Investigation of Electrical Properties and Structure of Vacuum Evaporated C₆₀ Films

Angiras D. Pandya

Western Michigan University

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INVESTIGATION OF ELECTRICAL PROPERTIES AND STRUCTURE OF VACUUM EVAPORATED C₆₀ FILMS

By

Angiras D. Pandya

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Angiras D. Pandya
C$_{60}$ is an important electronic material and its properties can be tuned by thermal annealing process and solid phase crystallization process. These properties were investigated as a function of thermal annealing temperature and solid phase crystallization. However, there is no systematical study on annealing effect and Solid Phase Crystallization of C$_{60}$ films. In this study, the effect of thermal annealing on formation of nanocrystalline C$_{60}$ thin films were investigated for annealed samples and solid phase crystallized samples. The C$_{60}$ films described here were prepared by vacuum thermal evaporation method. The structural properties of C$_{60}$ films were investigated with Raman spectroscopy. The electrical properties of C$_{60}$ films were investigated with current–voltage characteristics and electrical conductivity –temperature measurements. The result indicated that the thermal annealing and solid phase crystallization process bring structural changes in the C$_{60}$ films and that resulted in change in electrical properties. The performance of the electrical properties was varied because of the transfer of the structural properties by thermal annealing and solid phase crystallization.
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CHAPTER 1

INTRODUCTION

Fullerenes are closed carbon-cage molecules containing only pentagonal and hexagonal rings, of which the celebrated icosahedral \( C_{60} \) is archetype [1]. \( C_{60} \) is a molecule that consists of 60 carbon atoms, arranged as 12 pentagons and 20 hexagons. The shape is the same as that of a soccer ball. The black pieces of leather are the pentagons, the hexagons are white. (Figure 1.1) For \( C_{60} \) there is 1812 possible structure but only one in which all the pentagons are non adjacent and thus it is the most stable isomer[2]. There are 60 different points where three of the leather patches meet. Imagine a carbon atom situated at each of these points, and you have a model of the \( C_{60} \) molecule. That model, however, is vastly out of scale. If the \( C_{60} \) molecule were the size of a soccer ball, then the soccer ball in turn would be roughly the size of the earth.

\( C_{60} \) molecules form a face-centered-cubic (FCC) solid (Figure 1.2). Here the buckyballs are represented by spheres, and the size of the spheres approximately corresponds the size of the \( C_{60} \) molecules, 10 Angstrom.[1] There is plenty of empty space between the fullerene molecules. \( C_{60} \) molecules condense to form a solid of weakly bound
molecules. This crystalline state is a new form of solid carbon, besides the long known diamond and graphite. It is called Fullerite.\cite{14} Much of the work in physics is centered on the solid phases of C\textsubscript{60}.

Figure 1.1: Fullerene (C\textsubscript{60}) molecule\cite{14}. 20 hexagons and 12 pentagons are clearly seen.

Figure 1.2: FCC Unit cell of Fullerene [14].
Structural Properties of C\textsubscript{60}

Ultrasonic measurements have revealed that the elastic module of C\textsubscript{60} polymer increase with the polymerization degree which depends on the polymerization pressure and temperature.[7] It has been showed that amorphous C\textsubscript{60} synthesized at very high pressure and temperature (~13GPa, 1850K) can scratch the diamond surface easily, with hardness exceed that of diamond making the ultra hard C\textsubscript{60} amongst the hardest known materials.[1]

The inverse transmission spectra for 1D and 2D polymers indicate that raising the polymerization temperature shifts the absorption edge to lower energies, showing that the polymers are semiconductors [8]. The distance between each pair of atoms in the C\textsubscript{60} molecule is about 1.37-1.44 Å[15].X-ray diffraction studies show that C\textsubscript{60}, as is expected, has a face center cubic (fcc) crystalline -structure and the center of the cubes are more than 10.4 Å[15] Raman studies shows that will increase in the pressure and temperature strongly affects the degree of polymerization and thereby other properties related to polymerization[4].
Electrical Properties of C$_{60}$

If we talk about electrical properties, the very first time that we would like to know about is it’s conductivity properties. Generally, the conductivity of C$_{60}$ increases with the degree of polymerization and depends on their structure and the type of the bonds between carbon atoms[1][4][12]. Strong covalent bonding between the cages and, as a consequence, the reduction of number of π-electrons in C$_{60}$ change the electronic properties of the fullerite.[16] A linear C$_{60}$ chain has been found to be semiconductive with a finite band gap of 1.148 eV and almost pure σ-type intermolecular bonding.[16]

1D plasma-polymerized C$_{60}$ acts as a p-type semiconductor in contradiction to the n-type semiconductor behavior of pristine C$_{60}$.[1] In addition, it has been demonstrated that electron-doping by alkali-metals of pristine C$_{60}$ forms 1D polymer spontaneously and causes a metallic conductivity.[1][4][6]

Highly-oriented C$_{60}$ polymer shows a gigantic conductivity anisotropy. Conductivity in the polymerized planes shows super conducting behavior and the out-of-plane one is semiconductor-like behavior.[1] A randomly oriented polymer shows a semiconductor behavior and obeys the Arrhenius law [4].
Both semimetallic and semiconducting behaviors have been observed in the electrical resistivity measurement on samples with disordered structures synthesized from pure C$_{60}$[1].

