CHAPTER 4

STRUCTURAL AND COMPOSITIONAL ANALYSIS

4.1 INTRODUCTION

The structural studies of materials always play a prominent role as their physical properties depend very much on their structure. The knowledge about the structure of the film is important to understand and predict the nature of the films. A number of analytic techniques are available for the structural characterization of thin films. These include X-Ray Diffraction (XRD), Energy Dispersive Analysis using X-Rays (EDAX), Fourier Transform Infrared spectroscopy (FTIR), etc.

X-ray diffraction (XRD) is used to determine the crystalline and amorphous structure of different phases in organic thin films. Energy Dispersive Analysis using X-rays (EDAX) is used to understand the elemental composition of the thin film samples. Fourier Transform Infrared (FTIR) absorption spectroscopy offers the advantage of identifying polymorph as well as to provide information about absorbed species.

This chapter deals with the structural and compositional studies of PbPc and CuPc thin films prepared by vacuum evaporation technique. PbPc and CuPc are organic semiconducting materials which have various functional groups. So this chapter also deals with the Fourier transform infrared spectroscopy of functional group analysis.
4.2 X-RAY DIFFRACTION

Diffraction is one of the most powerful methods for investigation of internal structure of material. The relative ease and convenience, large diffraction angle, representation of the average crystalline lattice throughout the film and simultaneous display of diffraction pattern from the film make the XRD method a successful analytical technique for the study of thin films.

**Bragg’s Law**

Diffraction of coherent radiation by the three dimensional array of atoms in a crystal is governed by Bragg’s law (Figure 4.1.), which states that the incident beam is reflected by the set of lattice planes (hkl) if

\[ n\lambda = 2d \sin \theta \]  \hspace{1cm} (4.1)

![Figure 4.1 Schematic diagram for determining Bragg's law](image-url)
4.3 THEORY

4.3.1 X-Ray Techniques

In X-ray works, one can choose between white and monochromatic radiation. With white radiation “Laue Pattern” is obtained and the lattice planes are easily recognizable. The Laue technique is mainly used to determine the orientation of single crystal. It is a convenient tool because a pattern can be recorded in Polaroid film within a few minutes. X-ray techniques based on monochromatic radiations are generally more important because the ‘d’ spacing can be calculated from the observed diffraction angles.

An important feature of X-ray diffractometer is its ability to focus into a sharp diffraction line with the radiation, which is Bragg-reflected from an extended specimen area. This considerably improves the sensitivity and the signal to noise ratio. Focusing is achieved by making the specimen as a part of the circumference of a circle, so called focusing circle, so that all the beams diffracted in different areas by the same family of (hkl) planes, cross over again and are detected on this circle. Two different designs of diffractometers namely Bragg – Brentano diffractometer (Figure 4.2) and Seemann – Bohlin diffractometer (Figure 4.3) are used in thin film work.

It is worthwhile to note that for X-ray diffraction a film can remain on its substrate and allows 'nondestructive testing' of the film-substrate system, the ‘d’ spacing of films attached to the substrate usually contains contribution of homogeneous strains caused either by intrinsic stresses in the film or by differential thermal expansion if the temperature of the fabrication and observation are different. One of the main applications of X-ray diffractometer techniques in thin films is that to make use of their good resolution of d spacing to investigate strains in thin films (Maissel and Glang (1983)).
Figure 4.2 Bragg – Brentano focusing on a powder diffractometer

Figure 4.3 Schematic diagram giving details regarding formation of X-ray diffraction pattern and focusing method.
4.3.2 Structural parameters

4.3.2.1 Grain size (D)

The grain size (D) can be calculated using the Scherrer’s formula (Culity (2001), Wellier (1994)) from the full width at half maximum (FWHM)

\[ D = \frac{k\lambda}{\beta \cos \theta} \]  

(4.2)

where the constant \( k \) is the shape factor \( \approx 0.94 \), \( \lambda \), the wavelength of the X-rays (1.5406 \( \text{Å} \) for Cu K\( \alpha \)), \( \theta \), the Bragg’s angle and \( \beta \), the FWHM.

4.3.2.2 Dislocation density (\( \delta \))

The dislocation density (\( \delta \)) can be evaluated from the crystallite size (D) by the following relation (Nelson and Riely (1945), Oza et al (2005)).

\[ \delta = \frac{1}{D^2} \]  

(4.3)

4.3.2.3 Strain (\( \varepsilon \))

The origin of the micro strain is related to the lattice misfit, which in turn depends upon the deposition conditions. The micro strain (\( \varepsilon \)) can be calculated from the following relation.

\[ \varepsilon = \frac{\beta \cos \theta}{4} \]  

(4.4)

4.3.2.4 Interplanar spacing (hkl)

From the XRD profiles, the interplanar spacing \( d_{hkl} \) is calculated using the Bragg’s relation
where $\theta$ is the bragg’s angle and $n$, the order of diffraction.

