CHAPTER 4

Experimental Results of Aluminium Oxide

\((\text{Al}_2\text{O}_3)\) Thin Films
Chapter: IV

Experimental Results of Aluminium Oxide (Al₂O₃) Thin Films

4.1 Introduction:
In this chapter the results have been given on the observations based on the experimental studies on aluminum oxide thin films. The details of thin film deposition have been given in chapter 2. Vacuum evaporated aluminium thin films were oxidized by using hot water oxidation method. The Al₂O₃ thin films were characterized for their crystal structure, surface morphology, optical and mechanical properties. The surface roughness was measured by using AFM. Optical signal loss was studied by prism coupling method for optical waveguide application. Similar to MgO thin film vapor chopping technique was used during deposition of Al₂O₃ thin films also. The ambient air exposure effects on the thin films properties have also been undertaken.

4.2 Crystal structure using X-ray diffraction (XRD):
X-ray diffraction patterns of vapor chopped and nonchopped Al₂O₃ thin films are shown in Fig. 4.1. From fig. 4.1 it is seen that, the vapor chopped and nonchopped thin films have different crystal structure. In the case of vapor chopped Al₂O₃ thin films (220), (620) and (422) cubic phases was also observed. The strong α-Al₂O₃ phase and (116) rhombohedral phase were observed. On the other hand (220) cubic and (211) rhombohedral phases were observed in nonchopped Al₂O₃ thin films. (620), (422) and α-Al₂O₃ phases were not present in nonchopped Al₂O₃ thin films.
Figure 4.1: XRD patterns of vapor chopped and nonchopped Al₂O₃ thin films of 300 nm thickness.

The thickness variation effect is plotted in figure 4.2. For lower thicknesses i.e. 200 and 100 nm XRD patterns were blueprints of the 300 nm thickness deposited vapor chopped and nonchopped Al₂O₃ thin films. A small intensity variation was observed, as thickness increases intensity of XRD peak increases. The intensity increment is an indication of thin film’s crystallinity improvement.

Figure 4.2 XRD patterns for vapor chopped and nonchopped Al₂O₃ thin films for different thicknesses.
Aluminium metal peak was observed, indicating the complete oxidation of aluminium metal films.

4.3 Surface morphology by scanning electron microscope (SEM):

The surface morphology of vapor chopped and nonchopped aluminium oxide thin films were studied by using scanning electron micrographs. Fig. 4.3 shows the surface morphology of VC and NC Al\textsubscript{2}O\textsubscript{3} thin films.

![SEM images of vapour chopped and nonchopped Al\textsubscript{2}O\textsubscript{3} thin films of 300 nm.](image)

Figure 4.3 SEM images of vapour chopped and nonchopped Al\textsubscript{2}O\textsubscript{3} thin films of 300 nm.

From figure it is seen that, nonchopped Al\textsubscript{2}O\textsubscript{3} thin films shows fibril surface morphology whereas vapor chopped Al\textsubscript{2}O\textsubscript{3} thin film gives smooth, dense continuous thin film surface morphology.

4.4 Atomic Force Microscopy (AFM):

The surface roughness gives additional information about surface morphology of thin films. Fig. 4.4 shows 2-dimensional and 3-dimensional atomic force micrographs for vapor chopped and nonchopped aluminium oxide thin films.

From the fig. 4.4 it was observed that, the surface roughness of vapor chopped thin film was lesser than the nonchopped Al\textsubscript{2}O\textsubscript{3} thin film. The granular structured grains were observed in vapor chopped as well as nonchopped Al\textsubscript{2}O\textsubscript{3} thin films. The grain size of nonchopped thin film was higher than the vapor
chopped Al₂O₃ thin films. Vapor chopped thin film was found to be denser than the nonchopped Al₂O₃ thin film. Thickness variation effect on surface roughness in Al₂O₃ thin films was not so prominent.