**Application of C$_{60}$ Thin Films**

High-quality crystalline C$_{60}$ thin films have been grown successfully on many substrates and studied extensively for the understanding of growth mechanisms of fullerene films and for their unique properties and potential electronic applications. Electronic devices comprising C$_{60}$ films in their structures such as rectifying electronic diodes[10], photo-diodes and solar cells[10], Metal-insulator-semiconductor[10], field-effect transistors (MISFETs)[9], showing very stable, reproducible performances and excellent device characteristics, has been manufactured.

In the present work, we concentrate our interest in electronic properties and structural changes because of different Annealing temperature and solid phase crystallization. It is now well known that if pure C$_{60}$ is subjected to a high temperature, some intramolecular bonds may break up and re-form as intermolecular bonds, such that the material is converted into a pure carbon polymer consisting of
covalently linked fullerene cages [4][12]. A large number of different structural phases, both crystalline and amorphous, have been observed, and some of these have already been well studied and characterize. Structural changes in C₆₀ films were investigated using Raman spectroscopy because Raman spectroscopy is quite sensitive to the structure of crystalline carbon and therefore, it is a powerful tool to examine the structural changes in carbon.
CHAPTER 2

PREPARATION AND EXPERIMENTAL BACKGROUND

The experimental procedure followed in the present research are shown in figure 2.1.

![Flowchart of experimental procedure.](image)

Figure 2.1: Flowchart of experimental procedure.
Preparation of The Specimen

Substrate Cleaning

It is very important to clean the substrate carefully because any leftover impurity on the substrate may give some erroneous result in investigation of C$_{60}$. Substrates were cleaned using following process.

1. Immersion in concentrated acid for 30 seconds.

2. 5 minutes of ultrasonication with distilled water

3. 5 minutes of ultrasonification with acetone

4. Drying with N$_2$ Gun

Types of Substrate used:

1. n type Silicone substrate
2. alkaline glass substrate

Preparation of Filament

In whole study we deposited only C$_{60}$ and Aluminum on above mentioned substrates. The C$_{60}$ was available in powdered form. There
fore, it was deposited using commercial tantalum boat and Aluminum was available in wire form, therefore, it was deposited using tungsten wire of 0.5mm diameter. It was made in V-shape and aluminum wire was wrapped over the V-shape to be evaporated. It is essential to clean tungsten wire to avoid contamination during the process. Therefore, tungsten wires were baked for 30 minutes at 10 amps inside the evaporator under $10^{-4}$ to $10^{-5}$ mtorr vacuum before we started deposition of aluminum.

**Vacuum Thermal Evaporation**

Vacuum thermal evaporation technique was utilized for the preparation of thin film of $C_{60}$. In this technique $C_{60}$ was deposited by resistance heating until it evaporated. Vapor of $C_{60}$ condenses on the substrates and gets deposited. Vacuum is an essential factor in vacuum thermal evaporation in order to avoid the oxidation of the $C_{60}$ or any material to be deposited. The vacuum system that was utilized to create vacuum includes one diffusion pump and one mechanical pump which is capable enough to create the vacuum of $10^{-5}$ to $10^{-7}$ mtorr.

The Vacuum evaporation equipment that was utilized to deposit films at clean room laboratory at western Michigan university is shown in Figure 2.1.
Substrate used:

➔ n type Si substrate
➔ Glass substrate

Commercial C$_6$O powder from Alfa Aesar was 99.95 % pure according to the company grade. Tantalum boat filament was used to evaporate this grade of C$_6$O as already mentioned above. The current passed through the filament was kept 25 amp for 45 minutes under the vacuum of the $10^{-5}$ to $10^{-7}$ m torr. The filament and the substrate were kept 7 cm apart and right over the filament to ensure uniform deposition process.

Figure 2.2 : Vacuum evaporation system available at clean room facility laboratory, Western Michigan University.
**Types of Samples.**

1. C₆₀ were deposited on glass and Silicone substrate to characterize the effect of annealing temperature

2. First C₆₀ was deposited on glass and silicone substrate and then Aluminum was deposited to characterize solid phase crystallized sample.

