CHAPTER 5

CHARACTERIZATION OF C\textsubscript{60}, C\textsubscript{60}/C\textsubscript{70} CRYSTALS AND C\textsubscript{60}/GaAs HETEROJUNCTIONS

5.1 INTRODUCTION

Characterization of a material can be defined as a complete description of its physical and chemical properties. In the case of crystals, a thorough characterization is very much essential to assess their quality and hence to find their feasibility for device applications. Also it provides the necessary feedback to improve the method of preparation to obtain the right material. In the present work, the C\textsubscript{60} crystals were analyzed for their spectroscopic and mechanical properties. For this purpose FTIR and Raman spectroscopy and Vickers microhardness were used respectively. The materials' stability and hardness are sensitive to contamination and the surrounding atmosphere and hence attention has been paid to study the effect of impurities (mainly higher fullerenes) on these two important properties. For this, pure C\textsubscript{60} and mixed C\textsubscript{60}/C\textsubscript{70} crystals exposed to air were characterized and the results are compared. Current-Voltage measurements (I-V) were carried out on C\textsubscript{60}/n-GaAs, C\textsubscript{60}/p-GaAs and Ti/C\textsubscript{60}/Ti structures in order to assess if they possess any useful property for applications in electronics.

5.2 VIBRATIONAL PROPERTIES OF SOLID C\textsubscript{60}

The vibrational properties of C\textsubscript{60} have been studied extensively by optical spectroscopies, inelastic neutron scattering and theoretically by various dynamical calculations (Weeks and Harter 1989; van Loosdrecht
et al. 1992, 1992a). A detailed understanding of the vibrational properties of solid C60 would improve the understanding not only of the C60 solid itself but also the properties of related compounds. The sensitivity of the optical scattering processes to the crystal field makes Raman spectroscopy together with infrared spectroscopy a powerful means to study the solid state vibrational properties of condensed matter, as well as to detect the structural phase transitions.

The high molecular symmetry of C60 is the origin of their unusual properties. The symmetry of C60 is described by that of the regular icosahedron: the icosahedral-reflection group Iₙ = Iₐc, the product of the icosahedral rotation group I (60 rotations around 2-fold, 3-fold and 5-fold axes, Figure 5.1) and the reflection Cₐ. There are two types of distinguishable carbon-carbon bonds for an isolated C60 molecule. The pentagon-hexagon or single bonds (1.44 Å) and hexagon-hexagon or double bonds (1.40 Å). Because of the high molecular symmetry, the 174 internal modes (3.60 - 3 rotations - 3 translations) fall into 46 distinct eigen frequencies. All vibrational modes of C60 are distributed (Weeks and Harter 1989) as

\[ T_{\text{molecule}} = 2 A_g (R) + 3 T_{1g} + 4 T_{2g} + 6 G_g + 8 H_g (R) + A_u + 4 T_{1u} (IR) + 5 T_{2u} + 6 G_u + 7 H_u \]

Among which only the two non-degenerate \( A_g \) modes and eight five-fold degenerate \( H_g \) modes are Raman active and four \( T_{1u} \) modes are infrared active. Vibrations with predominantly radial displacements of carbon atoms have excitation energies of 200-900 cm\(^{-1}\), whereas the high-energy modes (980-1600 cm\(^{-1}\)) consist of mainly tangential motions. The \( A_g \)-symmetry mode frequency in C60 observed at 1461 cm\(^{-1}\) involves a tangential breathing mode of the five carbon atoms around each of the 12 pentagons and has therefore been referred to as the pentagonal pinch (PP) mode.
Figure 5.1 Truncated icosahedron and its 2-, 3- and 5-fold axes
5.2.1 **Infrared Spectroscopy**

The IR spectra of the C$_{60}$ crystals in the region 400 to 4000 cm$^{-1}$ were obtained by KBr pellet technique using the Bruker Model IFS 66V FTIR spectrometer. Figure 5.2 represents the IR spectra of vapor grown C$_{60}$ crystals exposed to ambient atmosphere for about one month. All the four IR active modes, characteristic of C$_{60}$, have been observed. In addition to this, a peak at about 1745 cm$^{-1}$ and other minor peaks have also been observed. This may be attributed to oxidised C$_{60}$.

