Chapter 3
Dip Coating Deposition and Characterizations of CuAlS$_2$ Thin Films
3.1. INTRODUCTION

The CuAlS$_2$ has been widely investigated because of their potential applications in solar cells [1], photovoltaic detectors [2], building blue and green light emitting devices [3], modulators, filters such as optical light eliminator filters [4] and optical frequency conversion applications in solid-state-based tunable laser systems [5]. CuAlS$_2$ is used as oxygen gas sensor, working at room temperature [6] and in targeted “in vitro” imaging of cancer cells as its potential application in cancer diagnostics without any intrinsic toxicity rendered to cells [7].

Up to now, a number of methods have been used to deposit CuAlS$_2$ thin films, including, iodine transport [8], metal organic decomposition (MOD) [9], single source thermal evaporation [6], sulfurization of precursors in H$_2$S flow [10], sulfurization of sputtered metallic precursors by sulfur vapors in hermetically sealed ampoules [11], thermal evaporation of elemental mixture [12], spray pyrolysis [13], pulsed plasma deposition [14], horizontal Bridgman method [15], chemical bath deposition (CBD) [16, 17] and two stage thermal evaporation technique [18]. The literature shows no report of deposition or study of CuAlS$_2$ thin films by dip coating technique. Thus the author deposited CuAlS$_2$ thin films on glass substrates by dip coating technique. The as deposited dip coating thin films were characterized by energy dispersive analysis of X-rays (EDAX), X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and atomic force microscopy (AFM). The optical properties and electrical transport properties study was also undertaken on the dip coating deposited thin films.

3.2. EXPERIMENTAL

Cupric chloride (CuCl$_2$·2H$_2$O) [S D Fine-Chem. Ltd., Mumbai, India], triethanolamine (TEA) (C$_6$H$_{15}$NO$_3$) [Sisco Chem. Pvt. Ltd., Mumbai, India], aluminium chloride (AlCl$_3$·6H$_2$O) [Oxford Laboratory, Mumbai, India], ammonia liquid (NH$_3$) [Chiti-Chem Corporation, Vadodara, India] and thiourea (NH$_2$CSNH$_2$) [Chiti-Chem Corporation, Vadodara, India] were used for the synthesis of CuAlS$_2$ thin films by dip coating technique.
In the synthesis of CuAlS$_2$ thin film by dip coating technique, initially 10 ml of 0.5M copper (II) chloride (CuCl$_2$•2H$_2$O) solution was mixed with 5 ml of 3.7 M TEA solution under continuous stirring for 5 minute by taking them in a 100ml clean glass beaker. The CuCl$_2$•2H$_2$O acts as precursor for Cu and TEA acts as capping agent to slow down the release of the metal ions resulting in slow precipitation of the compound by ion-ion reaction and to prevent the agglomeration of the desired metal ions. Then in the above solution, 16 ml of 10M NH$_3$ solution was added and stirred for 5 minute. Here NH$_3$ (liquid ammonia) is used as reagent to adjust the pH of the solution. The pH of the solution is kept 9.5, reason being if pH < 7 the solution becomes acidic due to which it can corrode the deposited thin film. In continuous stirring, 10 ml of 0.7M aluminium chloride (AlCl$_3$•6H$_2$O) solution was added and stirred for 5 minutes. Finally under continuous stirring, 10 ml of 1.0M thiourea solution was mixed and stirred for 5 minute. At last, 48 ml of deionised water was added to make the final solution to 100 ml. The final solution of 100 ml was kept under programmed dip coating unit apparatus for 5 hours for thin films deposition. The dip coating parameters maintained for films deposition is, dip speed 9 mm-sec$^{-1}$; return speed - 9 mm-sec$^{-1}$; dip duration 10 sec; dry duration 5 sec and 600 dips in total was done.

During the deposition of CuAlS$_2$ thin films the following reaction is expected to have occurred:

\[
\text{CuCl}_2\cdot2\text{H}_2\text{O} + 2\text{NH}_3\text{OH} + \text{TEA} \rightarrow [\text{Cu (TEA)}]^{+2} + 2\text{OH}^{-1} + 2\text{NH}_4\text{Cl} + 2\text{H}_2\text{O}
\]

\[
\text{AlCl}_3\cdot6\text{H}_2\text{O} + 3\text{NH}_3\text{OH} \rightarrow \text{Al}^{+3} + 6\text{H}_2\text{O} + 3\text{OH}^{-1} + 3\text{NH}_4\text{Cl}
\]

\[
2(\text{NH}_2)\text{CS} + 2\text{OH}^{-1} \rightarrow 2\text{C}_2\text{H}_2\text{N}_2 + 2\text{H}_2\text{O} + 2\text{HS}^{-1}
\]

\[
2\text{HS}^{-} + 2\text{OH}^{-1} \rightarrow 2\text{S}^{-2} + 2\text{H}_2\text{O}
\]

\[
[Cu (\text{TEA})]^{+2} + \text{Al}^{+3} + 2\text{S}^{-2} \rightarrow \text{CuAlS}_2 \downarrow + \text{TEA}
\]

