EVALUATION OF FULLERENE-BASED FILMS ABILITY TO SUPPRESS SPONTANEOUS POLYMERIZATION

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ABSTRACT

The aim of the EU-FP7 Marie Curie project is ‘finding fullerene–coated surfaces with maximum photosensitizing activity.’ The effectiveness of fullerene as the singlet oxygen generator decreases in the case of fullerene is condensed to the bulk material form due to polymerization ability. In this thesis, the task is about finding fullerene coated surfaces with reduced ability to polymerize.

In order to study the polymerization, Raman spectroscopy which provides non-destructive, fast and very informative method to get structural and electronic information about the fullerene-based structure was used. The films were irradiated with green laser (514 nm) at the laser power 1.8 mW which is close to the brightest sunlight irradiation, and results show that hydrogen plasma treated C\textsubscript{60}:H films presents less polymerization ability under the daylight irradiation.

The fullerene films co-evaporated with CdS, CdTe, HNO\textsubscript{3}, TPP (tetraphenylporphyrin) or treated with the hydrogen plasma were produced in St. Petersburg, Russia. Their properties were compared with “C\textsubscript{60} pure” sample.

The assessment of the texture was made by atomic force microscopy (AFM).

We used spectroscopic ellipsometry which is also a non-destructive method for characterization. The refractive index, extinction coefficient, absorption coefficient and thickness of the films were determined. The films except the “C\textsubscript{60} pure” were nearly transparent in the visible-near UV spectral regions.

Keywords: fullerene, CdS, CdTe, HNO\textsubscript{3}, TPP, hydrogen plasma, Raman spectroscopy, spectroscopic ellipsometry, polymerization.
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1. INTRODUCTION

1.1 BUCKMINSTERFULLERENE ($C_{60}$)

For quite a long time, the known phases of carbon were limited to graphite and diamond although carbon is the most abundant element in the world. A new form of carbon, buckminsterfullerene ($C_{60}$) which is also called in a short form as fullerene, was predicted initially by Eiji Osawa in 1970. However, the discovery of fullerenes was materialized in 1985 by Robert F. Curl Jr., Harold W. Kroto and Richard E. Smalley with his group. Surprisingly, the astrophysical study which was conducted by Smalley and his co-workers revealed the unusual infrared lines from large carbon clusters in the red giant stars and led to the discovery of $C_{60}$ [1-3]. This discovery was rewarded with the Nobel Prize in 1996 [1-4].

The fullerenes are preferable materials for the several reasons. The first reason is fullerenes are based on carbon which is one of the most abundant elements in nature. The other reason is discovering of the doping fullerene with the alkali metals which provides the superconducting transition in low temperatures under pressure.

Additionally, fullerene presents the most interesting property that some double bonds in the molecule break up and form the covalent bonds between the molecules in the case of irradiation with light. This phenomenon is called photo polymerization [1]. The structure of the photopolymerized $C_{60}$ has not been detailed yet and is still on the process of investigation [5-7]. Especially, when the $C_{60}$ molecules are intercalated or chemically modified, for example with hydrogen plasma.

The other interesting property of fullerenes is that they promote the transition of molecular oxygen from triplet state to singlet state if irradiated with visible light [8-10]. This property of fullerene is used in photodynamic therapy to inactivate the viruses and bacteria [11-14]. Photodynamic therapy (PDT) is one kind of the phototherapy using a non-toxic and also light sensitive compound which is called photosensitizier (PS). PDT contains three main points: PS, light source and tissue oxygen. In this therapy, PS are targeted either systemically, locally or topically to the lesion (usually in cancer cell, not always) and then lesion is illuminated with visible light for some time that leads to activate the PS [8, 10, 15]. Additionally, presence of oxygen enables to obtain cytotoxic reactive oxygen species (ROS) and leads to
death of cell and destruction of tissue. The possible applications of fullerene that is used as PS in PDT are illustrated in figure 1.1.

![Figure 1.1. Possible applications of fullerene in PDT [8].](image)

The process of PDT can be explained in detailed form: the PS absorbs the light and an electron jumps to the first excited singlet state. In this state, the energy is lost either by fluorescence or internal conversion and the excited singlet state relaxes to long-lived triplet state by a process called intersystem crossing (isc). In the excited triplet state, the reactive oxygen species (ROS) can be generated due to the interaction of excited singlet state between ground state molecular oxygen [8].

Although this method was discovered in 1997, the method has not been industrialized. Some investigations [8, 11-13] were made in liquid environments by biologists but the high cost of water-soluble derivatives of fullerene limited the applications. Then, pristine solid $C_{60}$ has been shown as an efficient photodynamic agent and also the surface of thin films was showed an antibacterial activity. Thus, the topic for inactivation efficiency of viruses and bacteria can be extended to bulk $C_{60}$ films in the air environmental conditions.

The field of fullerenes has started to occur in 1987 and it still has been developing year by year both in research and industrial areas [1, 2].

1.2 Raman Spectroscopy

The history of the spectroscopy started with the introducing the ‘spectrum’ term by Isaac Newton in 1666. Newton expressed the spectrum as continuous series of colours that
appeared when sun light passed through a prism. From 17\textsuperscript{th} century to until today, spectroscopy has been developed with lots of the innovations in optics and has been used as an efficient tool to characterize the sample \[16\].

Spectroscopy gives information about the interactions of the light-matter and the radiated energy and leads to characterize the sample. Different types of light-matter interactions (absorption, emission, scattering e.g) as well as the type of the matter (atoms, molecules, crystals, e.g) provide distinguishable types of spectroscopy.

The molecules which consist of atoms are connected to each other by valence forces. Atoms vibrate by exciting the molecule thermally and lead generation of several resonant vibrations that are analogous of the vibrations in the mechanic. Vibrational frequencies of a sample are characteristic so vibrational spectroscopy presents a very versatile method for sampling. Raman spectroscopy studies the vibrational spectra of the sample so provides a ‘fingerprint’ structure for each molecule \[17\].

In 1923, Smekal predicted the Raman effect theoretically and in 1928, Sir C. V. Raman discovered it experimentally depending on his extended the molecular light-scattering studies. Then, Landsberg and Mandelstam observed the Raman effect in quartz in recent times with Raman but the studies of Raman were accepted as more accomplished and awarded with the Nobel Prize in 1930 \[18\].

During the years, lots of improvement has been made in Raman spectroscopy to overcome the problems of fluorescence, poor sensitivity or reproducibility. Near infrared (NIR) and red excitation lasers are used to avoid the problem by fluorescence. Improvement of the spectrometer part using highly sensitive detectors coupled with optical fibres and microscopes increased the sensitivity of analysis. There are two big branches of Raman technologies which are called Dispersive Raman spectroscopy and Fourier transform Raman spectroscopy (FT-Raman spectroscopy). They are classified due to their laser excitation source and which Raman scattering is detected. These techniques are preferred according to the detecting sample. Nowadays, it is possible to get more sensitive spectra in a less time and easier to use it \[19\].

Raman spectroscopy is used in a wide range from ancient archaeology \[20\] and advanced nanotechnology \[19, 20\]. In nowadays, it is applied in a broad range in the scientific area such
as forensic science, medical and clinical chemistry, material science, surface analysis, biotechnology [21], mineralogy, food and beverages and forensic science [19, 20].

Irradiation of a substance by a monochromatic light (usually in visible region), if nearly all of the light will pass from sample but a few part of it is scattered to different directions from incident light, the scattered light gives the same frequency with the monochromatic light that is presented in the term of $\nu_0$. This process is called as ‘Rayleigh scattering’.

In Raman’s studies, the spectrum of the scattered light was found with the shifted frequencies that are specific of the substances. Shifted frequencies ($\Delta \nu$) can be either positive or negative values corresponding to the scattering light [2].

1.3 ELLIPSMOMETRY
The meaning of ‘Ellipsometry’ word is measuring the ellips of polarization and presents an effective property for studying the surfaces and thin films. The experimental technique of ellipsometry was introduced by P. Drude in 1889 and at the beginning it was used both determination of the surface layers and to characterize them. In 1945, Rothen introduced the ellipsometer which provides to measure the film thickness in a more sensitive way [22, 23]. Until today, development of more sophisticated analysis tools which are suitable for computer programs and there has been developed so much in the ellipsometry and it has been started to use in many areas of research. Especially, spectroscopic ellipsometry which provides unique possibilities has been used widespreadly in applications such as measuring the thickness of an oxide film grown by on a silicon wafer [23, 24].

Ellipsometry does not only determine the polarization change, it also determines the sample which leads to change the polarization state thus providing the characterization of sample. The optical properties of materials, thicknesses of layers, the composition of a heterogeneous material and also the electronic bandstructure of materials can be obtained from spectroscopic ellipsometric data [23, 25]. The other advantage of ellipsometry from many surface sensitive techniques is that the experiments in vacuum, in air or liquid environments. It is also a non-destructive technique and suitable for in situ measurements but however, it is an indirect technique so that the information cannot get obtained directly from the data, one needs to use expressions from electromagnetic theory of light for complex amplitude reflections to characterize sample in specific conditions [23].
In ellipsometry measurements there are two limited cases. In the first case, fullerene film is transparent so the extinction coefficient \( k \) is zero and the unknown parameters are refractive index \( n \) and thickness \( d \). In the second case, film is ultimately non-transparent and the parameters are \( n \) and \( k \). The case which is in between is very difficult because it serves three parameters and ellipsometry measures only two parameters which are called psi and delta.

1.4 Outline of the Thesis

In this thesis, chapter 2 presents the theoretical information about Raman spectroscopy and spectroscopic ellipsometry. Additionally, the information about fullerenes and the polymerization process of fullerene are expressed in the chapter 2. In chapter 3, the experimental part is served and the setups of the Raman spectroscopy and ellipsometry are presented. All of the results are expressed in chapter 4 which is called ‘Results and Discussion’ and chapter 5 gives the summary and conclusions of this thesis.
2. THEORY AND BACKGROUND

2.1 FULLERENES

\( C_{60} \) consists of 60 atoms in the closed-cage form. The molecular structure of the molecule is truncated icosahedron that is constructed by 12 pentagons and 20 hexagons [1-3]. The molecular structure of \( C_{60} \) is illustrated in figure 2.1.

![Molecular structure of \( C_{60} \) molecule](image)

In figure 2.1, each carbon atom is bonded covalently to the other three atoms. Carbon atom has four valance electrons that enable to form the two single bonds and one double bond. The slightly shorter double bond is formed by the two hexagons and single bond is formed between hexagons and pentagons. The bonding type of \( C_{60} \) is sp\(^2\) hybridization which is the strongest bond in nature, even stronger than the sp\(^3\)- hybridized diamond bond, providing useful properties for producing of hard, light and incompressible materials [1].

Some physical properties of the \( C_{60} \) molecule are classified in table 2.1 [2].

<table>
<thead>
<tr>
<th>Physical property (( C_{60} ))</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C single bond length</td>
<td>1.46 Å</td>
</tr>
<tr>
<td>C-C double bond length</td>
<td>1.40 Å</td>
</tr>
</tbody>
</table>
Mean ball diameter 7.10 Å
Ball outer diameter 10.44 Å
Number of distinct C sites 1
Number of distinct C-C bond types 2
Binding energy per atom 7.40 eV
Optical absorption edge 1.70 eV

All of the carbon atoms on the C\textsubscript{60} molecule are located geometrically identical to each other. The molecule presents the high symmetrical property which is called as icosahedral point symmetry group (I\textsubscript{h}) with 120 symmetry operations. The symmetry operations for I\textsubscript{h} are presented in table 2.2 [27].

