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Electrical properties of thin film $C_{60}$

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Rice University, 1993
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Electrical Properties of Thin Film C\textsubscript{60}

by

Dipankar Sarkar

A THESIS SUBMITTED
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Electrical Properties of Thin Film $C_{60}$

Dipankar Sarkar

Abstract

The fabrication of solid $C_{60}$ device structures by vacuum sublimation methods is described. The experimentally determined threshold of intrinsic conductivity of solid $C_{60}$ is $\sim 1.5$eV. The observations of ohmic contact and photoinduced voltages in $C_{60}$ sandwich structures are observed and explained. The diffusion of silver into $C_{60}$ thin films is quantitatively studied. The activation energy for diffusion of silver into $C_{60}$ is estimated at $2.5\pm0.5$ eV. Experiments on KrF excimer laser-induced ablation and the laser-induced conductivity change in solid $C_{60}$ are done for the first time.
Acknowledgments

I wish to take this opportunity to thank all those people and things that have motivated me to live in the wonderful world of science. The process of enumeration of names is unfair, since it implies a hierarchical sequence which is strictly unintentional:

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I enjoyed the short but successful adventure with high power excimer lasers while working with Harvey Phillips and Dr. Roland Sauerbrey during the study on excimer laser radiation induced changes in solid C60.

My sincere thanks to Mr. Clyde Altemus and his people, and Mr. Dwight Dear of the Research Support Shop for their help in executing the design and fabrication of several critical components for this research. Special thanks go to Mr. B. Brinson and Mr. Hubert Daugherty for their expert technical assistance.

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Chapter 1

Introduction

1.1 Historical development in C_{60} research

Carbon is a remarkable element. Its solid state manifests diverse properties in various allotropic forms. Diamond, an insulator, and graphite, a fairly good conductor, were the two known forms of natural allotropes. Recent discovery of large stable carbon clusters [19, 48] consisting of even numbers of carbon atoms (C_{60}, C_{70}, C_{84}), and the capability to obtain macroscopic quantities by a simple technique [52], has spurred intense scientific interest in studying the physical and chemical properties of the third stable elemental form of carbon in the solid state—fullerene solids. Fullerene solids exhibit semiconducting properties in its intrinsic form and superconductivity with alkali metal doping.

1.2 Physical information on fullerenes and C_{60}

The structure of C_{60} has been identified as a soccer-ball shaped molecule with 12 pentagonal and 20 hexagonal faces. Pentagons provide the curvature to close a two dimensional hexagonal carbon surface onto itself. C_{60} belongs to the icosahedral point group I_h, and its energy levels have up to fivefold degeneracies. The average carbon-carbon distance on the surface of the molecule is essentially the same as the carbon-carbon distance (1.42 Å) between the threefold-coordinated interplanar carbon atoms in graphite. Nuclear magnetic resonance experiments have shown the existence of two different bond lengths in C_{60}: 1.46 Å and 1.40 Å [39].

In the solid state, C_{60} is held together by weak van der Waals forces. The calculated cohesive energy per C_{60} cluster is 1.6 eV, much smaller than the typical C-C bond energy (> 3eV) [41]. The low cohesive energy is also evident from the low sublimation temperature (∼ 400°C) of C_{60}. The crystalline form of solid C_{60} is a disordered mixture of hcp and fcc lattices [52]. Amorphous solid C_{60} has also been observed [21]. The calculated density, based on a hcp lattice is 1.678g cm^{-3} which is
close to a measured value of $1.65 \pm 0.05 \text{ g cm}^{-3}$[52]. The nearest neighbor distance is 10.02Å and the diameter calculated for the carbon cage is 7.1Å[41].

Calculations of many physical properties have been made, including electron energies [42, 10, 24, 20], the optical spectrum [24], the vibrational modes [53, 45, 50, 51, 5, 6], and the electric and magnetic properties [7, 37]. A large number of experiments have revealed detailed information on many of the properties.

Alkali metal doped C$_{60}$ is superconducting and has a critical temperature of $\sim 30$K [23, 14, 29]. The discovery of superconductivity in doped fullerenes has reopened the scientific questions regarding the mechanisms responsible for such unexpectedly high transition temperatures. On the other hand, the understanding of ordinary electrical conductivity in the fullerenes is an equally important question that has attracted a lot of research. In many respect, C$_{60}$ behaves as a semiconductor, showing photoconductivity in the visible frequency range. Fullerenes are easily soluble in many organic solvents like benzene, toluene etc., and the possibility of growing solvent cast thin films imply low-finance technologies for semiconductor applications like photovoltaics.

Central to an understanding of conductivity in crystalline solids is knowledge of the electronic structure. For C$_{60}$ in the gas phase, there are 60 $\pi$ orbitals, that have mostly p-type character, and project radially from the surface of the molecule. The $\pi$ electrons pair up to fill 30 energy states. The degeneracy of the angular momentum $L = 5$ level, which contains 11 states, is removed by the icosahedral symmetry of the molecule, giving rise to three separate levels: $h_u$, or the highest occupied molecular orbital (HOMO), containing 10 electrons; the triply degenerate $t_{1u}$, the lowest unoccupied molecular orbital (LUMO), which can accomodate 6 electrons; and a triply degenerate $t_{2u}$ orbital at a higher energy. Energy band calculations indicate a direct gap of 1.5eV at the Brillouin-zone boundary(X-point)[41], with forbidden transitions. Experiments and theory also indicate narrow bands ($\sim 0.4eV$), not uncommon for organic semiconductors [3, 41, 25].

There lies ahead the interesting possibiility of putting atoms inside the C$_{60}$ cage itself. A spherical void of $\sim 3.5$Å inside the C$_{60}$ cage could accomodate any atom, in principle. It is not yet possible to produce endohedrally-doped fullerenes in macroscopic quantities, so its properties in the solid state are a matter of speculation at the moment.
1.3 Contributions and outline of the thesis

It is the aim of this thesis to study some of the basic electrical properties of C\textsubscript{60} in order to clarify and understand certain issues related to its electronic applications.

Questions of doping and diffusion arise when one tries to modify electrical properties of most semiconducting materials. It is important to understand the properties of electrical contacts to a sample in order to probe it electrically without ambiguity. The criteria for ohmic contacts within the context of C\textsubscript{60} is addressed. The thesis addresses issues related to thermal excitation of charge carriers in C\textsubscript{60} that contribute to conductivity. The unexpected phenomenon of doping the C\textsubscript{60} with metal atoms during the contact-making process, uncommon among ordinary solids, is studied. The first study of the metal-insulator phase transition of intrinsic C\textsubscript{60} by excimer laser irradiation, resulting in a change in electrical conductivity of at least six orders of magnitude is also reported.

The chapters that follow are arranged in this order:

- The experimental chamber for fabrication of C\textsubscript{60} thin films related devices and in-situ electrical measurements, is outlined in Chapter 2. C\textsubscript{60} is a new material, and this implies the evolution of a number of new techniques in the fabrication and characterization process.

- Chapter 3 addresses the issue of electrical conductivity in solid C\textsubscript{60} based on a band-like model. Based on further evidence from published literature, the validity of the band picture is argued.

- Diffusion of silver into C\textsubscript{60} interstices is studied Chapter 4. Contrary to the commonsense notion of a noble metal, silver is observed to significantly interact with C\textsubscript{60}.

- The experiment on changing the electrical conductivity of C\textsubscript{60}, by over seven orders of magnitude due to excimer laser irradiation is studied in Chapter 5.

- Chapter 6 concludes the thesis by pointing out the improvements that could be made in the apparatus and experiments in the future.
Chapter 2

Experimental setup

2.1 Introduction

In order to do research in any frontier area, such as solid $C_{60}$ research, one has to build the necessary apparatus. Some general design criteria were followed in the construction of our deposition chamber, based on information available at the time. Improvements came only later, after a fair amount of knowledge was already obtained through previous experience.

2.2 Design Criterion

The first-generation apparatus was designed for a broad range of experiments, to be accomplished without great difficulty. An outline of the design criteria for individual subsections follow:

Vacuum Sublimation $C_{60}$ is a molecular solid with fairly low sublimation temperature ($\sim 400-500^\circ C$), suitable for vacuum sublimation for film growth. Pure solid $C_{60}$ powder is available commercially for film growth.

Multiple furnaces To study the electrical properties of thin films, metallic electrodes are necessary, and to complete all the processing steps without breaking vacuum requires shuttered furnaces that can be independently operated.

Thickness measurements To grow very thin films (few hundred Angstroms or less) of known thickness, commercially available quartz crystal thickness monitors are used, which requires calibration.

Multiple substrates This is necessary for efficiency when a set of similar samples are to be grown or fabricated.

View ports are needed for two reasons:
Alignment To be able to see the samples for alignment of the masks and the substrates during a particular deposition sequence.

Calibration To be able to carry out a calibration procedure of the thickness monitor using laser interferometry.

Substrate temperature To grow films at different substrate temperatures, and also to heat or cool the substrates during in-situ measurements.

Electrical connections In-situ electrical measurements require several electrical feedthroughs that electrically connect the samples on the substrate holder to the outside of the chamber.

Shadow Masks Fabrication of structures or devices require the ability to pattern each deposition. This is usually accomplished by bringing in different shadow-masks in the beam of effusing atoms or molecules.

O-ring seals There was no immediate need to work at vacuum of better than $1 \times 10^{-6}$ torr, and so the design of the vacuum chamber could employ rubber O-ring seals as opposed to metal seals for UHV, for high temperature baking.

Special Furnace High temperature for effusion and protection of rubber O-ring seals from excessive heat required special furnaces. Also, effusion cell temperature had to be monitored.

Effusion cells The effusion cells were required to be made of suitable refractory and non-reacting materials like alumina and graphite.

2.3 Description of apparatus for fabrication of C$_{60}$ devices

The vacuum deposition chamber was built satisfying the above design criteria. The various components used to build the system was either purchased or fabricated in the workshop. Most of the components were made of stainless steel, and stainless steel welds were used to give added strength to resist mechanical and thermal stress.

One can grow five independent samples for each pump down of the chamber. There can be a maximum of three independent furnaces for subliming either C$_{60}$ or a variety of metals. There are six different shadow-mask patterns available for patterning substrates. The capacity to measure in-situ electrical resistance by two a point method for all five substrates exist. Resistances of the order of a hundred
gigaohms can be measured. A brief description of the vacuum chamber subsystems follow.

2.3.1 The vacuum chamber

The vacuum chamber was built around a four-way cross with two additional, smaller nipples attached, to allow connection of an ionization gauge and a thermocouple gauge. One of the flanges has an adapter chamber that is large enough to accommodate three furnaces and the shutters. A schematic is given in Fig 2.1. The sample holder could be brought into the chamber from the top flange on the cross.

A schematic of the chamber with the different vacuum components is shown in Fig 2.2. The vacuum was maintained by a 60liter/sec turbo pump (Varian Turbo-V60), backed by a mechanical pump. To reduce contamination of sample substrates by dust or other small particles, fast initial roughing that can create turbulence inside the vacuum chamber is avoided. A needle valve in parallel to the main roughing line valve is used for initial pumpdown of the chamber. Only after the pressure was

![Schematic of Vacuum Chamber for Film Deposition](Top view)
reduced to 20 inches of mercury or less does the faster roughing valve take over. The turbo pump is switched on when pressure inside the chamber is less than 10 millitorr.

It typically takes approximately two hours for the vacuum to reach the lower $10^{-6}$ torr range. Thermocouple vacuum gauges are used both inside the vacuum chamber and on the roughing line. The roughing line also contains the venting valve. It is put on the roughing line in order to eliminate the possibility that small leaks from this valve would affect the pressure inside the chamber. An Ion Gauge is used to measure the vacuum pressure below $10^{-4}$torr. A Varian 880RS Vacuum Ionization Gauge controller is used to interface to the two thermocouple gauges and the ionization gauge. A molecular sieve trap in the roughing line prevents oil vapor from the mechanical pump from contaminating the vacuum chamber.

Figure 2.2: Vacuum Chamber showing the pumps and valves
2.3.2 Electrical measurements

The measurements of in-situ resistance are carried out using a Model 196 Keithley digital multimeter (DMM) and a high voltage DC power supply. The resolution of the DMM in its dc current measurement mode is 1 nA, and together with the high voltage dc power source, is capable of providing up to 300 Volts dc, in order to measure resistance well over a few thousand gigaohms. Thus one is able to measure the current through the samples directly, and not require a lock-in detection method. The Keithley DMM employs filtering/averaging techniques that give 6-7 digits of accuracy for the measured quantity. The wires to and from the substrates and the electrical feedthroughs are placed inside teflon tubing. This provides both good electrical insulation in the gigaohm range and also protects the wires when the substrate holder is heated to high temperatures not suitable for otherwise standard insulation materials.

2.3.3 The sample holder

The substrate holder is a hollow cavity, accessible from outside the vacuum chamber, into which one could either pour liquid nitrogen to cool the substrates or place a heater to heat the substrates. A schematic drawing illustrating the arrangement of the various components for the sample holder is given in Fig 2.3.

The substrate holder has a large thermal mass, so temperature variation is not very convenient, but it can hold temperatures steady at a given value. The heater is a custom made heater from Watlow(400W) with provision for protection of the leads. Temperatures of a few hundred degrees Celsius can be obtained. Stainless steel welds in the substrate holder were preferred, anticipating the thermal stresses that occur in a rapid liquid nitrogen cooling sequence. Cajon fittings allow free rotation and manipulation of the substrate holder from outside the vacuum chamber. A schematic drawing illustrating the arrangement of the various components of the sample holder is given in Fig 2.3.

2.3.4 Furnaces

The furnaces have been specially designed for this application. High melting point metals like tantalum or molybdenum were used for the heater element. The current required for the furnaces was available from 20:1 step down transformers with 1KVA capacity. The primary was connected to a variac. Alternating current was used for
heating the furnaces, to avoid any possible electrolysis of the cooling water that came in direct contact with the electrodes. These furnaces are capable of a maximum temperature of approximately 1600 degrees celsius, sufficient for the deposition of the materials to be used. The cooling water was arranged to be delivered continuously by a recirculating water pump from a small reservoir. Stainless steel or brass was used for the external electrodes and other components. The remainder of the furnace was made of welded stainless steel. These replaced earlier brass furnaces, whose silver solder joints were prone to damage due to thermal stress. A schematic for the furnaces used and the relative position of the effusion cell and heater geometry is illustrated in Fig 2.4.

The entire unit was constructed within a custom made unistrut table and support structure. This allowed convenient location of both the chamber and associated control electronics in one place.
2.4 Cleaning procedure for substrates

A controlled cleaning procedure for substrates is important to avoid contamination of samples and unreliable results. The cleaning procedure was partly borrowed from the standard wafer cleaning procedure followed in any Si processing laboratory, and partly evolved from a trial and error iterative process. A different but optimal procedure for each substrate material was developed.

For silicon substrates, we borrowed part of the ‘standard’ RCA cleaning procedure followed in most semiconductor labs. A brief outline of the procedure is as follows:

1. Ultrasonic cleaning in acetone for 10 minutes, to remove organic contaminants.

2. Silicon substrates were submerged into a fresh mixture of $H_2O - NH_4OH - H_2O_2$, in the ratio 5:1:1, in a fused silica beaker. DI (de-ionized) water was used. The solution was heated to 75-80 degrees Celsius. The bubbling of the solution was allowed for about 10 minutes after which the substrates were overflow-quenched in DI water for about 1 min.

3. The silicon substrates were submerged into a 2% HF solution for 20–30 seconds. This was done to strip a thin hydroxide film that forms due to oxidation. After this treatment the silicon surface becomes hydrophobic, and water molecules are not able to attach itself to the silicon. This prevents small dust particles from attaching to the silicon surface.

4. Baking the substrates in a vacuum oven for about 30 minutes to dry them completely.
5. Immediate transfer of the substrates onto the substrate holder in finally put inside the vacuum chamber for further processing.

For quartz or glass substrates, one cannot use a process that requires HF in its cleaning steps. The following steps were followed:

1. Ultrasonic cleaning in acetone for 15–20 minutes. This was to remove organic contaminants like finger grease etc, that are nearly always present.

2. Ultrasonic cleaning for 30 min in a 5% soap solution—commercially known as CONTRAD 70 ultrasonic cleaning reagent. Soap helps to remove tiny dust particles by soap-action. The soap/detergent also helps remove any residual grease from the surface. The substrates were held in small beakers so that only the edges could touch any surface, and thereby reduce contamination.

3. Thorough rinsing in DI water.

4. Drying in a vacuum oven or inside the vacuum chamber.

All cleaning was carried out inside a clean bench or laminar flow hood, in order to reduce contamination from dust. The glass or quartz substrates were usually obtained by cutting 75mm x 25mm microscope slides into three 25mm x 25mm squares. The silicon wafers were cleaved along the crystallographic planes which minimized contamination from silicon dust. However, SEM photographs of the silicon surface showed contamination from certain spherical objects, ranging in size from 1 to 10 microns in diameter which were possibly contamination from the factory during the wafer polishing stages. Once cleaned, the substrates were held only by pairs of clean tweezers. Electrical contacts were made to the substrates with colloidal silver paste. Silver paste is often used for SEM samples in vacuum environment. There was not significant outgassing of the substrates with silver paste at pressures of 1X10⁻⁶ torr.

2.5 Calibration of the thin film thickness monitor

The thin film thickness monitor was calibrated using interferometry. If a laser beam is allowed to reflect off the substrate as the film is deposited, the intensity of the reflected beam is modulated by the depositing film. The intensity modulation of the reflected beam is due to interference between the reflected light from the front and rear interfaces of the thin film. Thus a change in the thickness of the thin film would
cause the optical path lengths of the two reflected beams to differ. If the difference in the optical path length is equal to half a wavelength of the light being used, a minimum in the intensity is observed. Another half wavelength difference would lead to a maximum in the net reflected intensity. The experimental arrangement shown in the schematic in Fig 2.5 explains the principle behind the calibration procedure. The ratio of the maximum to the minimum in the reflected intensity decreases with time. This is expected since the component reflected from the inner interface is gradually attenuated, so that the amplitude of the interference pattern decreases. Eventually only the intensity of the component reflected from the top surface, without any modulation, should result, since the transmitted component will have been attenuated by the C$_{60}$ film.