Figure 4.4: 2-dimensional and 3-dimensional atomic force micrographs for vapor chopped and nonchopped aluminium oxide thin films for 300 nm.

The variation in surface roughness of thin film plays an important role in optical coatings. It enhances the optical absorbance and affects the optical properties of thin films.
4.5 Optical properties:

Aluminium oxide has enormous potential to be of use in optoelectronics and microelectronics devices. Al₂O₃ thin film combines many properties such as high dielectric constant, high thermal conductivity, wear resistance and protective coating, mechanical strength, chemical inertness, good adhesion to glass substrate and transparency over wide wavelength range [1-5]. The refractive index (1.76) of these films is in the range suitable for optical waveguide purpose [4, 5].

As already mentioned in chapter I, the properties of deposited Al₂O₃ thin films depend on the deposition process and optimized parameters. To use the optical coating thin films in optoelectronic device formation having minimum optical signal transmission loss due to scattering of light, the reduction in defects and voids formation and improved surface morphology are the basic requirement.

4.5.1 Optical transmittance:

The optical transmission properties of vapor chopped and nonchopped Al₂O₃ thin films showed in figure 4.5

![Figure 4.5 Optical transmittance of vapor chopped and nonchopped Al₂O₃ thin films thickness 300nm.](image-url)
In fig. 4.5 it has been clearly seen that, the transmittance go on increasing with wavelength. It was also found that, the vapor chopped thin films showed higher transmittance than the nonchopped Al₂O₃ films. Vapor chopped thin films showed transmittance in 80-90% range whereas it was in between 55-60% for the nonchopped thin films.

The given transmittance graph (fig. 4.5) is an average transmittance values of 4-5 samples of vapor chopped and nonchopped Al₂O₃ thin films. The actual values of all the 5 samples of 300 nm thickness are plotted in figure 4.6. It is seen that sample to sample variations are more in the NC films than in the VC films.

Figure 4.6 Scatter diagram for vapor chopped and nonchopped Al₂O₃ thin films for 300 nm.

The thickness variation effect on Al₂O₃ thin films are plotted in Fig. 4.7. It shows the optical transmittances spectra for vapor chopped Al₂O₃ thin films of 100, 200 and 300 nm thin film thickness. It is clear that, as thickness of thin film increases, optical transmittance goes on decreasing whereas it increases with respect to wavelength for all thicknesses.
Figure 4.7 Optical transmittance spectra for vapor chopped Al$_2$O$_3$ thin films for different thicknesses.

Figure 4.8 Optical transmittance spectra for nonchopped Al$_2$O$_3$ thin films for different thicknesses.

Fig. 4.8 shows the optical transmission spectra for nonchopped Al$_2$O$_3$ thin films for 100, 200 and 300 nm thickness. The optical transmittance spectra have
same behaviour as vapor chopped thin films. In nonchopped thin films also optical transmittances varies with thickness variation and was in between 55-85 %.

4.5.2 Optical band gap:

Figure 4.9 shows the absorbance of vapor chopped and nonchopped Al₂O₃ thin films for different thicknesses. It was observed that, absorbance increases with increase in thickness of the thin film. Increase in absorbance with decrease in transmittance is co-related with each other with respect to thickness variation. Vapor chopped thin films showed the lower absorbance than nonchopped thin films.

Figure 4.9: Optical absorbance of vapor chopped and nonchopped Al₂O₃ thin films for different thicknesses.

Fig. 4.10 a, b and c shows the thickness variation effect in optical band gap for 100, 200, and 300 nm. Vapor chopped and nonchopped Al₂O₃ thin films showed same band gap patterns with different values. The absorption parameter \((\alpha \nu)^2\) shows the absorption edge moves to shorter wavelength region.
Figure 4.10 a) \((\alpha \theta h)^2\) against \(h\theta\) for vapor chopped and nonchopped Al\(_2\)O\(_3\) thin films for 100 nm thin film thickness

Figure 4.10 b) \((\alpha \theta h)^2\) against \(h\theta\) for vapor chopped and nonchopped Al\(_2\)O\(_3\) thin films for 200 nm thin film thickness.