![Diagram](image)

**Figure 2.3:** Types for substrate prepared.
Microlithography

Clean room laboratory of Western Michigan University has facility of performing microlithography on various substrates. Lithography is a technique that is used to transfer a pattern from photomask to various substrates.

Photomask Making

As discussed above, a photomask is an essential tool to be fabricated in order to transfer a pattern on to any substrate. In the Present research, we need to fabricate the microstructure of aluminum film as shown in figure 3. Therefore, a photomask is required to transfer the same kind of pattern on to different substrate. A photomask in accordance to the pattern was fabricated using CAD designing.

Coating of Photoresist

An important step of microlithography process is a coating of photoresist layer. A photoresist is a polymeric material and it is very sensitive to the exposure of UV light. Here we need to get a uniform and thin layer of photoresist on to samples. The clean room laboratory
of Western Michigan University has a spin coater available as shown in diagram 2.4. It is a two-stage spin coater.

The two stage spinning coater means for the first stage it spins at certain speed and then later in second stage it spin at relatively faster speed in our case it was more than 3000 rpm for second stage and the duration of spin was selected 30 seconds.

Figure 2.4: Two-stage spinning coater.

With this much high speed and limited amount of photoresist materials were able to get the uniform and thin coating of photoresist on the samples.
**Exposure of UV Light**

The photoresist is a polymeric material and it is very sensitive to the exposure to the UV light. Depending upon its type it goes under chemical bond breaking or linking upon exposure. In over case polymeric material's bonds gets broken upon exposure. And it forms the dissolvable product of photoresist material in developing solution.

**Development of Pattern**

Another important step for the microlithography process is development of micro photoresist pattern. Once photoresist is coated on the substrate with spin coater, it was kept in an oven for 20 minutes at 80°C for polymerization. The oven that was used was available at clean room laboratory at Western Michigan University.

The photomask as above mentioned was kept over the surface of this baked samples and exposure to the Ultraviolet light as discussed above was provided for 12 seconds. This treatment would break the chain linking of the Exposed polymeric material. The unexposed portion of the film which has not been exposed because of the mask will remain polymerized. Then again the above prepared samples were baked again in the same oven at 120°C to remove
moisture and to improve bonding between photoresist and the
substrate. Then finally, the photoresist pattern was achieved by
developer solution. The photoresist in polymerized form is insoluble
in the developing solution and exposed photoresist is soluble in the
developing solution. The developing solution was prepared with 40 %
of NaOH and 60 % of water. Thus, the samples were kept immersed in
the above mentioned developing solution until all exposed photoresist
went away. And finally we got the desired photoresist pattern.

**Aluminum Etching**

We need to get the Aluminum patterns over the surface of the
sample and Al was etched by chemical etching process.

An etching solution especially for Al etching was prepared and
its composition ratio was as shown bellow.

\[
H_3PO_4 : CH_3COOH : HNO_3 :: 1 : 3 : 1 \quad (1)
\]

This kind of solution was prepared in a suitable beaker and this
beaker was used only for aluminum etching. This solution needs to be
mixed therefore, it was heated on a hot plate at 50°C with some degree
of stirring, simultaneously. The samples prepared were cleaned
thoroughly with distilled water before we started etching. The samples
were immersed in aluminum etching solution and simultaneous mild hand agitation was provided. That portion of photoresist on surface which has not been exposed remains coated on the surface while other part starts to be etched off by etching solution and thereby turning the surface darker. Thus, photoresist act as protective coating on the surface and save the aluminum from being etched off while uncovered aluminum gets removed in the etching solution.

This was very tedious process and was done repeatedly until clear and uniform pattern of aluminum was achieved. The substrates were cleaned with acetone to remove all photoresist coating and finally the pattern of aluminum as shown in the diagram was examined under optical microscope to confirm proper etching of aluminum layer.

**Annealing Process**

The annealing temperature was systematically changed in 100°C to 400°C range in oxygen ambient for three hours. In this study the annealing time was kept 3 hours with a step of 1 hr to get the desired temp and the films were characterized as a function of temperature.
Solid Phase Crystallization

The crystallization from an amorphous phase to a (poly)-crystalline phase occurs through two processes—nucleation and grain growth. Both have characteristic activation energies. The nucleation activation energy is extracted from the time to onset of crystallization, i.e., the incubation time, while the grain growth rate is extracted from grain progression data. For the SPC C₆₀ system, the nucleation activation energy is larger than the grain growth activation energy. To achieve the largest possible grains, it is desirable to suppress nucleation relative to grain growth. In our case we used Aluminum induced crystallization. We fabricated a system of Glass/C₆₀/Al. The annealing of Glass/ C₆₀ /Al stack was done in same furnace and in oxygen ambient and annealing temperature was changed from 100°C to 400°C for three hours and with a step of 1 hour to get desired temperature.

