X-RAY DIFFRACTION STUDIES
ON LEAD PHTHALOCYANINE, ZINC PHTHALOCYANINE
AND MAGNESIUM PHTHALOCYANINE THIN FILMS

5.1 Introduction

The properties of phthalocyanine thin films are greatly influenced by the film morphology which in turn is determined by the preparation parameters such as substrate temperature and post-deposition annealing. Phthalocyanine thin films consist of organic molecules loosely bound by van der Waals or London-type forces. It is found that the structural properties affect the performance of a thin film as a functional material. The diversity of morphology that is characteristic of phthalocyanines is of great interest and controls the film structure during the fabrication of organic thin film devices. Many metal-substituted phthalocyanines, due to their thermal stability and sensitivity to a variety of gases are potential candidates for thin film gas sensors.\textsuperscript{1-4} The technique of X-ray diffraction (XRD) allows accurate determination of lattice d-spacings, lattice parameters, crystallite size and phase identification. X-ray diffraction patterns are characteristic of the atomic arrangement in the given film. X-ray diffraction studies have shown that phthalocyanine is a planar molecule having $D_{4h}$ symmetry. The molecular arrangement is determined by two factors: (i) electrostatic
interaction between substrates and molecules and (ii) van der Waals interaction between neighbouring molecules.\textsuperscript{5}

5.2 Theory

In a crystal, the atoms are arranged in a regular and periodic manner. X-ray diffraction in a crystal occurs when the wavelength of X-rays used is of the same order of magnitude as the interplanar distance. The scattered X-rays do not interfere constructively in all directions. The possible directions in which a crystal can diffract a beam of monochromatic X-rays are determined by Bragg’s condition.

\[ 2d \sin \theta = n \lambda \] \hspace{1cm} 5.2.1

where \( d \) is the distance between the atomic planes, \( \theta \) is the angle of incidence relative to the concerned plane, \( n \) is the order of diffraction and \( \lambda \) is the wavelength of the incident monochromatic X-rays.

The factor \( d \) is related to the \((hkl)\) indices of the plane by the relation

\[ \frac{1}{d^2} = \frac{1}{\sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right) \] \hspace{1cm} 5.2.2

and

\[ \sin^2 \theta = \frac{\lambda^2}{4 \sin^2 \beta} \left( \frac{h^2}{a^2} + \frac{k^2 \sin^2 \beta}{b^2} + \frac{l^2}{c^2} - \frac{2hl \cos \beta}{ac} \right) \] \hspace{1cm} 5.2.3

where \( a, b, c \) are lattice constants and \( \beta \) is the angle between \( a \) and \( c \).
The diffraction directions are determined by the structure and size of the unit cell. Intensities of the diffracted beams are determined by the position of the atoms within the unit cell.

The microcrystalline grain size $L$ of the film is determined from the full width at half maximum (FWHM) of the most intense peak in the XRD pattern using the Scherrer formula

$$L = \frac{K\lambda}{\eta/2 \cos \theta}$$

where $K$ is a constant equal to 0.9, $\lambda=1.54059 \text{Å}$, $\eta/2$ is the full width at half maximum in radians and $\theta$ is the diffraction angle of the most intense peak.

5.3 Experiment

PbPc, ZnPc and MgPc in the powder form (purity 99%) procured from Aldrich Chemical Company Inc., WI, USA are used as the source materials for the preparation of thin films. Thin films of these materials are prepared using a “Hind Hi Vac” vacuum coating unit (Model No.12 A4) by thermal evaporation technique at a base pressure of $10^{-5}$ Torr as discussed in section 2.14 of Chapter 2. The rate of evaporation is controlled within 10 - 15 nm/minute. Microglass slides are used as substrates which are cleaned according to the procedure described in section 2.15 of Chapter 2. A molybdenum boat of dimensions 29 mm x 12 mm x 5 mm is used as the source and the substrates are kept at a distance of 12 cm from it.
Thicknesses of the films are controlled by a single crystal thickness monitor and are crosschecked by Tolansky's multiple beam interference technique as described in section 2.19 of Chapter 2. Thin films deposited at room temperature are annealed in vacuum for one hour. Also thin films are prepared at different elevated substrate temperatures using a substrate heater, a detailed description of which is given in section 16 of Chapter 2. The temperature is monitored using a copper-constantan thermocouple.