The optical band gap values are given in table 4.1 It shows that, optical band gap increases with increase in thin film thickness as well as due to chopping. This optical band gap for vapor chopped Al\(_2\)O\(_3\) thin films was in between 4.7-5.8 eV whereas it was in 4.5-5.6 eV range for nonchopped films. There was small variation in band gap due to vapor chopping whereas thickness effect was found to be more prominent.
Figure 4.10 c) \((\alpha h \nu)^2\) against \(h \nu\) for vapor chopped and nonchopped \(\text{Al}_2\text{O}_3\) thin films for 300 nm thin film thickness

<table>
<thead>
<tr>
<th>Thin film thickness (nm)</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nonchopped</td>
</tr>
<tr>
<td>100</td>
<td>4.5</td>
</tr>
<tr>
<td>200</td>
<td>5.0</td>
</tr>
<tr>
<td>300</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Table 4.1: Optical Band gap values of vapor chopped and nonchopped \(\text{Al}_2\text{O}_3\) thin films

Number of worker has been reported the optical band gap of aluminum oxide [8-11]. Obtained band gaps in our case are lesser than the band gap of bulk aluminium oxide 9.5 eV [12] and are in the reported range.

4.5.3 Refractive index:

The refractive index values of vapor chopped and nonchopped \(\text{Al}_2\text{O}_3\) thin films have been given in table 4.2. Table shows that, the refractive index of vapor chopped thin films were lower than the nonchopped \(\text{Al}_2\text{O}_3\) thin films for 100, 200 and 300 nm thicknesses. It was also observed that, refractive index increases with increase in thickness of thin film for vapor chopped as well as nonchopped \(\text{Al}_2\text{O}_3\)
thin films. The refractive index for vapor chopped thin films was in the range 1.59-1.66 whereas it was 1.63-1.69 for nonchopped thin films. As per the references, these values are in acceptable range [4, 14-18].

<table>
<thead>
<tr>
<th>Thin film Thickness (nm)</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NC</td>
</tr>
<tr>
<td>100</td>
<td>1.63</td>
</tr>
<tr>
<td>200</td>
<td>1.66</td>
</tr>
<tr>
<td>300</td>
<td>1.69</td>
</tr>
</tbody>
</table>

Table 4.2: Refractive index of vapor chopped and nonchopped Al₂O₃ thin films for different thicknesses

4.6 Optical waveguiding properties:

The optical transmission loss was measured by prism coupling method [19]. Here the deposited Al₂O₃ thin films act as a optical planar waveguide. The difference between input optical signal and output signal intensity gives the clear idea about the optical transmission loss. The columnar grain growth and defects i.e. voids and cracks obtained in thin film during manufacturing process, scatters the optical signal which results in transmission loss. The optical transmission loss was measured in 4-5 samples for to check the results reproducibility.

The optical transmission loss study of Al₂O₃ thin film waveguide showed that, optical transmission loss of vapor chopped thin film (3.73 dB/cm) was less than the nonchopped Al₂O₃ (6.01 dB/cm) thin film waveguide. These optical transmission loss values of both VC and NC thin films were lesser than those reported (10 dB/cm) by Kersten et al. [5]. The effect of thickness variation i.e. 100, 200 and 300 nm is negligible. It differs by ~0.5-0.8 dB/cm. so it can be neglected.
4.7 Mechanical properties:

4.7.1 Adhesion:

Adhesion of vapor chopped and nonchopped Al$_2$O$_3$ thin films were also studied. For each case the adhesion of Al$_2$O$_3$ thin films were plotted by measuring 4-5 samples each. The scatter diagram is plotted in fig. 4.11. It can be observed that, adhesion increases with increase in thickness of thin film as well as due to vapor chopping.