5.2.2 **Raman Spectroscopy study**

Raman scattering has played an important role in the study of the solid state properties of C$_{60}$ from the initial stage. Much of the Raman spectroscopic measurements have been carried out on C$_{60}$ crystals. Two major problems are dealt with in most of the Raman scattering study of C$_{60}$ crystals: (1) the effect of oxygen contamination and photo-illumination on the Raman spectra of solid (2) the change in the Raman spectra during phase transition. There exists contradictory reports on the stability of the compound and as well on the phase transition. In the present investigation, with an aim to address these two problems and also to confirm the purity and crystallinity of the grown crystals, Raman spectroscopic measurements were made on high purity C$_{60}$ crystals both at room temperature (fcc phase) and low temperature (sc phase) structures.

5.2.1.1 **Experimental details**

The Raman spectroscopic experiments were performed in the backscattering geometry by employing the 514.5 nm line of an Ar-ion laser, Ramnor double monochromator and the usual photon-counting electronics. The monochromator was calibrated using strong plasma lines of the argon-ion laser. The experiments were performed on a vapor grown high
Figure 5.2 IR spectrum of vapor grown C$_{60}$ crystals.
purity C$_{60}$ crystal on its (111) face. The surface of the crystal was clean and optically planar. The as grown crystal was mounted on the cold finger of a flow cryostat. Subsequently the cryostat is evacuated down to $10^{-6}$ torr. The C$_{60}$ crystal structure is known to be sensitive to the laser heating due to the strong absorption in the green part of the spectrum which results in qualitative changes of the Raman spectra (van Loosdrecht et al 1992). In order to avoid this problem, the intensity of the excitation laser was fixed at 20 mW/cm$^2$. The laser beam was focused to a spot of 50 µm. With these precautions, the Raman spectra were reproducible for different spot positions on the crystal.

Figures 5.3 and 5.4 show the unpolarized Raman spectra of C$_{60}$ single crystal recorded on a crystal surface exposed to air. The upper curve represents the room temperature spectra (290 K, fcc phase) and the lower curve represents the low temperature spectra of sc phase (T = 50 K). All the ten modes assigned by Bethune et al (1990) are clearly observed in both the spectra. A sharp line at 1461 cm$^{-1}$, characteristic of C$_{60}$, has been observed and the signal (1572 cm$^{-1}$) corresponding to C$_{70}$ was completely absent. This confirms the purity of the C$_{60}$ crystals.

5.2.1.2 Photopolymerization in C$_{60}$ Crystals

Photo illumination on the surface of C$_{60}$ single crystals leads to the instability of the surface resulting in polymerization. The polymerized surface exhibits a high resistance to thermal sublimation and is not soluble in most of the well known solvents of C$_{60}$. Due to the high sensitiveness of C$_{60}$ to oxygen exposure and to photo illumination, the identification of the 1469 cm$^{-1}$ and 1459 cm$^{-1}$ peaks of the pentagonal pinch (PP) mode of high-frequency Ag symmetry has been the subject of controversy eversince the Raman spectroscopy of C$_{60}$ was explored. Few reports suggest that the 1469 cm$^{-1}$ peak, originally attributed to pure C$_{60}$, shifts to 1459 cm$^{-1}$ due to photopolymerisation of C$_{60}$ in air (Rao et al 1993; Zhou et al 1992). The
Figure 5.3 Unpolarized Raman spectra of vapor grown & 5.4 C$_{60}$ single crystal recorded at room temperature (T=290 K, fcc phase) and at low temperature (T=50 K, sc phase)
others attribute the 1469 cm$^{-1}$ peak to oxygen contamination and the 1459 cm$^{-1}$ peak to pure C$_{60}$ (Duclos et al 1991; Hamanaka et al 1993). In the present case, the strongest PP-mode frequency has been observed at 1461 cm$^{-1}$, which is less by 8 cm$^{-1}$, supporting the former results that the downward shift was due to photopolymerisation of C$_{60}$ in air. More recently, Li et al (1994a) reported that the 1469 cm$^{-1}$ peaks originally observed for pure pristine C$_{60}$ shifts to 1459 cm$^{-1}$ after photopolymerization in argon and to 1461 cm$^{-1}$ in air. The mechanism of polymer formation was proposed to be [2+2] cycloaddition of the 6:6 double bonds on two adjacent C$_{60}$ molecules to form a cyclobutane linkage (Rao et al 1993).