**Table 2.2.** The representation of icosahedral (I\textsubscript{h}) symmetry.

<table>
<thead>
<tr>
<th>( I_h )</th>
<th>( E )</th>
<th>12( C_5 )</th>
<th>12( C_5^2 )</th>
<th>20( C_3 )</th>
<th>15( C_2 )</th>
<th>( I )</th>
<th>12( S_{10} )</th>
<th>12( S_{10}^3 )</th>
<th>20( S_6 )</th>
<th>15( \sigma )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_g )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>( F_{1g} )</td>
<td>3</td>
<td>( \frac{1+\sqrt{5}}{2} )</td>
<td>( \frac{1-\sqrt{5}}{2} )</td>
<td>0</td>
<td>-1</td>
<td>3</td>
<td>( \frac{1-\sqrt{5}}{2} )</td>
<td>( \frac{1+\sqrt{5}}{2} )</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>( F_{2g} )</td>
<td>3</td>
<td>( \frac{1-\sqrt{5}}{2} )</td>
<td>( \frac{1+\sqrt{5}}{2} )</td>
<td>0</td>
<td>-1</td>
<td>3</td>
<td>( \frac{1+\sqrt{5}}{2} )</td>
<td>( \frac{1-\sqrt{5}}{2} )</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>( G_g )</td>
<td>4</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>4</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>( H_g )</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>( A_u )</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>( F_{1u} )</td>
<td>3</td>
<td>( \frac{1+\sqrt{5}}{2} )</td>
<td>( \frac{1-\sqrt{5}}{2} )</td>
<td>0</td>
<td>-1</td>
<td>-3</td>
<td>( \frac{\sqrt{5}-1}{2} )</td>
<td>( -\frac{\sqrt{5}-1}{2} )</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>( F_{2u} )</td>
<td>3</td>
<td>( \frac{1-\sqrt{5}}{2} )</td>
<td>( \frac{1+\sqrt{5}}{2} )</td>
<td>0</td>
<td>-1</td>
<td>-3</td>
<td>( -\frac{\sqrt{5}-1}{2} )</td>
<td>( \frac{\sqrt{5}-1}{2} )</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>( G_u )</td>
<td>4</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>-4</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>( H_u )</td>
<td>5</td>
<td>0</td>
<td>0</td>
<td>-1</td>
<td>1</td>
<td>-5</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>-1</td>
</tr>
</tbody>
</table>
In this table, \( E \) is the identity operation and the inversion operator is indicated by \( i \). The rotation is served by \( C_n \) term and twofold, threefold and fivefold rotations are presented by \( C_2, C_3, C_5 \) and \( C^2_5 \) terms, respectively. The improper rotation which is given by \( S_n \) term is presented by \( S_3, S_{10} \) and \( S^2_{10} \) terms and also \( \sigma_v \) is the vertical mirror plane [2, 27].

Each point group can be presented in numerous ways but one can reduce all possible transformations into the irreducible sub-matrices to get less complicated representation. The Mullikan symbols \( A, B, E \) and \( F \) are used to show these representations with subscripts \( 1, 2, u \) and \( g \) and superscripts ' and ". \( A \) and \( B \) correspond to the one-dimensional symmetric and anti-symmetric symbols, respectively and \( E \) and \( F \) are the representations of 2- and 3-dimensional symmetries. The subscript terms, \( g \) and \( u \) are called as the gerade and ungerade modes, depend on even and odd symmetry due to the inversion. \( 1 \) and \( 2 \) terms indicate the symmetry and antisymmetry due to the additional rotation or mirror symmetry [1, 2].

The icosahedral symmetry group is presented by ten irreducible representations: \( A_g, A_u, F_{1g}, F_{1u}, F_{2g}, F_{2u}, G_g, G_u, H_g \) and \( H_u \) [1, 2, 28].

### 2.1.1 Photophysical Properties of \( C_{60} \)

Fullerene, \( C_{60} \) is used as a very efficient photosensitizer (PS) in the antimicrobial activities and drugs [8, 14, 15]. When the \( C_{60} \) is irradiated by the light, it is excited from ground singlet state to the excited singlet state. There are three possibilities for deactivation of PS: fluorescence, internal conversion and inter-system crossing [8-10]. These processes are shown schematically in figure 2.2.

![Figure 2.2. Schema of the deactivation process of fullerene [9].](image)

- 12 -
In the figure 2.2, the Oxygen also called as dioxygen \((O_2)\) is the strong oxidant that destroys the organic compounds in a quick way. Although there is the 21% percentage of dioxygen in the air, people can breathe without burning and this is explained by spin chemistry that dioxygen is a magnetic molecule.

Triplet oxygen \(^3O_2\) which is presented in the figure 2.2 is the ground state of the oxygen molecule. Triplet oxygen has 16 electrons in the shell and due to Hund’s rule, two electrons in the outer shell are placed parallel to each other which gives the total spin of the system equal to 1 \((S = 1)\). The spin value of 1, provides the aerobic life in nature [26].

Singlet oxygen, \(^1O_2\), is the excited state of the dioxygen, its total spin is zero \((S = 0)\) that enables to show singlet behavior like very reactive behaviour. Strong reactivity led to use singlet oxygen in different areas from polymer science to cancer therapy.

The electronic configurations of the triplet and singlet oxygen are illustrated in figure 2.3.

![Electronic Configurations of Triplet and Singlet Oxygen](image)

**Figure 2.3.** The electronic configurations of triplet and singlet oxygen [26].

In \(C_{60}\), fluorescence is negligible situation. Although no fluorescence emission was detected originally from \(C_{60}\), some groups have reported about very weak fluorescence emission which has an argument because of the quantum yield. The reason of the weak fluorescence can be explained by the short lifetime of the singlet state and the high symmetry which causes to forbid the lowest energy transition. The other possibility, internal conversion, is the radiationless decay process and the energy is lost by heating [10].

In the photodynamic therapy (PDT), PS plays the main role, absorbing the light and transferring the energy. The processes of PS are illustrated in the form of Jablonsky diagram.
in figure 2.4. In the ground state of PS, two electrons with the opposite spins are located that is called as singlet state. After the interaction between PS and light, the light is absorbed and one of the electrons in the ground state is gone into a higher energy level preserving its spin. This step is called as first excited singlet state, unstable and short-lived (nanoseconds) situation where the energy is lost either emitting light (fluorescence) or converting into heat (internal conversion) and the electron returns to the ground state. The PS in the excited singlet state can also undergo to the intersystem crossing where the spin of the electron is inverted, turned into excited triplet state with the two parallel spins. The lifetime of this state is long-lived (microseconds to milliseconds) due to forbidden spin transition process which is called phosphorescence. The phosphorescence is occurred by emission of light and PS jump from triplet to singlet state.

![Jablonsky diagram for PS](image)

Figure 2.4. Jablonsky diagram for PS [8].

The photophysical properties of fullerene molecule are easier to understand, in contrast to bulk form of fullerene where the ‘inter-molecular type exciton’ is formed in the crystal lattice through neighbor molecules. This type of exciton where the electron and hole are existed on neighbor molecules is called charge transfer (CT) excitons. In the solid state structure, self-trapping of CT exciton that is also the precursor of the photopolymerization play main role in fast relaxation dynamics with the relaxation of the crystalline lattice. Preventing of these CT excitons and photopolymerization can be obtained adding the intercalated molecules. One example for this process is given in figure 2.5. In this figure, although C_{60} has two CT excitons in 2.64 and 2.94 eV, the intercalated molecule, C_{60}Br_x, does not present any CT exciton.
The other possibility for photophysical reaction is the photodegradation which is a degradation reaction due to the absorption of photons in UV, visible and infrared region. Additionally, this reaction includes the photodissociation reaction which breaks up the molecules into the small pieces via photons and also common reaction in the Sun and also changes the structure of molecule irreversibly like intercalating the other molecules into the substate, too.

The photodegradation is a process of adsorption of particles on the surface which may interact with the sample or hydroxyl radicals. Oxidation is also known as a common photodegradation reaction.

The most known $C_{60}$ is with the high symmetric and soccer-ball shaped, presents the fcc structure in molecular crystals providing one octahedral and two hexagonal voids per $C_{60}$ molecule. These voids can be filled by intercalating the alkali metals into the $C_{60}$ that leads to the compound of $C_{60}$ with tetrahedral and octahedral sites filled, containing 3 ions inside per $C_{60}$ molecule. The presence of oxygen affects the physical properties of fullerene and depends on the oxidation reactions. The oxidation process of fullerene is important to understand the chemical reactivity of fullerene and also to characterize the property of fullerene material [29-31].

The kind of photodegradation that we used in this project is oxidation. After the oxidation, ‘the intercalated oxygen molecules are located above of the hexagons of the $C_{60}$ molecules which are facing with the octahedral voids of the $C_{60}$ lattice’ [26]. A complete thermally induced oxidation reaction for the fullerene in presence of oxygen is illustrated in figure 2.6.
In this figure, the process is ranged starting from the intercalation of oxygen to the complete oxidative degradation of fullerene.

**Figure 2.6.** A complete oxidative degradation of fullerene with oxygen [29].

### 2.1.1.1 POLYMERIZATION OF \( C_{60} \)

\( C_{60} \) molecular crystals with f.c.c structure and weak Van der Waals intermolecular bonds can be transformed into different polymeric structures. The polymeric phases change the structure, mechanical and electronical properties of the pristine form of the \( C_{60} \) [1].

Three principal methods are used to polymerize \( C_{60} \): photopolymerization, pressure polymerization and intercalation of \( C_{60} \) structure with guest compound. In this project, photopolymerization method is used and described in details in chapter 2.1.1.1.1.

#### 2.1.1.1.1 PHOTOPOLYMERIZATION

In this method, thin films of \( C_{60} \) were irradiated by light in the UV or visible region for polymerizing \( C_{60} \). In the table 2.1, the optical absorption edge of \( C_{60} \) is presented as 1.7 eV that means the excitation wavelength of light must be nearly equal to 730 nm, so the electrons will jump to excited single state that is short-lived state. The electrons will drop to the lowest excited triplet state fast which is both very reactive and long-lived state. In this type of polymerization, the important point is hiding \( C_{60} \) from the direct exposure of \( O_2 \) during the phototransformation process because \( O_2 \) is an effective quencher which leads to change the electron population in the triplet state [1].
In photopolymerization, some of the double bonds are broken and connected to an adjacent molecule forming a square ring which contains four carbon atoms. This intermolecular bond creation is called [2+2] cycloaddition [1, 2, 5-7, 32, 33] and illustrated in figure 2.7.

![Figure 2.7. [2+2] cycloaddition in C\textsubscript{60} molecule [34].](image)

In the cycloaddition process, double bonds of the adjacent molecules are orientated parallel to each other. The complete polymerization leads to the decrease of distance between the molecules to 9.1-9.2 Å which is served as 10 Å in the case of unpolymerized state. This bond connects the two pair bonds which connects two hexagons and is called as 66/66 bond and in another way, one or both bonds may connected due to the cycloaddition process and shared between a hexagon and a pentagon. These bonds may be in the form of 65/66 or 65/56 [35]. The bond lengths of the 66/66, 65/56 and 65/66 bonds in the relaxed form are listed in table 2.3.

**Table 2.3.** Bond lengths of the 66/66, 65/56 and 65/66 bonds [35, 36].

<table>
<thead>
<tr>
<th>Type of the bond</th>
<th>Length (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>66/66</td>
<td>9.19</td>
</tr>
<tr>
<td>65/56</td>
<td>9.17</td>
</tr>
<tr>
<td>65/66</td>
<td>9.26</td>
</tr>
</tbody>
</table>

The creation of the intermolecular bonds provides to stop the rotation of molecule and lowers the symmetry [1, 2, 5, 28, 32]. Additionally, the formation of the new bonds leads to change the frequency of molecular vibrations, especially A\textsubscript{g} (2) mode which enables a consecutive
stretching at the same time and connects the double bonds on a C₆₀, presents the characteristic downshift in Raman spectra. The downshift of the A<sub>g</sub>(2) depends on the number of double bonds that are broken and connected outwards which is a characteristic Raman property for all polymeric phases like orthorhombic phase (1D), tetragonal phase (2D) and rhombohedral phase (2D) [1, 2]. The shifted positions of A<sub>g</sub> (2) mode of different C₆₀ structures are illustrated in figure 2.8.

Figure 2.8. Shifted frequencies of the A<sub>g</sub> (2) mode in different polymer structures of fullerene [2].

2.1.2 Method of Production of Films

In this project, the films were produced by collaboration group in St.Petersburg, Russia using the quasi-closed volume vacuum evaporation technique. Films were prepared by discrete evaporation in a quasi-closed volume providing vacuum chamber pressure 10⁻⁷ Torr. The semiconductor fullerene films were grown on glass substrates / ITO and silicon substrate and coevaporated with cadmium sulfide (CdS), cadmium telluride (CdTe), nitric acid (HNO₃), tetraphenylporphyrin (TPP or H₂TPP) or treated in the hydrogen plasma discharge (C₆₀:H). The synthesis parameters for some of these films are listed in table 2.4.
Table 2.4. The synthesis parameters for films.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>Content</th>
<th>Composition ratio</th>
<th>T_{evaporator}, °C</th>
<th>T_{substrate}, °C</th>
<th>Deposition time, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>C\textsubscript{60}HNO\textsubscript{3}</td>
<td>-</td>
<td>500</td>
<td>130</td>
<td>10</td>
</tr>
<tr>
<td>113</td>
<td>C\textsubscript{60}HNO\textsubscript{3}</td>
<td>-</td>
<td>500</td>
<td>130</td>
<td>5</td>
</tr>
<tr>
<td>114*</td>
<td>C\textsubscript{60}</td>
<td>-</td>
<td>510</td>
<td>200</td>
<td>12</td>
</tr>
<tr>
<td>149</td>
<td>C\textsubscript{60}:CdS 1:1</td>
<td></td>
<td>560</td>
<td>240</td>
<td>4</td>
</tr>
<tr>
<td>151</td>
<td>C\textsubscript{60}:CdS 1:3</td>
<td></td>
<td>520</td>
<td>210</td>
<td>3</td>
</tr>
<tr>
<td>154</td>
<td>C\textsubscript{60}:CdS 1:10</td>
<td></td>
<td>520</td>
<td>215</td>
<td>4</td>
</tr>
<tr>
<td>02_69</td>
<td>H\textsubscript{2}TPP</td>
<td>-</td>
<td>320</td>
<td>150</td>
<td>5</td>
</tr>
</tbody>
</table>

In the table 2.4, ‘*’ term means that the sample was exposed to hydrogen plasma after the evaporation.

In table 2.4, TPP is tetraphenylporphyrin and can be shown in abbreviated way either TPP or H\textsubscript{2}TPP. The molecular formula of TPP is C\textsubscript{44}H\textsubscript{30}N\textsubscript{4} and this compound can act as a photosensitizer in production of the singlet oxygen in photodynamic therapy as well as commonly used HNO\textsubscript{3}. The combination of CdS with sulfate ion (SO\textsubscript{4})\textsuperscript{2-} is used in order to inactivate the bacteria and viruses. Depending on to the structures of donor-acceptor complex of TPP and the combination of both CdS and CdTe, which are also used as photoresistor. Additionally, CdTe provide a good opportunity in order to use in organic solar cells and other light-controlled molecular devices such as molecular switches.

The process of the hydrogen treatment is explained in details below and also is presented in figure 2.9 where (a) illustrates the chamber of fullerene production and (b) shows the plasma reactor and the position of the sample inside the reactor.

![Figure 2.9](image)

Figure 2.9. (a) The chamber for fullerene production and (b) the plasma reactor.
In the figure 2.9 (a), the initial powder was under the tantalum screen while the substrate was above and (b) illustrates that the sample was placed outside of the main discharge in order to reduce the amount of reacted hydrogen.

The plasma chemical reactor which is formed by a d.c. diode system with tungsten electrodes and operates at the current density in the case of it is lower than 0.3 \( \text{A/cm}^2 \). The treatment was done at very low H pressure \( (p = 3 \div 10 \text{ kP}) \) and the samples were on the periphery of the plasma discharge. The aim of the experiment was to produce samples with very low concentration of hydrogen – not \( \text{C}_{60}\text{H}_{36} \) or \( \text{C}_{60}\text{H}_{24} \) as is usually obtained in previous works - but creating the conditions where the fullerenes attach as small amount of hydrogen as possible. With this aim, the hydrogen pressure was as small as possible and reducing pressure any more could lead to the quenching of the discharge.

### 2.2 Analysis Methods

#### 2.2.1 Raman Spectroscopy

When the molecule collides with the light, in the energy of \( h\omega_0 \), a photon may be scattered in the form of elastic or inelastic scattering. In elastic scattering, there is no change of energy and called as Rayleigh scattering where the lines appear more intense.

The Raman effect is observed, collision of a molecule with light led to the interactions of electron cloud and bonds of the molecule with the light. The scattering process for spontaneous Raman effect, a photon enables to excite the molecule to the virtual state. After the relaxation process of molecule, a photon is emitted and undergo to the the specific rotational or vibrational transition state. If the transition of a molecule is ended up with a higher vibrational state, it emits a photon which has got a less energy \( (\omega_0 - \omega_{\text{vib}}) \) than laser.

This process is called as ‘Stokes scattering’ and enables to give one photon in a million so the obtaining Raman effect is weak. In the inverse situation which is called ‘Anti-Stokes scattering’, the molecule is in the excited vibrational energy in the initial state and goes to the lower state that leads to get more scattered energy \( (\omega_0 + \omega_{\text{vib}}) \) and the frequency shift is positive [18]. The process of Rayleigh, Stokes and anti-Stokes scattering are presented in figure 2.10.
Figure 2.10. Presentation of the scattering processes of Rayleigh, Stokes and anti-Stokes [37].

The rough ratio of the vibrational mode intensities in anti-Stokes and Stokes parts are presented in equation (2.1). Intensity of the light can be changed by the angle of scattering, the electronic polarizability and the directions of polarization, etc [1].

\[
\frac{I_{\text{vib,at}}}{I_{\text{vib,st}}} = \left(\frac{\omega_0 + \omega_{\text{vib}}}{\omega_0 - \omega_{\text{vib}}}\right)^4 e^{-\frac{\hbar \omega}{k_B T}} \quad (2.1)
\]

In Raman spectroscopy, the polarizability of the molecule must change during the interaction of incident light on the molecules with the electrical field in the virtual state. This situation is explained by the formula,

\[
P = \alpha E \quad (2.2)
\]

where \(P\) is the induced dipole moment, \(\alpha\) is the polarizability of the molecule and \(E\) is the electrical field. In the classical description, both \(E\) and \(P\) that is inside of the molecule are oscillating in the interaction process. The oscillating function of \(E\) depending on the frequency of light, \(\nu_0\), is presented in equation (2.3),

\[
E = E_0 \cos 2\pi \nu_0 t = E_0 \cos \omega_0 t \quad (2.3)
\]

where \(E_0\) is the interacted electric field with the molecule and time is \(t\). Equation (2.3) is inserted into the (2.2) and the obtaining equation is labeled in equation (2.4).

\[
P = \alpha E_0 \cos \omega_0 t \quad (2.4)
\]
Polarizability, $\alpha$, is a parameter that changes due to the motion of the nuclei in the molecule and also presents the bounding ability of them [38]. This term can be given by an expression depending on the internal vibrational mode, $q$, which is presented as $q = q_0 \cos 2\pi v_{vib}t$ where $v_{vib}$ term presents the eigenfrequency of the nuclei. The equation for expanded series, $\alpha$ is presented in (2.5).

$$\alpha = \alpha_0 + \left( \frac{\delta \alpha}{\delta q} \right) q + \text{higher order terms}$$  \hspace{1cm} (2.5)

Inserting the equation (2.5) into the (2.4), a complex equation for the dipole moment is obtained and served as equation (2.6).

$$P = (\alpha_0 E_0 \cos \omega_0 t) + \frac{1}{2} E_0 q \frac{\delta \alpha}{\delta q} [\cos(\omega_0 + \omega_{vib}) t + \cos(\omega_0 - \omega_{vib}) t]$$  \hspace{1cm} (2.6)

First term in the equation (2.6) presents the equilibrium condition for the molecule and in the second term $\omega_0 - \omega_{vib}$ and $\omega_0 + \omega_{vib}$ expressions are the Stokes and anti-Stokes shifts which are also illustrated in figure 1.1, respectively [17].

Variations of the polarizability can be understood by the vibration process and the molecule symmetry. According to the ‘a centre of symmetry’ for molecules, symmetric vibrations present the intense Raman bands but unsymmetrical vibrations leads to increase the negligible Raman bands and the other rule is Raman active vibrations are inactive in infrared.

Wavenumber ($\nu$) whose unit is in inverse centimeters [cm$^{-1}$] is used in Raman spectroscopy to present the Raman shift. The equation which shows the relation between the wavenumber and energy is expressed in equation (2.7).

$$E = \frac{hc}{\lambda} = hce\nu$$  \hspace{1cm} (2.7)

Conversion between the energy and wavenumber term can be calculated using the expression that is labeled in (2.8).

$$8059 \text{cm}^{-1} = 1 \text{eV}$$  \hspace{1cm} (2.8)

According to the equation (2.8), the vibrations in the range of 200 – 4000 cm$^{-1}$ have energies of 24 – 496 meV [1].
2.2.1.1 Raman Spectroscopy on C\textsubscript{60}

In a non-linear molecule, motion of the molecule has six degrees of freedom which contains three translations and three rotations [27]. The number of the vibrational modes for a molecule with N atom is presented by the formula, \(3N - 6\) so for fullerene, C\textsubscript{60}, that contains 60 atoms has 174 vibrational degrees of freedom. Fullerene is presented by icosahedral symmetry, I\textsubscript{h}, which is also called as highest possible symmetry for a molecule. Due to the high symmetry, leads to degenerate many of the vibrational degrees of freedom of the fullerene and gives 46 vibrational modes [1, 2, 27, 28, 32]. The expression for vibrational modes of fullerene is expressed in below (2.9) [1, 2, 28].

\[
\Gamma^\text{vib}_{\text{C}_{60}} = 2A_g + 3F_{1g} + 4F_{2g} + 6G_g + 8H_g + A_u + 4F_{1u} + 5F_{2u} + 6G_u + 7H_u. \quad (2.9)
\]

The letters in the expression serves the different degeneracy of modes as \(A\) is 1, \(F\) is 3, \(G\) is 4 and \(H\) is 5. The \(g\) and \(u\) operators presents the gerade and ungerade modes which explains the changing of the sign due to their vibration directions. If the molecule is in the point group which consists of the inversion centre, Raman active vibrations must be gerade [1, 27]. According to the group theory, expression in (2.9) four \(F_{1u}\) modes are active in IR, ten modes \((8H_g + 2A_g)\) are Raman active and the other 32 modes are considered as optically silent. Raman active modes of single crystal of C\textsubscript{60} in the upper part and the polycrystalline C\textsubscript{60} film are illustrated in figure 2.11.

**Figure 2.11.** Raman active modes of single crystal C\textsubscript{60} in upper part and polycrystalline film of C\textsubscript{60} in lower part [28].

- 23 -
In consequence of high symmetry structure of fullerene, Raman spectroscopy provides to probe the changes chemical environment of \( C_{60} \). Lowering the symmetry with using the chemical changes will present the new Raman active modes. At the same time, the structure of \( H_g \) (5-fold degenerate) modes will change and split into different structures and the frequencies of some modes may shift. Different types of polymerization and the intercalation with the different molecules can be given examples for lowering the symmetry [1, 2, 32].

2.2.1.1 Polymeric Phases of \( C_{60} \)

\( C_{60} \) is entitled as very Raman active material due to its large Raman cross section of many of the vibrations in the molecule. When the molecules are connected covalently bonded, lead to lower the symmetry structure which presents more Raman allowed lines and the resulting spectra provides the characteristic information for the polymerization process of different phases. Lowering the symmetry, low frequency optical chain modes may be created near 100 cm\(^{-1}\) or modes may be connected by the intermolecular bonds in the region of 900-1000 cm\(^{-1}\). Silent modes may be Raman allowed modes and degenerate \( H_g \) modes may take the different energies and original line splits into several components. The shift in the vibrational frequencies leads to change the electron distribution and it may cause to change the some bonds strengths [1].

In the Raman spectrum, some modes are useful probing for the polymerization and intercalated phases of \( C_{60} \). \( A_g \) (2) which is also called as pentagonal pinch mode is placed in 1469 cm\(^{-1}\) for pristine \( C_{60} \). This mode cannot be split, but a number of \( A_g \) (2)-derived modes appear due to different processes connected with the changes of the electronic structure. In the polymerization process of \( C_{60} \), some double bonds are occurred by breaking the bonds and bonded covalently to the neighbor molecule and this process effect the characteristic vibrational states of the molecule. After the polymerization process, the effecting of \( A_g \) (2) mode is not obvious but the researches present that \( A_g \) (2)-derived mode is shifted down linearly due to the number of polymer bonds on the molecule [1, 5, 7, 32]. The shifted positions of the \( A_g \) (2)-derived mode depending on the formation of polymer bonds are listed in table 2.5.
Table 2.5. Shifted positions of the $A_g(2)$-derived mode for different $C_{60}$ phases [1].

<table>
<thead>
<tr>
<th>Phase</th>
<th>Number of polymer bonds</th>
<th>$A_g(2)$ mode position (cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine</td>
<td>0</td>
<td>1469</td>
</tr>
<tr>
<td>Dimers</td>
<td>1</td>
<td>1464</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>2</td>
<td>1459</td>
</tr>
<tr>
<td>Branched chains</td>
<td>3</td>
<td>1454</td>
</tr>
<tr>
<td>Tetragonal</td>
<td>4</td>
<td>1448</td>
</tr>
<tr>
<td>Rhombohedral</td>
<td>6</td>
<td>1407</td>
</tr>
</tbody>
</table>

2.2.2 ELLIPSOMETRY

2.2.2.1 PRINCIPLES OF ELLIPSOMETRY

Ellipsometry measures the polarization change which is reflected from sample surface [39]. The schema which presents the basic process of light-matter interaction of sample in the surface is illustrated in figure 2.12.