Measurement Of Electrical Properties

Electrical Conductivity

Electrical conductivity of thin film materials depends on several factors such crystal structure and some of mechanical
properties. Thus electrical conductivity measurement could be used to investigate crystalline structure, crystalline imperfection and various other structural properties. Measurement of the temperature-dependent resistivity provides much information like electron scattering mechanism; mean free path and so on. Huang [18] and Tanak [19] shown that inter molecular vibration modes play the main role in determination of temperature dependent resistivity [1]. We know that resistivity is inversely proportional to conductivity. Thus, electrical conductivity must be definitely related to the structural changes. In our case we tried to measure structural changes with the aid of Raman spectroscopy and X-ray diffraction.

In order to measure the electrical conductivity [17], it is necessary to make a constant section area electrode. We fabricated such kind of electrodes with aluminum by vacuum microlithography process as discussed earlier. The diagram 2.5 shows the configurational picture of aluminum electrodes. The gap between two electrodes is 100 µm and the length is 100 mm. Electrical resistivity were measured with change in thermal energy on a hot plate at clean room laboratory, Western Michigan University. The temperature change was monitored by a thermocouple contacted with the surface of the specimens and a multi-meter to take data. Values of electrical resistivity were measured with changes in temperature from room
temperature to 400°F to calculate the electrical conductivity with an equation shown below.

\[ R = \rho \frac{l}{A} \]  

(5)

Where, \( R \) is the resistant of the measured area of the thin film, 
\( \rho \) is the conductivity at the constant conductive section area, 
\( A \) is cross section area of thin film, 
\( l \) is the gap of the electrodes.

Figure 2.5: Electrode configuration on the thin films to measure conductivity.
**Ohmic Contact of Al/C$_{60}$ Interface**

Our aim is to get good and conductive contacts to measure electrical conductivity and current voltage characteristics because better the conductivity of the contacts, the more the accurate results we get for electrical properties measurements. In the present research, we employed aluminum/C$_{60}$ contacts to measure electrical properties of C$_{60}$.

The interface of Al/C$_{60}$ has been very interesting because of enhanced bond strength of these materials. The bonding of these two materials is of covalent character and cause rehybridization of C$_{60}$ orbital with Al orbital [1]. We have carried out I/V measurements for the samples annealed and recrystallized at different temperatures. In these experiments, we have used Keithy electrometer and extra DC power supplies for this propose. Also Maxwell [20] has calculated the work function change for various textured surfaces of aluminum upon adsorption of C$_{60}$ and they found that the work function for Al/ C$_{60}$ is of the first order due to fundamental dielectric response of the fullerene layer [1].

In order to have ohmic contact the, the metal-semiconductor material should have linear I/V characteristics, thus by measuring
current-voltage characteristics for any interfaces we can determine whether the junction has ohmic contacts. We carried out series of I/V measurement for the different annealed samples and solid phase crystallized samples at diff temperature. And we found that Al/ C₆₀ has ohmic contacts. The measurement was done with Keithy electrometer – model 5516.

**Thermal Activation Energy of Electrical Conductivity**

Conductivity follows Arrhenious relationship with temperature\[17\] and at constant temperature electrical conductivity does not alter, it stays constant, and therefore to change electrical conductivity some amount of energy is required. In our case the minimum amount of energy the cause the change in conductivity was provided thermally by increasing temperature. And this minimum amount of energy that cause changes in conductivity is called thermal activation energy. This thermal activation energy can be calculated with the change in thermal energy that is temperature. In this case, we measured conductivity from room temperature to 400°F range. The Arrhenious relationship between electrical conductivity and temperature is described as,

\[
\sigma = \sigma_0 \exp(-\Delta E /kT) \tag{7}
\]
Where, \( \Delta E \) is thermal activation energy,

\( k \) is boltzmann Constant,

\( \sigma \) is the conductivity of the test film at heating temperature (T),

\( \sigma_o \) is the co-factor.

The calculated values of conductivity from the resistivity measurements were plotted for \( \ln \sigma \) and \( 1/T \) coordinates and the thermal activation energy for change in conductivity was calculated from the slope of Arrhenious plot.

**Instrumentation for The Structural Characterization**

**Raman Spectroscopy**

The applications of Raman spectroscopy are widespread and range over chemical, physical, biological and medical sciences[4]. Often is employed to identify a particular chemical species and its bond structure. Each different scattering molecular species gives its own characteristic Raman spectra. In favorable instances vibrational assignments enable quantitative information about intramolecular and inter molecular forces to be obtained and thermodynamic functions to be calculated[5]. It is a convenient tool for the identification of
crystal or molecule, for obtaining structural information or noncrystalline solids, for identifying molecular species in aqueous solutions, and for characterizing solid–liquid interfaces [17].