Figure 1 shows the deposited CuAlS$_2$ thin film on glass substrate by dip coating technique.
3.3. RESULTS AND DISCUSSION

3.3.1. ENERGY DISPERSIVE ANALYSIS OF X-RAY (EDAX) ANALYSIS

The chemical compositions of the as deposited CuAlS$_2$ thin film were determined by energy dispersive analysis of X-rays (EDAX) technique.

![EDAX spectrum](image)

**Figure 1:** Deposited CuAlS$_2$ thin film on glass substrate by dip coating technique.

**Figure 2:** EDAX spectrum along with inset table of chemical composition of as deposited CuAlS$_2$ thin film.

<table>
<thead>
<tr>
<th>Element</th>
<th>EDAX Weight (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Standard</td>
</tr>
<tr>
<td>Cu</td>
<td>41.09</td>
</tr>
<tr>
<td>Al</td>
<td>17.44</td>
</tr>
<tr>
<td>S</td>
<td>41.47</td>
</tr>
</tbody>
</table>
The EDAX spectrum is shown in Figure 2. The observed weight% of the elements with standard values is tabulated as inset of the Figure 2. The observed extra peaks of other elements like Si, Na, Mg, O, Ca, etc. in the EDAX spectrum is due to glass substrate. The values of Cu, Al and S are tabulated after deleting the glass substrate elements. The data clearly states that the deposited CuAlS\(_2\) thin film is nearly stoichiometric but slightly rich in aluminium and deficient in sulphur.

3.3.2. STRUCTURAL ANALYSIS

Figure 3 shows the XRD pattern of CuAlS\(_2\) thin films taken employing Philips X-pert-MPD X-ray diffractometer.
All the peaks of XRD could be indexed as those of CuAlS$_2$ with tetragonal unit cell structure. The lattice parameters determined using Powder – X software from the recorded XRD pattern are $a = b = 5.33$ Å and $c = 10.40$ Å. They are in good agreement with the reported values [$a = b = 5.325$ Å and $c = 10.390$ Å, JCPDS Card No. 25-0014]. Other parameter like Miller indices, $2\theta$ angle, inter planer spacing ($d$) and $d\%$ errors for prominent peaks are tabulated in Table 1.

**Table 1**: Miller indices, $2\theta$ angle, inter planer spacing ($d$), and $d\%$ error determined for as deposited CuAlS$_2$ thin film.

<table>
<thead>
<tr>
<th>Thin films</th>
<th>(hkl)</th>
<th>$2\theta$</th>
<th>$d$ (Å)</th>
<th>$d%$ error</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAlS$_2$</td>
<td>112</td>
<td>29.32</td>
<td>3.04</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td>33.64</td>
<td>2.66</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>47.57</td>
<td>1.91</td>
<td>1.34</td>
</tr>
<tr>
<td></td>
<td>204</td>
<td>49.73</td>
<td>1.83</td>
<td>1.57</td>
</tr>
<tr>
<td></td>
<td>312</td>
<td>57.56</td>
<td>1.60</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>116</td>
<td>58.52</td>
<td>1.58</td>
<td>0.07</td>
</tr>
</tbody>
</table>

The highest $d\%$ error is 1.57 $\%$, which states that the deposited CuAlS$_2$ thin film is single phase but the error may be due to presence of dislocations in the grain size. The calculated X-ray density `$\rho$' of as deposited CuAlS$_2$ thin film is 3.48 gm·cm$^{-3}$. The calculated value of X-ray density is in good agreement with the reported value of 3.43 gm·cm$^{-3}$ [19] for bulk CuAlS$_2$.

The peak broadening in XRD pattern occurs due to decrease in crystallite size arising owing to the dislocation generated lattice strain [20]. The crystallite size of the as deposited CuAlS$_2$ thin film was determined from the XRD peak broadening employing Scherrer’s equation [20];

$$D = \frac{K \lambda}{\beta_{hkl} \cos \theta}$$  \hspace{1cm} (1)
Where $D$ is the crystallite size, $K$ is shape depended parameter and is taken here as 1 considering the particles to be spherical in shape, $\lambda$ is the wavelength of X-ray (1.5405 Å), $\beta$ is the angular line width at half maximum intensity and $\theta$ is the Bragg angle in degree.