### 4.4 ENERGY DISPERSIVE X-RAY (EDAX) ANALYSIS

EDAX analysis stands for Energy Dispersive X-ray analysis. It is sometimes referred as EDS or EDAX analysis. It is a technique used for identifying the elemental composition of the specimen, or an area of interest thereof. The EDAX analysis system works as an integrated feature of a scanning electron microscope (SEM) and cannot operate on its own without the latter.

#### 4.4.1 EDAX Process

During EDAX analysis, the specimen is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the specimen atoms, own electrons, knocking some of them off in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher-energy electron from an outer shell. To be able to do so, however, the transferring outer electron must give up some of its energy by emitting an X-ray.

The EDAX spectrum is just a plot of how frequently an X-ray is received for each energy level. An EDAX spectrum normally displays peaks corresponding to the energy levels for which the most X-rays had been received. Each of these peaks is unique to an atom, and therefore corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the specimen.
An EDAX spectrum plot not only identifies the element corresponding to each of its peaks, but also the type of X-ray to which it corresponds. For example, a peak corresponding to the amount of energy possessed by X-rays emitted by an electron in the L-shell going down to the K-shell is identified as a K-Alpha peak. The peak corresponding to X-rays emitted by M-shell electrons going to the K-shell is identified as a K-Beta peak.

The following Figure 4.4 shows the identification of elements in an EDAX spectrum based on the energy content of the X-rays emitted by their electrons as these electrons transfer from a higher energy shell to a lower-energy level.

![Figure 4.4 Energy released by an electron in various shells](image)

**4.5 FOURIER TRANSFORM INFRARED (FT-IR) SPECTROSCOPY**

FT-IR stands for Fourier Transform Infra Red, the preferred method of infrared spectroscopy. In infrared spectroscopy, IR radiation is passed through a sample. Some of the infrared radiation is absorbed by the sample and some of it is passed through (transmitted). The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample. Like a fingerprint no two unique molecular
structures produce the same infrared spectrum. This makes infrared spectroscopy useful for several types of analysis. The information that FT-IR can provide are

(i) Identification of unknown materials
(ii) Check the quality or consistency of a sample
(iii) Determine the amount of components in a mixture

4.5.1 Theory

Infrared spectroscopy has been a workhorse technique for material analysis in the laboratory for over seventy years. An infrared spectrum represents a fingerprint of a sample with absorption peaks which correspond to the frequencies of vibrations between the bonds of the atoms making up the material. Because each different material is a unique combination of atoms, no two compounds produce the exact same infrared spectrum. Therefore, infrared spectroscopy can result in a positive identification (qualitative analysis) for every different kind of material. In addition, the size of the peaks in the spectrum is a direct indication of the amount of material present. With modern software algorithms, infrared is an excellent tool for quantitative analysis.

Fourier Transform Infrared spectrometry was developed in order to overcome the limitations encountered with dispersive instruments. The main difficulty was the slow scanning process. A method for measuring all of the infrared frequencies simultaneously, rather than individually, was needed. A solution was developed which employed a very simple optical device called an interferometer. The interferometer produces a unique type of signal which has all of the infrared frequencies "encoded" into it. The signal can be measured very quickly, usually on the order of one second or so. Thus, the
use of the interferometer results in extremely fast measurements. Fourier transformation using of "decoding" of the individual frequencies is accomplished. Schematic diagram of FTIR spectrometer arrangement is shown in Figure 4.5.

![Schematic diagram of FTIR spectrometer arrangement](image)

**Figure 4.5 Schematic diagram of fourier transform infra red spectroscopy arrangements**

### 4.6 MEASUREMENTS

Samples were analyzed by using Shimadzu XRD-6000 X-ray diffractometer. Samples mounted on the specimen holder using silica gel were scanned at a rate of 5 deg/minute with CuK\(\alpha\) radiation. The radiation is filtered using a 1° divergence slit, a 1° scatter slit, and 0.15 mm receiving slit. All the films were analysed in the 10° – 80° (2θ) scale-range. The generated raw data files were then computer processed to smooth data points, remove amorphous background scatter. Integrated intensities were calculated using Shimadzu profile fitting software package that performs mathematical modeling of the diffractogram pattern. EDAX analysis were carried by using JEOL SEM / model JSM-35 CF, fitted with energy dispersive spectrometer 7000 series for elemental analysis. FTIR spectra were recorded on a Perkin Elmer 1600 spectrometer in the 3500-450 cm\(^{-1}\) range; resolution 4 cm\(^{-1}\); 1024 scans, interval 0.2. The size of the IR beam was 15 mm in diameter.
4.7 RESULTS AND DISCUSSION