The material to be studied doesn’t need to be virtually colorless or of good optical quality and only small quantity of the sample is necessary, the sample may be in any physical state and can be measured with a wide range of temperature and pressure conditions, a small wavenumber shifts can be measured with a same facility with a large wavenumber shifts and even week scattering is unlikely to escape the detection [5]. Also the wavenumber of the shifts is not the only characteristics parameter of the raman spectra but also the intensity, contour of raman band and it’s state of polarization are now susceptible to precise measurement and in case of crystal fruitful orientational studies have been made easy [5][6].

The spectrum is sensitive to chemical bonds. Raman spectroscopy provides details of defect or disorder rather than to trace of impurities and related imperfections [17].

The Raman spectroscopy that was used in this research has an excitation laser beam of 633nm and spectrum was recorded in conjunction with interferometer.
X-ray Diffraction

X-ray diffraction technique is a unique non-destructive and analytical technique for the structural characterization of any thin film materials like C₆₀. Traditionally this method has been used for phase identification and determination of structural imperfections. In recent years its application has been extended for the identification of crystal structures of thin film materials. For most applications, the amount and type of information that could be possible to extract depends not only on the nature of the sample microstructure (crystallinity, structure imperfections, crystallite size, texture) but also the complexity of the crystal structure (number of atoms in the asymmetric unit cell, unit cell volume) and the quality of the experimental data (instrument performances, counting statistics). The principle of x-ray diffraction technique can be explained with the Bragg's law as shown bellow. We used Cu kₐ radiation and 2θ angle was kept from 10 to 60°.

\[ n\lambda = 2dsin\theta. \]

Where, \( \lambda \) = wavelength of radiation ( for Cu kₐ=1.542 Å)

\( d \) = spacing between planes of crystal lattice.
n = order of diffraction and it is an integer

θ = Incident angle that is angle between incident x-ray beam and crystal surface.

In this project XRD pattern helps us to understand the crystalline structure of annealed and solid phase crystallized samples.
CHAPTER 3

RESULT AND DISCUSSION

Raman Results with Annealing Temperature

The fullerene molecules is fundamental building block of the crystalline phases which held together by weaker van der Waal forces that couple the fullerene molecules to each other [4]. Thus many of the properties of C_60 including their Raman spectra, are closely related to the molecular properties of isolated C_60 molecules [4]. Here we used Raman spectroscopy to investigate chemical bonding and crystalline structure of C_60, moreover, Raman spectroscopy is a very powerful tool to probe the polymerization of C_60 also. The Raman Spectrum of unpolymerized C_60 sample (not shown here) contains 10 peaks while upon polymerization the Raman spectra shows new peaks and may of original peak spit[12]. This indicates lowering of molecular symmetry though the formation of covalent bond between molecules.[12] The Raman spectra for pristine C_60 shows two major shifts at 520 cm^{-1} and 1469 cm^{-1}. In our investigation we tried to get these two shifts for different annealing temperature and different solid phase crystallizing temperature. In this study, we have concentrated on the only one peak that is pentagonal pinch mode at 1469 cm^{-1}. 
Raman spectra for as deposited C$_6$O film and annealed samples (100°C to 400°C for 3 hours) are given in the diagram 3.1.

It can be seen that as deposited film and as we go on increasing temperature we get sharp peak that shows characteristics of crystalline structure of C$_6$O while temperature at 400°C we do not get Raman shift at 1458 cm$^{-1}$, instead we get two peaks that is characteristics of linear carbon chains so called Carbyne. Thus C$_6$O no longer exists at 400°C. Linear carbyne chain may made up of either an polyne sequence of single and triple bond or a comulene chain of double bonds [4].
In the Figure 3.2 shown below, we have concentrated only peaks area of annealed sample. For as received samples we get shift at 1456 cm\(^{-1}\), and for 100\(^{\circ}\)C and 200\(^{\circ}\)C we get shift at 1454 cm\(^{-1}\) and even for 300\(^{\circ}\)C we get Raman shift at 1452 cm\(^{-1}\). This is not a significant change with increase in temperature, though the shift does occur just from 1456 to 1452 cm\(^{-1}\). And this could be because of little polymerization effect (yet we can not conclude) with increasing temperature or oxygen ambient effect during annealing process. Sharp peaks suggest good crystallizing condition of the film, yet we could not decide degree of crystallization with just Raman studies.