The value of crystallite size $D$ was evaluated from the slope of the Scherrer’s plot of $\frac{\cos \theta}{\lambda}$ versus $\frac{1}{\beta_{hkl}}$ for as deposited CuAlS$_2$ thin film, Figure 4. The graphical and analytical determined crystallite sizes are tabulated in Table 2.

![Scherrer’s plot of the as deposited CuAlS$_2$ thin film.](image)

**Figure 4:** Scherrer’s plot of the as deposited CuAlS$_2$ thin film.

The source of strains in thin films is due to crystalline imperfections and distortion. The dependence of full width at half maxima on strain and grain size is related by the Hall – Williamson relation [21], which represents the Uniform Deformation Model (UDM). The material properties are independent of the direction because the strain was assumed to be uniform in all crystallographic directions.
Table 2: Parameters of CuAlS\textsubscript{2} thin film.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Crystallite size D (nm)</th>
<th>Strain $\varepsilon \times 10^{-3}$</th>
<th>Stress $\sigma$ (MPa)</th>
<th>Energy Density $u$ (kJm\textsuperscript{-3})</th>
<th>Dislocation Density $\delta \times 10^{-4}$ (nm)$^{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scherrer's method</td>
<td>Graphical</td>
<td>20.86</td>
<td>-</td>
<td>-</td>
<td>27.56</td>
</tr>
<tr>
<td></td>
<td>Analytical</td>
<td>17.27</td>
<td>-</td>
<td>-</td>
<td>33.52</td>
</tr>
<tr>
<td>Hall-Williamson relation</td>
<td>UDM</td>
<td>18.32</td>
<td>0.23</td>
<td>-</td>
<td>29.79</td>
</tr>
<tr>
<td></td>
<td>USDM</td>
<td>17.98</td>
<td>0.21</td>
<td>21.99</td>
<td>30.94</td>
</tr>
<tr>
<td></td>
<td>UDEDM</td>
<td>18.19</td>
<td>0.28</td>
<td>23.03</td>
<td>30.23</td>
</tr>
<tr>
<td>Size-Strain Plot method</td>
<td>Graphical</td>
<td>16.68</td>
<td>0.22</td>
<td>-</td>
<td>23.27</td>
</tr>
</tbody>
</table>

The graph of $\left(\frac{4\sin\theta}{\lambda}\right)$ versus $\left(\frac{\beta_{hkl}\cos\theta}{\lambda}\right)$ was plotted for the prominent XRD peaks of CuAlS\textsubscript{2} thin films, Figure 5. The slope and ordinate intercept of the fitted line gave the strain and crystallite size, respectively. The positive slope value shows presence of tensile strain produced due to tensile stress. This external tensile force tends to increase inter atomic distance as observed in the values of the XRD determined lattice parameters. The origin of extrinsic stress in a thin film comes mainly from adhesion to substrate, while the intrinsic stress comes from defects such as dislocations in the film. The results of the UDM analysis for the CuAlS\textsubscript{2} thin film are tabulated in Table 2.

The Hooke’s law relates the linear proportionality between the stress ($\sigma$) and strain ($\varepsilon$):

$$\sigma = Y_{hkl}\varepsilon$$  \hspace{1cm} (2)

Where $Y_{hkl}$ is the modulus of elasticity or Young’s modulus.
The equation (2) is valid for a significantly small strain. Assuming a small strain to be present in the deposited CuAlS$_2$ thin films, Hooke’s law can be used here. Applying the Hooke’s law approximation to Hall–Williamson relation gives:

$$\frac{R_{hl} \cos \theta}{\lambda} = \left( \frac{K}{D} \right) + \sigma \left( \frac{4 \sin \theta}{4Y_{hkl}} \right)$$

(3)

The equation (3) is known as the Uniform Stress Deformation Model (USDM). For a tetragonal unit cell structure, Young’s modulus [22] is evaluated by the following equation (4),

$$Y_{hkl} = \frac{(h^2+k^2+l^2)^2}{s_{11}(h^4+k^4)+(2s_{12}+s_{66})h^2k^2+(2s_{15}+s_{44})(h^2+k^2)L^2+s_{33}L^4}$$

(4)

Where $L = a/l$

Here a and c are the lattice parameters; h, k and l are miller indices taken from XRD analysis. The elastic compliance constants $S_{ij}$ (m$^2$N$^{-1}$) of CuAlS$_2$ were taken from the reported values [22], which are tabulated in Table 3.

Figure 5: The modified form of Hall-Williamson analysis plot representing UDM for CuAlS$_2$ thin film.
Table 3: Elastic constants of CuAlS\(_2\) thin film.

<table>
<thead>
<tr>
<th>S(_{11}) (m(^2)N(^{-1}))</th>
<th>S(_{12}) (m(^2)N(^{-1}))</th>
<th>S(_{13}) (m(^2)N(^{-1}))</th>
<th>S(_{33}) (m(^2)N(^{-1}))</th>
<th>S(_{44}) (m(^2)N(^{-1}))</th>
<th>S(_{66}) (m(^2)N(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.421 \times 10^{-11}</td>
<td>-4.938 \times 10^{-12}</td>
<td>-5.802 \times 10^{-12}</td>
<td>1.467 \times 10^{-11}</td>
<td>1.769 \times 10^{-11}</td>
<td>1.860 \times 10^{-11}</td>
</tr>
</tbody>
</table>

The determined value of the Young’s modulus, Y\(_{hkl}\), for CuAlS\(_2\) thin film having tetragonal unit cell came out to be 102.52 GPa, which is nearly equal to the reported value 102.13 GPa\([22]\) and 106.91 GPa\([23]\). The USDM plot of \(\left(\frac{\beta_{hkl}\cos\theta}{\lambda}\right)\) versus \(\left(\frac{4\sin\theta}{\lambda Y_{hkl}}\right)\) for the CuAlS\(_2\) thin film is shown in Figure 6. The parameters like, stress calculated from the slope of the fitted line, the strain calculated using equation (2) and crystallite size determined from intercept are tabulated in Table 2. They are in good agreement with the values obtained from UDM.

Figure 6: The modified form of Hall-Williamson analysis using USDM for CuAlS\(_2\) thin film.
Another model known as Uniform Deformation Energy Density Model (UDEDM) was used to determine the crystallite size, strain and stress. The energy density can also be determined by this model. For an elastic system that follows Hooke’s law, the energy density \( u \) can be given as,

\[
u = \frac{(\varepsilon^2 Y_{hkl})}{2}.
\]

The equation of Hall – Williamson relation [21], can be rewritten using equation (5);

\[
\frac{\beta_{hkl}\cos\theta}{\lambda} = \left(\frac{K}{D}\right) + \sqrt{u} \left(\frac{4\sin\theta}{\lambda} \sqrt{\frac{2}{Y_{hkl}}}\right)
\]

Plot of \( \frac{\beta_{hkl}\cos\theta}{\lambda} \) versus \( \left(\frac{4\sin\theta}{\lambda} \sqrt{\frac{2}{Y_{hkl}}}\right) \) of equation (6) is shown in Figure 7. The square of the slope of fitted line gave the energy density \( u \) and the reciprocal of the \( y \)-intercept provided the crystallite size \( D \). Then stress and strain were calculated by using equations (2) and (5) respectively. All the obtained values are tabulated in Table 2. The value of the crystallite size determined using UDEDM is in good agreement with the values determined using other models.

![Figure 7: The modified form of Hall-Williamson analysis using UDEDM for CuAlS2 thin film.](image-url)
The grain size and strain can also be evaluated using Size-Strain Plot (SSP) method. In this estimation, it is assumed that the crystallite size profile is illustrated by a Lorentzian function and the strain profile by a Gaussian function [22]. Hence we have,

\[
(d_{hkl} \beta_{hkl} \cos \theta)^2 = \frac{K}{D} (d_{hkl}^2 \beta_{hkl} \cos \theta) + \left( \frac{\varepsilon}{2} \right)^2
\]  

(7)

Where K is a constant that depends on the shape of the particle; for spherical particles it is taken as 1. In Figure 8, the graph of \((d_{hkl} \beta_{hkl} \cos \theta)^2\) versus \(d_{hkl}^2 \beta_{hkl} \cos \theta\) was plotted by using equation (7) for the prominent XRD peaks of CuAlS₂ thin film. In this case, the crystallite size was determined from the slope of the line and square root of y-intercept gave the strain. The obtained values are tabulated in Table 2.

![The SSP plot of CuAlS₂ thin films.](image)

*Figure 8: The SSP plot of CuAlS₂ thin films.*
Figure 9: (a) TEM image and (b) selected area electron diffraction (SAED) pattern of CuAlS$_2$ thin film.
The grain size (D) and dislocation density (δ) of the films were calculated for preferential orientations to have information about their crystallinity levels. The dislocation density (δ), defined as the length of dislocation lines per unit volume of the films, was evaluated from the equation (8) [24]

\[
\delta = \frac{1}{D^2 (nm)^{-2}} \quad (8)
\]

The crystallization levels of the as deposited thin films are good because of their small δ values determined from the Scherrer’s formula, H-W plot and SSP plot, Table 2, which represent the amount of defects in the film.

The TEM and SAED image of the as deposited CuAlS\(_2\) thin films is shown in Figure 9, respectively. The TEM image and SAED pattern of as deposited CuAlS\(_2\) thin film were recorded using Philips, Tecnai 20 transmission electron microscope.

The TEM image shows that the deposited thin film is uniform without any cracks. The selected area electron diffraction (SAED) pattern for CuAlS\(_2\) thin film (Figure 9(b)) shows ring pattern along with spots, confirming the deposited thin film are polycrystalline in nature with large grain size. The rings were indexed as (112), (200), (220), (312), (116) and (400) indices associated with tetragonal structure. All indexed planes except (400) are in agreement with the XRD planes.

Figure 10: (a) SEM image of large area (b) and (c) SEM image of small selected area of CuAlS\(_2\) thin film.
The Figure 10 shows the SEM images of CuAlS$_2$ thin films deposited on glass substrates at room temperature. Figure 10(a) clearly shows that the film covers the whole of the substrates having pocketed morphology variation. Figure 10(b & c) shows a magnified image of pocketed thin films morphology. The Figure 10(b) shows presence of rod like structure whereas Figure 10(c) shows beautiful bunch of rods originating from the film surface.

**Figure 11:** AFM images of the as deposited CuAlS$_2$ film: (a) 2D AFM image (b) height profile (c) 3D (x-y-z) AFM image (d) 3D (y-x-z) AFM image
The AFM image of the as deposited CuAlS$_2$ thin films was recorded by Nano Surf Easyscan-2 by tapping mode. The AFM has been unique technique to analyse surface morphology of thin films, which provides the surface structure and roughness of thin films. Figure 11(a); shows two dimensional (2D) and Figure 11(c & d) shows three dimensional (3D) AFM images of the as-deposited CuAlS$_2$ thin films, respectively. The height profile variation is shown in Figure 11(b). The Figure 11(a) shows 2D image of film area 1.98 μm × 1.98 μm. The 2D image shows presence of spherical grains having coalescences between them. The Figure 11(c & d) shows 3D image of film area 256 μm x 256 μm. The 3D image shows presence of structures like hills and mountains having valleys between them. The height profile parameters, Figure 11b, taken along the horizontal line of the AFM image of CuAlS$_2$ thin film is tabulated in Table 4. The parameters like peak p, valley z or v (Rp-v), root mean square (rms), roughness (Rq) and average roughness (Ra) values indicate roughness in vertical direction. The Figure 11(b) shows rise in heights at the two ends of the viewed horizontal scale. These increased heights may be due to presence of bunch of nanorods features as observed in the SEM image at the sites.

**Table 4:** Surface and line roughness’s analysis of the AFM profiles of as-deposited CuAlS$_2$ thin film.

<table>
<thead>
<tr>
<th>Surface Roughness</th>
<th>Line Roughness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sa (nm)</td>
<td>Ra (nm)</td>
</tr>
<tr>
<td>34.971</td>
<td>26.767</td>
</tr>
<tr>
<td>Sq (nm)</td>
<td>Rq (nm)</td>
</tr>
<tr>
<td>46.325</td>
<td>34.339</td>
</tr>
<tr>
<td>Sy (nm)</td>
<td>Ry (nm)</td>
</tr>
<tr>
<td>384.91</td>
<td>172.68</td>
</tr>
<tr>
<td>Sp (nm)</td>
<td>Rp (nm)</td>
</tr>
<tr>
<td>193.13</td>
<td>104.88</td>
</tr>
<tr>
<td>Sv (nm)</td>
<td>Rv (nm)</td>
</tr>
<tr>
<td>-191.79</td>
<td>-67.801</td>
</tr>
<tr>
<td>Sm (pm)</td>
<td>Rm (pm)</td>
</tr>
<tr>
<td>223.57</td>
<td>223.4</td>
</tr>
<tr>
<td>Area (pm$^2$)</td>
<td></td>
</tr>
<tr>
<td>3.959</td>
<td></td>
</tr>
</tbody>
</table>
3.3.3. OPTICAL ANALYSIS

The optical absorption spectrum, Figure 12, of CuAlS\textsubscript{2} thin films deposited by dip coating has been recorded in the wavelength range 200nm to 3200nm. The spectrum shows high absorption in the ultra violet range with absorption edge lying at 290nm corresponding to energy 4.28 eV.

![Absorbance spectrum of CuAlS\textsubscript{2} thin film.](image)

Figure 12: Absorbance spectrum of CuAlS\textsubscript{2} thin film.

The energy bandgap $E_g$ was determined from the optical absorption data using the near-band edge absorption relation (9) [21],

$$(ahv)^n = A(hv - E_g) \quad (9)$$

Where, $n$ characterizes the transition. For direct allowed and forbidden transitions, $n = 2$ and $2/3$ respectively, and $n = 1/2$ and $1/3$ for indirect allowed and forbidden transitions respectively. The absorption coefficient ‘$\alpha$’ was calculated employing the Beer-Lambert equation (10) [25-27].

$$\alpha = 2.303 \frac{A}{t} \quad (10)$$
Where $A$ is the absorbance of the light through sample, $t$ is path length of light which travelled through the sample (thickness of the thin film = 260 nm) of CuAlS$_2$ thin film.

**Figure 13:** The plot of (a) direct bandgap (b) indirect bandgap of CuAlS$_2$ thin film.
The analysis of equation 8 shows that \( n = 2 \) and \( \frac{1}{2} \) fits well for the as deposited CuAlS\(_2\) thin films stating that the as deposited CuAlS\(_2\) thin films possess direct and indirect allowed optical bandgaps. The plot of \((\alpha h\nu)^2\) versus \( h\nu \) and \((\alpha h\nu)^{1/2}\) versus \( h\nu \) are shown in Figures 13(a & b) respectively. The value of direct allowed optical bandgap was evaluated by extrapolating the straight line portion of \((\alpha h\nu)^2\) versus \( h\nu \). The obtained value of the direct optical bandgap is 3.78 eV for the CuAlS\(_2\) thin films in present investigations which is more than the reported value of 3.49 eV for bulk material [28]. This shows that blue shift occurred due to film thickness. The value of indirect allowed optical bandgap of 2.98 eV was evaluated by extrapolating the straight line portion of \((\alpha h\nu)^{1/2}\) versus \( h\nu \) for as-deposited CuAlS\(_2\) thin films.

![Graph of transmittance (T%) and reflectance (R%) spectra of CuAlS\(_2\) thin film.](image)

**Figure 14:** The transmittance (T%) and reflectance (R%) spectra of CuAlS\(_2\) thin film.

The transmittance (T%) and reflectance (R%) spectra of as deposited CuAlS\(_2\) thin film are shown in Figure 14. The drop in the transmittance for wavelengths higher than 700 nm may
be presumably due to absorption by free carriers. After 1200 nm wavelength transmittance is stable and so this material can be utilised as infrared window. The data from the spectra have been used to determine the optical constants of the film. The refractive index is an important parameter for materials to be used for optical applications. In the region of interband transition that has strong absorption, refractive index of the film can be determined by below equation [29] only when the illumination of electromagnetic waves are perpendicular to the surface of film,

$$\eta = \frac{1+\sqrt{R}}{1-\sqrt{R}}$$  \hspace{1cm} (11)

The plot of refractive index (\(\eta\)) and extinction coefficient (\(k = \alpha\lambda/4\pi\)) versus wavelength (\(\lambda\)) is shown in Figure 15.

**Figure 15:** The plot of refractive index (\(\eta\)) and extinction coefficient (\(k\)) versus wavelength of CuAlS\(_2\) thin film.
Figure 16: The variation of real and imaginary part of the dielectric constant with wavelength of as deposited CuAlS$_2$ thin film.

The plot shows that the refractive index ($\eta$) and extinction coefficient ($k$) varies with wavelength in the range 290–3200 nm for as-deposited thin films. The variation shows that refractive index decreases in the wavelength range of 290 nm to nearly 700 nm. The static refractive index $\eta(0)$ determined using the optical dispersion relationship is found to be $\eta(0) = 1.84$. This obtained value is less than the reported value of 2.12 [30]. This variation may be due to surface dissimilarity of the as deposited thin film and reported thin film. The dielectric constant dependence on frequency is defined by below equation (12),

$$\varepsilon(\omega) = \varepsilon_r(\omega) + i\varepsilon_i(\omega)$$  \hspace{1cm} (12)

where $\varepsilon_r$ and $\varepsilon_i$ are the real and imaginary parts of the dielectric constant, respectively and these values were calculated using the below formulas of equation (13) [31],

$$\varepsilon_r(\omega) = n^2(\omega) - k^2(\omega) \hspace{1cm} \text{and} \hspace{1cm} \varepsilon_i = 2n(\omega)k(\omega)$$  \hspace{1cm} (13)
The variations of $\varepsilon_r$ and $\varepsilon_i$ values of the as deposited CuAlS$_2$ thin film with wavelength are shown in Figure 16. The $\varepsilon_r$ values are higher than that of $\varepsilon_i$ values.

### 3.3.4. ELECTRICAL ANALYSIS

The d. c. electrical resistivity variation with temperature in the temperature range from ambient to 427 K were studied for CuAlS$_2$ thin film using four probe set-up, Model DFP-02 (Scientific Equipment & Services, Roorkee, India). Using the measured voltage keeping constant current, the resistivity ($\rho$) at each temperature was evaluated by taking into consideration the correction factor. The plot of $\log \rho$ versus $1000/T$ for as deposited CuAlS$_2$ thin film is shown in Figure 17. The resistivity decreases with increase in temperature, stating the thin films material to be semiconducting in nature. The determined activation energy value is tabulated in Table 5, which is in good agreement with reported value of 0.70 eV [32]. The activation energy value and nature of curve clearly shows the presence of shadow level in as-deposited thin films.

![Figure 17: Log $\rho$ versus 1000/T plot for CuAlS$_2$ thin film.](image-url)
Table 5: Calculated activation energy of as deposited CuAlS$_2$ thin film.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature region (K)</th>
<th>Activation Energy $E_a$(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuAlS$_2$ Thin film</td>
<td>310 to 427</td>
<td>0.81</td>
</tr>
</tbody>
</table>

The Hall Effect analysis was carried out on the as-deposited CuAlS$_2$ thin film by employing the Hall Effect set up, DHE-22 (Scientific Equipment, Roorkee, India) at room temperature. Graphite conductive adhesive alcohol based (Alfa Aesar) paste was used for taking the Ohmic contacts in van der Pauw geometry. The Ohmic nature of the electrical contacts made on the sample were confirmed by measuring I-V characteristic between $R_{12,12}$, $R_{23,23}$, $R_{34,34}$ and $R_{41,41}$ contacts of thin film (Figure 18) for both polarity in the current range of -5 μA to +5 μA.

Figure 18: I-V characteristics between different pair of contacts for CuAlS$_2$ thin film.
Figure 19: Hall voltage induced as a function of applied magnetic field for CuAlS$_2$ thin film.

The samples under investigation were kept in magnetic field which modifies the path of the majority carriers which produce Hall voltage. Figure 19, shows the graph of Hall voltage ($V_H$) versus magnetic field ($B$). The Hall coefficient ($R_H$), the mobility of charge carriers ($\mu_H$) and carrier concentration ($\eta$) were evaluated employing standard formulae using the value of the slope of the plot of Figure 19, thickness of the samples and constant current. The obtained values are tabulated in Table 6, the positive Hall coefficient confirmed the thin film to be p-type in nature which was also confirmed by hot probe method. The evaluated carrier concentration of thin film came out to be in the order of $10^{16}$ cm$^{-3}$ stating the samples to be semiconductor. The electron mobility value determined from the Hall Effect measurement was 4.39 cm$^2$V$^{-1}$s$^{-1}$ for as deposited thin film. This mobility value is in good agreement with the reported value ($< 5$ cm$^2$V$^{-1}$s$^{-1}$) [32].
Table 6: The room temperature Hall parameters of as deposited CuAlS$_2$ thin film.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Hall coefficient $R_H$ (cm$^3$C$^{-1}$)</th>
<th>Carrier concentration $\eta$ (cm$^3$)</th>
<th>Hall mobility $\mu$ (cm$^2$V$^{-1}$s$^{-1}$)</th>
<th>Semiconductor Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin film</td>
<td>103</td>
<td>$6.08 \times 10^{16}$</td>
<td>4.39</td>
<td>P</td>
</tr>
</tbody>
</table>

The variation of thermoelectric power ‘S’ as a function of temperature were measured on the as deposited CuAlS$_2$ thin films using the experimental set up, TPSS-200, (Scientific Solution, Mumbai, India). The variation of potential difference between the two probes keeping temperature difference ($\Delta T$) as 7 K constant were measured from 310 K to 425 K temperature.

![Figure 20: Plot of Seebeck coefficient ($S$) versus 1000/T of CuAlS$_2$ thin film.](image)
The determined Seebeck coefficient (S) variation with inverse of temperature (1000/T) is shown in Figure 20 for the as deposited CuAlS$_2$ thin film. The plot showed that the Seebeck coefficient values increases with temperature stating semiconducting nature of the samples. The absolute values of the Seebeck coefficient at all evaluated temperature is positive stating the sample to be p-type in nature, which further uphold the results of the Hall Effect and hot probe methods. The values of Fermi energy (E$_F$) and constant (A) were evaluated from the slope and intercepts of the Figure 20, respectively. Using the value of ‘A’ and carrier concentration (η) obtained from Hall Effect measurements, the scattering parameter (s), effective density of states (N$_A$) and effective mass of holes (m$_h^*$) were evaluated by employing standard equations. The calculated values are tabulated in Table 7.

<table>
<thead>
<tr>
<th>CuAlS$_2$</th>
<th>Fermi Energy E$_F$ (eV)</th>
<th>A</th>
<th>Scattering constant (s)</th>
<th>S (µVK$^{-1}$)</th>
<th>N$_A$ (cm$^{-3}$)</th>
<th>m$_h^*$ (kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thin film</td>
<td>0.007</td>
<td>0.383</td>
<td>2.117</td>
<td>10.96</td>
<td>5.68 × 10$^{17}$</td>
<td>7.3 × 10$^{-32}$</td>
</tr>
</tbody>
</table>

The I-V characteristics study on the CuAlS$_2$ thin film was carried out in dark as well as under white and UV electromagnetic illuminations. The I-V measurements under white illumination (Philips) was made using 4W lamp having intensity on the sample surface of 6614 Lux. Whereas the UV illuminated (Model: UVSL-14P, Ultra-Violet Products Ltd. Cambridge CB4 1TG, UK) I-V measurement was carried out employing 4W lamp having intensity of 31 Lux on the sample surface. The intensity measurement was done by light Luxmeter (Model: MECO-930, MECO Meters Pvt. Ltd., Navi Mumbai, India). The recorded I-V characteristics in dark, for white and UV illuminations are shown in Figure 21. In case of dark and white illumination, the sample just behaves as a simple resistor unaffected by the external illumination, thus both I-V plots nearly overlap. The UV illumination of thin films shows I-V deviation. The slope of UV illuminated line is more
than the dark and white illumination. This indicates that UV-illumination produces more number of electron–hole pairs. The reason being the optical energy bandgap of the deposited CuAlS$_2$ thin films is 3.78 eV which matches to the wavelength of ultra violet radiation (~329 nm). The effect of the illumination on the CuAlS$_2$ thin film shows that it can be used as a photovoltaic material for absorption of UV range and also as window material for IR range.

![I-V plots of CuAlS$_2$ thin film in dark as well as under white and UV illuminations.](image)

**Figure 21:** I-V plots of CuAlS$_2$ thin film in dark as well as under white and UV illuminations.

### 3.4. CONCLUSIONS

The CuAlS$_2$ thin films were deposited by dip coating technique at room temperature. The EDAX analysis showed that deposited CuAlS$_2$ thin film is nearly stoichiometric but slightly rich in aluminium and deficient in sulphur. The X-ray diffraction showed that the unit cell of
the deposited CuAlS$_2$ thin film possesses tetragonal structure. The determined lattice parameters, Miller indices, 2θ values and inter planer spacing (d) are in good agreement with the reported data. The crystallite size determined from XRD data employing Scherrer’s formula, Hall-Williamson modified forms like; uniform deformation model (UDM), uniform stress deformation model (USDM), uniform deformation energy-density model (UDEDM) and the size-strain plot method (SSP) were in good agreement with each other. The TEM image shows that the deposited thin film is uniform without any cracks. The selected area electron diffraction (SAED) pattern shows ring pattern along with spots, confirming the deposited thin film are polycrystalline in nature with large grain size. The SEM image of the as deposited CuAlS$_2$ thin films shows that the film covers the whole of the substrates having pocketed morphology variation. Higher magnification shows presence of rod like structure on the surface of the thin film. The AFM study shows spherical grains having coalescences between them. The AFM also showed presence of hills and mountain like structure having valleys between them. The optical absorbance study showed that the as deposited CuAlS$_2$ thin film possesses both direct and indirect allowed transitions. The direct and indirect optical bandgap values were found to be 3.78 eV and 2.98 eV. Both the bandgap values are in good agreement with the reported value. The d. c. electrical resistivity variation with temperature in the temperature range from room temperature to 427 K showed continuous decrease of resistivity value with increase in temperature stating semiconducting nature of the samples. The determined activation energy value is 0.81 eV, which is in good agreement with reported value of 0.70 eV. The room temperature Hall Effect measurements showed the samples to be p-type in nature having carrier concentration of the order of $10^{16}$ cm$^{-3}$ further corroborating semiconducting nature of the samples. The p-type nature of the semiconductor was also confirmed by hot probe method. The Seebeck coefficient variation with temperature showed that the Seebeck value increases with increase in temperature further confirming semiconducting nature of the samples. The absolute values of the Seebeck coefficient all through the analyzed temperature were positive stating the samples to be p-type in nature. The effect of the illumination on the CuAlS$_2$ thin film shows that it can be used as a photovoltaic material for absorption of UV and also as window material for IR (infrared) range.
REFERENCES:


