TBA⁺) nor the 'dimeric' films are conductive i.e. before the peak maximum for the first reduction in figure 5. In situ Raman measurements of the sandwich structures correlate with these observations, indicating that the C₆₀ lattice is unstable to charge injection. At low temperatures, however, the system is seen to be stable and a high conductivity state may be induced at relatively low voltages. The results presented here highlight the importance of the characterization of the charged species in understanding the transport processes. While they do confirm that a high conductivity state can be generated in fullerene films, the importance of lattice stabilization is highlighted.

ACKNOWLEDGEMENTS

The Focas Institute was funded under the Irish government NDP 2000 – 2006 with assistance from European Regional Development Fund. The work was also carried out with help from the DIT Seed Fund and Enterprise Ireland.

REFERENCES

1. H.W Kroto, J.R Heath, S.C O'Brien, R.F. Curl, and R.E. Smalley, Nature 318,162, (1985).
2. Handbook of Organic Conductive Molecules and Polymers. Volume 1 Charge transfer salts, Fullerenes and Photocinductors. Edited by H.S. Nalwa 1997, John Wiley and Sons Inc.
3. H.J. Byrne, W.K. Maser, M. Kaiser, W.W. Rühle, L. Akselrod, A.T. Werner, J. Anders, X.-Q. Zhou, G.Mahler, T. Kuhn, A. Mittelbach and S. Roth, Appl. Phys. A, 57, 303 (1993)
4. J. H. Schoen, Ch Kloc, B. Batlogg, Nature 408, 549 (2000)
5. www.nd.edu/~jbarkai/schonquestions.

6. H.J. Byrne, in *Physics and Chemistry of Fullerenes and Derivatives*, H. Kuzmany, J. Fink, M. Mehring and S. Roth eds., World Scientific Signapore, p183(1995)
7. A. Smie and J. Heinze, *Physics and Chemistry of Fullerenes and Derivatives*, World Scientific Singapore (1995)
8. M. Kaiser, W.K. Maser, H.J. Byrne, A. Mittelbach and S. Roth, *Solid State Commun.*, 87, 281 (1993)
9. A.J. Bard, L.R. Faulkner. 'Electrochemical methods, fundamentals and applications' John Wiley and Sons Inc. (1980)
10. C. Johoulet. A.J. Bard, F. Wudl, *Am. Chem Soc* 113, 5456, (1991).
11. C. Johoulet. Y.S. ObengY-Tkim, F.Zhou A.J. Bard, *J Am. Chem. Soc* 114, 4237, (1997).
12. Kuzmany, M. Matus, T. Pichler and J. Winter, in *Physics and Chemistry of Fullerenes*, K. Prassides ed., Kluwer Academic, Dordrecht(1994).

*j_moghal@hotmail.com; phone 01 402 7929; fax 01 402 7901