![Figure 2.12. The light-matter interaction between two surface.](image)

In the figure 2.12, the polarization of a monochromatic light wave on the surface plane in two different medium is illustrated. The interaction of incident light with matter, one portion of the incident light will form the reflected wave ($r$) while remaining part will transmit through...
the sample and form the transmitted wave \( t \). At the interface, the laws of electromagnetic theory are essential to get the correlations between the incident and reflected wave and between the incident and refractive wave, in order. In all of the light forms, it is possible to determine the electrical fields into the components of linearly polarized parallel \( E_p \) and perpendicular \( E_s \) to the incident plane wave. The subscripts of \( p \) and \( s \) present the reference axes of the system due to the direction of the incident plane wave which is parallel and perpendicular, respectively. The coefficients for complex reflection for polarized light through \( p \) and \( s \) directions are given in equation (2.10).

\[
R_p = \frac{E_{rp}}{E_{ip}} = |R_p|e^{i\delta_p} \tag{2.10}
\]

\[
R_s = \frac{E_{rs}}{E_{is}} = |R_s|e^{i\delta_s}
\]

where \( R_p \) and \( R_s \) are the complex reflection coefficients in parallel and perpendicular directions, respectively. These coefficients depend on the incident angle, the energy of photon and optical properties such as the dielectric function of two media. Additionally, the structure of the media have to take consider because being in an anisotropic property, consisting of different materials causes to inhomogeneous property and also surface roughness is another important parameter for these coefficients.

In the ellipsometer, reflected polarized light will be analyzed due to its polarization state. The reflected light is generally elliptically polarized which provides one component parallel and one component perpendicular with respect to the plane of incident wave. Nevertheless, the determination of the amplitude and phase of these components are not possible so the ratio of these components which presents as \( \rho \) are using and given in equation (2.11).

\[
\rho = \left| \frac{R_p}{R_s} \right| e^{i(\delta_p - \delta_s)} \tag{2.11}
\]

The complex ratio of reflectance, \( \rho \), is often written in a short form that is presented in equation (2.12).

\[
\rho = \tan \varphi e^{i\Delta} \tag{2.12}
\]
In equation (2.12), the amplitude ratio is \( \tan \varphi \), and served as \( \frac{R_p}{R_s} \). The phase difference, \( \Delta \), between the components of \( p \) and \( s \) directions are presented by the formula, 
\[ \Delta = \delta_p - \delta_s \] \( \varphi \) and \( \Delta \) are the ellipsometric angles and taken values from 0° to 90° and from 0° to 360°, respectively [23].

Ellipsometry provides several advantages like measuring the only polarization changes without the intensity changing which gives a measurement independent from the intensity variations of light source. One of the advantages of ellipsometry is the measurement of phase difference that enables to detect very thin films on their substrates. Additionally, it is non-destructive and suitable for in-situ measurements [23, 24, 39, 40].

Spectroscopic ellipsometry provides to determine the complex reflectance ratio with respect to the photon energy in the infrared (IR), visible and near ultraviolet (UV) range. Determining of two ellipsometric angles \( (\varphi \) and \( \Delta \) ) facilitates to obtain the information both the real and imaginary parts of the dielectric function of a material without Kramer-Kronigs dispersion integrals. Furthermore, the data from spectroscopic ellipsometer presents more detailed information than experimental results and some complex therotical models can be created [23].

**2.2.2.1 THE INTERACTION OF LIGHT WITH MATTER**

The propagation and excitation of a plane electromagnetic wave is governed by Maxwell’s equations and ‘hold at every point in whose neighborhood the physical properties of the medium are continuous [40]. ’ Maxwell’s equations due to the space and time derivatives are presented in below.

\[ \nabla \times E = -\frac{\partial B}{\partial t} \] \hspace{1cm} (2.13)

\[ \nabla \times H = \frac{\partial D}{\partial t} + J \] \hspace{1cm} (2.14)

\[ \nabla \cdot B = 0 \] \hspace{1cm} (2.15)

\[ \nabla \cdot D = \rho \] \hspace{1cm} (2.16)
In equation (2.13) $E$ term presents the intensity of electric field and $B$ term both in equation (2.13) and (2.15) is magnetic flux density. The terms of $\rho$ and $J$ serve the electric charge and density of current in the medium which are not obtaining from the origin of electromagnetic field. $D$ and $H$ fields are called as densities of electric flux and magnetic flux, respectively. Maxwell’s equations are expressed by relations that are related to the property of medium under the effect of the field. These expressions are called as ‘constitutive relations’ and given in equations (2.17) and (2.18) in their general forms.

\[
D = D(E, B) \quad (2.17)
\]

\[
H = H(E, B) \quad (2.18)
\]

In the case of linearly related between equations (2.17) and (2.18), the superposition principle applies and the medium is manifested as linear [23, 40].

### 2.2.2.1 The Dielectric Function

If the field is weaker than the ferroelectrics and ferromagnets, it provides the property of linear medium so the constitutive relations that are presented in equations (2.17) and (2.18) will form as,

\[
D(k, \omega) = \varepsilon_0 \varepsilon(k, \omega) \cdot E(k, \omega) \quad (2.19)
\]

\[
H(k, \omega) = \mu_0^{-1} \mu^{-1}(k, \omega) \cdot B(k, \omega) \quad (2.20)
\]

where $\varepsilon_0$ and $\mu_0$ terms are the physical constants which are called as electric permittivity and magnetic permeability of free space, equal to $8.854 \cdot 10^{-12} \, \text{F/m}$ and $4\pi \cdot 10^{-7} \, \text{H/m}$, respectively. The functions of $D(k, \omega), E(k, \omega), H(k, \omega)$ and $B(k, \omega)$ are the Fourier transforms of the field quantities due to the space and time. $\varepsilon(k, \omega)$ and $\mu^{-1}(k, \omega)$ are the tensors of dielectric and inverse magnetic permeability which present the linear property of a material related both the inter and intra-molecular structure of it.

If the wavelength is sufficiently long to allow the long-range effects in a material, in the case of most materials at the optical frequencies, the wave vector $(k)$ can be neglected. According to neglection, dielectric and inverse magnetic permeability tensors are written in dependence of frequency and served in equations (2.21) and (2.22).
\[ \varepsilon(k, \omega) = \varepsilon(\omega) \quad (2.21) \]

\[ \mu^{-1}(k, \omega) = \mu^{-1}(\omega) \quad (2.22) \]

In the optical frequency range for electromagnetic waves, the magnetic moments can be neglected. The magnetic moments in para- or ferromagnetic materials, the relaxation time is too long that causes preventing to follow the rapid oscillations of the electromagnetic field and remaining part in diamagnetic materials are not sufficiently enough to effect the optical behavior so the optical properties of solids can be expressed in one parameter, \( \varepsilon \).

The Maxwell’s equations for the monochromatic plane waves in the frequency range are formed again with depending on the time related factor, \( e^{i\omega t} \) and neglecting both the electric charge and current, presented in below.

\[ \nabla \times E = -i \omega \cdot B \quad (2.23) \]

\[ \nabla \times H = i \omega \cdot D \quad (2.24) \]

\[ \nabla \cdot B = 0 \quad (2.25) \]

\[ \nabla \cdot D = 0 \quad (2.26) \]

Using the equations in above, the dielectric tensor can be presented in matrix tensor,

\[ \varepsilon = \begin{pmatrix} \varepsilon_{11} & \varepsilon_{12} & \varepsilon_{13} \\ \varepsilon_{21} & \varepsilon_{22} & \varepsilon_{23} \\ \varepsilon_{31} & \varepsilon_{32} & \varepsilon_{33} \end{pmatrix} \quad (2.27) \]

where all of the components of \( \varepsilon \) determines the complex expression of the dielectric tensor. The form of matrix changes due to the crystal structure. In the case of isotropic material, all the \( \varepsilon_{ij} \) will be equal and dimesionless complex quantity of a complex dielectric function is served in equation (2.28).

\[ \varepsilon = \varepsilon_1 - i\varepsilon_2 \quad (2.28) \]

In the equation (2.28) that is also the common expression for \( \varepsilon \), \( \varepsilon_1 \) and \( \varepsilon_2 \) are the real and imaginary parts of the complex dielectric function [23].
2.2.2.1.1 The complex refraction index

The complex index of refraction, \( N \), can be expressed more convenient using the relation due to the \( \varepsilon \). This expression is presented in equation (2.29).

\[
N = \sqrt{\varepsilon}
\]  

(2.29)

The result of equation (2.29) is labeled in equation (2.30).

\[
N = n - ik
\]  

(2.30)

In the equation in below, \( n \) is the refraction index of medium depends on the phase velocity of the medium, \( v \). The \( n \) term is explained by the formula, \( n = \frac{c}{v} \) where \( c \) is the light speed in vacuum. The other term in equation (2.30), \( k \), is the extinction coefficient of the medium and presents the attenuation of wave while propagating in the medium. The attenuation can also written by another formula related to the absorption coefficient, \( \alpha \),

\[
\alpha = \frac{4\pi k}{\lambda_{\text{vac}}}
\]

(2.31)

where \( \lambda_{\text{vac}} \) presents the light vacuum wavelength and expressed by the formula, \( \lambda_{\text{vac}} = \frac{2\pi c}{\nu} \).

Using the equation (2.29), the real and imaginary parts are equated and the results are presented in equations (2.32) and (2.33).

\[
\varepsilon_1 = n^2 - k^2
\]

(2.32)

\[
\varepsilon_2 = 2nk
\]

(2.33)

For another method, the formulas for \( n \) and \( k \) are labeled as in equations (2.34) and (2.35) [23].

\[
n = \sqrt{\frac{1}{2} \left( (\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2}) \right)}
\]

(2.34)

\[
k = \frac{\varepsilon_2}{\sqrt{2(\varepsilon_1 + \sqrt{\varepsilon_1^2 + \varepsilon_2^2})}}
\]

(2.35)
2.2.2.2 Optical Models in Isotropic Planar Structures

2.2.2.2.1 The Fresnel Equations

In figure 2.12, the propagation of an optical plane wave through one material which acts as an interfacial layer between two media is illustrated. In this figure, the plane wave propagated between two homogeneous optically isotropic media and the medium in reflected part is called with ‘0’ subscript while the other medium that is in transmission part is called as ‘1’ with the complex refraction indices of \( N_0 \) and \( N_1 \) respectively. The incident angle and angle of refraction is presented as \( \varphi_0 \) and \( \varphi_1 \), in order. The equations of Maxwell are essentials in the media and must fulfill the boundary conditions that provide to get Snell’s Law which is presented in equation (2.36).

\[
N_0 \cdot \sin \varphi_0 = N_1 \cdot \sin \varphi_1
\]  
(2.36)

In case of known amplitude and polarization of an incident plane wave, the amplitude and polarization of both reflected and transmitted waves can be calculated using the boundary conditions. These parameters are calculated in two different situations to get a more convenient expression and presented in below.

\[
r_{abp} = \frac{E_{Ep}}{E_{ip}} = \frac{N_1 \cos \varphi_0 - N_0 \cos \varphi_1}{N_1 \cos \varphi_0 + N_0 \cos \varphi_1}
\]  
(2.37)

\[
r_{abs} = \frac{E_{Es}}{E_{is}} = \frac{N_0 \cos \varphi_0 - N_1 \cos \varphi_1}{N_0 \cos \varphi_0 + N_1 \cos \varphi_1}
\]  
(2.38)

\[
t_{abp} = \frac{E_{Ep}}{E_{ip}} = \frac{2N_0 \cos \varphi_0}{N_1 \cos \varphi_0 + N_0 \cos \varphi_1}
\]  
(2.39)

\[
t_{abs} = \frac{E_{Es}}{E_{is}} = \frac{2N_1 \cos \varphi_1}{N_0 \cos \varphi_0 + N_1 \cos \varphi_1}
\]  
(2.40)

The equations in above, present the Fresnel complex-amplitude coefficients of reflections, \( r \), and transmissions, \( t \), in p- and s- directions, respectively. However, according to the property of media such as absorbing etc., the incident and refracted angles will form a complex expression and the physical picture of the fields and ray propagation will be more complicated, too.
2.2.2.2 The Two-Phase Model

In figure 2.12, two-phase model which is known as most basic is presented. In this model, the reflection coefficients in the equation (2.10) are given in the form of Fresnel coefficients and labeled in equation (2.41).

\[
R_p = r_{01p} \\
R_s = r_{01s}
\]  

(2.41)

Fresnel equations (2.37-40) are inserted into equation (2.11) with applying the Snell’s Law in the equation (2.36), a new and useful expression for the complex refraction index of substrate, \(N_1\), is expressed in the terms of \(N_0\) which is the ambient (air) complex refraction index and \(\rho\).

\[
N_1 = N_0 \sin \varphi \sqrt{1 + \left(\frac{1 - \rho}{1 + \rho}\right)^2 \tan^2 \varphi}
\]  

(2.42)

The equation (2.42) presents that calculating of the complex dielectric function of a material is possible by ellipsometry.