![Scatter diagram of adhesion of vapor chopped and nonchopped Al$_2$O$_3$ thin films for different thicknesses.](image)

The adhesion values for different thin film thickness (100, 200 and 300 nm) have been given in table. 4.3. The table shows that vapor chopped thin films have higher adhesion than the nonchopped thin films. The average values are given here.
<table>
<thead>
<tr>
<th>Thin film Thickness (nm)</th>
<th>Adhesion ($\times 10^3$ N/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NC</td>
</tr>
<tr>
<td></td>
<td>VC</td>
</tr>
<tr>
<td>100</td>
<td>158 ± 7</td>
</tr>
<tr>
<td>200</td>
<td>205 ± 3</td>
</tr>
<tr>
<td>300</td>
<td>286 ± 8</td>
</tr>
</tbody>
</table>

Table 4.3: Adhesion of vapor chopped and nonchopped Al$_2$O$_3$ thin films for different thicknesses

4.7.2 Intrinsinc stress:

The intrinsic stress of vapour chopped and nonchopped Al$_2$O$_3$ thin films were also studied. The effect of thin film thickness has been given. The fig. 4.12 gives the intrinsic stress of vapor chopped and nonchopped Al$_2$O$_3$ thin films for different thicknesses.

![Scatter diagram](image)

Figure 4.12: Intrinsic stress of vapor chopped and nonchopped Al$_2$O$_3$ thin films for different thicknesses.
Similar to MgO thin film, the stress of Al$_2$O$_3$ thin films were also studied. The calculated thermal stress for aluminum oxide thin film was very small, it was (-1.004 x 10$^7$ N/m$^2$). The negative sign indicates the type of the stress. It was comprehensive stress. The obtained intrinsic stress values are average values for 100nm, 200nm and 300nm thicknesses have been given in table 4.4. It was observed that, intrinsic stress decreases with increase in thin film thickness whereas vapor chopped Al$_2$O$_3$ thin films showed lesser intrinsic stress than nonchopped thin films.

<table>
<thead>
<tr>
<th>Thin film thickness (nm)</th>
<th>Intrinsic stress (x 10$^7$ N/m$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>VC</td>
</tr>
<tr>
<td>100</td>
<td>58 ± 9</td>
</tr>
<tr>
<td>200</td>
<td>36 ± 3</td>
</tr>
<tr>
<td>300</td>
<td>31 ± 8</td>
</tr>
</tbody>
</table>

Table 4.4: Intrinsic stress of vapor chopped and nonchopped Al$_2$O$_3$ thin films for different thicknesses.

4.8 Ambient air exposure effect:

When the prepared thin film is exposed to ambient air, the properties of thin film changes with respect to exposure duration. We have already has seen in the case of magnesium oxide thin films in chapter III. The effect of air exposure on Al$_2$O$_3$ thin film was also studied. For this measurement, the films were kept in a dust free container at room temperature and measurements were taken before and after exposure period. The variation in measurement gives the exposure effect. The affinity of deposited thin film to adsorb and/or absorb the moisture as well as other gases is mainly affecting the changes in thin film properties. Aluminium oxide is an environmentally stable oxide. It shows very small variation in the optical and mechanical properties.
4.8.1 Crystal structure:

Crystal structure of vapor chopped and nonchopped fresh and air exposed Al₂O₃ thin films were studied. Figure 4.13 showed that, the effect of 30 days air exposure was almost negligible. Thin film was highly stable. There were no changes in respective phases.

Figure 4.13: Fresh and 30 days air exposed vapor chopped and nonchopped Al₂O₃ thin films.