Figure 3.2: Raman shift 1452 cm\(^{-1}\) for 300\(^{\circ}\)C and 1456 cm\(^{-1}\) for as deposited.
Raman Results for Solid Phase Crystallized Samples

Below Figure 3.3 shows Raman shifts for solid phase crystallized sample. All samples were heated with Al layer on C₆₀ (aluminum induced crystallization) at 100°C, 200°C and 300°C and 400°C. We get sharp peaks for as deposited sample and as we go on increasing temperature. But at 400°C SPC sample shows no sharp peak it shows characteristics of carbine structure as discussed earlier. Again we concentrate on the peak position in the diagram shown bellow we can see that the SPC sample as deposited shows peak at 1456 cm⁻¹ and As we go on increasing temperature we get raman shifts at 1454 cm⁻¹. Two-dimensional polymerization gives a large shift of the line, down to bellow 1449 cm⁻¹. In our case, at 300°C we get (annealed sample) a shift at 1452 cm⁻¹, which can not be conclude with just Raman data that it is characteristics of some degree of polymerization.
Figure 3.3: Raman shifts for Solid phase crystallized sampled with increase in temperature.

Figure 3.4: Raman shift 1454 cm\(^{-1}\) for most of the Solid phase crystallized samples.
Comparison of Annealed and Solid Phase Crystallized Samples

If we look at the as deposited annealed sample and solid phase crystallized sample we get same peak position in both the cases. There is no significant Raman shift and at 100°C and in chase if 300°C we get Raman shift from 1452 cm\(^{-1}\) (annealed sample) to 1454 cm\(^{-1}\) (Solid Phase Crystallized Sample)

This shows that Solid phase crystallized samples have better crystallizing conditions of C\(_60\) than in case of Annealed sample.

Figure 3.5 (a): Comparison of raman result for solid phase crystallized and annealed as deposited sample.
Figure 3.5 (b): Comparison of Raman result for solid phase crystallized and annealed as deposited sample.

Thus from Raman results we can say that with increasing annealing temperature has very little effect on crystallization of C₆₀ molecules while in case of Solid phase crystallization peak position does not change significantly. Thus solid phase crystallized sample has sharp peak shows high degree of crystallinity.
X-Ray Diffraction Patterns for C\textsubscript{60} Thin Films

The x-ray diffraction analysis was carried out with monochromatic beam of Cu k\(\alpha\) radiation. And XRD pattern was taken for 100\(^\circ\)C annealed and 100\(^\circ\)C solid phase crystallized samples for \(\theta\) from 10 to 60\(^\circ\) angle.

![100 C annealed sample](image)

Figure 3.6: XRD pattern for for 100\(^\circ\)C annealed sample.

Figure 3.6 above shows XRD pattern for 100\(^\circ\)C annealed sample and we get some what broaden peaks at \(\theta=18.12\) and 21.1 for planes (221) and (222) respectively. Figure 3.7 bellow shows \(\theta=18.18\) and
21.13 for planes of (221) and (222) as in previous case but here we got another peak for (112) planes at $2\theta = 15.12$ angle.

Figure 3.7: XRD pattern for 100°C solid phase crystallization.

Moreover, we get a sharp peak of Si(100) at two theta angle 33.33 for single crystal of silicone substrate for both annealed and solid phase crystallize samples. Also the we got comparatively sharp and intense peaks in case in solid phase crystallized sample that shows relatively higher degree of crystallization. Thus solid phase crystallized samples exhibits better recrystallizing condition than annealed samples.
Electrical Properties with Conductivity

Temperature Dependence of Electrical Conductivity

Following the Arhenious equation (2) shown earlier, we plotted $\ln(\sigma)$ Versus $1/T$ for different samples of annealed condition and different samples of solid phase crystallized conditions. Straight line in all the plots clearly indicated the temperature dependence on conductivity followed the Arhenious equation. The profile of the Arhenious relationship has a negative slope distribution with the thermal change. All the samples showed abrupt negative slope suggesting that C$_{60}$ has good semiconducting properties. As we annealed the sample to high temperature, that slope increases and so the semiconducting properties.

Similarly for solid phase crystallized sample we plotted $\ln(\sigma)$ Versus $1/T$ as shown in diagram. Even in this case we get straight line and it indicated temperature dependence of conductivity followed the Arhenious equation. Profile was found to be same the negative slope distribution with thermal change. Slope value were seemed to be decreased than in case of annealed sample. This could be the effect of crystallization as it was understood by Raman shifts.
Figure 3.8: Arrhenious plots for samples annealed at different temperature.
Figure 3.9: Arrhenious plots for solid phase crystallized samples at different temperatures.
Change in Conductivity

Bellow diagram shows the change in electrical conductivity at room temperature for C₆₀ thin film annealed at different temperatures and for solid phase crystallized samples at different temperature. First when annealing temperature was increased, electrical conductivity was found to increase up to 300°C and so is the case of solid phase crystallized samples for different temperature. Conductivity increases with solid phase crystallizing temperature up to 300°C. Raman study of thin film of C₆₀ shows that at high temperature amorphization of C₆₀ takes place and the results in carbone structure. Therefore, conductivity of film at higher temperature is not displayed for characterization of C₆₀ thin films. Nevertheless, graphite is known for high conductivity even more than C₆₀. Moreover, as x-ray studies showed that solid phase crystallization increases the degree in crystallinity, therefore, crystalline phase might be resulted in to decrease in the conductivity.
Figure 3.10: Electrical conductivity annealed samples and solid phase crystallized samples as a function of temperature.