### 5.2.1.3 Rotational ordering transition in C$_{60}$ single crystal

Solid C$_{60}$, being composed of nearly spherical molecules, undergoes a phase transition involving orientational ordering. Earlier X-ray diffraction and calorimetric experiments showed that solid C$_{60}$ undergoes a first order phase transition from the high temperature free-rotor fcc phase (Fm3) to the orientationally ordered simple cubic phase (P2$_1$/a3) at around 250 K (Heiney et al 1991). This transition is classified as order-disorder phase transition with the development of orientational order in the sc phase. In the ordered state, electron rich double bonds between two hexagons (6:6 double bonds) are adjacent to the electron deficient pentagonal faces on nearest neighbor molecules. The phase transition in solid C$_{60}$ has been studied using Raman spectroscopy (van Loosdrecht et al 1992a; Hamanaka et al 1993).

According to the results of the factor-group analysis, for sc structure which has four molecules per primitive cell and site symmetry S$_h$, 145 modes are expected to be Raman active. Similarly for fcc phase with T$_h$ site symmetry, 37 Raman-active modes are expected. However, all these peaks cannot be expected to have present in the Raman spectra due to the resolution limitation of the experiments, thermal broadening and possible degeneracies. In the present work, 19 clear bands and signatures are
observed in the fcc phase whereas there are 26 clear peaks in the low temperature spectra. The newly activated modes and splittings in the original peaks reflects the reduced symmetry of solid C$_{60}$ in sc phase. In going from the orientationally disordered to orientationally ordered phase, frequency of the Raman modes increases abruptly accompanied by a step-like decrease in the line widths. The abrupt hardening of the modes, first attributed to the decrease in the unit-cell volume near the transition, later ascribed to be partly due to the laser induced electronic excitations into the metastable triplet state (van Loosdrecht et al 1992a).

5.3 MICROHARDNESS STUDY

The resistance offered by a material to indentation by a much harder body is known as hardness. The hardness properties are basically related to the crystal structure of the material and hence microhardness studies are often used to study the plasticity of the crystals. Hardness measurements can be done by a wide variety of tests such as Brinell test, Meyer test, Knoop test, Rockwell test and Vickers microhardness test. The equipment and the detailed test conditions for most of the hardness tests in use may be found in references (Mott 1956; O'Neill 1967; Williams 1942). In principle, in spite of the differences in detail, hardness tests measure largely the same physical property; the materials’ resistance to plastic deformation under combined stresses, which is related to the yield stress in simple tension. Among the other methods, Vickers microhardness test is found to be the most suitable for the measurements of microhardness of crystals.

In this test, microindentation is made on the surface of the crystals with the help of diamond pyramid indentor. The Vickers pyramid indenter where opposite faces contain an angle $\alpha$ (=136°) is the most widely accepted pyramid indenter for two reasons namely,
(i) The contact pressure for the pyramid indenter is independent of indent size

(ii) Pyramid indenters are less affected by elastic release than other indentors.

Hardness is generally defined as the ratio of the load applied to the surface area of indentation. Vickers hardness number is defined as

\[
H_v = \frac{1.8544 \, P}{d^2} \text{ Kg/mm}^2 \quad (5.1)
\]

where \( P \) is the load and \( d \) is the mean diagonal length of the indentation made on the crystal surface.

### 5.3.1 Microhardness study of C\(_{60}\) and C\(_{60}/C_{70}\) crystals

At room temperature C\(_{60}\) crystallizes in a cubic face centred lattice as is the case with gold and other metals. In contrast to the crystals made of atoms, the individual C\(_{60}\) molecules have a high rotational mobility in their crystal lattices. Owing to this mobility, the interaction between the individual fullerene molecules is weakened and thus the hardness is reduced.

Li et al (1992) were the first to report the microhardness value of pure C\(_{60}\) crystals grown from vapor phase. They reported the Vickers hardness (\( H_v \)) value of 17.5 Kg/mm\(^2\) on (111) habit face of C\(_{60}\) crystal. Bobrove et al (1995) reported the hardness values in the range of 1.2-1.8 Kg/mm\(^2\) for polycrystals grown by solution growth method. The recent report by Tachiba et al (1994) indicates that the hardness value of C\(_{60}\) crystal on the (111) face is 22 Kg/mm\(^2\) and is independent of load at room temperature under nitrogen atmosphere for the load in the range of 3 to 14 gm. Extended studies by the same authors (1995) on the behavior of plastic deformations
of C_{60} single crystals reveal that the slip systems are formed around indentation and they are found to be independent of temperature in the range 240-450 K. Thus there exists a very few reports on the mechanical property of fullerenes and even those results are contradictory to each other.