The laser used was a 1mW He-Ne laser. A beam splitter was used for two reasons: 1) to attenuate the overall intensity of the laser beam from affecting either the sample or saturating the detector and 2) to allow the incoming and the outgoing beams to be at normal incidence on the substrate. A silicon photodiode detector was used. The laser beam was incident on the quartz crystal sensor head, so that the thickness measured by the thickness monitor(TM) and the interference experiment referred to the same spot. Once the effusion from the furnace attained a steady state, the TM was used to record the flux rate. Then the substrate was rotated into the

![Diagram of laser setup](image)

**Figure 2.5:** Calibration experiment for thin film thickness monitor
same position and deposition continued. The reflected laser beam was directed to
the photodetector and the output was monitored on a X-Y plotter. Usually the max-
ima in the graphs are noisier, so the time-period of the intensity variation was made
between the successive minima.

Comparing the results obtained from the optical interference measurement with
that obtained from the TM, one could obtain a 'correction factor' for the thickness
monitor reading. Usually, these monitors have a feature that is called the tooling
factor, which allows a constant scaling of the values automatically as it is displayed.
Thus the calibration procedure could allow a proper tooling factor value to be obtained
thereby allowing absolute measurement of the flux rate to be read read directly off the
thickness monitor. The tooling factor feature also allows the possibility of locating
the thickness monitor sensor head at a convenient location other than where the
substrate would be located.
Chapter 3

Intrinsic C$_{60}$ as a semiconductor

3.1 Introduction

Recent studies on electronic properties of solid C$_{60}$ demonstrate its semiconductor-like behavior. Intrinsic C$_{60}$ exhibits n-type behavior[26, 34]. There have also been reported results of forming heterojunction devices with p-type polymers [33].

Several electrical and optical measurements have been performed on solid C$_{60}$, and there are currently considerable investigations into its properties [20, 26, 31, 22, 30, 54]. In this chapter experiments pertaining to the semiconducting properties of C$_{60}$ are described.

3.2 Bandgap measurements

One of the fundamental parameters that characterize a semiconductor is its bandgap. The electrical, optical and thermal behavior of a semiconductor are directly related to its bandgap. A large bandgap (> 6 – 7eV) implies an insulator; zero bandgap or overlapping bands gives metallic behavior. However, experiments on organic semiconductors have shown that the band model, as it applies to inorganic semiconductors like silicon and germanium, is strictly inapplicable [9]. The corresponding ‘auto-ionization’ model proposes that an excited state that forms an ion-pair, can be separated under the combined action of thermal energy and electric field. This gives rise to the threshold of intrinsic conductivity. Time-resolved carrier relaxation studies on C$_{60}$[35] indicates that solid C$_{60}$ is similar to disordered systems like a-Si [56] where typical carrier relaxation is associated with localized states. Fig 3.1 is a schematic of energy levels in an amorphous solid indicating localized states in the band tails responsible for hopping transport. The low sublimation temperature of C$_{60}$ indicates that the molecules are held together by weak Van der Waals forces, and it is likely that the solid falls within the domain of organic semiconductors with amorphous characteristics.
Figure 3.1: Schematic of density of states distribution in amorphous solids.

It has been reported [43] that thin films of C_{60} retain molecular signatures, such as the vibronic transitions found in isolated molecules. We will refer to the energy gap $E_G$ (or simply the 'gap'), as the energy required to excite the crystal giving an excess electron and a hole that are sufficiently separated for coulombic interactions to be negligible.

There are standard methods to measure the bandgap of a semiconductor. The gap measured depends on the method used. Thus, a strong optical absorption threshold could indicate the bandgap, provided such optical transitions are allowed. Thermal excitation, by heating the solid, does not require to satisfy the constraint of 'vertical' transitions[43, 11], and so depicts the minimum separation between a valley in the conduction band and a crest in the valence band. This is not necessarily the same as the optical absorption threshold.

From basic semiconductor theory, we obtain an expression for the intrinsic conductivity, $\sigma(T)$ as a function of temperature, in the high temperature regime ($\geq 300K$),

$$\sigma(T) = \sigma_0 \exp \left( -\frac{E_G}{2k_BT} \right)$$

(3.1)

where $\sigma_0$ is a constant.

Thus a simple experiment, in which we measure the conductivity of a sample as a function of temperature, can provide us a measure of the gap. On plotting the logarithm of the current through the a C_{60} solid against $1/T$ where $T$ is in Kelvin, the slope should be numerically equal to $E_G/2k_B$.
3.2.1 Experiment to determine the threshold of intrinsic conductivity

The experiment involved growing a C\textsubscript{60} thin film and making contacts to its ends, without breaking vacuum. The details of the sample fabrication process has been given in chapter 4. To summarize: on a cleaned quartz substrate, electrodes were deposited with silver using a shadow-mask. Subsequently, C\textsubscript{60} was sublimed onto the substrate. The current between the electrodes was monitored as a function of film thickness. It increased faster initially but saturated after some time. Fig 3.2 shows the measured current as a function of growth time. This latter observation indicates that bulk conductivity could be measured without the complication of surface effects. Film thickness was greater than a few thousand Ångstroms (2000Å – 1\textmu m).

The sample was heated to about 100\textdegree C above room temperature and then allowed to cool down. Measurement of the current through the thin film at different temperatures was made. Typically, a measurement was performed for every 2\textdegree C fall in the temperature. A type-K thermocouple, mounted on the substrate, monitored the substrate temperature. The sample was maintained inside the chamber without illumination. Fig 3.3 shows the data from such a measurement.

3.2.2 Results and discussion

A Boltzmann-type model as in Eqn 3.1 provides a value for the measured threshold for intrinsic conductivity. The measured value is approximately 1.3–1.6eV, varying

![Graph](image)

**Figure 3.2:** Conductance saturation as a function of film thickness
from sample to sample, and also with the processing history of the individual samples. When the sample is maintained at elevated temperature (\(\sim 100^\circ C\) above ambient) for long duration (\(\sim 12-36\) hours), the gap would decrease with time. There was no significant decrease for short duration heating cycles. This decrease was of the order of 0.2eV. The reason for this downward change in the gap is not clear at the moment. However, studies[43] indicate that processing conditions influence the energy levels within the gap (or the sub-gap). Reported ESR signals from thin films indicate the presence of dangling carbon bonds [43]. The optical absorption spectrum below 1.5eV is strikingly similar to the silicon dangling bond absorption in amorphous-Si:H. There is also reported results of an Urbach edge, typical of amorphous solids, in the optical absorption spectrum of thin film C\(_{60}\) [43]. Based on such observations, it is possible that the processing history or the heating of C\(_{60}\) samples might give rise to additional gap states that effectively lower the threshold for intrinsic conductivity. Exposure to ambient increases the gap and results in a corresponding, almost immediate, decrease in the conductivity of the thin film. The experimentally measured value for the threshold for intrinsic conductivity, is in agreement with other published works:

**Figure 3.3: Measurement of intrinsic gap of C\(_{60}\).**
1. Band structure calculations\cite{41} by Saito et. al. provides a direct bandgap of 1.5eV, with optically forbidden transitions.

2. Measurement of bulk photoconductivity threshold\cite{31} indicates a steep rise at 1.5eV. The C\textsubscript{60} films by this group were exposed to ambient, and as other researchers have shown \cite{11}, oxygen can combine with C\textsubscript{60} and introduce asymmetry that allows optical transitions at the bandgap energy.

3. Photothermal deflection spectroscopy(PDS) \cite{43} by Skumanich indicates a direct bandgap of 1.6eV, which includes forbidden transitions.

4. In-situ measurements, in vacuum of $\sim 10^{-7}$ torr, for the thermal activation energy for intrinsic C\textsubscript{60} gives a value of 1.2eV\cite{11}. The samples in this study were maintained at high temperatures ($\sim 200^\circ$C), and as our study indicates, there is a decrease in the effective gap for such heat treatment.

5. High-Resolution Electron-Energy-Loss Spectroscopy(HREELS) on thin films of C\textsubscript{60}\cite{8} indicate lowest excitations at 1.55eV.

It has been argued \cite{40} that the observed feature at 1.5eV in optical absorption studies and HREELS data is due to Frenkel excitons and that these excitonic states are common in molecular crystals. Frenkel excitons are excited states of molecules and can hop between sites. Thus excitons can cause energy transport within a solid, and they would be detected in the optical absorption or electronic excitation or photoemission studies. They would not necessarily contribute to a net transport of electrical charge for conduction. For transport of charge carriers there has to exist a mechanism for the dissociation of the excitons at the electrical contacts to the external circuit. The device structure employed for our experiment was completely symmetrical and had ohmic contacts (i.e. no strong electric field to dissociate an exciton), and so it is unlikely that the mechanism for charge transport is due to Frenkel excitons. Unlike other spectroscopic techniques, the simple measurement of Arrhenius behaviour is a direct measurement for electronic excitation across a gap and its subsequent transport through the solid. Based on these arguments, it is safe to say that the threshold for intrinsic conductivity has the activation energy of $\sim 1.5eV$. 
3.3 Ohmic Contacts to C\textsubscript{60} thin films

Metal-semiconductor junctions can be of two types; either Schottky barrier or ohmic contacts. The type of semiconductor, n or p type, and the relative magnitude of the work functions of the metal and the semiconductor determine the type of contact that results. Fig 3.4 illustrates the different work function combinations that give rise to ohmic or non-ohmic interfaces.

For a measurement of the temperature dependence of the conductivity of undoped C\textsubscript{60}, it is required to employ ohmic contacts, so as not to interfere with the conduction process. Schottky barriers are rectifying and can obscure measurements done at small applied voltages (~1 – 2 Volts). An I-V (current vs voltage) measurement on the C\textsubscript{60} samples indicates no observable rectification occurs for electrodes made of silver. Measurements were performed on both sandwich structures (Chapter 4) and with electrodes in the form of electrical contacts placed laterally (7mm apart) on a C\textsubscript{60} film. Measurements were typically carried out at high voltages (~200 Volts) to minimize the error due to possible voltage drops at various contacts in the circuit.