4.7.1 XRD Analysis

4.7.1.1 Effect of thickness

The X-ray diffraction patterns of thermally evaporated PbPc and CuPc films of thicknesses 150 nm, 300 nm and 450 nm prepared at room temperature are shown in Figure 4.6 (a, b and c) and 4.7 (a, b and c). The PbPc patterns at lower thickness (150 nm) shows peaks at 2θ values 6.85°, 14.16° and 24.55° that were assigned to monoclinic (001), (320) and (111) lines respectively. The patterns at thickness (300 nm) shows an extra peak at 2θ value 17.49° and is assigned to the monoclinic (420) line. A peak at 2θ value 30.26° coinciding with the triclinic (400) line is seen for higher thicknesses (300 nm and 450 nm). The peak values are in good agreement with the previous literature works (Colins et al (1990), Miyamoto et al (1995)).

The CuPc patterns at lower thickness (150 nm) shows peaks at 2θ values 8.69°, 12.98° and 25.18° that were assigned to monoclinic (001), (320) and (111) lines respectively. The patterns at thickness (300 nm) shows an extra peak at 2θ value 31.58° and is assigned to the monoclinic (400) line. A peak at 2θ value 26.78° coinciding with the triclinic (420) line is seen for higher thicknesses (450 nm). The peak values are in good agreement with the previous literature works (Ambily and Menon (1990)).

From the XRD patterns of PbPc and CuPc films of different thicknesses, it is clear that as thickness increases, triclinic grains (T) are seen along with monoclinic (M) forms. Thus evaporated films at room temperature are monoclinic at lower thickness or a mixture of monoclinic and triclinic forms at higher thicknesses (Ambily and Menon (1998), Colins et al (1993)).
These evaporated films are polycrystalline in nature so some of the peaks are broad.

Figure 4.6  XRD patterns of PbPc films of various thicknesses
Figure 4.7 XRD patterns of CuPc films of various thicknesses
A weak intensity of (320) reflection and absence of (h00) reflections in all thicknesses implies a low degree of crystallinity of the monoclinic film compared with the triclinic film. The XRD patterns show weak diffraction peaks for (320) and (420) monoclinic lines of PbPc and (320) and (400) of CuPc. PbPc and CuPc molecules in the monoclinic modification are composed of well-defined structure which clusters themselves, consist of orderly arranged molecular stacks. Within the stacks there exist two substructures which have opposite orientations of the shuttlecock Pc structure. Such a structure explains the weak diffraction peaks of monoclinic crystals (Colins et al (1993), Miyamoto et al (1995), Collin and Belgachi (1989), Hamann et al (1978)). In this phase, the molecules stack linearly to form a molecular column parallel to the c axis (Ambily S et al (1999)).

Table 4.1 and 4.2 shows the structural parameters of PbPc and CuPc films for different thicknesses. From the table it is clear that full width half maximum value (FWHM) decreases with the film thickness. Such a decrease reflects the decrease in internal micro strain within the films and an increase in grain size.

Figure 4.8 and 4.9 shows the variation in grain size and dislocation density as a function of thickness. From this we conclude that as thickness increases, grain size increases and defects like dislocation density and strain decreases. This may be attributed to increase in crystallinity in the films (Prabahar and Dhanam (2005)).
Figure 4.8  Variation in grain size (D) and dislocation density (δ) as a function of thickness of PbPc

Figure 4.9  Variation in grain size (D) and dislocation density (δ) as a function of thickness of CuPc
4.7.1.2 Effect of temperature

The XRD patterns of PbPc and CuPc films for thickness 450 nm at different annealed temperatures are shown in Figure 4.10 (a, b and c) and 4.11 (a, b and c). The peaks obtained at 303 K are assigned to the monoclinic phase films with some triclinic grains, as already mentioned.

The XRD pattern of PbPc at 323 K shows peaks at 2θ values 14.9°, 22.4° and 30.3° assigned to the triclinic (200), (300) and (400) lines respectively. Here some peaks are of small range. When temperature is increased to 373 K one more peak at 2θ value 7.43° arise which gets assigned to the (100) reflection of triclinic phase. The results are consistent with the previous literature works (Colins et al (1993), Miyamoto et al (1995)). The XRD pattern of CuPc at 323 K shows peaks at 2θ values 26.12°, 27.63° and 34.21° assigned to the triclinic (300), (200) and (400) lines respectively. In 323 K annealed film, the diffraction peaks appeared at 26.12° corresponding to the (300) lattice planes of α-phase CuPc. These facts indicate that the CuPc thin film annealed at 323 K is highly ordered along the c-axis in a direction perpendicular to the substrate surface (Deokjoon Cha et al (2005), Lulu deng et al (2011)). The structural difference is in the diffraction angle of the molecular stacks 26.12° and 34.21° for α phases. The Pcs form long flat ribbon-like monoclinic crystals, the surface of the ribbon being the (300) (400) plane (Kedar Manandhar et al (2006)). Here some peaks are of small range. When temperature is increased to 373 K one more peak at 2θ value 26.83° arise which gets assigned to the (100) reflection of triclinic phase. The results are consistent with the previous literature works (El-Nahass M.M et al (2002), Puigdollers J et al (2006)).
Figure 4.10 XRD patterns of PbPc films for thickness 450 nm at annealed temperatures