Bruker (Model D8 Advance) and Philips Analytical X-ray diffractometers with CuKα radiation of wavelength λ=1.54059 Å are used for the diffraction measurements. X-ray diffractograms of PbPc, ZnPc and MgPc thin films are recorded and are analysed.

5.4 Results and Discussion

The metal-substituted phthalocyanine molecule is a square planar molecule consisting of a divalent metal ion surrounded by four benzopyrrrole units. Phthalocyanines commonly exist in three different polymorphic forms depending on their molecular stacking arrangements and are designated as α, β and γ phases. The α-form is metastable and can be converted to β-form by annealing. The β-form is thermodynamically stable. The γ-phase is not yet well understood.
Figure 5.4.1 shows the X-ray diffractogram for PbPc thin film deposited at room temperature. A prominent peak at $2\theta = 12.5^0$ is observed. Ottaviano et al.$^8$ have reported a peak at $2\theta = 12.61^0$ for as-deposited PbPc thin film. They further suggest that the film is monoclinic. PbPc in the monoclinic modification are composed of clusters of well defined structure. These clusters consist of orderly arranged stacks. Within the stack there exists two substructures, which is a possible explanation for weak diffraction intensity of PbPc monoclinic peak. The PbPc molecule has a unique shuttlecock shaped structure with two crystal structures.$^9$ The position of lead atom in the PbPc skeleton differs from the position of the central metal atom in other phthalocyanines. Most metal-substituted phthalocyanines have planar molecules. But in the case of a free PbPc molecule, the lead atom deviates by 0.27 - 0.40 Å from the plane and the rest of the molecule distorts away from it.$^{10}$ Figure 5.4.2 and Figure 5.4.3 give the X-ray diffractograms of ZnPc and MgPc thin films deposited at room temperature. The MgPc as-deposited film is observed to be almost amorphous in nature. The values of a, b and c could not be determined due to insufficient data.
Figure 5.4.1  X-ray diffractogram of PbPc thin film deposited at room temperature

Figure 5.4.2  X-ray diffractogram of ZnPc thin film deposited at room temperature
Figure 5.4.3 X-ray diffractogram of MgPc thin film deposited at room temperature

5.4. A Effect of Substrate Temperature

The X-ray diffractograms are recorded for films deposited at different substrate temperatures. Figure 5.4.A.1 shows the X-ray diffractogram for PbPc thin film deposited at 348 K. Well-defined peaks are observed at $2\theta = 6.81^\circ$, $2\theta = 7.41^\circ$ and at $2\theta = 12.55^\circ$. Figure 5.4.A.2 and Figure 5.4.A.3 give the X-ray diffraction patterns for PbPc thin films deposited at 398 K and 448 K respectively. The peak at $2\theta = 7.41^\circ$ becomes more intense in these cases. Figure 5.4.A.4, Figure 5.4.A.5 and Figure 5.4.A.6 give the X-ray diffractograms for ZnPc thin films prepared at 348 K, 398 K and 448 K respectively. An increase in the peak intensity is observed up to 398 K and then a decrease is observed for the film deposited at 448 K. Figure 5.4.A.7 shows the XRD pattern for MgPc thin
film deposited at 348 K. A small peak is observed at $2\theta = 7.24^0$. The XRD pattern for a sample deposited at 398 K is given in Figure 5.4.A.8 which shows a peak with a slightly increased intensity. Figure 5.4.A.9 shows the XRD pattern for MgPc thin film prepared at 448 K, which again shows an amorphous nature. The grain size of the microcrystallites for these films are calculated using equation 5.2.4 and are collected in Table 5.4.A.

![X-ray diffractogram of PbPc thin film deposited at substrate temperature 348 K](image)

**Figure 5.4.A.1** X-ray diffractogram of PbPc thin film deposited at substrate temperature 348 K
Figure 5.4.A.2 X-ray diffractogram of PbPc thin film deposited at substrate temperature 398 K

Figure 5.4.A.3 X-ray diffractogram of PbPc thin film deposited at substrate temperature 448 K
Figure 5.4.A.4 X-ray diffractogram of ZnPc thin film deposited at substrate temperature 348 K

Figure 5.4.A.5 X-ray diffractogram of ZnPc thin film deposited at substrate temperature 398 K
Figure 5.4.A.6 X-ray diffractogram of ZnPc thin film deposited at substrate temperature 448 K