2.2.2.2.3 The Three-Phase Model

In this model, there is a thickness between the ambient and substrate presented by the term of \(d_1\). One example for this model is served in figure 2.13.

![Figure 2.13. The model for three phase.](image)

In this situation, the complex reflection coefficients in the equation (2.41) will take a new form that is labeled as equation (2.43).
In the equation (2.43), Fresnel coefficients are presented by the subscripts that the numbers show the media, ambient film is (0-1) and the interface part of film is (1-2) for polarized light in p and s directions. The other term, $\beta_i$, is the phase thickness of film and served in the equation (2.44).

$$\beta_i = 2\pi \left( \frac{d_i}{\lambda} \right) N_i \cos \phi_i$$  \hspace{1cm} (2.44)

In the case of the film has layer more than three, multiple reflections occur which causes to get infinite series in the formulas [23].

The functions of $R_p$ and $R_s$ are periodic that enable to return to the initial point in the case of film thickness is equal to the ellipsometric period. The thickness can be calculated using the period formula labeled in equation (2.45) where $\lambda$ presents the wavelength term [22].

$$T = \frac{\lambda}{2\sqrt{N_i^2 - \sin^2 \phi_0}}$$  \hspace{1cm} (2.45)

According to this equation, it can be concluded that the ellipsometric period changes due to the wavelength and the from complex refractive index. The periodic form of ellipsometry is illustrated in figure 2.14.

**Figure 2.14.** An ellipsometric nomogram for the thickness calculation with the period.
In this figure, the graphic with psi versus delta expresses that thickness can take several values depending on the period. Additionally, the graphic presents two same measurements in the range of between 0 to 360° which leads two cases for calculating of thickness. In the case of ∆ = 0°, thickness formula is \( d = (m - \frac{1}{2})T \) and when ∆ = 180° the formula turns the form of \( d = mT \) where \( m \) is given by the numbers \( (m = 1, 2,...) \).

The delta which explains phase shift is more convenient for calculation of the thickness and psi which expresses the changes in amplitude related to the ratio of the refraction indexes [39].

In the spectroscopic ellipsometry, the film can present the different properties either transparent or absorbing in different ranges. In transparent films, oscillation patterns whose depend on the thickness and refractive index occur due to the interference of thin films and in the thicker films more oscillation patterns are obtained. In figure 2.15, the effect of thickness is presented for oxide on Si in the thickness of 100 nm, 500 nm and 3 microns. It is obtained that if the thickness is big, more interference oscillations are obtained.

![Figure 2.15. Thickness effect on the interference [41].](image)

Figure 2.15 is presented wavelength versus psi angle. The peak values of psi decreases with the bigger refractive index and affects the number of oscillations.

Spectroscopic ellipsometry presents different performances related to the thickness. If the thickness of the film is smaller than 10 nm and until to 200 nm, this region is called ultra thin, the ellipsometer just fits the thickness and gives correlated index data. The region between 50 nm to 2 μm enables a perfect region for spectroscopic ellipsometry obtaining refraction index and thickness. If the thickness is bigger than 2 μm, this region is so-called thick and leads to get many interference signals which are reduced by using uniform film [41].
2.2.2.3 Surface Roughness

This parameter is also called in a short form ‘‘roughness’’ and measures the textile of the surface on the film presenting the vertical deviations from its ideal surface forms. The vertical deviations identify the roughness in the films due to the quantity of deviations and determine that in the large deviations, surface is rough and in the small deviations, the surface is smooth. In the statistically surface rough, the roughness can be presented with \( \delta \) that is surface roughness in r.m.s unit and the distance of correlation \( R \). Surface roughness is illustrated with its term in figure 2.16.

![Figure 2.16. The statistic rough surface.](image)

The roughness is an important parameter that cannot negligible. In the case of neglecting the roughness produces so much error and the study about it has been expressed by Fenstermaker and McCrackin in 1969. According to the results, ellipsometry is so sensitive to the roughness and real surfaces of the optical planes even in the basic models are not smooth that is at least on the atomic scale. Surface roughness affects data of the ellipsometry and modeled with the EMA (Bruggeman Effective Medium Approximation) in the case of thickness is between 0.1 nm to 50 nm [23].

2.2.2.4 Modelling of the Films

Our fullerene films present the 4-layer thickness where a layer of fullerene lies on silicon which has a native oxide and surface roughness. In turn, fullerene has also a surface layer with a certain roughness which influences the light reflection.

The first assumption for modeling that films have got the two-layer structure which means the refractive index of upper layer in the film is much smaller than the refractive index of main film. The obtained value of refractive index of upper layer from ellipsometry presents the nearly same value for several samples which is between 15 and 20 nm. This value, 15-20 nm, is also obtained from the AFM measurements for surface roughness. Thus, the sub-surface
part of the films can be modeled as a ‘porous microstructural layer’ and explained by the model of Bruggeman effective media approximation (EMA) which presents the mixture of C\textsubscript{60} and the fraction, \( f \), of the empty space. Using the dielectric constant in equation (2.29), obtained the equation (2.46) is presented in below.

\[
\varepsilon = (n - ik)^2
\]  

(2.46)

Equation (2.46) can be expressed in the terms of \( \varepsilon_1 \) and \( \varepsilon_2 \) which present the optical dielectric constants of the main layer of fullerene and free space, respectively. The optical dielectric constant of free space is equal to one. The expression with these terms are given in below and labeled as equation (2.47).

\[
\varepsilon = (n - ik)^2 = f\left(\frac{\varepsilon - \varepsilon_1}{\varepsilon + 2\varepsilon_1}\right) + (1 - f)\left(\frac{\varepsilon - 1}{\varepsilon + 2}\right)
\]  

(2.47)

In the case of exact structure with the small extinction coefficient is unknown, the refractive index can be obtained by a simple formula that is labeled in equation (2.48),

\[
n = n_1 + n_2 / 2
\]  

(2.48)

where \( n_1 \) is the refractive index of fullerene and \( n_2 \) presents the term of refractive index of voids (air). Using the equation (2.48), the roughness for our case is found 1.5.

The results present that the upper layer can be described satisfactorily as the layer of surface roughness which is modeled as an effective medium of the film with a portion of %50 void. In the figure (2.17), this result is presented which shows the model of fullerene film on silicon substrate from a combined study of AFM, spectroscopic ellipsometry and Rutherford backscattering spectroscopy.

![Figure 2.17. Model of the fullerene films on silicon substrate.](image)

- 36 -
The figures of the initial structure of the film and after modeling are illustrated in figure 2.18 (a) and (b), respectively.

**Figure 2.18.** The structure of the films in (a) initial and (b) after modeling.
3. EXPERIMENTAL PART

3.1 Raman Spectroscopy

In this thesis, the single grating Raman spectrometer (Renishaw 1000 Raman system) which is denoted with the three different lasers (Argon-ion, He-Ne and infrared lasers) and a CCD-detector was used and illustrated in figure 3.1.

![Figure 3.1. The experimental setup for Raman spectroscopy.](image)

In these experiments, only Argon ion laser (green) in the model of (SPECTRA PHYSICS LASERS, 1350W, 163-M42-010, SERIAL NO: X0643351) was used. The specifications of this laser are presented in table 3.1.

**Table 3.1.** The specifications of the green laser.

<table>
<thead>
<tr>
<th>Laser</th>
<th>Colour</th>
<th>Wavelength</th>
<th>Wavenumber</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon-ion</td>
<td>Green</td>
<td>514 nm</td>
<td>19407 cm(^{-1})</td>
<td>163-M42-010, X0643351</td>
</tr>
</tbody>
</table>

Laser light is directed in the spectrometer and sent to the optical microscope. Then, the laser light is focused on the sample surface using the one of the microscope lenses. In this setup, close-view lenses with the magnification 20× and 50× and the magnification of distance-view lenses are 5×, 20× and 50×. The difference of these lenses can be expressed as larger
distance between the sample and lens does not provide a better scattered focusing and the intensity of signal is lower if it is compared with the close-view lenses. The models of the lenses that are used in the experiment are expressed in table 3.2.

Table 3.2. The model of the lenses.

<table>
<thead>
<tr>
<th>Lens</th>
<th>Model</th>
</tr>
</thead>
<tbody>
<tr>
<td>5×</td>
<td>OLYMPUS IC 5, MD PLAN 5 (0.10)</td>
</tr>
<tr>
<td>20×</td>
<td>OLYMPUS IC 20, MS PLAN 20 (0.46)</td>
</tr>
<tr>
<td>50×</td>
<td>OLYMPUS IC 50, MD PLAN 50 (0.75)</td>
</tr>
</tbody>
</table>

The choice of focal length depends on the aim of the experiment. Using of higher focal length lenses enables to give more magnification and the better laser spot focusing.

The principle of Raman spectroscopy is illustrated comprehensively in figure 3.2 in below.

Figure 3.2. The schematic setup of Renishaw 1000 micro-Raman grating spectrometer.

The laser spot position is controlled by a video camera and the translation stage where the sample is laid. After the interaction between the light and the sample the backscattered light is pointed back to the spectrometer where the Notch filter provides to cut the laser light in the vicinity of its wavelength and leads to avoid the saturation by the Rayleigh high intensity scattering in the CCD- detector. After that, laser light is passed through a slit into the single
grating and then directed to the CCD-detector. Thus obtaining data can be recorded with the intensities of each wavenumber values individually and scans the desired range of the spectrum and also provides collecting the data in a short time without using high power that causes damage on the sample [2].

In this thesis, spectral range was determined in 200-1800 cm\(^{-1}\) region, time is inserted as 30 seconds and accumulation is given in 50. Cosmic ray is presented in ‘On’ mode and only ten percentage of the laser was used for power where the laser power is arranged on 18 mW. The given parameters in the Gram program (GRAMS/32, Version: V1.3.33, 1993) is illustrated in figure 3.3.

![Figure 3.3. Inserting values for Raman spectra.](image)

The same values were used for the spectral range in 2000-4000 cm\(^{-1}\).

### 3.2 Ellipsometry

There are several types of spectroscopic ellipsometers are used to get acquire spectroscopic data. The ellipsometer that we used in this thesis is type of the rotating analyzer ellipsometer. The basic schema for an rotating analyzer ellipsometry setup is presented in figure 3.4.

![Figure 3.4. Basic setup of ellipsometry.](image)
According to this figure, the electromagnetic wave is emitted from light source and pass through the monochromator which enables to get the wavelength in desired range and send to the polarizer to polarize linearly. The compensator is optional part for the ellipsometry device, either a quarter wave plate or retarder can be combined in the setup. Then, the light is passed through the compensator and falls to the sample. The reflected light from the sample passes the second polarizer which is also so-called analyzer and reach to the detector. The complex dielectric function of $\varepsilon$, can be obtained directly using the ellipticity of the reflected light from inverse Fresnel equations.

In this project, the rotating analyzer ellipsometer in the model of (J. A. Woollam Co., Inc. Ellipsometry Solutions, $\alpha$ - SE™) was used and the picture of this ellipsometry is presented in figure 3.5.

![Figure 3.5. The ellipsometer.](image-url)

The light source of this model provides the spectral range between 380 nm to 900 nm and also enables three options to get the rate of data acquisition such as 3 sec., 10 sec., and 30 sec. which are called fast, standard and high precision mode, respectively. The angle of incident can be oriented in the angles of 65°, 70°, 75° and 90°, in that case, the incident light was chosen as 70°. Combining the setup with the rotating analyzer, the CCD detector is used for detection of data. Additionally, optical fiber which is used to align of the setup better and also beam modulator that enables to produce harmonic waves are combined in this type of ellipsometry [42].
Ellipsometry presents an indirect technique property which requires an evaluated optical model fixing with the experimental data in order to get significant physically information so the program which is called as CompleteEASE Version 4.41 was used. The basic modeling was arranged adding the silicon substrate and silicon with native oxide files whose thickness is 200 Å in ‘Analysis’ menu in this program. The interface of this program is illustrated in figure 3.6.

![Figure 3.6. The interface of the CompleteEase program.](image)
4. EXPERIMENTAL RESULTS AND DISCUSSIONS

The results are served in two different chapters for Raman spectroscopy and ellipsometry, respectively and used films for these experiments are listed in table 4.1.

Table 4.1. The list of used films for each experiments.