Fig 3.5 is a schematic of the energy levels of a C\textsubscript{60}–silver contact. The Fermi level for other metals like gold and platinum is also indicated. The work function of C\textsubscript{60} is taken as equal to its ionization energy of 6.8eV [27], and for intrinsic semiconductors this corresponds to a mid-gap value or the intrinsic Fermi level. The work functions of various metals are obtained after Michaelson [12]. The bandgap of C\textsubscript{60} is assumed to be 1.5eV based on the arguments in the previous section. It is clear from the diagram and Fig 3.4 that Ag and Au would form ohmic contacts with C\textsubscript{60}. The elements with the highest known work function, Selenium(5.9eV) and Platinum(5.7eV) are also indicated on the same diagram. Buckminsterfullerene has been demonstrated to be an n-type semiconductor which acts as a relatively strong acceptor[26, 34]. It may therefore be speculated that all known metals would form ohmic contacts with C\textsubscript{60} if it is assumed to be n-type. It has been experimentally verified that Ag, Ni, Al and Au form ohmic contacts with C\textsubscript{60}[11, 54, 31].

3.4 Photovoltage from sandwich structures

There has been considerable effort to study photovoltaics in sandwich structures of organic solids [9]. The observation of photoconductive response linear in bias voltage and light intensity on sublimed films bridging metals, and photovoltaic response typical of n-type semiconductors in liquid junction cells [26], indicate the possibility of
Figure 3.4: The conditions for formation of Schottky and Ohmic contacts.
Figure 3.5: Relative energy band diagram of C\textsubscript{60} and electrode metals.

using C\textsubscript{60} for photovoltaic applications. Photovoltages in amorphous semiconductors like a-Si, and the various experimental and theoretical evidence about the semiconducting properties of C\textsubscript{60} being similar to amorphous semiconductors [43], provides further motivation.

Sandwich structure devices were fabricated on Si using silver for the top and bottom electrodes. Fig 3.6 illustrates the experimental arrangement for the study of photovoltage generation in sandwich structures. The device structure employed was symmetrical, assuming the top silver electrode to be a normal semi-transparent electrode. Fig 3.7 shows the obtained photovoltage data. The photovoltage indicated is in units of microvolts, and the incident power in units of microwatts. The response is not normalized, and the power spectrum incident from the source and monochromator is also indicated. The photovoltage generated is in the range of 10 – 100\(\mu\)V and the incident power \(\sim 10 – 100\mu\)W. A silicon detector based power meter, that has calibrated correction factor for different wavelengths, was used. The photovoltage response from devices A and B were qualitatively similar.

An explanation of this photovoltaic response in these structures is based on the photodiffusion or the Dember effect. The device structure employed was symmetrical with both the top and bottom electrodes made of Ag. It was also verified that both electrodes made an ohmic contact with C\textsubscript{60}, and so there could not occur a charge sep-
Figure 3.6: Experiment to study the spectral response of C$_{60}$.

Figure 3.7: Spectral response of C$_{60}$ photovoltage generation.
ination as at a Shottky barrier. If the penetration depth $\alpha^{-1}$ of the incident radiation is smaller than the thickness of the thin film, then there would be a larger concentration of electron-hole-pairs generated on the side at which the light is incident. In general, the diffusion coefficients of both carriers are different. The concentration gradient due to photogeneration would therefore cause the faster diffusing particle to move away from the end where photogeneration is occurring. This would show up in the external circuit as a voltage difference between the electrodes. The polarity of the voltage would be determined by the two diffusion coefficients. In connection with a study on xerographic process on $C_{60}$[22], it has been demonstrated that the schubweg for holes (schubweg: average distance moved in unit electric field, $\mu\tau$), as compared to electrons in $C_{60}$, is smaller by a factor of about $10^2$. Thus, if the photodiffusion process is responsible for the photovoltage observed, then the illuminated electrode should be positive with respect to the other. For the samples studied, this was observed and so makes the Dember effect explanation plausible.

Experimentally reported values for the absorption coefficients, $\alpha$, in $C_{60}$ thin films from ellipsometric measurements [44] can be used to explain the observed photovoltage profile illustrated in Fig 3.7. The photovoltage response curve normalized with respect to the power spectrum has a steep rise between $\lambda \approx 525\text{nm}$ ($\sim 2.35 \text{ eV}$) and $\lambda \approx 425\text{nm}$ ($\sim 2.9 \text{ eV}$). At $\lambda \sim 425 \text{ nm}$, the penetration depth ($= \alpha^{-1}$) is $\sim 150 \text{ nm}$, and therefore photo-generation would be confined near the surface at which photons are incident. Subsequent diffusion of carriers can give rise to a photovoltage. At the longer wavelengths the incident light would cause approximately uniform generation of electron-hole pairs inside a film thickness of $\sim 1\mu\text{m}$, and exhibit no Dember effect.

In order to prove this, the experiment should be repeated for different thicknesses of $C_{60}$ films and also with contacts of different metals that form ohmic contacts with $C_{60}$, to see if the photoresponse is similar, and not dependent on the contact. Even if one of the contacts is some what non-ohmic, a photovoltaic effect would be measured instead of the Dember effect.
Chapter 4

Diffusion of Silver into C_{60}

4.1 Introduction

The process of diffusion of atoms or molecules in solids is a very extensively studied subject. Unlike the gas and liquid phases, where the process of diffusion of is easily observed, diffusion into the solid phase is relatively difficult to characterize experimentally. The process of diffusion in solids is very important however and its understanding and control has found many uses in science and technology such as in the fabrication of pn junction devices.

C_{60} solid films are interesting solids for the study of diffusion. The lattice, assuming a crystalline solid, is a relatively open structure: C_{60} molecules are spheres of approximately 7 Å located on a lattice with lattice constant of approximately 10 Å [14, 52]. There are large interstices between the C_{60} molecules that could accommodate almost any atom. Thus the effective activation energy involved in the diffusion process should be smaller, relative to other covalent or ionic solids with smaller lattice constants.

People have demonstrated that alkali metals and oxygen can diffuse into C_{60} readily, altering the electrical and optical behavior of C_{60}[14, 52, 36] [13, 29, 23]. Diffusion of alkali metal atoms into C_{60} results in the formation of ionic compounds of the form A_{x}C_{60} where A is an alkali metal and x is between 3 and 6. Controlled ambient studies of the conductivity decrease in C_{60}, demonstrate that oxygen can easily diffuse into the bulk of C_{60} films [11].

X-ray and electron diffraction studies on thin films of C_{60} reveal a somewhat disordered mixture of hexagonal-close-packed(hcp) lattice [52], and face-centered-cubic(fcc) lattice [14]. STM images of C_{60} thin films provide additional evidence for this randomness[28, 55, 21]. It is well known that the positions taken up by the third layer in stacking of close-packed lattices determine the ratio of different types[49]. STM studies have also shown that very amorphous films of C_{60} are produced for certain growth conditions[21]. This is consistent with the spherically symmetrical shape
of C$_{60}$, since the two arrangement ABABAB (for hcp) or ABCABC... (for fcc) would be equally likely to nucleate in the absence of any symmetry breaking species. In an fcc lattice there are three interstitial sites available per each C$_{60}$ molecule. Two of the sites provide tetrahedral coordination (four nearest neighbors) and one allows octahedral coordination (six nearest neighbors)[14]. However, the intercalating species can often overcome the weak van der Waals forces holding the lattice, and cause it to expand and transform to a different structure like the bcc (body-centered-cubic) lattice[14].

Diffusion of particles into a solid is critically dependent upon the crystal structure, which determines the atomic forces and therefore the activation energy for hopping of diffusants. It is our purpose in this chapter to study the process of diffusion of silver into C$_{60}$.

4.1.1 Sandwich structures

To study a semiconducting material's electrical and optical properties, it is convenient to employ what we call a sandwich structure. The material of interest is grown as a thin film sandwiched between two conducting planes that constitute the electrodes. Thus one could apply strong electric fields. By employing partially-transparent electrodes, one can subject the material to simultaneous optical excitation. Sandwich structures are also important for studying metal-semiconductor contacts. The choice was to build structures of C$_{60}$ sandwiched between noble metals like silver or gold that are good conductors and not chemically very reactive in atmosphere. Fig 4.1 depicts an ideal sandwich structure.

![Figure 4.1: An ideal Sandwich structure](image)
4.1.2 Observations that indicated diffusion of silver into C\textsubscript{60}

The goal of our initial experiments was to fabricate reliable sandwich structures of C\textsubscript{60}. A bottom metal layer was deposited, followed by deposition of the C\textsubscript{60} layer and then using a shadow-mask, deposit an array of silver contacts of area \(\sim 5\text{mm}^2\) onto the top surface of the C\textsubscript{60} layer. This pattern of metallization would constitute the top electrode. A single one 2.5cm\(\times\)2.5cm substrate could make over forty such sandwich structures.