(a) 303 K

(b) 323 K

(c) 373 K
Figure 4.11 XRD patterns of CuPc films for thickness 450 nm at annealed temperatures.
Table 4.1. Structural parameters of thermally evaporated PbPc films for different thicknesses

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>(hkl)</th>
<th>2θ (degrees)</th>
<th>Interplanar Spacing d (Å)</th>
<th>FWHM β ×10⁻³ (radians)</th>
<th>Grain size D (nm)</th>
<th>Dislocation density δ ×10¹⁵ (lines/m²)</th>
<th>Strain ε ×10⁻⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>(001)</td>
<td>6.9</td>
<td>6.89</td>
<td>12.75</td>
<td>8.648</td>
<td>16.760</td>
<td>3.5560</td>
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<td></td>
<td>(420)</td>
<td>17.492</td>
<td>16.58</td>
<td>5.06</td>
<td>16.232</td>
<td>44.350</td>
<td>0.5083</td>
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<tr>
<td></td>
<td>(111)</td>
<td>25.438</td>
<td>24.15</td>
<td>3.49</td>
<td>2.975</td>
<td>49.874</td>
<td>0.4020</td>
</tr>
<tr>
<td>450</td>
<td>(001)</td>
<td>6.981</td>
<td>6.89</td>
<td>12.65</td>
<td>5.8855</td>
<td>24.641</td>
<td>1.6469</td>
</tr>
<tr>
<td></td>
<td>(320)</td>
<td>12.718</td>
<td>12.59</td>
<td>6.95</td>
<td>4.9594</td>
<td>29.369</td>
<td>1.1593</td>
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<tr>
<td></td>
<td>(111)</td>
<td>25.706</td>
<td>24.155</td>
<td>3.46</td>
<td>2.3769</td>
<td>62.465</td>
<td>0.2562</td>
</tr>
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</table>

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### Table 4.2. Structural parameters of thermally evaporated CuPc films for different thicknesses

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>(hkl)</th>
<th>20 (degrees)</th>
<th>Interplanar Spacing d (Å)</th>
<th>FWHM β ×10⁻³ (radians)</th>
<th>Grain size D (nm)</th>
<th>Dislocation density δ ×10¹⁵ (lines/m²)</th>
<th>Strain ε ×10⁻⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>150</td>
<td>(001)</td>
<td>8.516</td>
<td>8.69</td>
<td>13.25</td>
<td>12.621</td>
<td>12.454</td>
<td>3.5426</td>
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<tr>
<td></td>
<td>(320)</td>
<td>12.436</td>
<td>12.98</td>
<td>7.64</td>
<td>5.857</td>
<td>26.125</td>
<td>1.4516</td>
</tr>
<tr>
<td></td>
<td>(111)</td>
<td>26.354</td>
<td>25.18</td>
<td>5.42</td>
<td>6.436</td>
<td>22.714</td>
<td>1.4521</td>
</tr>
<tr>
<td>300</td>
<td>(001)</td>
<td>8.970</td>
<td>8.94</td>
<td>13.12</td>
<td>8.895</td>
<td>16.451</td>
<td>2.5756</td>
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<td></td>
<td>(320)</td>
<td>11.924</td>
<td>11.24</td>
<td>5.46</td>
<td>15.245</td>
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<td>0.8253</td>
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<td></td>
<td>(111)</td>
<td>27.382</td>
<td>29.97</td>
<td>4.58</td>
<td>22.475</td>
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<td>450</td>
<td>(001)</td>
<td>8.891</td>
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<td>13.18</td>
<td>6.215</td>
<td>22.859</td>
<td>1.8459</td>
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<td></td>
<td>(320)</td>
<td>11.876</td>
<td>11.48</td>
<td>7.54</td>
<td>5.689</td>
<td>23.989</td>
<td>1.2546</td>
</tr>
<tr>
<td></td>
<td>(111)</td>
<td>26.854</td>
<td>26.54</td>
<td>4.49</td>
<td>3.954</td>
<td>61.452</td>
<td>0.8457</td>
</tr>
</tbody>
</table>
From the XRD patterns at different annealed temperature it is verified that as temperature increases the additional of peaks for triclinic phase increases. In the triclinic structure, the molecular stack along the a-axis orient their convex and concave sides alternatively. Annealing at 373 K changes the structure to triclinic with (100) as the direction of preferential orientation. So when annealing is carried out in air at 373 K, triclinic phase becomes predominant. The annealed films also exhibit polycrystalline nature. As mechanical strength increased triclinic peak size increased.
Table 4.3 Structural parameters of thermally evaporated PbPc film of thickness 450 nm at different annealed temperatures