Vickers hardness measurement is also of interest to know because it is known to be quite sensitive to the presence of impurities and the crystal structure of the material. Especially, in the case of fullerenes, the purification of individual fullerenes being a difficult job, hardness study of both pure C_{60} and mixed crystals (C_{60}/C_{70}) will give a valuable information on the effect of impurities on the mechanical property of C_{60}. The requirement of high quality crystals of sufficiently large size restricts the systematic studies, especially, the load dependence of hardness.

In the present investigation, microhardness measurements were carried out on both C_{60} and mixed C_{60}/C_{70} crystals by subjecting them to the static indentation tests in air at room temperature (T = 290K). Leitz Wetzler microhardness tester fitted with Vickers pyramidal indenter and attached to a Leitz incident light microscope was used for the purpose. Crystals with well developed facets were selected for the hardness measurements and fixed on clay to keep the desired crystal face perpendicular to the diamond indentor. The indentations were made for different loads (5, 10, 25, 50 and 100 gm) and the contact period of the indentor with the specimen was maintained as 10 seconds for all the cases. The microhardness value was taken as the average of the indentations made, with both diagonals being measured. Several trials of indentations at each load were carried out and the Vickers hardness numbers were estimated using equation 5.1.

Figure 5.5 shows the variation of Vickers hardness H_v with applied load on the (111) face of pure C_{60} crystal and mixed crystal. It is seen from the figure that the hardness value increases with the increase of load for both pure C_{60} and mixed crystals. A systematic crack develops at the load
Figure 5.5  Microhardness $H_v$ as a function of indentation load for pure $C_{60}$ crystals and mixed $C_{60}/C_{70}$ crystal
of 100 gm and above for pure C$_{60}$ crystal and for mixed crystals, the cracks
develop at 50 gm (Figure 5.6a). It can be noticed that the hardness value of
pure C$_{60}$ crystal is more than that of the mixed crystal for all applied loads.
Contrary to the results of Tachiba et al (1994), the hardness values of both
the crystals depend much on the applied load. This can be attributed to the
surface hardening due to photopolymerization. Very often slip lines were
found around the indentation mark on the crystal surface. This kind of slip
systems are suggested to be \{111\}<110> for both fcc and sc structures
(Tachiba et al 1995). This indicates that the slip systems are independent
of temperature. However, the slip systems are reported to be more distinct
and visible at higher temperature than they are at lower temperatures. In
the present case, the slip systems are clearly observed with high slip steps
for higher loads. For lower loads of 5 gm and less, no slip systems found
while the higher load of 10 and 20 gm induce little slip lines with lesser step
heights. The results are in accordance with the literature that the C$_{60}$/C$_{70}$
crystals are soft and fragile materials (Bobrove et al 1995).

5.4 SURFACE DEGRADATION OF C$_{60}$ AND C$_{60}$/C$_{70}$ CRYSTALS

For any material to be of use in practical applications, the stability
against degradation is the most important requirement. Several studies
have already been carried out on C$_{60}$'s air oxidation behavior under different
conditions and many controversial results have been reported. Taylor et al
(1991) illustrated that C$_{60}$ in solution is affected by light and oxidation.
Later it was shown that even the pure C$_{60}$ powder kept in standard
conditions (at room temperature and ambient pressure) absorb a few
percentage of oxygen leading to non-sublimable residues (Li et al 1994a).
Irradiation of C$_{60}$ thin films to UV/visible light under ambient pressure
produces toluene insoluble amorphous carbon (a-C) product (Rao et al 1993).
The photosensitive nature of C$_{60}$ single crystals results in different changes
with respect to the conditions to which the crystals are exposed viz. 1)
cracks develop on the surface when exposed to light (Li et al 1994a;
Figure 5.6  
(a) Indentation mark for an applied load of 50 gm on a $C_{60}/C_{70}$ mixed crystal surface  
(b) $C_{60}$ oxide layer, the remain of a $C_{60}$ crystal after sublimation

Figure 5.7  
(a) Optical microscopic picture of degraded $C_{60}/C_{70}$ mixed crystal  
(b) an enlarged picture of the same surface

Figure 5.8  
Cracks observed on pure $C_{60}$ crystals
Verheijen et al. (1993). 2) the exposition of C_{60} crystals to UV/visible light results in toluene insoluble residues and the polymerized crystal surfaces exhibit high resistant to thermal sublimation than the interior portion of the crystal (Li et al. 1994a). 3) The laser irradiation of C_{60} single crystals yields an amorphous carbon in oxygen atmosphere while the inert atmosphere leaves the crystal unaffected (Manfredi and Milani 1995).

In most of the above cases, C_{60} crystals have been subjected to the said conditions comparatively for a shorter duration and also there has been no mention about the role of impurities (especially higher fullerenes) on the surface degradation of fullerene crystals.