It was often found that the two electrodes were electrically short-circuited. Dust incorporated into the structure can cause pinholes in the C\textsubscript{60} and cause devices to be shorted. However, there would be instances when all devices on a substrate would turn out not to be short-circuited. This kind of binary behavior indicated that dust was not the reason for short-circuited devices, in which case the yield of 'good' and 'bad' devices would be statistical. Furthermore, the batch of devices on a substrate that would turn out to be 'good', exhibited variations in resistivity that are much larger than would be expected from the variation in thickness of C\textsubscript{60} from the center to the edge of the substrate. The thickness variation was about a factor of two, as evident from the optical fringe pattern on the substrate. However, the variation in resistivity was often in excess of one thousand.

Capacitance and conductance of each of these devices was measured. A Hewlett-Packard 4280 1MHz C-Meter/C-V plotter was used for these measurements. The devices were held by a vacuum chuck inside a light-proof box and probed using tungsten tipped(\(\sim 200\mu\text{m}\)) Micromanipulator XYZ probe holders. The devices were kept in the dark during the measurement to avoid errors due to photoconductivity and other possible effects. The idea was to obtain information on the material properties of C\textsubscript{60} that did not depend on precise sample geometry. Capacitance, \(C \sim \epsilon A/d\) where \(\epsilon\) is the permittivity of the medium, \(A\) is the effective area and \(d\) the effective distance between the electrodes. Similarly, Conductance, \(G \sim \sigma A/d\), where \(\sigma\) is the conductivity of the medium. Thus the ratio of the capacitance to the conductance, \(C/G = \epsilon/\sigma\), a value which should depend upon material properties of C\textsubscript{60} only. The \(C/G\) ratio on devices differed from substrate to substrate by a factor of 2–5. The conclusion drawn was that the electrical properties of C\textsubscript{60} were modified by the fabrication process.
4.1.3 Explanation based on a diffusion model

The above observations could be reconciled if one assumed diffusion of silver atoms into C_{60} during the top-metallization step. Fig 4.2 illustrates a non-ideal sandwich structure in the presence of diffusion of atoms. The electrical permittivity and conductivity of undoped C_{60} would be different from the ‘doped’ case, in general. Radiative heating of the substrate from the hot furnace could cause diffusion of metal atoms into the lattice. The experimentally verified temperature rise of substrates, measured by a type-K thermocouple attached to the substrate, for different furnace temperatures used for the sublimation of silver was in the range of 100-150°C. Also, as experimentally observed, the doping process tends to give metallic conductivity to C_{60}. This has been demonstrated for the alkali metals[36, 13, 29, 23]. Thus in effect we have our top electrode reaching below the top surface of the C_{60} layer. This could give rise to large variations in observed resistance across the sample, from the center to the edge of the substrate, as indicated in Fig 4.2.

4.2 Theoretical study of Diffusion in solids

For the purpose of analysis we will assume that the one-dimensional solution of the diffusion equation is valid for the experiments’ geometry. If the diffusion coefficient, D, is independent of the concentration, N(x,t), of the diffusing particles, at time t, Fick’s equations can be stated in the form:

Figure 4.2: Non-ideal Sandwich structure
\[ J(x, t) = -D \frac{dN(x, t)}{dx} \]  

(4.1)

and

\[ \frac{dN(x, t)}{dt} = D \frac{d^2N(x, t)}{dx^2}. \]  

(4.2)

Equation 4.1 is known as Fick's first law and describes the rate of permeation under steady state. Equation 4.2 is known as Fick's second law and it describes the rate of accumulation of the diffusing species at different points in the medium and as a function of time. This equation therefore applies to transient processes. Employing the separation of variables technique the above equations can be solved [3] for the boundary conditions of a semi-infinite medium to give us the general solution of the concentration as a function of position and time:

\[ N(x, t) = \frac{1}{2\sqrt{\pi Dt}} \int_{0}^{\infty} [N(\xi, 0)e^{-\frac{(\xi-x)^2}{4Dt}} + N_1(-\xi, 0)e^{-\frac{(\xi+x)^2}{4Dt}}]d\xi. \]  

(4.3)

The solution contains the unknown function \( N_1(-\xi, 0) \) which is often evaluated by applying the appropriate boundary conditions. For our problem of incoming silver atoms onto a C_60 medium, we have essentially a constant source and diffusing species enter the semi-infinite body at the plane \( x = 0 \). Thus our boundary and initial conditions could be stated as:

\[ N(0, t) \big|_{t \neq 0} = N_0 \]  

(4.4)

\[ N(x, 0) = 0 \]  

(4.5)

The solution under the indicated boundary and initial conditions take the form:[3]

\[ N(x, t) = N_0 erfc \left( \frac{x}{2\sqrt{Dt}} \right), \]  

(4.6)

where \( erfc(x) \) is defined by the following equation:

\[ erfc(x) = 1 - \frac{2}{\sqrt{\pi}} \int_{0}^{x} e^{-z^2} dz. \]  

(4.7)

Here \( N_0 \) is the concentration of the diffusing particles at \( x = 0 \). Thus \( N_0 \) would depend upon the incident flux rate and would be limited by the solid solubility limit of the silver in C_60. The total number, \( Q(t) \), of diffusants entering the body, per unit area, at the boundary \( x = 0 \), at time \( t \), will be given by:
\[ Q(t) = \int_0^t J(x, t) \mid_{x=0} \, dt \]  \hspace{1cm} (4.8)

where \( J(x, t) \) is obtained from Fick's first law to be:

\[ J(x, t) \mid_{x=0} = DN_0 \left( \frac{d}{dx} \left[ \text{erfc} \left( \frac{x}{2\sqrt{Dt}} \right) \right] \right) \mid_{x=0} \]  \hspace{1cm} (4.9)

The final closed form expression for \( Q(t) \) is given by:

\[ Q(t) = 2N_0 \sqrt{\frac{Dt}{\pi}}. \]  \hspace{1cm} (4.10)

The important conclusion is this: if a certain property or phenomenon under study depends linearly on the number of diffusing particles within the body, and if Fick's laws hold, then that property itself should have the square-root dependence on time that \( Q \) has.

### 4.3 Device structure employed to study diffusion

In order to study diffusion in solids, researchers have employed several techniques [3, 1]. There are several direct methods such as radiochemical, chemical, and X-ray methods, ion mass spectroscopy, atomic absorption, etc. Traditionally, radiotracers were used in accurate determinations of the depth profile of the diffused species. At present ion beam techniques of almost equal precision are used. In microelectronics, diffusion into semiconductors is often determined by step-wise etching of the surface and determining the concentration of the diffusing particle by suitable methods[4]. Indirect, non-destructive, determinations of diffusion profiles is popular in semiconductors using techniques such as measurement of diode-capacitance, conductivity, or optical reflectance. One convenient method to study diffusion is by measurement of resistivity of the sample into which diffusion is allowed to occur [3]. However, this technique is necessarily limited to diffusants that act as donors or acceptors in the host lattice. Based on the empirical observation that silver modifies the conductivity of \( C_{60} \), it was decided to use resistivity measurements to study the diffusion of silver into \( C_{60} \) thin films. The steps followed to fabricate the samples are illustrated in Fig 4.3. Everything was done in a vacuum of \( \sim 10^{-6} \) torr, to avoid possible complication from atmospheric oxidation[11, 46].

The structure of the device employed to study diffusion is indicated in Fig 4.4. Approximate dimensions for the devices fabricated were: \( a = c = 3.5 \text{mm}; w = 10 \text{mm}; \)
1 = 7mm; and the film thickness, $t \sim 0.5\mu m$. When the temperature of the film is raised to 50 – 60°C above room temperature, there would be significant conductivity between the bottom electrodes due to thermal excitation of carriers in $C_{60}$ and a current could flow across the planes P1 and P2. Typically, one would measure about 100 MΩ between the bottom electrodes before the top electrode is deposited. If one considers the sections between the planes P1 and Q1, the resistance of this structure between the bottom and top electrode would be $\sim 10^{-7} - 10^{-8}$ times the resistance measured between the bottom electrodes, i.e. about a few ohms at the most. Planes P1 and P2 would be almost equipotential surfaces, and one could consider the conductivity modulation, due to diffusion of silver, between the equipotential planes P1 and P2 only.

Fig 4.5 illustrates the region between planes P1 and P2. Silver atoms diffuse into the ‘slab’ at $x=0$ and establish a concentration profile indicated by $N(x, t)$, at a given time $t$. If one models the conductance between the planes P1-P2 as due to several conductances in parallel, one could obtain an expression for the conductance as a function of time. The conductance of a differential element at $x, \Delta G$, would be given by the expression:
\[ \Delta G(x,t) = \sigma(x,t) \frac{w \Delta x}{l} = (N(x,t)q\mu) \frac{w \Delta x}{l} \] (4.11)

Where \( q \) is the charge carrier contributed to the C_{60} lattice per each silver atom, and \( \mu \) is the mobility of the charge carrier at the temperature of the lattice and \( w \) and \( l \) are the width and length of the device, indicated in Fig 4.5. Since, conductances add up in parallel, the total *additional* conductance due to introduction of ‘dopant’ atoms could be obtained by integrating \( \Delta G(x,t) \) over \( x \). This gives the conductance as a function of time:

\[ G(t) = \int_0^{\infty} \Delta G = \int_0^{\infty} \left( \frac{q\mu w}{l} \right) N(x,t)dx = \left( \frac{q\mu w}{l} \right) \int_0^{\infty} N(x,t)dx. \] (4.12)

However, \( Q(t) = \int_0^{\infty} N(x,t)dx \) and so the final expression for the total additional conductance, \( G(t) \), is given by Eqn 4.13. This also shows a dependence on the square-root of time:

\[ G(t) = \left( \frac{2N_0q\mu w}{b\sqrt{\pi}} \right) \sqrt{Dt}. \] (4.13)
4.4 Assumptions of the model

The model assumes the following:

1. The C$_{60}$ film is a semi-infinite medium in the calculation. This approximation would be valid only for the initial deposition. As $t$ increases, there would be 'reflection' of diffusants from the substrate end of the C$_{60}$ thin film.