<table>
<thead>
<tr>
<th>Raman Spectroscopy</th>
<th>C_{60}:H</th>
<th>02_{69}</th>
<th>111, 113_</th>
<th>149, 151, 154_{C_{60}CdS}</th>
</tr>
</thead>
<tbody>
<tr>
<td>114_a, b</td>
<td></td>
<td></td>
<td>C_{60}TPP</td>
<td></td>
</tr>
<tr>
<td>111, 113_C_{60}:H</td>
<td></td>
<td></td>
<td>C_{60}HNO3</td>
<td></td>
</tr>
<tr>
<td>111, 113_C_{60}:H</td>
<td></td>
<td></td>
<td>C_{60}CdS</td>
<td></td>
</tr>
<tr>
<td>Ellipsometry</td>
<td>114_a C_{60}:H</td>
<td>149, 151,</td>
<td>212, C_{60}_{pure}</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>154_{C_{60}CdS}</td>
<td>213_{C_{60}CdTe}</td>
</tr>
</tbody>
</table>

4.1 RAMAN SPECTROSCOPY

The Raman spectra of the films which are presented in table 4.1 were taken in the range between 200 and 1800 cm\(^{-1}\) in order to determine the polymerization ability. The important parameters for the polymerization process are time, accumulation and power. The effect of accumulation in the 114_a C_{60}:H film is presented in figure 4.1. This figure presents that the spectra of different accumulation times with maximum 800 (20 min), 25000 (80 min) and 200000 (24 hours) counts. The obtained result that short accumulation time is noisier. Additionally, different accumulation times lead to qualitative changes in the spectra.

Figure 4.1. Effect of accumulation on the Raman spectra.
Additionally, ageing effect of the films was compared. The films except the CdTe intercalated ones were produced in 2008 and CdTe films were produced in 2012. The ageing effect of 114_a C_{60}:H film is illustrated in figure 4.2.

![Figure 4.2](image)

**Figure 4.2.** The ageing effect of 114_a C_{60}:H film.

Figure 4.2 presents that the position of the modes did not change generally. But, being normalized for the A_g (1) intensity, the H_g modes decreased their height. The ageing affect of both H_g (1), (2), (3), (4), (8) and A_g (1) modes are served in panel 4.1.

**Panel 4.1.** The ageing effects on the H_g and A_g modes.
The figure (a) in panel 4.1 presents that after plasma treatment the $H_g (1)$ mode got additional features at 260 cm$^{-1}$ which was disappeared four years later. In the spectral range of $H_g (2)$ and $A_g (1)$ mode, there are no noticeable changes. Additionally, the silicon peak which is located on 520 cm$^{-1}$ is presented in this region to confirm the calibration was made for all of the measurements. In the region of $H_g (3)$ and $H_g (4)$ modes, all spectra are similar to each other. The $H_g (8)$ mode is strongly enhanced in hydrogen treated fullerenes. This enhancement is predicted by the calculations and the mode decreases tending to its initial value due to ageing. In the spectral range of $H_g (5)$ and $H_g (6)$ modes present more differences although the spectra which are plotted with red and blue are nearly same. This means that hydrogen treatment brings additional features which are reversible. The figure for this spectral range is given in figure 4.3.

**Figure 4.3.** Ageing effect in the $H_g (5)$ and $H_g (6)$ spectral range.
In figure 4.3, the positions on 948 and 984 cm$^{-1}$ are sometimes ascribed to 4-membered ring which appears when fullerenes polymerize but the strong objections against the polymerization is given in figure 4.3. The H$_g$ (5) mode which is located at 1098 cm$^{-1}$ was enhanced after the plasma treatment and has been preserved during four years. Additionally, two prominent features which are situated around 1200 cm$^{-1}$ and a peak at 1267 cm$^{-1}$ are appeared after the hydrogen treatment but disappear later due to aging. A$_g$ (2) mode is the fingerprint of the polymerization process and expressed detaillly in chapter 2.2.1.1.1. The ageing effect on the A$_g$ (2) mode is shown in figure 4.4.

![Figure 4.4. Ageing effect on A$_g$ (2) mode.](image)

In figure 4.4, the pristine film shows an unpolymerized peak at 1469 cm$^{-1}$ and a shoulder at 1461 cm$^{-1}$, the plasma treated film shows a single peak at 1469 cm$^{-1}$ and the aged film presents the peaks both 1463 cm$^{-1}$ and 1469 cm$^{-1}$ where the first peak is twice larger in the peak area. Using these data, it can be concluded that the plasma treatment suppress the ability of polymerization. However, some spectral features of the plasma treatment films have disappeared during four years, the fullerene films polymerize easily again. The spectra of all of the films in the table 4.1, is presented in figure 4.5.
The silicon peak appears on 520 cm\(^{-1}\) [43] so the silicon peaks were calibrated on the 520 cm\(^{-1}\) in the figure 4.5. In the Raman spectra of the fullerene films present no mode between 772 and 1099 cm\(^{-1}\). However, in the case of long irradiation on the fullerene film leads to create distinct modes at 945 and 974 cm\(^{-1}\) which is also seen both in figure 4.3 and figure 4.5. Some authors explain it by the formation of the 4-membered cyclobutane rings appeared during [2+2] cycloaddition [1, 5, 6, 32].

For polymerization process in fullerene-based structures, \( A_g (2) \) mode presents the characteristic property for each structure and downshifted as it mentioned in theory part in chapter 2.2.1.1.1. The peaks in the region of \( A_g (2) \) mode have been determined using a peak fitting program whose model is (PeakFit\(^{TM}\) program, Version 4 for Win32) and fitted by Voigt lineshapes. In the graphics which are presented in panel 4.2, the black line presents the
experimental data, red line illustrates the Voigt line shapes and green lines are served by the peak-fitting program.

Panel 4.2. The $A_g(2)$ peak modes of the films.
The figures in panel 4.2 present that deconvolution of $A_g(2)$ modes give several peaks. The $A_g(2)$ mode is a non-degenerate peak so it cannot split. The appearance of a satellite is explained by the appearance of the $A_g(2)$ derived modes. These modes appear when the sample polymerizes. The results in panel 4.2 are compared with the spectrum of $C_{60}_\text{pure}$ film and the results are presented in panel 4.3.

**Panel 4.3.** The comparison of $A_g(2)$ modes (a) $C_{60}_\text{pure}$ film and (b) hydrogen treatment and CdS intercalated samples.

C$_{60}_\text{pure}$ film in panel 4.3 (a) presents an unpolymerized peak at 1468 cm$^{-1}$, dimers and linear chains at 1462 and 1457 cm$^{-1}$ in order and even the signs of two-dimensional polymerization around 1450 cm$^{-1}$. It can be concluded that the pure fullerene film has the strongest ability for polymerization and the plasma treatment films have the narrowest peaks in the vicinity of $A_g(2)$ mode.

The detail explanations for polymerization process for all of the films are presented in below classifying them in the different chapters.

**4. 1.1 Films in the CT-complex structure**

In this chapter, fullerene films with intercalated HNO3, CdS and TPP are determined.
4.1.1.1 

**HNO$_3$ Intercalated Films**

The first difference between the films with HNO$_3$ is the structure of them. The spectra of film in the 111$_{C_{60}}$:HNO$_3$ are clear but 113$_{C_{60}}$:HNO$_3$ presents more polymerized structure where the $H_g$ modes split and even $A_g$ modes have got a satellite. The mode positions of two films are given in table 4.2.

**Table 4.2.** The mode positions of 111$_{C_{60}}$ and 113$_{C_{60}}$:HNO$_3$ films.

<table>
<thead>
<tr>
<th>Modes of the films (cm$^{-1}$)</th>
<th>111$<em>{C</em>{60}}$:HNO$_3$</th>
<th>113$<em>{C</em>{60}}$:HNO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$H_g$ (1)</td>
<td>269</td>
<td>269</td>
</tr>
<tr>
<td>$H_g$ (2)</td>
<td>-</td>
<td>429</td>
</tr>
<tr>
<td>$A_g$ (1)</td>
<td>-</td>
<td>493</td>
</tr>
<tr>
<td>$H_g$ (3)</td>
<td>707</td>
<td>707</td>
</tr>
<tr>
<td>$H_g$ (4)</td>
<td>772</td>
<td>771</td>
</tr>
<tr>
<td>$H_g$ (5)</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>$H_g$ (6)</td>
<td>-</td>
<td>1247</td>
</tr>
<tr>
<td>$H_g$ (7)</td>
<td>1423</td>
<td>1423</td>
</tr>
<tr>
<td>$A_g$ (2)</td>
<td>1469</td>
<td>1469</td>
</tr>
<tr>
<td>$H_g$ (8)</td>
<td>1568</td>
<td>1572,1602,1627</td>
</tr>
</tbody>
</table>

The structure in the $H_g$ (1) mode for both 111$_{C_{60}}$ and 113$_{C_{60}}$:HNO$_3$ films are similar as the hydrogenated fullerenes which gives the peak in 269 cm$^{-1}$ as well as weak peaks in 254 and 295 cm$^{-1}$. However, the structure in the 113$_{C_{60}}$:HNO$_3$ film presents more splitter structure which means the polymerization.

In the panel 4.1, 111$_{C_{60}}$:HNO$_3$ film near the $A_g$ (2) mode are fitted and the positions are located in 1399, 1423 ($H_g$ (7)), 1451, 1463 and 1469 ($A_g$ (2)) cm$^{-1}$. $A_g$ (2) mode is shifted 6.4 cm$^{-1}$ as the hydrogenated fullerene films and this position of peak is located in 1463 cm$^{-1}$. The $H_g$ (8) mode of this film was downshifted nearly 10 cm$^{-1}$ and the downshifted of other modes are determined approximately 3-6 cm$^{-1}$.

In the case of $A_g$ (2) mode of 113$_{C_{60}}$:HNO$_3$ film, the fitted peaks has been situated approximately at 1354, 1385, 1424 ($H_g$ (7)), 1461 and 1469 ($A_g$ (2)) cm$^{-1}$. The pinch mode is shifted approximately 8 cm$^{-1}$ which presents more polymerized structure than other HNO$_3$ film. $H_g$ (8) mode of 113$_{C_{60}}$:HNO$_3$ film presents the big polymerized structure and gives three peaks in 1571, 1600 and 1621 cm$^{-1}$ where the $H_g$ (8) mode is downshifted 7 cm$^{-1}$ and
situated at 1571 cm\(^{-1}\) while the other peaks are the result of polymerization. Additionally, there is a shoulder peak between 1300 and 1400 cm\(^{-1}\). According to the reference [44], in the case of (C-(NO\(_2\))) vibration mode gives strong Raman peaks in the region of 1340-1380 cm\(^{-1}\) which means the interaction between the molecules and leads to polymerization. Raman spectra of the 113\(_{60}\)HNO\(_3\) film is served in figure 4.6 with the inset part which gives the strongly enhanced H\(_g\) (8) mode.

![Raman spectrum of 113\(_{60}\):HNO\(_3\) film.](image)

**Figure 4.6.** The Raman spectrum of 113\(_{60}\):HNO\(_3\) film.

As a result, the modes except the A\(_g\) (2) and H\(_g\) (8) modes for two films are shifted approximately between 3-6 cm\(^{-1}\).

### 4.1.1.2 CdS Intercalated Films

Raman spectra of CdS films are shown in figure 4.7 with an inset part which presents the A\(_g\) (2) modes of CdS films. In 149\(_{60}\) and 151\(_{60}\)Cd\(_S\) films, the modes are presented clearly, except H\(_g\) (5) mode and also H\(_g\) (6) mode in 151\(_{60}\)Cd\(_S\) film.
Figure 4.7. Raman spectra of CdS films.

In the 149_C60CdS which contains the components in the half portion, presents more peaks in 1300-1400 cm\(^{-1}\) region which can be occurred by both shift of the \(A_g\) and \(H_g\) modes and inactive vibration modes. However, 154_C60CdS film which contains mostly CdS in the %91 ratio presents more polymerized structure with disappearing all the modes except \(H_g(7)\), \(A_g(2)\) and \(H_g(8)\). The additional peaks are appeared at 1450-1451 cm\(^{-1}\) for 149, 151 and 154_C60CdS films, respectively which may related either shifted of \(A_g\) (2) mode or the process of charge transfer between the molecules. The pinch mode is downshifted 10 and 8 cm\(^{-1}\) for 149, 151 and 154_C60CdS films, respectively. The \(H_g(8)\) modes of the films are situated at nearly 1568 cm\(^{-1}\) which means 10 cm\(^{-1}\) shifted that can be explained by the interaction between either C\(_60\) molecules or C\(_60\) and CdS. The approximate mode positions are illustrated in table 4.3.

Table 4.3. Mode positions for 149, 151 and 154_C60CdS.