In the present work, the effect of surface degradation due to the prolonged exposition of C_{60} and mixed C_{60}/C_{70} crystals to air at room temperature have been investigated. For this, a few good quality crystals with mirror polish surfaces were kept exposed to the ambient atmosphere for about two years. The surface features of the exposed crystals have been studied with optical microscope.

Figure 5.7a shows the optical micrograph of the mixed C_{60}/C_{70} crystal after two years of exposition to air. The surface got deteriorated completely (Figure 5.7b) and turned "brownish" in color. Oxidation on the outer surface of the crystal must be the cause for the destruction of the outer surface.

The pure C_{60} crystal has not been affected to this extent. Also there has been no observable changes in the color of the crystal surface. A few specks have been observed on the crystal surface which might be the atmospheric impurities condensed during the prolonged exposition to ambient. Crack lines have also been observed on pure C_{60} crystals as shown in Figure 5.8. These kind of cracks have already been reported for the crystal which has been exposed to light. In present case, the cracks have not
appeared on all the crystals. So the observed cracks might have developed internally due to the thermal strain during growth and has become more significant and visible when exposed to the ambient atmosphere. The above surface features suggest that better the purity of the sample \((C_{60})\), more the resistant to oxidation and the impurities such as higher fullerenes (mainly \(C_{70}\)) promote the oxidation leading to the degradation of the \(C_{60}\) crystal surface (Sekar et al 1996). This result is in accordance with the reports that the \(C_{70}\) is more sensitive to the oxidation than \(C_{60}\) (Huffman and Ganske 1995; Werner et al 1992). In order to study the thermal stability of the degraded \(C_{60}\) crystal, a tiny crystal has been heat treated at about 600°C for a few hours. Figure 5.6b shows the remains of the crystal after sublimation. The oxidized layer is found left while the interior portion has been completely sublimed out. This result indicates that the oxidized layers of \(C_{60}\) are thermally more stable than the pure \(C_{60}\).

5.5 ELECTRICAL CHARACTERIZATION OF \(C_{60}/GaAs\) HETEROJUNCTIONS

Current-Voltage measurements (I-V) of \(C_{60}/n\)-GaAs, \(C_{60}/p\)-GaAs and Ti/\(C_{60}/Ti\) structures were performed with Keithley Electrometer model 617.

Figure 5.9 shows a typical I-V curve (semi-logarithmic plot of current versus bias voltage) of Ti/\(C_{60}/n\)-GaAs junction at room temperature. The bias voltage is the voltage on the titanium electrode with respect to the GaAs substrate. The junction was found to be conducting when the titanium electrode was at a positive bias voltage while the current for a negative bias voltage was much smaller. This indicates that the Ti/\(C_{60}/n\)-GaAs structure behave as a rectifier. The log(I) versus V curve is almost linear for forward bias voltage exceeding 0.55 V, which can be interpreted as the series resistance effect. The forward current-voltage (I-V) characteristics have been analyzed using the following equations
Figure 5.9 Semilogarithmic graph of current-voltage characteristics for Ti/C$_{60}$/n-GaAs structure
where \( J \) is the current density (I/A), \( J_s \) is the saturation current density, \( \phi_b \) is the barrier height of the junction, \( V \) is the potential drop across the sample, \( A \) is the area of the titanium electrode, \( R \) is the series resistance of the sample, \( q \) is the electron charge, \( n \) is the ideality factor, \( k_B \) is the Boltzmann's constant, \( A^* \) is the Richardson's constant (8.4 A cm\(^{-2}\)K\(^{-2}\) for n-type GaAs and 120 A cm\(^{-2}\)K\(^{-2}\) for p-type GaAs) and \( T \) is the absolute temperature. The determined barrier height, ideality factor and saturation current density values are given in Table 5.1. The sum of the barrier heights (n-type and p-type) gives the band gap of GaAs (\( E_g = 1.42 \) eV). The series resistance values have been determined using \( dV/d\ln(J) \) vs. \( J \) plot (Cheung and Cheung 1986).