2. Sufficiently low deposition of silver is assumed, otherwise one could form a highly conducting plane at $x=0$, that would short-circuit the conductance between the planes P1 and P2.

3. The diffusant is a donor. If the electronic interaction of the diffusant causes a reduction in the total number of carriers, that are already present by virtue of thermal excitation, then $\Delta G(t)$ would have a negative sign.

4. The mobility is independent of the concentration of the diffusants. This is not a bad approximation if we are working at above-room-temperature regime. Only at low temperatures does impurity scattering play a significant role in mobility changes.

5. The diffusant atoms are chemically non-reactive with the C$_{60}$ molecules.
6. Complications from non-crystallinity and grain-boundaries in C₆₀ are absent.

4.5 Experiment

A quartz substrate, 2.5cm × 2.5cm was cleaned by the standard procedure described in Chapter 2. Compared to glass, quartz had a low leakage current at the temperatures of interest. Electrical contacts were made to the substrate with colloidal-silver. After reaching a base vacuum of \( \sim 10^{-6} \) Torr, the bottom electrodes were deposited using a shadow-mask. A type-K thermocouple was mounted on top of the substrate to allow more accurate determination of the substrate temperature. Fig 4.6 indicates the electrical connections made to the substrate.

Before silver deposition, there was infinite (> 200GΩ) resistance between terminal T1 and TC1 or TC2. After deposition of a few hundred angstroms of silver through a shadow mask, the resistance between TC1 or TC2 and T1 would be only a few ohms. However, the resistance between T1 and T2 would continue to be > 200GΩ, since there would be no conducting bridge between them. This procedure ensured that the bottom electrodes are good and there is no leakage between the T1 and T2 terminals.

This was followed by deposition of the C₆₀ layer. C₆₀ layers of thicknesses of about 0.5μm were typically grown. An Arrhenius plot of the 'intrinsic' sample indicated that the threshold of intrinsic conductivity was about 1.5–1.6 eV. Fig 4.7 shows the plot obtained in the temperature range 324–396K.

![Figure 4.6: Electrical connections for diffusion experiment](image-url)
Figure 4.7: Arrhenius plot of sample just before silver diffusion

Next, the substrate was heated to 70–80°Celsius. The silver furnace was heated to the sublimation temperature, and the system was allowed to reach thermal equilibrium.

Deposition of silver was made in small increments. At intervals of 10–15 minutes, silver was deposited for about 1 min at a time, and then turned away from the furnace. The flux rate from the silver furnace, typically 1–5 Å/min, determines the quantity of silver deposited in that time interval. So a 1 min exposure would imply a deposition corresponding to about a monolayer of silver. Radiative heating from the furnace would also cause the conductivity to increase, due to thermal excitation, and also diffusion to proceed during the small time intervals when the substrate receives silver atoms. Subsequently, the substrate would be allowed to cool down to its initial, equilibrium temperature, and diffusion would be practically quenched. Once the sample reaches equilibrium, one may assume the thermally activated current to have reached its initial value. Any change in the conductivity would therefore be due to diffusants within the C\textsubscript{60}. Fig 4.8 is the plot of the current against t\textsuperscript{\frac{1}{2}}. Arrhenius plot of the sample immediately following the compensation of C\textsubscript{60} indicated little change in the 'gap'.

Next, the sample was subjected to further doses of silver until the current through the device increased exponentially with total dose of silver. At this stage, silver
deposition was stopped and an Arrhenius plot was immediately obtained. Fig 4.9 shows the plot. The ‘gap’ decreased by ~0.5eV. On maintaining the device at ~100°C for several hours, and subsequently measuring the Arrhenius behavior, one observes the tendency for the ‘gap’ to recover to its intrinsic value as indicated in Fig 4.10.

4.5.1 Observations

For temperatures in the neighborhood of 380K, initial deposition of silver causes a reduction in the total current. This reduction would continue until the total silver deposition is about a few tens of monolayers. Subsequent to this, the current would increase exponentially with additional silver flux. The onset of this exponential rise is dependent on substrate temperature, and is delayed for higher temperatures. On plotting the current against the square-root of the number of silver atoms deposited, we observe a straight line, the slope of which is larger at higher temperatures. The gap does not change significantly when the dose of silver atoms is still in the square-root regime, but decreases significantly for doses in the exponential regime of conductivity. Also, the Arrhenius plot indicates a distinct curvature (Fig 4.9 shows a steeper slope at higher temperatures). Maintaining the substrate at high temperature for long times...
Figure 4.9: Reduction in threshold of intrinsic conductivity with Ag doping

Figure 4.10: Recovery of 'gap' towards intrinsic value
causes the gap to increase and tend to recover towards the initial intrinsic value. Undoped samples that are kept at elevated temperatures for long times however, show a reduction in the gap.

4.5.2 Results and Explanation

The resistance, at room temperature, between the bottom electrodes, before the top silver deposition, was measured to be approximately $\sim 5G\Omega$. Assuming a film thickness of $1\mu m$, the intrinsic conductivity, $\sigma$, at room temperature, in the dark, is calculated to be $5.6 \pm 1.0 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$. This is in good agreement with conductivity values obtained by in-situ measurements by other researchers [11], reporting $\sigma$ at room temperature to be approximately $8.3 \times 10^{-7} \Omega^{-1} \text{cm}^{-1}$. There is a very large change in the conductivity for samples exposed to oxygen and light[11] [31, 22, 30]. The quantity of silver deposition that causes almost zero resistance between the bottom electrodes is $\sim 50 - 100\AA$. On a control substrate with no C$_{60}$ layer, this quantity of silver produced no conduction between the bottom electrodes. It would take $\sim 400 - 500\AA$ of silver to show conduction between the bottom electrodes of the control sample. Assuming $\sigma = 1\Omega^{-1} \text{cm}^{-1}$, the resistance between the bottom electrodes at room temperature would be a few k$\Omega$. However, the measured resistance between the bottom electrodes decrease all the way to a short-circuit. Thus it could be estimated that the conductivity of C$_{60}$ changes by at least six orders of magnitude by doping with silver. More accurate estimates are possible when the diffusion profile is precisely known.

We interpret our data and observations as follows: The decrease in the current with initial doses of silver is due to compensation of holes in the 'valence band' of C$_{60}$. At elevated temperatures, where the diffusion experiment was carried out, there would be many electrons and holes available due to thermal excitation across the gap. Assuming the electron mobility in C$_{60}$ is $\sim 100 \text{ V}^{-1}\text{cm}^{2}\text{sec}^{-1}$, at 400K there would be $\sim 10^{17}\text{cm}^{-3}$ number of electrons and holes. At room temperature it would be smaller by 4-5 orders of magnitude. Thus the initial dose of silver, assuming the silver energy level is well inside the bandgap of C$_{60}$, would tend to contribute its valence electron to compensate the large number of holes present. This would lead to a reduction in the total number of free carriers, and so cause the conductivity to decrease. The reduction in the current would be directly proportional to the number of compensated holes, which would be proportional to the number of silver atoms.
introduced, and so exhibit a square-root dependence on the dose of silver atoms. Similar systems consisting of compensation due to diffusion of mercury in selenium has been reported[3]. This square-root regime is consistent with the observation that the measured threshold of conductivity, that does not show significant change from its intrinsic value—all the silver atoms are ionized and so they are not able to donate electrons to the conduction band. However, at increasing dosage, the compensation process ceases and the silver is able to donate its electron into the conduction band of C$_{60}$. The activation energy measured for silver is $\sim 0.61$ eV in the low temperature regime, and increases continuously to $\sim 1.06$ eV in the high temperature regime as indicated in Fig 4.9. Fig 4.11 explains why this might occur.

At higher temperatures, more and more silver levels within the gap would be ionized and this would effectively increase the activation energy for the next lowest levels. From the experiment, $E_{\text{min}} = 0.61$ eV, $E_{\text{max}} = 1.06$ eV and $E_i = 1.62$ eV for this sample. The introduction of energy levels within the gap proves that silver interacts electronically within the C$_{60}$ lattice.

The recovery phase of the threshold for intrinsic conductivity is probably due to migration and subsequent clusterring of silver atoms within the interstices of C$_{60}$, due to continued hopping of the silver atoms at elevated temperature. It is probably energetically favorable for the silver atoms to cluster together, as compared to

![Diagram](image_url)

**Figure 4.11:** Explaining the increase in activation energy with temperature
remaining isolated or ionized. Once in cluster form, the energy levels would change, and the mechanism of interaction with the C60 could be different.