Moreover, as we discussed earlier in Raman spectroscopic and X-ray diffraction studies, we found solid phase crystallized sample are more crystallized at high temperature than they are in case of normal annealing. Therefore SPC samples we got less conductivity values than it is in case of annealed samples.
**Activation Energy with Annealing Temperature and Solid Phase Crystallizing Temperature:**

Below table lists the activation energy of electrical conductivity deduced from figure. The activation energy was found to decrease with increase in annealing temperature. And in the case of 400°C we got drop in activation energy shows increase in conductivity. This effect of sudden increase in conductivity may be because of amorphization of the C₆₀ at 400°C. Same effect was observed in case of Solid phase Crystallizing temperature. With increase in the temperature the energy was found to decrease All of the activation energy data Variation of the activation energy is may be because of the ambient gas effect. When these films were annealed in oxygen ambient, the stoichiometric composition was made by oxidation process and the films exhibited semiconducting properties.

The Tables shown as in the next page summarizes the activation energy values and it's respective conductivity values for both annealed and Solid Phase Crystallized samples.
Table 1: Change in Activation Energy for conductivity of C₆₀ films as a function of annealing temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation Energy(eV)</th>
<th>Conductivity (Ωcm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As deposited C₆₀</td>
<td>0.404</td>
<td>2.2×10⁻⁶</td>
</tr>
<tr>
<td>Annealed at 100°C</td>
<td>0.420</td>
<td>9.2×10⁻⁶</td>
</tr>
<tr>
<td>Annealed at 200°C</td>
<td>0.440</td>
<td>9.6×10⁻⁶</td>
</tr>
<tr>
<td>Annealed at 300°C</td>
<td>0.494</td>
<td>1.3×10⁻⁵</td>
</tr>
</tbody>
</table>

Table 2: Change in Activation Energy for conductivity of C₆₀ films as a function of annealing temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Activation Energy(eV)</th>
<th>Conductivity (Ωcm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Deposited SPC</td>
<td>0.401</td>
<td>1.8×10⁻⁶</td>
</tr>
<tr>
<td>100°C SPC</td>
<td>0.410</td>
<td>5.5×10⁻⁶</td>
</tr>
<tr>
<td>200°C SPC</td>
<td>0.431</td>
<td>9.4×10⁻⁶</td>
</tr>
<tr>
<td>300°C SPC</td>
<td>0.492</td>
<td>1.2×10⁻⁵</td>
</tr>
</tbody>
</table>
Electrical Properties

I/V Characteristics of all Annealed Samples

I/V characteristics for all annealed samples are shown in bellow diagram. According to the I/V test for as deposited C$_{60}$ film suggests that, aluminum contacts are ohmic. This results suggested that the aluminum contacts can serve for measuring the conductivity.

![IV characteristics for annealed samples](image)

Figure 3.11: I/V characteristics of C$_{60}$ thin films as a function of different annealing temperature.
Raman spectroscopic result showed that as we go on increasing annealing temperature the C$_{60}$ molecules get polymerized. Therefore, with increasing annealing temperature we get higher conductivity. The result showed that the 300°C annealed sample showed highest level of current with increasing temperature. And the 400°C was found to decrease the level of current with increasing voltage. This may be because of amorphization of the molecules of C$_{60}$ at high temperature. Raman results showed that we got Raman shift from 1456 cm$^{-1}$ to 1452 cm$^{-1}$ in case of 300°C annealed because of either polymerization or effect of oxygen ambient the C$_{60}$ molecules. Thus with highest level of annealing temperature we got highest level of electric current with increasing voltage.

**I/V Characteristics for Solid Phase Crystallized Samples**

Similar chart was plotted for Solid phase crystallized samples of C$_{60}$ deposited on glass substrate for different temperatures as shown in diagram bellow. Results showed that even in case of SPC samples level of electric current with increase in voltage was found to increase with increase in solid phase crystallizing temperature. We got highest level of electric current in case of 300°C SPC sample
Raman studies showed us that aluminum induced crystallization of C$_{60}$ is more effective to crystallize the sample than in case of annealed samples. Our study showed us that in case of 200°C annealed sample we get some degree of crystallization and for 300°C we got...
highest degree of crystallization. Diagram shown bellow were plotted for 300°C Annealed and SPC and 200°C annealed and SPC samples.