### Table 5.1

<table>
<thead>
<tr>
<th>Structure</th>
<th>( n )</th>
<th>( \phi_b ) eV</th>
<th>( J_s ) A/cm(^2)</th>
<th>( R ) ( \Omega )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_{60}/n-\text{GaAs} )</td>
<td>1.6</td>
<td>0.80</td>
<td>2.7x10(^{-8})</td>
<td>3.6x10(^3)</td>
</tr>
<tr>
<td>( C_{60}/p-\text{GaAs} )</td>
<td>3.1</td>
<td>0.62</td>
<td>4.8x10(^{-4})</td>
<td>0.3x10(^3)</td>
</tr>
</tbody>
</table>
The Ti/C$_{60}$/p-GaAs structures was also found to be rectifying but its direction of rectification was opposite to that of Ti/C$_{60}$/n-GaAs, i.e. a negative bias applied to the Ti electrode with respect to the GaAs substrate corresponds to forward direction. Figure 5.10 shows the typical I-V curve for Ti/C$_{60}$/p-GaAs at room temperature.

In order to confirm that the rectifying behavior is not due to the potential barrier but due to the Ti/C$_{60}$ interface, I-V behavior of Ti/C$_{60}$/Ti has been measured and the result shows a linear characteristic (Figure 5.11) indicating that Ti/C$_{60}$ contact is ohmic. The fact that Ti/C$_{60}$/n-GaAs and Ti/C$_{60}$/p-GaAs have opposite directions of rectification implies that there are potential barriers preventing electron and hole diffusion at the C$_{60}$/n-GaAs and C$_{60}$/p-GaAs interfaces respectively. These two barriers can be reduced under forward bias and increased under reverse bias, thus providing an interpretation of the observed rectification in the C$_{60}$/GaAs heterojunctions.

Both the junctions have different barrier height and the sum of Ti/C$_{60}$/n-GaAs and Ti/C$_{60}$/n-GaAs junctions' barrier heights is equivalent to the band gap of gallium arsenide (Arulkumaran et al. 1996).

Capacitance-Voltage characteristics of Ti/C$_{60}$/p-GaAs structures were investigated with high frequency (1 MHz) capacitance meter. The total capacitance of the Ti/C$_{60}$/p-GaAs structure can be considered as a series combination of the C$_{60}$ layer capacitance, denoted as $C_{C_{60}}$, and the p-GaAs depletion layer capacitance denoted as $C_{GaAs}$, i.e.

$$\frac{1}{C} = \frac{1}{C_{C_{60}}} + \frac{1}{C_{GaAs}} \quad (5.6)$$

Since C$_{60}$ film was undoped and thin (1929 Å), the whole layer of C$_{60}$ must be depleted due to the built-in potential of the C$_{60}$/p-GaAs heterojunction. $C_{C_{60}}$ is then given by the relation,
Figure 5.10 Semilogrithmic graph of current-voltage characteristics for Ti/C₆₀/p-GaAs structure.
Figure 5.11 Current-Voltage characteristics of Ti/C$_{60}$ structure
\[ C_{C_{60}} = \frac{A \varepsilon_{C_{60}} F_0}{d} \]  

where \( \varepsilon_{C_{60}} \) and \( d \) are the dielectric constant and the thickness of the \( C_{60} \) layer respectively. Thus \( C_{C_{60}} \) should remain constant and correspond to the maximum total capacitance of the Ti/\( C_{60}/p \)-GaAs structure. The dielectric constant of \( C_{60} \) can be evaluated to be 4.53 from the maximum total capacitance of Ti/\( C_{60}/p \)-GaAs structure and found to comparable with the reported value (Hebard et al 1991).

### 5.6 CONCLUSION

FTIR and Raman spectroscopic measurements were made on the high purity \( C_{60} \) single crystals. In the first case, the spectra confirm the purity of the grown crystals. The Raman spectra further reveal that the crystallinity of the sample was good. The low temperature Raman spectra (\( T=50 \) K) gave a number of new peaks and splittings in the original peaks compared to fcc phase in accordance with the crystal symmetry of solid \( C_{60} \).

The pentagonal-pinched mode (pp-mode), characteristic peak of \( C_{60} \), has been observed at 1461 cm\(^{-1}\). This confirms the proposal that the photopolymerization takes place in \( C_{60} \) crystals when exposed to air. Vickers microhardness studies show that the pure \( C_{60} \) crystal is harder than the \( C_{60}/C_{70} \) mixed crystal. Simple optical microscopic studies reveal that the \( C_{60} \) crystals offer more resistant to oxidation than the \( C_{60}/C_{70} \) mixed crystals. Current-Voltage characterization of \( C_{60}/GaAs \) heterojunctions show that they are having good rectifying behavior. The dielectric constant of \( C_{60} \) has been evaluated to be 4.53 from the maximum total capacitance of Ti/\( C_{60}/p \)-GaAs structure.