By performing the experiment at different substrate temperatures, one could obtain the activation energy, $E_a$ for the diffusion process. Equation 4.13 gives the temperature dependence of the slope in a plot of Current vs $\sqrt{t}$, as shown in Fig 4.8. If $D = D_0 \exp(-E_a/k_BT)$ is the assumed temperature dependence for the diffusion coefficient, then for identical flux rates, and for mobility, $\mu = $ constant within the temperature range being considered, one arrives at the condition that the slope $\propto \sqrt{D}$. Thus, slope $S$ satisfies:

$$S \propto \exp \left( -\frac{E_a}{2k_BT} \right).$$

(4.14)

Plotting a graph of $\ln S$ against $1/T$, the slope should be numerically equal to $E_a/2k_B$. Fig 4.12 shows such a plot with experimentally obtained data points. The units for $S_I$ does not matter, since any constant multiplier would feature as a constant intercept in such a plot, and is therefore irrelevant for obtaining the activation energy for the hopping process in diffusion. Experimentally a value of approximately 2.5 eV is obtained, which is in the same range, 2–4 eV, as that for other diffusing species in germanium[3]. However, since C60 has a large lattice constant 5 times an ‘atomic’

![Figure 4.12: Obtaining the activation energy from diffusion data](image-url)
solid, the diffusion coefficient at a given temperature would be approximately 25 times larger [3] since one could write [3],

\[ D = \frac{\delta^2}{6\tau_0} \exp \left( -\frac{E_a}{k_B T} \right), \]  

(4.15)

where \( \delta \) is the shortest distance between two equilibrium positions (neighboring lattice or interstitial sites), and \( \tau_0 \) is a constant of the same order of magnitude as the natural period of vibration of the atoms in the crystal lattice, approximately \( 10^{-13} \) seconds. In summary, one can say that silver readily diffuses into C\(_{60}\) thin films.

4.6 Discussion

It is observed that silver diffuses readily through C\(_{60}\) solid films. The property we measure is indirect. We measure the resistance of the sample, and estimate the quantity of silver that diffused into the sample. It is clear that silver is interacting electronically with the C\(_{60}\) host. Also, at temperatures around 300K, C\(_{60}\) molecules rotate at very high rate(\( \sim 1.8 \times 10^9 \) revolutions per second). Thus the silver atom, assuming it occupies some interstitial site in the C\(_{60}\) lattice could not be attached to any specific carbon atom on the C\(_{60}\) cage. All the silver could conceivably see is a cloud of charge around the cage. Any interaction between the two species could at best be in the timescale of nanoseconds. And so silver could interact electronically with the C\(_{60}\) molecule. It has been reported that at low temperatures, silver does form a complex of the kind AgC\(_{60}\) and such a complex seems to be nonexistent at higher temperatures[18].
Chapter 5

Excimer Laser Induced Electrical Conductivity in Thin-Film C\textsubscript{60}

5.1 Introduction

The fabrication of solid structures with typical dimensions well below the 1\(\mu\)m range is of great interest for a number of fascinating applications. There is constant ongoing research for new methods and processes to shrink device size in microelectronics. Excimer lasers have found their way into this domain for two reasons:

1. As an alternative to the usual sophisticated photolithographic process employed in fabrication of sub-micron structures and patterns.

2. As a tool to modify material properties.

It has been demonstrated that periodic line structures with periods as small as 30 \text{nm} can be produced in polyimide by direct ablation using an interferometric technique\cite{15, 16}. Traditionally, more sophisticated photolithographic techniques are used to generate such structures. Excimer laser processing of materials could also modify physical properties, such as electrical conductivity, through a laser induced metal-insulator transition\cite{32}. Coupled with the 0.1 \(\mu\)m spatial resolution, new potential applications may be considered.

Previously, laser induced metal-insulator phase transitions have been demonstrated exclusively with polymers like Kapton\cite{47, 17}. Laser processing of fullerenes presents not only many potential new applications, but also an opportunity to investigate the physics involved in laser induced modifications of a fullerenes and other semiconducting material.

The technological uncertainty involved in the fabrication of electrodes to C\textsubscript{60} sandwich cells was discussed in Chapter 4. Excimer laser induced conductivity change in C\textsubscript{60} films allow the possibility to fabricate electrodes to such structures that are essentially ‘impurity’ free. In principle, the change in conductivity could be carried
out inside vacuum by directing excimer laser radiation through a quartz window and onto the sample. In this chapter we present the results of utilizing excimer lasers to increase the electrical conductivity of thin film C₆₀.

5.2 Experimental Setup and Discussion

C₆₀ films were grown on quartz or glass substrates by sublimation of commercially available solid purified C₆₀ (Polygon Enterprise) with labelled purity of 99%. Trace amounts of C₇₀ were present. It was assumed that the controlling species would be C₆₀. The C₆₀ powder was ‘conditioned’ to remove trace amounts of solvents by keeping it in a heated vacuum dessicator at above 200°C for several days. The vacuum was ~10 millitorr. Subsequently the powder was stored in bottles and kept inside a dessicator, in the dark. This procedure was followed based on experimental evidence that trace amounts of solvents used during purification stages are responsible for degradation of the films kept in oxygen[38, 11]. The sublimation was carried out in our vacuum chamber with furnace temperature at about 460–475°C. The base vacuum during sublimation was ~ 10⁻⁶ torr.

The substrates were 2.5cm by 2.5cm in size. Quartz substrates were used for the experiments to determine the ablation threshold, and glass was used for the conductivity measurement experiments. The procedure outlined in Chapter 2, section 2.4, was followed to clean the substrates. During sublimation, the flux rate of C₆₀ was monitored at intervals of 30min–1hr using the quartz crystal thickness monitor. Because the flux of C₆₀ decreased with time, such measurements allowed fairly accurate (within ~10%) estimate of the film thickness by approximating the flux rate in a given interval as equal to the average of the starting and ending flux rates for that interval of time. Typically, average flux rates of ~30 Å/min was used. Once the films were grown, they were stored inside a vacuum dissicator till they were ready for use in the experiment.

5.2.1 Determination of the Ablation Threshold and Absorption Coefficient

A uniform portion of the output of an injection controlled KrF laser was attenuated, using a beam-splitter, and then focussed slightly to a 3mm diameter spot on films deposited on quartz. By rotating the beam-splitter, variable amount of power could be transmitted, without changing the spot size on the sample. Fig 5.1 illustrates the arrangement.
Irradiation was performed in air. The incident fluence was calculated by dividing the energy transmitted through the focusing lens by the spot size on the sample. Different fluences were obtained by varying the attenuation of the beam, while maintaining a constant spot size. The C₆₀ films used were deposited on quartz substrates with a thickness of approximately 3000 Å, and were optically thick at the fluences used. The etch rate was determined by counting the number of laser shots required to obtain transmission of the laser light through the C₆₀ film. A uv fluorescent business-card was used to 'see' the ultraviolet light (248nm) The results of these experiments are shown in Fig 5.2. The etch depth per pulse increases linearly with the logarithm of the fluence, for the fluences used.

Each laser shot ablates a certain depth of the C₆₀ film, for fluences above a threshold fluence, \( F_{th} \). Assuming a Beer's law type of absorption:

\[
F(x) = F_0 \exp(-\alpha x),
\]

(5.1)

where \( F_0 \) is the fluence incident on the thin film. We have, by definition of etch depth per shot or ablation depth, \( d \), the equation:

\[
F_{th} = F_0 \exp(-\alpha d). 
\]

(5.2)

Equation 5.2 tell us that since \( d \) is the etch depth, for \( x > d \) the fluence would be below the threshold fluence, \( F_{th} \), and so there would be no more ablation for \( x > d \). Rewriting Eqn 5.2 gives the relation for etch depth per shot as a function of the incident fluence \( F_0 \):

\[
d(F_0) = \frac{1}{\alpha} \ln \left( \frac{F_0}{F_{th}} \right).
\]

(5.3)
Figure 5.2: Etched depth per laser shot as a function of incident fluence.

Thus assuming an exponential penetration depth of the laser radiation, the etch depth per shot plotted against the logarithm of the incident fluence, $F_0$, should give a straight line whose intercept on the fluence axis, corresponding to zero etch depth per shot, would give $F_{th}$. The experimentally measured threshold fluence for ablation is $20\pm2$ mJ/cm$^2$. Furthermore, the absorption coefficient, $\alpha$, at 248nm can be determined to be $6.2\pm0.6\times10^5$ cm$^{-1}$, obtained by using Eqn 5.3 with known incident fluence and etch depth per shot. This result may be compared with a previously reported value of $4.7\times10^5$ cm$^{-1}$ obtained by ellipsometric measurements at the same wavelength[44].

The fit with experimental data confirms the assumptions of Beer's law in the range of fluences used in this experiment($\sim100$mJ/cm$^2$). For higher fluences there could be deviation from linearity due to effects like saturation—number of photons available in excess of what could be absorbed by the medium, etc.

5.2.2 Changing Electrical Conductivity of C$_{60}$ Thin Films

Once the ablation threshold was known, experiments were conducted with C$_{60}$ thin films by exposing them to varying amounts of excimer laser radiation with each
shot below the threshold fluence. Thus the change in material property like electrical conductivity can be studied as a function of total dose.

C₆₀ films with thicknesses of 4000-5000Å was deposited on glass substrates and irradiated in air with a fluence of 17mJ/cm², which is slightly below the ablation threshold. Fig 5.3 illustrates the experimental arrangement for this part of the experiment.

In these experiments, a uniform portion of the laser output was expanded with a diverging lens. The fluence was determined by measuring the energy through a fixed aperture (6mm dia.) located in the sample plane. Samples were rotated at ~10 revolution/min to ensure more uniform irradiation. The KrF laser emitted 30ns full width half maximum (FWHM) pulses with a repetition rate between 0.5 and 8 Hz. A slower repetition rate was chosen (~1Hz) to allow easy counting of the number of laser shots, manually. Samples were obtained that had doses equivalent to 50,100,150,200,300,400,600,800 and 1000 shots. A 3 mm by 5 mm aperture was placed over the sample to define the irradiated area. The irradiated regions had a visibly different appearance, and were somewhat less reflecting as compared to bare C₆₀.