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Temperature (K)</th>
<th>(hkl)</th>
<th>2θ (degrees)</th>
<th>Interplanar spacing (d) (Å)</th>
<th>FWHM ((\beta) \times 10^{-3}) (radians)</th>
<th>Grain size (D) (nm)</th>
<th>Dislocation density ((\delta) \times 10^{15}) (lines/m²)</th>
<th>Strain ((\varepsilon) \times 10^{-4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>323</td>
<td>(200)</td>
<td>13.775</td>
<td>14.94</td>
<td>5.86</td>
<td>32.008</td>
<td>0.9760</td>
<td>11.305</td>
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<td></td>
<td></td>
<td>(300)</td>
<td>22.760</td>
<td>22.46</td>
<td>3.86</td>
<td>47.204</td>
<td>0.4487</td>
<td>7.666</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(400)</td>
<td>30.589</td>
<td>30.26</td>
<td>2.92</td>
<td>26.925</td>
<td>1.3793</td>
<td>13.400</td>
</tr>
<tr>
<td>450</td>
<td>373</td>
<td>(100)</td>
<td>7.775</td>
<td>7.43</td>
<td>11.36</td>
<td>37.148</td>
<td>0.7246</td>
<td>9.7420</td>
</tr>
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<td></td>
<td></td>
<td>(200)</td>
<td>15.315</td>
<td>14.94</td>
<td>5.70</td>
<td>71.876</td>
<td>0.1935</td>
<td>5.0349</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(300)</td>
<td>22.770</td>
<td>22.46</td>
<td>3.90</td>
<td>50.368</td>
<td>0.3948</td>
<td>7.1850</td>
</tr>
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<td></td>
<td></td>
<td>(400)</td>
<td>32.221</td>
<td>30.26</td>
<td>2.77</td>
<td>85.023</td>
<td>0.1383</td>
<td>4.2564</td>
</tr>
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</table>
Table 4.4 Structural parameters of thermally evaporated CuPc film of thickness 450 nm at different annealed temperatures

<table>
<thead>
<tr>
<th>Thickness (nm)</th>
<th>Temperature (K)</th>
<th>(hkl)</th>
<th>2θ (degrees)</th>
<th>Interplanar spacing d (Å)</th>
<th>FWHM (β) ×10⁻³ (radians)</th>
<th>Grain size D (nm)</th>
<th>Dislocation density (δ) ×10¹⁵ (lines/m²)</th>
<th>Strain (ε) ×10⁻⁴</th>
</tr>
</thead>
<tbody>
<tr>
<td>373</td>
<td>(100) (200) (400)</td>
<td>26.832/30.437/34.431</td>
<td>26.74/30.01/35.94</td>
<td>8.452/5.542/2.874</td>
<td>3.8451/2.8345/1.9859</td>
<td>39.814/68.425/62.543</td>
<td>1.1245/0.9545/0.8153</td>
<td>9.548/5.344/4.875</td>
</tr>
</tbody>
</table>
Table 4.3 and 4.4 shows the structural parameters of PbPc and CuPc films of thickness 450 nm at annealed temperatures (323 K and 373 K). Figure 4.12 and 4.13 shows the variation in grain size and dislocation density as a function of temperature for PbPc and CuPc films respectively. From these we conclude that as temperature increases, grain size also increases.

4.7.2. EDAX Analysis

Energy dispersive analysis using X-ray (EDAX) helps us to determine the elemental contents in the specimen very accurately. A core level electron of a surface atom of PbPc and CuPc are removed by an impinging electron or an X-ray photon. The excited atom decays to a lower energy state through an electronic rearrangement in which an additional electron from a higher level is knocked out leaving the atom in a doubly ionized state and the ejected electron possesses the energy difference.