Figure 5.4.A.7 X-ray diffractogram of MgPc thin film deposited at substrate temperature 348 K
Figure 5.4.A.8  X-ray diffractogram of MgPc thin film deposited at substrate temperature 398 K

Figure 5.4.A.9  X-ray diffractogram of MgPc thin film deposited at substrate temperature 448 K
### Table 5.4.A Variation of Grain Size with Substrate Temperature

<table>
<thead>
<tr>
<th>Material</th>
<th>Substrate Temperature (K)</th>
<th>Microcrystalline grain size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbPc</td>
<td>303</td>
<td>16.59</td>
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<tr>
<td></td>
<td>398</td>
<td>39.83</td>
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<tr>
<td></td>
<td>448</td>
<td>41.37</td>
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<tr>
<td>ZnPc</td>
<td>303</td>
<td>18.06</td>
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<tr>
<td></td>
<td>348</td>
<td>20.91</td>
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<tr>
<td></td>
<td>398</td>
<td>22.96</td>
</tr>
<tr>
<td></td>
<td>448</td>
<td>23.79</td>
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<tr>
<td>MgPc</td>
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<tr>
<td></td>
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<td></td>
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<td>30.18</td>
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<tr>
<td></td>
<td>448</td>
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</tr>
</tbody>
</table>

It is observed that the microcrystalline grain size increases with substrate temperature for all the samples.

### 5.4.B Effect of Vacuum-annealing

X-ray diffractograms are recorded for PbPc, ZnPc and MgPc thin films annealed in vacuum at different temperatures for one hour. Figure 5.4.B.1 and Figure 5.4.B.2 show X-ray diffractograms for PbPc thin film annealed at 448 K and 498 K. For these samples small peaks are observed at $2\theta = 6.81^0$, $2\theta = 7.41^0$ and at $2\theta = 16.50^0$. Ottavino et al. suggest that PbPc thin films annealed at 443 K are triclinic in structure. The microcrystalline grain size is calculated in each case. Figure 5.4.B.3 and
Figure 5.4.B.4 show the X-ray diffractograms of ZnPc thin film annealed in vacuum at 348 K and 498 K respectively. Peaks are observed at $2\theta = 9.00^0$, $2\theta = 12.31^0$ and at $2\theta = 18.17^0$. El-Nahass et al.\textsuperscript{11} have reported similar peaks for annealed ZnPc films. Figure 5.4.B.5, Figure 5.4.B.6 and Figure 5.4.B.7 show the X-ray diffractograms for MgPc thin films annealed in vacuum at 348 K, 398 K and 498 K respectively. The peak at $2\theta = 6.53^0$ increases in intensity as the annealing temperature increases. The sample annealed at 498 K is almost amorphous in nature. The grain size is calculated and is given in Table 5.4.B.

![Figure 5.4.B.1 X-ray diffractogram of PbPc thin film annealed in vacuum at 448 K](image)
Figure 5.4.B.2  X-ray diffractogram of PbPc thin film annealed in vacuum at 498 K

Figure 5.4.B.3  X-ray diffractogram of ZnPc thin film annealed in vacuum at 348 K
Figure 5.4.8.4  X-ray diffractogram of ZnPc thin film annealed in vacuum at 498 K

Figure 5.4.8.5  X-ray diffractogram of MgPc thin film annealed in vacuum at 348 K
Figure 5.4.B.6  X-ray diffractogram of MgPc thin film annealed in vacuum at 398 K

Figure 5.4.B.7  X-ray diffractogram of MgPc thin film annealed in vacuum at 498 K
Table 5.4.B variation of grain size with Annealing Temperature

<table>
<thead>
<tr>
<th>Material</th>
<th>Annealing Temperature (K)</th>
<th>Grain Size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbPc</td>
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<tr>
<td></td>
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<td></td>
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</table>

5.5 Conclusion

X-ray diffractograms of PbPc, ZnPc and MgPc thin films deposited at different substrate temperatures and annealed in vacuum at different temperatures are studied. For PbPc and ZnPc thin films, it is observed that the microcrystalline grain size increases with increasing substrate temperature and annealing temperature. Also it can be inferred that the crystallinity increases in these cases. Most of the films are found to be polycrystalline in nature. For MgPc, the as-deposited film and the one annealed at 498 K are almost amorphous in nature.
References