Contacts were made with colloidal sliver such that a conducting region of 3 mm by 2 mm was measured. Care was taken to isolate each conducting ‘pad’ from the other conducting regions on the same substrate and from non-irradiated C₆₀. The simple method of cutting through the thin film using a sharp razor blade, to create electrical discontinuity, was used. The electrical conductivities were determined by measuring the dc resistance between the contacts using a Hewlett Packard 4145A Semiconductor

![Diagram](image)

**Figure 5.3: Changing the electrical conductivity of C₆₀ films**
Parameter Analyzer. Voltage-current measurements of the highly conducting samples revealed that the contacts were ohmic. This was consistent with our earlier result that C\textsubscript{60} forms ohmic contact with silver, although not known currently, the detailed chemical nature of these conducting regions. Samples at the conductivity threshold, however, exhibited non-ohmic voltage-current characteristics.

Fig 5.4 shows the result of these measurements. Sheet conductivity (conductivity times depth) is plotted as a function of the number of laser shots at 17mJ/cm\textsuperscript{2} per shot. The measured sheet conductivity for unirradiated C\textsubscript{60} was limited by the accuracy of our equipment, but is on the same order as that of undoped C\textsubscript{60} in air, as measured in other experiments [11].

There was no significant change in the electrical conductivity of the irradiated samples, corresponding to currents less than \(~10\) pA at 5 V, until a critical number of laser shots of approximately 200 was reached. Above this critical number of shots, the conductivity increases sharply over seven orders of magnitude until it begins to saturate for more than 800 shots. This sharp change in conductivity is consistent with a laser induced metal-insulator phase transition as seen in other systems[32, 47]. The actual depth of the conducting region is unknown, but can be estimated to be on the order of the absorption depth of the laser which is approximately 20nm, obtained

![Figure 5.4: Change of sheet conductivity as a function of number of laser shots.](image)
earlier from $\alpha$. Assuming this depth for the conducting region, the conductivity of the highly irradiated samples are on the order of $10^{-1}$ cm$^{-1}$. This value for the conductivity is consistent with that of amorphous carbon or graphite[2]. These observations are analogous to the conductivity changes that were observed previously with excimer laser irradiated polymers[16, 47, 32].

Contrary to polymer samples, however, laser induced electrical conductivity in C$_{60}$ changed with time after irradiation. Fig 5.5 shows the electrical conductivity of six samples, each normalized to its conductivity on the first day, as a function of time. Immediately after irradiation, the samples were placed in a vacuum chamber at a pressure of $\sim 10^{-3}$ Torr. Electrical measurements were made each day and the samples again stored in vacuum. The time for each measurement, during which the samples were exposed to air, was less than one hour. After one week the samples were stored in air and the measurements were again made each day. Although the actual conductivities of the different samples varied by several orders of magnitude due to different irradiation doses, the normalized conductivity of samples irradiated well above the critical number of shots displayed similar conductivity decays. For these samples, after the first few days in vacuum, there was no additional degradation.

![Conductivity Decay on Exposure to Air](image)

**Figure 5.5:** Change of sheet conductivity on exposure to air.
of conductivity. Upon exposure to air, however, the conductivity again declined by $\sim 10\%$. The rate of decay again slowed after 7 days in air. Samples near the conductivity threshold revealed a more dramatic, and often erratic, change in the conductivity. In all cases, though, the conductivity remained orders of magnitude above the conductivity of the unirradiated $C_{60}$ thin films.

A decline in conductivity has been observed for unirradiated $C_{60}$ films exposed to oxygen[11]. Oxidation may also be responsible for the observed degradation of the laser induced conductivity. Experiments with controlled atmospheres allowing site selective chemical reactions to modify the laser induced conductivity might help elucidate how this occurs.

In conclusion, this experiment demonstrates that the electrical conductivity of thin film $C_{60}$ can be increased by seven orders of magnitude by excimer laser irradiation. The all-carbon semiconductor-metallic junction produced in this process may have important technological applications.
Chapter 6

Conclusion

To conclude, it is pertinent to point out the conceived future directions and improvements that could be made to the various aspects of these experiments:

6.1 Conceivable future improvements

6.1.1 Experimental Setup

The apparatus that we used for this project evolved over time to the present configuration. However, there are still a few design changes that, if incorporated, would make an improved 'second generation' apparatus. The following useful improvements could be made:

1. It is now fairly well established [11] that trace amounts of oxygen could affect the film quality. Although the reason for this is unclear at the moment, but growing films in UHV environment could definitely elucidate or eliminate the chemistry involved in such a process.

2. With the existing configuration, the furnaces that heat the effusion cells are located only about 10cm away from the substrates. During sublimation of high melting point solids, there is a substantial amount of radiative heating of the substrates, and of the thin film overlayer of C₆₀. This heating affected our experiments. Also, it is difficult to measure the temperature rise of the thin films, since attaching a thermocouple with very small thermal mass is a difficult experimental task. A second generation apparatus could minimize heating ambiguity by increasing the distance between the furnace and the substrates.

3. The heating also affects the flux rate measurements using the thickness monitor. The resonant frequency of the quartz crystal depends upon temperature, and so a heated quartz crystal would lead to incorrect measurement of the flux rate,
and so the thickness estimates of the films fabricated. One could solve this problem, either by having a thermally insulating material to mount the quartz crystal to the substrate holder, or by having the quartz crystal sensor head mounted elsewhere.

4. In order to study the temperature dependence of properties like conductivity, etc., it is better to have a temperature controller, preferably one that can be computer controlled. The present configuration is an open loop control system. Clearly this must be improved for more accurate control of the temperature of the substrate and the furnaces.

5. It is preferable to automate the data acquisition by using for example, a PC controlled GPIB card. This is very important to accurately study a process whose time scale is under a minute for each data point that we desire to obtain. It is impractical to do manual measurements for fast processes.

6. In order to prevent film contamination during experiments in ambient, we might want to add more ports to allow optical probes to reach the substrates and do in-situ optical measurements to characterize our films.

6.1.2 Measurement of intrinsic conductivity and ‘bandgap’

The experiments used commercially available C\textsubscript{60}, known to be purified by using methods that use solvents like toluene. Empirical observations indicate that traces (~1%) of residual solvent could cause the C\textsubscript{60} to degrade in air. The observed gap for these solids show fluctuations that are not well understood and characterized at the moment. By performing experiments on ‘solvent-free’ C\textsubscript{60} in very clean environments, one could elucidate the processes responsible for changing such properties.

In-situ measurement of the gap by thermal excitation has the advantage of preventing atmospheric contamination. However, it would be nice to be able to do additional characterization of the gap using other spectroscopies.

6.1.3 Diffusion of atoms into C\textsubscript{60}

At the moment there is a fair degree of speculation in the phenomena responsible for changes in conductivity and the ‘gap’ in C\textsubscript{60}. As a result of intercalation of silver atoms, changes in the conductivity and the gap are observed. To understand the phenomena better, it is necessary to employ similar systems with controlled changes in a
few parameters. A diffusion study with gold and copper could assist in understanding chemical trends in this process.

So far there has been little investigation of doping C\textsubscript{60} into a p-type semiconductor. Alkali metals give n-type conductivity to C\textsubscript{60}, and it is therefore worth investing systems that could be p-type.

6.1.4 Excimer laser processing of C\textsubscript{60}

The all carbon metal-semiconductor junction is an interesting system. It is conceivable to incorporate diamond films in a fullerene thin film system. This allows the very interesting possibility to fabricate metal-insulator-semiconductor structures entirely out of a single element—carbon.

The metal-insulator transition could be a percolation process in twodimensions. Since the change in conductivity is thought to be restricted to the surface layer only, such a system could be convenient to study percolation networks using experimental tools like the STM that is sensitive to conductivity of surfaces.

6.2 Summary

It was the purpose of this thesis to study properties of C\textsubscript{60} in the solid state. The primary emphasis was to study properties that relate directly to its possible future use as a semiconductor material. The study has clarified several issues concerning its basic physical properties. For example, as a result of doing in-situ electrical measurements of conductivity, the role of atmospheric oxygen in conductivity degradation is appreciated. Published literature gives conductivity values for intrinsic C\textsubscript{60} in the range $10^{-7} - 10^{-14}\Omega^{-1}\text{cm}^{-1}$, and was a puzzle until recently. It was also found that diffusion of silver atoms occur inside C\textsubscript{60}(outside the cage), changing its electrical properties. Understanding processes such as these is important since they are unique to C\textsubscript{60} and are not normally observed in the more common material systems.

The study of excimer laser induced conductivity changes is important as a technological discovery. From basic research point of view too, this would allow the fabrication of 'clean' electrical contacts to C\textsubscript{60} without the associated uncertainty involved in making electrodes from sublimation of metal atoms that could diffuse into the bulk. The importance of sandwich structures was emphasized and this technique would allow one to fabricate 'good' samples on which future experiments could be
done and a more detailed picture of C₆₀ is obtained. The mechanism for conductivity changes are interesting problems by themselves.

6.3 Final remarks

At the moment there is a sizeable population of researchers all over the world trying to unfold the mysteries of this unique molecule. Every good experiment helps the entire scientific community to understand and solve the problem better. It is our hope that the present study would help in the ongoing search for knowledge in this intricate system.
Bibliography