4.7.2.1 Effect of thickness

The elemental composition of the PbPc and CuPc films deposited at different thickness and annealed temperature were evaluated by EDAX technique. The Figure 4.14 and 4.15 shows the EDAX spectrum of the PbPc and CuPc films respectively. The percentage of lead and copper increases with thickness in both PbPc and CuPc films respectively (0.77, 1.30 and 6.18 for 150 nm, 300 nm and 450 nm of PbPc & 0.89, 1.93 and 8.78 for 150 nm, 300 nm and 450 nm of CuPc respectively). The percentage of carbon increases with thickness (30.93, 50.47 and 62.00 for 150 nm, 300 nm and 450 nm of PbPc & 38.34, 49.25 and 60.82 for 150 nm, 300 nm and 450 nm of CuPc respectively). In all the Pcs highest element percentage is obtained for carbon. Other peaks in the energy spectrum are due to glass substrate. Hydrogen is not detected due to its low atomic weight (Goldstein et al
The nitrogen amount is very poor in both films. The films deposited at 303 K with different thickness have uniform composition profile.

Figure 4.14. EDAX Patterns of PbPc Films of various thicknesses

(a) 150 nm

(b) 300 nm

(c) 450 nm
Figure 4.15. EDAX Patterns of CuPc Films of various thicknesses

(a) 150 nm

(b) 300 nm

(c) 450 nm

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The peak corresponding to carbon, silicon, sodium and oxygen shows a transition from L to the K-shell which can be termed as a K-Alpha peak (Kα). The peaks corresponding to lead and copper shows three types of transitions M-Alpha (Mα), M-beta (Mβ), M-Gamma (Mγ). All these transitions are shown in the EDAX patterns of PbPc and CuPc thin films of different thickness.

4.7.2.2 Effect of temperature

Figure 4.16 (a, b and c) and 4.17 (a, b and c) shows the EDAX patterns of PbPc and CuPc thin films of thickness 450 nm at room temperature (303 K) and annealed at 323 K and 373 K temperature. The percentage of lead and copper are same in both cases and its amount is low. Carbon present in CuPc and PbPc are observed in the EDAX. It is to be noted that the content of carbon observed with respect to temperature has no major change indicating that phthalocyanine is preserved. The presence of silicon, sodium and oxygen peaks are due to the glass substrates. The composition of the films deposited at higher thickness and annealed temperatures are found to be more in percentage. It is observed that the deposited annealed films of 373 K have slight deviation from stoichiometry and the film deposited at 303 K has a uniform composition picture. However, the film deposited at 303 K is required for the homogenization. In the films deposited and annealed at 373 K only, thermally stable phase is present and also it exhibited a microcrystalline structure with a uniform composition at the micrometer.

The peak corresponding to carbon, nitrogen, silicon, sodium and oxygen shows a transition from L to the K-shell which can be termed as a K-Alpha peak (Kα). The peaks corresponding to lead and copper shows three types of transitions – M-Alpha (Mα), M-beta (Mβ), M-Gamma (Mγ). All these transitions are shown in the EDAX patterns of PbPc and CuPc thin films.
Figure 4.16 EDAX patterns of PbPc films of thickness 450 nm at annealed temperature
Figure 4.17 EDAX patterns of CuPc films of thickness 450 nm at annealed temperature
4.7.3 FT-IR Analysis

The infrared spectrum of PbPc and CuPc thin films of 150 nm, 300 nm and 450 nm thickness prepared at room temperature and 450 nm annealed at 323 K and 373 K temperature is shown in Figures 4.18 to 4.27. The main peak at 725.23±4 cm\(^{-1}\) is attributed to non-planar deformation vibrations of the C–H bonds of benzene rings (Ahmad and Collins (1991b), Sidorov (1976)) and the C–H in plane bonding at 1112.93±4 cm\(^{-1}\) (Ahmad and Collins (1991b), Dann et al (1990)). A medium band at 771.53±4 cm\(^{-1}\) also corresponds to non-planar vibrations (Out-of-plane-bonding) of the C–H bonds (Ahmad and Collins (1991b), Meshkova et al (1997)). The following assignments can be made for the other ligand bands, the 3049.46±4 cm\(^{-1}\) band to aromatic C–H symmetric stretching vibrations and the 1606.70±4 and 1479.40±4 cm\(^{-1}\) band to C–C benzene ring skeletal stretching vibrations (Campbell and Collins (1997), Ahmad and Collins (1991b), Kroenke and Kenny (1964)). So it is expected to be intense compared to the C–N stretching at 1078.21±4 cm\(^{-1}\).

One strong intensity band at 881.47±4 cm\(^{-1}\) indicates the extraordinary stability of the metal phthalocyanines due to the strong bonding between the metal ion and the four surrounding nitrogen atoms in the pyrrole rings (Ahmad and Collins (1991b), Kobayashi et al (1970)). The peaks in the 700-400 cm\(^{-1}\) interval originate most probably due to vibrations in the benzene ring as they interact with the pyrrole ring (Ahmad and Collins (1991b)).

The band at 1332 ± 6 cm\(^{-1}\) is assigned to the C–C stretching in isoindole. The bands appearing at 882 ± 10 and 728 ± 5 cm\(^{-1}\) are assigned to the C–H bonding out of plane deformations. The bands appearing at 1284 ± 6 and 1162 ± 4 cm\(^{-1}\) is assigned to the C–N in isoindole and in plane band stretching vibration (Seoudi et al (2005)).
4.7.3.1 Effect of thickness

Figure 4.18 to 4.20 shows the referred spectrum of PbPc thin film of 150 nm, 300 nm and 450 nm respectively. The peaks are formed at 439.77±4 cm\(^{-1}\), 495.71±4 cm\(^{-1}\) and 605.65±4 cm\(^{-1}\) due to vibration of benzene ring as they interact with pyrrole ring. The intensity of the peak increases with increase in the thickness of the films. The strong intensity band at 881.47±4 cm\(^{-1}\) decreases with increase in the thickness indicates the stability of the metal Phthalocyanines due to the strong bonding. The intensity of the peak at 3049.46±4 cm\(^{-1}\) for aromatic C-H symmetric stretching vibration and peak at 2536.39±4 cm\(^{-1}\) decreases with increase in the thickness. The peaks at 1606.70±4 cm\(^{-1}\), 1479.40±4 cm\(^{-1}\) and 1330.88± 4 cm\(^{-1}\) correspond to C-C benzene ring skeletal stretching vibrations. The C-C and C-H benzene ring peak intensities increase with thickness. The intensity of C-N stretching at 1078.21±4 cm\(^{-1}\) decreases with increase in the thickness of the film. The absence of the band at 1006-1008 cm\(^{-1}\) and 1539±4 cm\(^{-1}\) suggest that the sample does not contain any metal free phthalocyanine. The peaks observed at 1078.21±4 cm\(^{-1}\), 1112.93±4 cm\(^{-1}\) and 1159.22±4 cm\(^{-1}\) depends on the molecular structure of the complexes and its chemical structure for the central metal.

Figures 4.21 to 4.23 show the spectrum of CuPc thin film of 150 nm, 300 nm and 450 nm respectively. In metal phthalocyanine, FTIR spectrums have a band at 1003 cm\(^{-1}\) which originates due to N–H bending vibration. This band is absent in metal phthalocyanine, because in Copper phthalocyanine, metal is replaced by metal cation. Metal ligand vibration band is observed in both copper and lead phthalocyanine at 940 and 960 cm\(^{-1}\). The peaks formed at 495.85±4 and 581.4571±4 cm\(^{-1}\) are due to vibration of the benzene ring interaction with the pyrrole ring. The intensity of the peak
increases with increase in the thickness of the films. The strong intensity band at 771.50±4 cm\(^{-1}\) decreases with increase in the thickness indicates the stability of the metal Phthalocyanines due to the strong bonding. The intensity of the peak at 3038.90±4 cm\(^{-1}\) corresponds to aromatic C-H symmetric stretching vibration and peak at 2678.89±4 cm\(^{-1}\) decreases with increase in the thickness of the film. The peaks at 1391.09±4 cm\(^{-1}\), 1490.00±4 cm\(^{-1}\) and 1900.25±4 cm\(^{-1}\) corresponds to C-C benzene ring skeletal stretching vibrations. The C-C and C-H benzene ring peaks intensities increases with thickness. The intensity of C-N stretching at 1091.34±4 cm\(^{-1}\) decreases with increase in the thickness of the film. The absence of the band at 1006-1008 cm\(^{-1}\) and 1539±4 cm\(^{-1}\) suggests that the sample does not contain any metal free phthalocyanine. The peaks observed at 1091.34±4 cm\(^{-1}\), 1391.09±4 cm\(^{-1}\) and 1491.22±4 cm\(^{-1}\) depends on the molecular structure of the complexes and its chemical structure for the central metal. 

The presence of bands at 712 and 739 cm\(^{-1}\) suggests the presence of \(\alpha\)-phase and the presence of bands at 730 and 752 cm\(^{-1}\) suggests that \(\beta\)-phase is also present in CuPc. The FTIR spectroscopic analysis of PbPc and CuPc suggest that these metal phthalocyanines contain both \(\alpha\)- and \(\beta\)-phases. The presence of band at 771 cm\(^{-1}\) in CuPc spectrum suggests the presence of \(\beta\) phase.
depends strongly on the molecular structure of the complexes and its chemical structure for the central metal. The middle peak originates from the vibration mode of a pyrrole ring and other two peaks are assigned to the in-plane deformation vibration of C-H bonding in the ring. The middle band has the highest intensity among the three peaks in the usual MPc's with D₄m molecular symmetry; however, the band shows lowest intensity in the case of PbPc and CuPc [29, 30, 31]. Due to an increase in the temperature, the absence of the band at 3049.46±4 and 2536.39±4 cm⁻¹ in the phthalocyanine complexes results in the replacement of hydrogen by metal cation [29].