Figure 3.13: Comparison I/V characteristics for solid phase crystallized samples and annealed samples for 300°C and 200°C.

It is easily evident from the chart that for both the 300°C and 200°C, the solid line goes down to dotted lines for solid phase crystallizing sample. Thus degree of crystallization is effective in case of solid phase crystallized sample. Thereby we can infer that aluminum induced crystallization brings the level of current down.
with increase in voltage. For 300°C annealed sample we got highest level of current with increasing temperature.

**Relationship of Crystallinity with Electrical Property**

Finally, the relationship between the structure and electrical properties of C₆₀ was compared. The change in crystallinity resulted in change of electrical conductivity. Activation energies were also found corresponding to the annealing temperature. There is an absolute change in conductivity at 300°C-annealed sample. Solid phase crystallization definitely changed the electrical properties of the C₆₀ films. The result obtained in this investigation further the knowledge of C₆₀ material, and therefore, the present project is beneficial for the application of C₆₀ films in different devices.
CHAPTER 4

CONCLUSION

The structure and the electrical properties of $C_{60}$ thin films fabricated by thermal evaporation method were studied as a function of annealing temperature and for solid phase recrystallizing conditions. We prepared two types of samples substrate/$C_{60}$ and substrate/$C_{60}$/Al and these stakes were annealed from 100 to $400^\circ$C in ambient of oxygen to study the effect of annealing temperature and to study the effect of Solid Phase Crystallization. It was found that electrical properties resulted from the change in structure of the films. Compared with the other electronic materials, $C_{60}$ undergoes recrystallization up to certain extent with increase in annealing temperature for some length of time. The Solid phase crystallization in our case, found effective to crystallize the specimen at different temperature. SPC treatment definitely changes the electrical properties of the $C_{60}$ film. In comparison with other processing methods of $C_{60}$ thin film such as reactive sputtering, thermal evaporation provides some unique advantages like precise control of the film composition, simplicity, low cost and scalability. Therefore, the preparation of the $C_{60}$ film by vacuum thermal evaporation followed by thermal annealing and solid phase crystallization provides
controllability of the structure and physical properties. Based on the experimental results of this study following main conclusions were made.

1) With increase in the annealing temperature we get significant Raman shift to conclude some extent of structural change in the C$_{60}$ molecules. As we went on increasing the temperature of annealing, we got sharp peaks at 1456 cm$^{-1}$ for 100$^\circ$C, 1454 cm$^{-1}$ for 200$^\circ$C and 1452 cm$^{-1}$ for 300$^\circ$C annealed samples and we got 1454 cm$^{-1}$ for 100$^\circ$C to 300$^\circ$C for solid phase crystallized samples. This are the characteristics of crystallized C$_{60}$ and thus C$_{60}$ was found to be a good Raman scatterer. We did not get sharp peaks for 400$^\circ$C annealed and 400$^\circ$C Solid phase crystallized samples, but we got characteristics of amorphous carbon. Thus C$_{60}$ get transformed to amorphous carbon between 300$^\circ$C to 400$^\circ$C yet we do not conclude anything on the nature of the transformation.

2) X-ray diffraction studies shows that we got sharp peaks for solid phase crystallized sample than in case of just annealed samples. Thus Solid phase crystallization found to be more effective to crystallize the C$_{60}$. 
3) Electrical conductivity was found to be increasing with increase in annealing and solid phase crystallizing temperature. Thus change in electrical conductivity can be concluded with corresponding structural change. Solid phase crystallization was found very effective to change the structural properties of the film. Electrical conductivity data was found to be in semiconducting nature and we got highest conductivity for amorphous carbon at 400°C.

4) I/V characteristics showed that the Al/C₆₀ junction has an ohmic contact. The I/V characteristics were found to be sensitive with structure of the films. I/V and activation energies for different sample showed that with C₆₀ is good semiconducting material.
CHAPTER 5

FUTURE WORK

In present research we tried to characterize the normal state properties of \( \text{C}_6\text{O} \) thin films. Here we got increase in electrical conductivity with subsequent change in structure. As we demonstrated that this material possesses interesting semiconducting properties more experiments should be performed in order to characterize it as a function of different. Further studies could be concentrated on effect of various dopants on the \( \text{C}_6\text{O} \) and subsequent structural change. Though we have not demonstrated any work on energy band structure, more studies with different dopants and their composition may open up new horizons in semiconductor devices. Polymerization was observed for some preparation conditions (e.g., pressure, controlled exposure to UV light). However, there is no conclusive evidence of polymerization in our experiments. This interesting process as well as the nature of transformation between 300\(^\circ\)C to 400\(^\circ\)C needs further investigation. Hence, I would like to say that it is not the end of my study this is just the beginning.
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2. Roger Tayler "Lecture notes on Fullerene chemistry" Imperial college press 1999