<table>
<thead>
<tr>
<th>Modes of the films (cm(^{-1}))</th>
<th>149_C60CdS</th>
<th>151_C60CdS</th>
<th>154_C60CdS</th>
</tr>
</thead>
<tbody>
<tr>
<td>(H_g) (1)</td>
<td>268</td>
<td>268</td>
<td>-</td>
</tr>
<tr>
<td>(H_g) (2)</td>
<td>429</td>
<td>428</td>
<td>430</td>
</tr>
<tr>
<td>(A_g) (1)</td>
<td>493</td>
<td>493</td>
<td>-</td>
</tr>
<tr>
<td>(H_g) (3)</td>
<td>707</td>
<td>707</td>
<td>708</td>
</tr>
<tr>
<td>(H_g) (4)</td>
<td>771</td>
<td>771</td>
<td>-</td>
</tr>
<tr>
<td>(H_g) (5)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(H_g) (6)</td>
<td>1244</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
The Raman spectra of TPP film present more different spectra than other films as it was expected. The molecular formula of TPP is C$_{44}$H$_{30}$N$_4$ which means there will be many shift in the modes due to the approximate number of intermolecular bonds. TPP molecule and its position are illustrated in figure 4.8 (a) and (b), respectively.

Near the range of the pentagonal pinch mode of TPP is fitted and obtained four peaks in the position of 1439, 1458, 1471, 1490 and 1500 cm$^{-1}$. The A$_g$ (2) mode may be downshifted to 1459 cm$^{-1}$. However, this probably does not mean polymerized long linear chains; instead the shift is likely due to the charge transfer [45]. The peaks in TPP film is presented in figure 4.9.

![Figure 4.8](image_url)  
**Figure 4.8.** (a) TPP molecule and (b) the position of TPP in fullerene.

![Figure 4.9](image_url)  
**Figure 4.9.** Raman spectra of TPP.
4.1.2 Hydrogen Treatment Films

The polymerization process in the case of hydrogenated films which are named as 111_C₆₀:H, 114_a and 114_b C₆₀:H, the situation is different because H:C₆₀ is a molecule that is covalently bonded. In the 111_C₆₀:H film, the peaks positions are located 1423.5 (H₉(7)), 1442.7, 1461.8 and 1468.2 (A₉ (2)) cm⁻¹. The position in 1461.8 shows the shifted position of the pinch mode and shifted 6.4 cm⁻¹ that is also compatible for the literature.

The similar results are obtained for 114_a and 114_b C₆₀:H films which give the downshift by 6.4 cm⁻¹ as well as the H₉(7) modes of them is located nearly in the same position – 1423 cm⁻¹. If for some reasons, buckminsterfullerene changes its spherical form, H₉ modes can split into up to 5 modes. One example for H₉ (1) mode in 114a_C₆₀:H is demonstrated in figure 4.10. This mode has situated at 270 cm⁻¹ with weak peaks at 254 and 295 cm⁻¹ which means that fullerenes lost their spherical shape and it again confirms the polymerization.

![Figure 4.10. The splitting of H₉ (1) mode.](image)

However, this splitting is much smaller than in fullerene film before the plasma treatment and comparing the results which are presented in panel 4.4 for pristine crystalline film and both CdS-intercalated samples and hydrogenated samples, it can be concluded that the H₉ (1) mode is less disturbed in the case for hydrogenated fullerenes.
Panel 4.4. Comparison of the Hg (1) modes of the films.

The other Hg modes are nearly in the same structure for the 114_a and 114_b C_{60}:H films but in the 111_C_{60}:H film, Hg(1) mode has situated in 269 cm\(^{-1}\) with very weak peaks at 253 and 295 cm\(^{-1}\) so it can be concluded that the polymerization in 111_C_{60}:H film is less than the other hydrogenated films. All mode positions of the hydrogenated films are presented in table 4.4. In this table, ‘-’ sign illustrates the disappearing mode which means polymerization so the peak is disappeared.

**Table 4.4. Mode positions for hydrogenated fullerenes.**

<table>
<thead>
<tr>
<th>Modes of the films (cm(^{-1}))</th>
<th>111_C_{60}:H</th>
<th>114a_C_{60}:H</th>
<th>114b_C_{60}:H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg (1)</td>
<td>269</td>
<td>268</td>
<td>268</td>
</tr>
<tr>
<td>Hg (2)</td>
<td>429</td>
<td>429</td>
<td>429</td>
</tr>
<tr>
<td>A_g (1)</td>
<td>493</td>
<td>493</td>
<td>493</td>
</tr>
<tr>
<td>Hg (3)</td>
<td>708</td>
<td>707</td>
<td>707</td>
</tr>
<tr>
<td>Hg (4)</td>
<td>771</td>
<td>771</td>
<td>771</td>
</tr>
<tr>
<td>Hg (5)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hg (6)</td>
<td>1247</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hg (7)</td>
<td>1424</td>
<td>1424</td>
<td>1424</td>
</tr>
<tr>
<td>A_g (2)</td>
<td>1468</td>
<td>1466</td>
<td>1468</td>
</tr>
<tr>
<td>Hg (8)</td>
<td>1569</td>
<td>1567</td>
<td>1567</td>
</tr>
</tbody>
</table>
The vibrational modes of the hydrogenated films except $H_g$ (8) modes of them were downshifted between $3-5\ \text{cm}^{-1}$ and $H_g$ (8) mode was downshifted by 11 cm$^{-1}$.

Finally, it can be concluded that films with hydrogen plasma treated are less polymerized than the other films. The pristine sample does not contain any features in the 1800 - 4000 cm$^{-1}$ region but plasma treatment which is hydrogen in our case provides a rich spectrum and some features are still remained on ageing. Therefore, the second spectra of hydrogen treatment films in the range of 2000-4000 cm$^{-1}$ were taken and shown in figure 4.11.

![Figure 4.11. 2nd spectra of the hydrogen treatment films.](image)

The peak positions in the 2800–3000 cm$^{-1}$ spectra are close to the carbon-hydrogen stretching modes reported for $C_{60}H_{36}$ [46]. However, there exists an alternative explanation, because second order modes may become active due to the C-H stretching vibration modes.

These measurements were compared with the measurements of the second order spectra made by I. B. Zakharova on freshly hydrogenated films. I took the old data and performed the deconvolution of the spectra. It turned out that plasma treated films showed very rich second order spectrum.

We emphasize that the observation of the second order peaks in fullerene films is a very rare phenomenon. Dong [46] observed these peaks under two conditions:
- very strong laser intensity
- suppressed ability to polymerize how was obtained (1) by cooling the samples below 40 K which is below the glass transition temperature and by (2) heating above 450 K when polymerization was thermally destroyed.

By contrast, very low laser intensity at room temperature was used in our experiments, and the appearance of the second order peaks may require special investigations. For an example, the peaks on the second spectra of 114a_C60:H (2008) film were determined using the PeakFit program and compared with the reference [46] which serves the peak values of the solid C60 films with the modes both in first and second order spectra. The detailed expression for the second order positions are served in panel 4.5 for 114a_C60:H (2008) film.


The graphic which is given in panel 4.5 (a) presents the peak positions at 1859, 1870, 1924, 1972 and 2014 cm\(^{-1}\). First and third positions are exactly same with the reference values but \(H_g(4) + H_g(5)\) mode is downshifted 6 cm\(^{-1}\) due to the reference. \(A_g(1) + A_g(2)\) mode is found
at 1972 cm\textsuperscript{-1} and also \( H_g(2) + H_g(8) \) mode is presented at 2014 cm\textsuperscript{-1} which mean the experimental positions are shifted \( \sim 4 \) cm\textsuperscript{-1} due to the reference work. In the graphic (b), four peak positions are presented in 2148, 2183 and 2214 cm\textsuperscript{-1} and the reference work presents the peak positions of these modes at 2181, 2137, 2201 and 2202 cm\textsuperscript{-1}. Most shifted peak position is situated at 2137 cm\textsuperscript{-1} which is downshifted approximately 11 cm\textsuperscript{-1} where the mode name of this position is \( H_g(3) + H_g(7) \). Additionally, \( A_g(2) + H_g(3) \) mode is downshifted as 2 cm\textsuperscript{-1}. The shift in the graphic (b) may be occurred due to the \( (C \equiv C) \) vibrational mode which presents strong Raman peaks in the spectral range of 2100-2250 cm\textsuperscript{-1} \cite{44}. The peak position on 2214 cm\textsuperscript{-1} can be correlated to the modes either \( H_g(4) + H_g(7) \) or \( 2H_g(5) \). The comparison of reference and experimental work are presented detail in the graphics (c) and (d). In graphic (d), the peak position in 2687 cm\textsuperscript{-1} may be correlated to \( H_g(6) + H_g(7) \) whose position is presented in 2676 cm\textsuperscript{-1} or \( H_g(5) + H_g(8) \) mode in 2678 cm\textsuperscript{-1}. All of these peaks are described by the second-order combinational modes but the peaks in the spectral range of 2800-3000 cm\textsuperscript{-1} which is the region of C-H stretching vibrations are much higher than the other. Additionally, all the second-order peaks disappear on ageing except the region of 2800-3000 cm\textsuperscript{-1}. The peaks in this region are illustrated in figure 4.12.

![Figure 4.12. The second order spectra of 114a\textsubscript{C_{60}}:H film in 2800-3000 cm\textsuperscript{-1} region. The peak positions are presented with their modes in figure 4.12. In the reference work, the peak positions for these modes are given in 2853, 2896, 2940, 3004, 3047 and 3155 cm\textsuperscript{-1}.](image-url)
As a final result, plasma treated samples lose the ability for polymerizing due to the plasma treatment and attached hydrogen which protects the active cites which are called $6=6$ bonds sterically. The absence of polymerization leads to appearance of large amount of second order modes in the Raman spectra whose confirmation was expressed by Dong and explained detail in above. The features especially in the spectral range of 2800-3000 cm$^{-1}$ are much stronger than the other regions due to the C-H stretching vibrations and the features only in this spectral range have been preserved for four years aging. The plasma treated films are unstable, and the spectra of four years aged films are very similar to the spectra of untreated films. Most probably, it can be occurred depending on the hydrogen detached and films restored the ability to polymerize. As shown in Fig. 4.11, only peaks in the 2800-3000 cm$^{-1}$ range are preserved in the second order spectra.

### 4.2 ELLIPSOMETRY

The CompleteEASE Version 4.41 program provides to get the experimental data and plot the graphics in the terms of both n-k and psi-delta versus wavelength. The obtained results from the program for each sample are listed in panel 4.6.

**Panel 4.6.** Experimental results from CompleteEase program.

212$_{C_{60}}$CdTe

213$_{C_{60}}$CdTe
In these experiments, some modeling was made and detailed in theory part in the chapter of 2.2.2.4. However, one more modeling was made to simplifying the modeling which explains surface layer can be treated as transparent layer $n = 1.5$ and $k = 0$ with the thickness of 20 nm. Then, the parameters of the fullerene layer were found starting from the silicon substrate using the experimental data. The parameters of the silicon are important and needed to check for each sample. The experimental data of the silicon versus wavelength is illustrated in figure 4.13.

![Figure 4.13. The figure for silicon substrate.](image)

The other program that is used for theoretical calculations of ellipsometric angles of given refractive indexes was created by Makarova, T.L and also the interface of it is presented in below and labeled in figure 4.14.
4.2.1 Determination of the n and k

A template enables to compare the experimental data with the theoretical values so one template is formed using the program which is illustrated in figure 4.15. The template is based on the incident wavelength is He-Ne laser wavelength 6328 Å and the angle of incidence is 70°. Delta and psi values are calculated in 1 nm step of film thickness.

The other important parameter for the thin films is surface roughness. Several pictures were taken for C$_{60}$ and C$_{60}$CdS film at the different places of the film in recent years and used for determination of approximate surface roughness. Surface roughness can be calculated automatically by the SPIP program (NanoScope 6.13R1(R), 2002, Digital Instruments/Veeco) and average surface roughness is served by the parameter ‘$R_q$’ [47]. The average value for surface roughness for every pictures were calculated using $R_q$ and obtained values are 200 Å and 100 Å for C$_{60}$ and C$_{60}$CdS films, respectively. The height pictures of the films are presented in panel 4.7. In the upper part of this panel, C$_{60}$ films and in the lower part C$_{60}$CdS films are presented.
Panel 4.7. The height pictures for (a) C$_{60}$ and (b) C$_{60}$CdS thin films.

In the ellipsometry measurements, the average roughness is taken as 200 Å and template was modeled with this value. In the case of requirement of shifting when the delta values of experimental and calculated data are not combined, some values for comparison were added or taken out.

The template is illustrated in figure 4.15 and used to characterize the properties of thin films.

Figure 4.15. The template for n and k determination for 20 nm roughness.
4.2.2 Determination of the Thickness (d)

The calculation of thickness is expressed in detail and also the formulas for it is given in the theory part which is labeled in equations (2.36) and (2.37). For an example of thickness calculation in the units of Å is presented in figure 4.16 for the 212\_C_{60}CdTe. The thickness in 8280 Å is also calculated in the program and 3480 Å is found without the surface roughness. When the surface roughness that is accepted as 200 in Å unit is added to the thickness of 3480 Å and obtained result is 3680 Å which is close to the calculated thickness of experimental data. For the thickness calculation, it is refined solving the exact equation at the final point of the spectrum.

![Figure 4.16. An example of thickness calculation for 212\_C_{60}CdTe.](image)

4.2.3 Characterization of the Films

4.2.3.1 CdTe Intercalated Films

Firstly, the result for 212\_C_{60}CdTe film is presented in this part. The illustration of the film is presented in figure 4.17.
In this graphic, firstly the measured data of delta is shifted by 10 degrees which means the roughness. Then, the graphic presents that experiment data and calculated data coincides very well in the spectral range from 8930 Å to 7800 Å so it is concluded that film is transparent in the region of higher values than 7800 Å. The very weak absorbance in the case of $k = 0.05$ starts at 7800 Å but at 6470 Å the value is becoming greater. In the spectral region between 6400—6470 Å, the calculated data is presented by the orange line in the figure 4.17 and shows that at 6470 Å the extinction coefficient gets the value $k = 0.085$. In the remain spectral range, more opaque part is presented and obtained that in the visible range the film is more opaque in the range of 4000—6000 Å.

The experimental data of 213_C₆₀CdTe films that is plotted with black are inserted into the template which was illustrated in figure 4.15 and approximate refractive index and extinction coefficient values are taken as 2.05 and 0, respectively. The thickness of film is refined and obtained value is 1880 Å. This value is inserted in the program of Makarova T.L as a second layer and the delta and psi values are calculated in the spectral range from 5000 to 9000 Å which is plotted with red in the figure 4.18. The figure 4.18 presents that film is transparent and at 5500 Å the quick increase of the extinction coefficient changes to a very weak increase. Additionally, very weak absorption is found in the spectral range of 8000—8550 Å.

*Figure 4.17. Results for 212_C₆₀CdTe.*
4.2.3.2 Cds Intercalated Films

The experimental data of 149_C60CdS film was inserted on the film and the approximate values for calculation were taken as $n = 2.01, k = 0$ and thickness is found 3630 Å, respectively. The graphic with this number that is plotted with pink is needed a little bit shift for psi values so the bigger refractive index value was given with the corresponding calculated thickness and plotted with the values $n = 2.05, k = 0$ and $d = 3580$ Å at red color. The graphic of 149_C60CdS film is presented in panel 4.8. According to figure 4.15, it can be concluded that refractive index value is between 2.01 and 2.05. In panel 4.8 (a), the graphic of experimental data is tilted which means the optical threshold at 6200 Å. Another important result for this film is presentation of the opaque property in the approximate spectral range of 3800 - 5000 Å and illustrated in the panel 4.8 (b).
Panel 4.8. The graphic of 149_C60CdS film (a) the characterization of transparent part and (b) opaque part.

The result for 151_C60CdS is presented in figure 4.19. After the comparison of experimental data with template in figure 4.15, n and k values are determined as 2.0 and 0, in turn and d is calculated as 2150 Å. In this figure, experimental data and calculated data are plotted with black and red, in turn and two optical thresholds where are appeared in the positions of 4460 Å and 6200 Å are illustrated with purple and blue arrows, respectively. Additionally, there is a weak absorption in the spectral range from 6500 Å to 7100 Å.

Figure 4.19. Results for 151_C60CdS film.
The result for 154_C_{60}CdS is presented in figure 4.20 where the black line and green line presents the experimental and calculated data, respectively. After the checking of the optical parameters $n$ and $k$ in the template that is shown in figure 4.15, $n$ and $k$ are found 1.9 and 0.1, respectively and $d$ is calculated as 2750 Å. The figure 4.20 presents that film is transparent and also shows that there are two optical shoulders in the positions of 4470 and 6200 Å which are also the same optical shoulder positions of 151_C_{60}CdS film.

![Figure 4.20. 154_C_{60}CdS film.](image)

**4.2.3.3 114_a C_{60}:H FILM**

Although the films that treated with hydrogen plasma seem so thin, 114_a C_{60}:H film was used for an example of the ellipsometry experiments. The experimental data is presented in figure 4.21 which is plotted with black and shows that film is totally transparent as it was expected. The film shows the opaque property in a short spectral range between 3800 Å to 4700 Å and also the optical threshold in 6200 Å shown with the pink arrow.
4.2.3.4 \textit{C}_{60} \textsc{pure} Film

The figure for \textit{C}_{60} \textsc{pure} is given in figure 4.22. The experimental and calculated data are illustrated with black and cyan colours. The optical parameters of the film are found at $n$ is 2 and $k$ is 0. Using those values, thickness is calculated and served as 1610 Å. The figure 4.22 shows two thresholds which can be occurred by the charge transfer reactions in 4200 Å and 5260 Å and illustrated with orange and pink arrows, respectively. The film presents the transparent property in the spectral range between 5260 Å to 9000 Å. Then its absorption abruptly increases, but after 4200 Å the absorption decreases.

The lower limit of optical transition for \textit{C}_{60} fullerenes occurs at nearly 3 eV. This transition is difficult to identify experimentally because of the oscillator strength is rather small about 3%
of that for the transition at 3.5 eV [48]. Thus, in principle, fullerenes must be transparent in the visible-UV region.

However, fullerenes are typical molecular crystals. The optical properties of fullerenes depend equally on intra- and intermolecular processes. The former lead to the formation of Frenkel excitons, and the latter give rise to charge-transfer excitons (CT-excitons) in which the two charges are localized on different molecules. Excitons of these two kinds were considered in detail in reference [49].

Measurement of the absorption in the visible region as a function of temperature, hydrostatic pressure, and magnetic field has shown that the spectral features near the absorption edge are due to excitons [50]. The optical absorption of fullerene films can be described in terms conventional for amorphous semiconductors.

The absorption edge, shifted to lower energy compared to fullerenes in solution, has been identified at approximately 1.8-1.9 eV for $C_{60}$ (6500 – 6870 Å).

Forbidden Frenkel excitons with energies of 1.55, 1.87, and 2.2 eV were reported inside the $C_{60}$ HOMO–LUMO band where the first allowed exciton is at 3.6 eV.

The absorption spectrum in the visible and ultraviolet (UV) ranges contains peaks related to allowed optical transitions at 3.5–5.6 eV and to excitons at energies below 3 eV and the most significant CT states have been identified at approximately 2.43 and 2.70 eV. The broad bands observed at 2.43 (5086 Å) and 2.70 eV (5457 Å) are assigned to the transitions of charge-transfer (CT) excitons consisting of an electron and a hole which are separated at the adjacent $C_{60}$ molecules. The splitting of CT-bands originated from two different configurations of the adjacent $C_{60}$ molecules: a five-ring/double-bond nearest-neighbor contact and a six-ring/double-bond nearest-neighbor contact [49].

It is worthwhile to mention that the triplet CT-exciton is one of the precursors with the long lifetime for the photopolymerization in $C_{60}$ solids. The process of transformation to the polymeric state involves an excitation by the photon (in our case, green laser). It produces the electron-hole excitations without spin flip (singlet excitons) and further they are converted to triplet excitons, which always have somewhat lower energies because of the absence of the exchange interaction. That’s why the triplet state is long-lived.
It was shown in reference [51] that the photoexcitations in solid $C_{60}$ are dominantly relaxed not into the intra-molecular triplet state but into triplet CT-excitons in which the electron and hole are separated at the adjacent molecules. This long-lived state is extended over the adjacent molecules and is regarded as responsible for the photodimerization.

4.2.4 Determination of the Absorption Coefficient

The results of the ellipsometric experiment were used to determine the excitons in the absorption spectra of fullerene films.

From the ellipsometric data, the film thicknesses have been determined and also the optical model which includes the surface roughness. Using this information, the optical absorption coefficients of fullerene films are calculated. Firstly, the transparency regions and the spectral positions of the main peaks are identified qualitatively and summarized in table 4.5. Then, the equation is solved one by one using the chosen model.

Table 4.5. Some features from ellipsometry experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Optical threshold (Å)</th>
<th>Peak in the spectrum (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{60}$ pure</td>
<td>5260</td>
<td>4200</td>
</tr>
<tr>
<td>C$_{60}$:H</td>
<td>6200</td>
<td>4700</td>
</tr>
<tr>
<td>C$_{60}$CdS</td>
<td>5500, further 6200</td>
<td>4470</td>
</tr>
<tr>
<td>C$_{60}$CdTe</td>
<td>7800 weak, 6470</td>
<td>After 5500 increase</td>
</tr>
</tbody>
</table>

In the first step, the extinction coefficient was calculated and the result is illustrated in figure 4.23.

![Figure 4.23. Extinction coefficient results of the films.](image-url)
From the obtained film thicknesses and ellipsometric parameters Psi and Delta we calculated the dependence of the extinction coefficient. Using the formula for absorption coefficient which is labeled in equation (2.31), the spectral dependencies for the crystalline $C_{60}$ film, CdS-intercalated, CdTe-intercalated film and hydrogenated film were calculated. The result is presented in figure 4.24.

![Absorption coefficient vs Energy](image)

**Figure 4.24.** The absorption coefficients of the films.

Pure $C_{60}$ film is highly transparent until 2.2 eV. Above 2.2 eV, we observe a very strong increase in absorption which is probably due to the absorption on excitons. The peak in the spectrum at 2.8 eV can be attributed to a charge-transfer electron.

The films intercalated with CdTe are weakly absorbing in the region of 1.5 – 2 eV. This can be due to CdTe itself which has an optical threshold at 1.5 eV. Additional mechanism of absorption switch on at about 2.2 eV.

CdS is more transparent than CdTe, its optical absorption starts at about 450 nm (2.74 eV). We clearly see this feature as a kink on the ellipsometric $\Psi$-$\Delta$ nomograms at 4470 Å (on both films). However, CdS-$C_{60}$ film starts absorbing already at 2 eV. This is possibly due to the impurity levels created in the $C_{60}$ molecular solids.

Hydrogen plasma treated fullerene film does not show any prominent features in the absorption in the investigated spectral range. The absorption is likely due to the Frenkel excitons, and there are no features of the charge-transfer excitons.
We note that the pure fullerene film shows the highest absorption in the region 2.5 – 3.5 eV. The intercalated and plasma treated films are more transparent. We can explain this phenomenon by the fact that in the C$_{60}$ pure film a charge transfer exciton is formed whereas in the intercalated films it is suppressed.
5. SUMMARY AND CONCLUSIONS

In this thesis, the fullerene films intercalated with CdS, CdTe, HNO$_3$, TPP and the hydrogen plasma treated films were studied. The aim of the study was to test these films before the complicated experiments on the determination of singlet oxygen generation by fullerenes. As both polymerization and singlet oxygen production uses the triplet state of fullerene molecule, we anticipated that the mechanical isolation by the molecules with weak charge transfer properties or dilute functionalization by hydrogen can suppress polymerization.

From the Raman spectra of the films we learned that the $A_g(2)$ was split in all cases, except freshly plasma treated fullerene films. This splitting was very strong in case of intercalation with HNO$_3$ and TPP (tetraphenylporphyrin). The films intercalated with CdS and CdTe are also presented the appearance of $A_g(2)$-derived modes. However, these features are weaker that for the pristine non-intercalated pure fullerene film. The films with the unperturbed position of the $A_g(2)$ modes were the plasma treated films, however it turned to be subjected to the aging effects.

From the ellipsometry analysis the thicknesses of the film and their optical parameters $n$, $k$ were determined. AFM studies were made to determine the surface roughness which was accounted in the ellipsometric analysis. Surface roughness value was determined using the AFM pictures of C$_{60}$ and C$_{60}$CdS and calculated using the SPIP program. The average value for roughness was taken as 20 nm and the modeling for the ellipsometry were made with this value. From this data the ellipsometric model was constructed and the spectral dependencies of absorption coefficient were determined. It was shown that the pure C$_{60}$ film has a prominent spectral band related to the charge-transfer excitons. For CdTe and CdSe films the absorption in the CT exciton band is much smaller, and it is totally absent in hydrogen plasma treated films.

According to the workplan of the EU Nano-Guard project, the best films characterized in this thesis, namely CdS-intercalated and hydrogenated films will be sent to the EPR (Electro-Paramagnetic Resonance) measurements for the evaluating the ability to produce singlet oxygen.
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7. REFERENCES

1. T. Wågberg, "Studies of polymeric and intercalated phases of C_{60}," (Umeå University, Umeå, 2001).


13. V. V. Z. PhD, I. M. Belousova, O. I. Kiselev, L. B. Piotrovsky, P. M. Anfimov, T. C. Krisko, T. D. Muraviyova, V. V. Rylkov, A. M. Starodubzev, and A. C. Sirotkin,


17. J. L. Koenig, Spectroscopy of Polymers (Elsevier Science Inc., USA, 1999).


27. D. J. Willock, Molecular Symmetry (John Wiley & Sons Ltd, United Kingdom, 2009).