**Figure 4.18 FTIR Spectrum of PbPc film of thickness 150 nm prepared at room temperature**
Figure 4.19 FTIR Spectrum of PbPc film of thickness 300 nm prepared at room temperature.
Figure 4.20 FTIR Spectrum of PbPc film of thickness 450 nm prepared at room temperature.
Figure 4.21 FTIR Spectrum of CuPc film of thickness 150 nm prepared at room temperature
Figure 4.22 FTIR Spectrum of CuPc film of thickness 300 nm prepared at room temperature
Figure 4.23 FTIR Spectrum of CuPc film of thickness 450 nm prepared at room temperature.
4.7.3.2. Effect of temperature

The FT-IR patterns of PbPc and CuPc thin films of 450 nm thickness at different annealed temperatures are shown in the Figures 4.24 to 4.27. The benzene ring peaks in the 700 - 400 cm\(^{-1}\) interval have increased the intensity with increase in the temperature. The main peaks at 725.23±4 cm\(^{-1}\) and 771.53±4 cm\(^{-1}\) is attributed to non-planar deformation vibrations of the C-H bonds. There is no change in this peak due to annealing. The strong bonding between the metal ion and the four surrounding nitrogen atom in the pyrrole ring peak at 881.47±4 cm\(^{-1}\) indicates increasing intensity with annealing temperature. The C-H in-plane bonding at 1112.93±4 cm\(^{-1}\) peak intensity increase with temperature. The spectral pattern in this region 1200-1000 cm\(^{-1}\) depends strongly on the molecular structure of the complexes and its chemical structure for the central metal. The middle peak originates from the vibration mode of a pyrrole ring and other two peaks are assigned to the in-plane deformation vibration of C-H bonding in the ring. The middle band has the highest intensity among the three peaks in the usual MPc’s with D\(_4\) molecular symmetry; however, the band shows lowest intensity into the case of PbPC and CuPc. This should be attributed to the molecular structure of PbPc and CuPc (Seoudi et al (2005), Moser and Thomas (1963), Janczak and Kubiak (2002)). Due to increase in the temperature, the absence of the band at 3049.46±4 and 2536.39±4 cm\(^{-1}\) in the phthalocyanine complexes results in the replacement of hydrogen by metal cation(Seoudi et al (2005)). The material characterization of these films by FT-IR spectroscopy clearly provides a convenient diagnostic technique in the development of PbPc and CuPc based thin film sensors (Seoudi et al (2005)).
Figure 4.24 FTIR Spectrum of PbPc film of thickness 450 nm annealed at 323 K
Figure 4.25 FTIR Spectrum of PbPc film of thickness 450 nm annealed at 373 K
Figure 4.26 FTIR Spectrum of CuPc film of thickness 450 nm annealed at 323 K
Figure 4.27 FTIR Spectrum of CuPc film of thickness 450 nm annealed at 373 K
4.8 CONCLUSION

XRD analysis confirmed that thermally evaporated PbPc and CuPc films at room temperature are of monoclinic nature at lower thickness and a mixture of monoclinic and triclinic nature at higher thicknesses. These evaporated films are polycrystalline in nature. Thickness increases, grain size increases and defects like dislocation density and strain decreases due to the increased in crystallinity nature in the films.

From the XRD patterns at different annealed temperature it is concluded that as temperature increases the number of peaks for triclinic phase increases. Annealing at 373 K changes the structure to triclinic with (100) as the direction of preferential orientation. So when annealing is carried out in air at 373 K, triclinic phase becomes predominant. The annealed films are also polycrystalline in nature. Various structural parameters such as grain size, dislocation density and strain have been estimated, and listed. It is found that as temperature increases, grain size increases.

EDAX analysis is used to find the elemental composition. The percentage of lead and copper were found to increase with thickness. The presence of Silicon, Sodium and Oxygen peaks are due to the glass substrates. The percentage of carbon is increased when annealed at high temperature (373 K). The composition of lead and copper in the deposited film at higher thickness and annealed temperatures are found to be of greater percentage.

FT-IR analysis identifies the presence of functional groups which absorb at definite frequencies. The spectral pattern depends strongly on the molecular structure of the complexes and chemical structure of the central metal. The FTIR spectroscopy analysis indicates the presence of both α and β-phases of phthalocyanines in both samples.
The CuPc and PbPc samples exhibit preferential orientation along parallel direction of the substrate surface in vacuum coated thin films. The metal ions play an important role in defining molecular orientation in thin films.