4.8.2 Optical Properties:

4.8.2.1 Optical transmittance:

The effect of ambient air exposure on optical transmittance properties of vapor chopped and nonchopped aluminium oxide thin films of 100 nm for different durations showed in fig. 4.15 The ambient air exposure for different duration 1 day, 10, 20 and 30 days were measured. The drastic effect of short term air exposure was observed on 100 nm as compared to the other 200 and 300 nm thin film thicknesses. The changes are more in the 300-400 nm wavelength range as compared to other wavelengths. Due to vapor chopping these changes became negligible even in the 300-400 nm range. The exposure effect on optical transmittance was very small so for further thicknesses exposure effect was studied only after 30 days.
Figure 4.15 Air exposure effect on optical transmittance of vapor chopped and nonchopped Al₂O₃ thin films for 100 nm for different durations.

Figure 4.16 Optical transmittance of nonchopped fresh and air exposed Al₂O₃ thin films for Air exposure effect study.

The optical transmittance was reduced due to air exposure. This is might be the adsorption of moisture over the surface of VC and NC Al₂O₃ thin films. The figure 4.16 showed very less air exposure effect on optical transmittance of fresh
and exposed nonchopped Al$_2$O$_3$ thin films for different thicknesses i.e. 100, 200, 300nm. The thickness variation effect also observed. Higher thicknesses were getting affected very less as compared to smaller thickness.

Fig. 4.17 showed the air exposure effect on vapour chopped Al$_2$O$_3$ thin films for different durations. It was observed that, air exposure effect on vapor chopped thin films was comparatively lower than the nonchopped Al$_2$O$_3$ thin films. There was almost no change due to air exposure on the vapor chopped thin films. The thickness wise variation are also shown in fig. 4.17

![Transmittance of fresh and air exposed Al$_2$O$_3$ thin films](image)

Figure 4.17 Optical transmittance of vapor chopped fresh (F) and air exposed (F) Al$_2$O$_3$ thin films for Air exposure effect study.

**4.8.2.2 Optical band gap:**

The effect of air exposure on optical band gap was studied for 30 days. The optical band gap of fresh and 30 days air exposed vapor chopped and nonchopped Al$_2$O$_3$ thin films for different thicknesses has been given in fig. The Al$_2$O$_3$ thin films of thickness 100 nm showed large changes in band gap as compared to the 200 and 300nm thicknesses films.
Figure 4.18 Optical band gap of vapor chopped and nonchopped fresh (F) and 30 days air exposed (A) Al₂O₃ thin films for different thicknesses.
The obtained values for optical band gap of vapor chopped and nonchopped thin films have been given in table 4.5. The vapor chopped thin films have higher band gap than the nonchopped Al₂O₃ thin films. Both vapor chopped and nonchopped Al₂O₃ thin films showed negligible variation in optical band gap due to air exposure. The Al₂O₃ thin films remains electrically stable after 30 days and very small change might be occur after 2 or 3 months in it. The vapor chopped thin films gives higher stability than the nonchopped thin films. The air exposure effect with respect to thickness variation on optical band gap was not prominent.

4.8.2.3 Refractive index:

The effect of air exposure on refractive index of vapor chopped and nonchopped Al₂O₃ thin film was also studied. Table 4.6 shows the refractive index for the films of various thicknesses viz. 30 days air exposed effect on VC and NC Al₂O₃ thin films. The refractive index of fresh thin films has been given in previous table 4.6. It was observed that, the variation in refractive index due to air exposure effect was comparatively higher in Al₂O₃ thin films of 100nm thickness. The exposure effect goes on decreasing with increase in thickness of thin film.

The vapor chopped thin films showed lesser air exposure effect than the nonchopped thin films. Compared to MgO thin films the exposure changes in Al₂O₃ thin films are smaller.

<table>
<thead>
<tr>
<th>Thin film thickness (nm)</th>
<th>Band gap (eV) after air exposure</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nonchopped</td>
</tr>
<tr>
<td>100</td>
<td>4.2</td>
</tr>
<tr>
<td>200</td>
<td>4.8</td>
</tr>
<tr>
<td>300</td>
<td>5.4</td>
</tr>
</tbody>
</table>
Table 4.6: Refractive index of vapor chopped and nonchopped Al₂O₃ thin films air exposed for 30 days.

4.8.3 Optical transmission loss:

The air exposure effect on optical transmission loss of vapor chopped and nonchopped Al₂O₃ thin film has shown that, there is very small change in transmission loss. Optical transmission loss increases due to air exposure. The fresh nonchopped Al₂O₃ thin films showed 6.01 dB/cm transmission loss; it became 8.47 dB/cm whereas vapor chopped thin films vary form 3.73 to 4.86 dB/cm. Again, vapor chopped thin films showed lower loss than the nonchopped thin films. The obtained transmission loss values were lesser than the reported loss i.e. 10 dB/cm [5]. The variation in surface roughness affects on the optical transmission loss.

4.8.4 Adhesion:

The air exposure effect study on adhesion of vapor chopped and nonchopped Al₂O₃ thin film has been shown that, there is very small change in adhesion due to air exposure. Adhesion of Al₂O₃ thin film decreased due to air exposure. The adhesion after 30 days air exposed Al₂O₃ thin films showed in figure 4.19.

There was very small change in adhesion was observed in short term exposure duration. It was unreadable so direct 30 days exposure effect has been given. It was also very small almost negligible

<table>
<thead>
<tr>
<th>Thin film Thickness (nm)</th>
<th>Refractive Index</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NC</td>
</tr>
<tr>
<td>100</td>
<td>1.651</td>
</tr>
<tr>
<td>200</td>
<td>1.668</td>
</tr>
<tr>
<td>300</td>
<td>1.693</td>
</tr>
</tbody>
</table>
Figure 4.19 Adhesion of Fresh (F) and air exposed (A) vapor chopped and nonchopped Al₂O₃ thin films for 30 days.

4.8.5 Intrinsic stress:

The air exposure effect on intrinsic stress of vapor chopped and nonchopped Al₂O₃ thin film has shown that, there is very small change in stress due to air exposure. Intrinsic stress almost remains same after 30 day air exposure, there was neither increment nor decrement was observed in Al₂O₃ thin films. The stress of thin films has been decreased with respect to thickness of thin film observed in fresh as well as air exposed thin films. Figure 4.20 showed the intrinsic stress variation with thickness variation after thin film air exposed for 30 days.
Figure 4.20: Intrinsic stress of vapor chopped and nonchopped Al$_2$O$_3$ thin film exposed for 30 days for different thicknesses

4.9 SUMMARY OF SOME IMPORTANT RESULTS:

The summary of some important results observed from the investigation carried out are as follows:

1. In the case of vapor chopped Al$_2$O$_3$ thin films (220), (620) and (422) cubic phases was also observed. The strong $\alpha$-Al$_2$O$_3$ phase and (116) rhombohedral phase were observed. On the other hand (220) cubic and (211) rhombohedral phases were observed in nonchopped Al$_2$O$_3$ thin films.

2. Nonchopped Al$_2$O$_3$ thin films showed fibril structure surface morphology whereas vapor chopped films showed smoothed surface morphology.

3. Surface roughness of vapor chopped thin films was found to be lesser than the nonchopped Al$_2$O$_3$ thin films.
4. Optical transmittance increases due to vapor chopping and decreases due to thickness.

5. Optical absorption decreases due to vapor chopping as well as decrease in thin film thickness.

6. Vapor chopped thin films showed comparatively higher band gap than nonchopped thin films.

7. Refractive index of Al$_2$O$_3$ thin films was found to increase with thin film thickness.

8. Vapor chopped thin films showed lower refractive index and lower transmission loss than nonchopped thin films.

9. Adhesion of Al$_2$O$_3$ thin film increases with increase in thin film thickness.

10. Vapor chopped thin films showed higher adhesion than nonchopped Al$_2$O$_3$ thin films.

11. Vapor chopped Al$_2$O$_3$ thin films showed lesser intrinsic stress than nonchopped thin films.

12. Al$_2$O$_3$ thin films properties remains stable after 30 days.
References:


