Chapter 6

STUDIES ON BILAYER FILMS IMPORTANT IN SOLAR CELL APPLICATION

Part I.

CdS/SnO₂ bilayer thin films

6.1 Introduction.

Transparent conducting film of metallic oxides such as SnO₂ or In₂O₃ etc have been studied for many years because of their practical applications [1-3]. An intrinsic and stoichiometric material does not show simultaneous high optical transparency and high electrical conductivity. Partial transparency and fairly good conductivity may be obtained in thin films of a variety of materials. But non-stoichiometric and doped films of oxides of Sn, In, Cd, Zn etc deposited by various techniques exhibit high optical transparency in the visible region, high optical reflectivity in the IR region and nearly metallic conductivity. The most prominent oxide materials are those mentioned at the beginig. The oxide films, which exhibit high conductivity along with high transparency in the visible region are widely used in making optoelectronic devices such as displays and solar cells [2,4,5] because of their high stability, hardness and adherence to many type of substrates. More than that, film of SnO₂ and other oxides find a number of applications such as transparent heating elements for air crafts and automobile windows, anti-static coating for instruments windows, heat mirrors for glass windows, anti-reflection coatings, gas sensors etc [2].

SnO₂ film can be produced by various deposition methods [6-10] including spray pyrolysis technique [11-14]. Spray pyrolysis involves spraying of a solution, (usually alcoholic/aqueous) containing soluble salt of the constituent
atoms of the desired compound onto a heated substrate. This is a very simple technique and more details are included in section 4.2. SnO$_2$ films prepared at low temperature are amorphous and while film prepared at high temperature are polycrystalline in nature [15,2]. It has also been noted that the grain size increases with substrate temperature. In order to increase the conductivity of the film various dopents are added like Sb [16,17], F [12,18] and In [11,19].

As satated in earlier chapters CdS thin film is widely used as a window material in several thin film heterojunction solar cells using the p-type materials like Cu$_2$S, CuInSe$_2$, CdTe etc. The most common problems in these cells are those occuring at interface in the pn junction and in the semiconductor-metal electrode contact region. The interface probleums occuring in the pn junctions and semiconductor-metal electrode contact region are reviewed by many others [20-23]. But there are not much studies aimed at the analysis of probleums occuring at the interface between SnO$_2$ and other semiconducting materials eg., (SnO$_2$/CdS interface). There die only few reports about this interface [24].

The drive for solar cells of high efficiency and long life has necessitated a more detailed understanding of CdS/SnO$_2$ interface. Very recently Niles et al reported the results of CdS/SnO$_2$ interface [24]. For high efficiency the CdS window layer must be very thin to allow maximum transmission into the absorber layer [25,26]. In these present work we have studied the interlayer diffusion of CdS and SnO$_2$ due to high temperature treatment.

6.2 Experiment.

6.21 Sample preparation.

The spraying technique is used for the preparation of CdS/SnO$_2$ samples. In the case of SnO$_2$ this technique
involves decomposition of alcoholic solution of stannic chloride at high temperature (450°C) in the presence of an oxidizing agent [27]. This endothermic reaction is given below

\[ \text{SnCl}_2 + 2\text{H}_2\text{O} \rightarrow \text{SnO}_2 \text{HCl} \]

Detailed description of experimental setup and theory of spray pyrolysis is given in section 4.2. The solution used for this contains \( \text{SnCl}_2 \cdot 5\text{H}_2\text{O} \) at a molarity of 0.9M. The distance from the spray head to substrate is kept at \(~30 \text{ cm} \) and the angle of incidence of solution droplets on the substrate is \(~75° \). The flow rate of the liquid is controlled to \(~10 \text{ ml/mts} \). 20 ml of the solution is sprayed for getting 450 nm thick \( \text{SnO}_2 \) film. Air is used as carrier gas. High scanning rate of spray head (100/mts) ensure a uniform film thickness. For optimizing the condition for good quality \( \text{SnO}_2 \) films, the films were prepared over glass substrates at different substrate temperature in the range 350-500°C.

Optical transmission and electrical resistivity show that the film prepared at 450°C has optimum results and this film is used for the bilayer (CdS/\( \text{SnO}_2 \)) preparation. For this purpose \( \text{SnO}_2 \) (thickness \(~450 \text{ nm} \)) film was prepared at 450°C on glass substrate and above this CdS film (thickness \(~400 \text{ nm} \)) was deposited at 300°C. The CdS films were also prepared by spray pyrolysis technique using a solution of thiourea (0.01M) and CdCl\(_2\) (0.01M). The details of CdS film preparation by spray pyrolysis is given in section 4.2. and also given elsewhere [28].

The CdS/\( \text{SnO}_2 \) film system was annealed at different temperatures in the range 100-300°C in air. The heating and cooling rates were \(2°C/\text{mts} \) for all cases. The details of annealing is described in section 4.2.

6.22 Measurements.

Spectrophotometer is used for transmission studies
of the films prepared at different substrate temperature. VASE is also used for the optical studies of the films. Electrical resistivity of the film is determined as described in section 5.35. VASE is used for the analysis of inter-diffusion taking place in the CdS/SnO$_2$ bilayer structure due to annealing. All VASE measurements were done at room temperature and in air. The sensitivity analysis of CdS/SnO$_2$ bilayer structure is given in section 3.4 and plots are given in Fig.3.10 to 3.13. These studies show that this system has high sensitivity over a wide range of wavelength and wide range of angle of incidence. The VASE measurements were done in the angle of incidence range 60-75° and the wavelength range 500-820 nm as suggested by sensitivity analysis.

6.3 Results and discussion.

The CdS/SnO$_2$ bilayer thin film system were prepared over glass substrate by spray pyrolysis technique. The summarised results of optical and electrical measurements of these films are given in Table 6.11. From this table, it is clear that the film prepared at 450°C has better properties. At low temperature the thickness of SnO$_2$ film is very low (In all cases same quantity of solution is used). Thickness of the film increases rapidly at 400°C and remain more or less constant. The electrical resistivity of the film at first decreases with increase in substrate temperature and reaches a minimum at 450°C and thereafter it increases slowly. Refractive index of the film measured using ellipsometer shows that the real part of refractive index has high value for the films prepared at 450°C. This may be due to the better structure of the film. The Fig.6.11 depicts the variation of optical transmission with wavelength for films prepared at different temperatures. The Fig.6.12 shows the refractive index spectrum of SnO$_2$ film prepared at 450°C determined using ellipsometer. In this calculation imaginary part k of complex
<table>
<thead>
<tr>
<th>Preparation Temperature (°C)</th>
<th>Thickness (nm)</th>
<th>Resistivity (Ω cm)</th>
<th>Index of Refraction 590 nm</th>
<th>Index of Refraction 620 nm</th>
<th>Index of Refraction 690 nm</th>
<th>Transmission (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>195</td>
<td>12 X10^-4</td>
<td>1.88</td>
<td>1.85</td>
<td></td>
<td>52</td>
</tr>
<tr>
<td>400</td>
<td>290</td>
<td>7.5 X10^-4</td>
<td>1.87</td>
<td>1.85</td>
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<td>450</td>
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<td>1.89</td>
<td>1.90</td>
<td></td>
<td>57</td>
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</tbody>
</table>

Table 6.11 Properties of SnO₂ film at different substrate temperatures. Table shows that the film prepared at 450°C has good optical and electrical properties.
Fig. 6.11 Transmission spectrum of SnO₂ film prepared by spray pyrolysis at different temperature. (a) 500°C (b) 450°C (c) 400°C and (d) 350°C
Fig. 6.12 Variation of real part (n) of refractive index of SnO$_2$ thin film prepared by spray pyrolysis technique at 450°C.
refractive index is taken as zero.

The Table 6.12 shows the results of CdS/SnO₂ interlayer analysis. Ellipsometrically calculated refractive indices of CdS and SnO₂ are used for the analysis. Different optical models are used for the analysis of CdS/SnO₂/glass system. The most important models are given below.

Model (a). air/CdS/SnO₂/glass.
Model (b). air/CdS/(CdS+SnO₂)/SnO₂/glass.

The ellipsometric data of the bilayer system is used for the analysis of these optical models and best fit of these models were determined using the technique given in section 3.2. At first the model (a) is selected. It is on the assumption that the two layers have sharp boundaries and there is no inter-diffusion. The other model (model (b)) is on the assumption that CdS and SnO₂ do not have sharp boundaries due to the inter-diffusion of CdS into SnO₂ or vice versa. The values of unbiased estimator $\delta$ [29] of different optical models derived from VASE analysis are shown in Table 6.12. From this $\delta$ value it is clear that the first optical model has the least value for $\delta$ compared to the other model. This shows that this model is best suited to the physical system, i.e., as prepared CdS/SnO₂ has sharp boundaries and CdS prepared over SnO₂ does not cause any inter-diffusion or chemical reaction.

The thermal stability of the CdS/SnO₂ interface is most important because the fabrication of thin film solar cell involves the thermal treatment [24]. The high temperature annealing is an attempt to simulate a common fabrication technique i.e., heat treatment. We have annealed the CdS (400 nm thick)/SnO₂ (450 nm thick) at different temperatures in the range 100-300°C in air. The results of post annealing VASE measurement are shown in Table 6.12. If CdS reacts with or diffuse into SnO₂, the structure of CdS/SnO₂ bilayer changes from model (a) to model (b). This will cause a
<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>CdS/SnO$_2$/glass model (a)</th>
<th>CdS/(CdS+SnO$_2$)/SnO$_2$/glass model (b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>unannealed</td>
<td>0.890</td>
<td>2.61</td>
</tr>
<tr>
<td>100</td>
<td>0.950</td>
<td>2.72</td>
</tr>
<tr>
<td>150</td>
<td>0.910</td>
<td>2.68</td>
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<tr>
<td>300</td>
<td>0.980</td>
<td>2.69</td>
</tr>
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</table>

Table 6.12 Results of VASE analysis of CdS/SnO$_2$/glass bilayer thin film system after annealing at different temperatures. This shows that CdS/SnO$_2$ interface is very stable.
considerable change in $\delta$ value of the optical model. But the unbiased estimator $\delta$ of different optical models has no considerable change due to annealing, as revealed by values in Table 6.12. This lack of change in $\delta$ value with temperature suggests that the CdS/SnO$_2$ system is highly stable and annealing does not cause any inter-diffusion that results in the degradation of the bilayer thin film system and ultimate failure of cell. Very recently Niles et al [24] have reported almost the same observation using soft x-ray synchrotron radiation photoemission technique. In this study we have used a very simple setup (VASE) for the diffusion study of CdS and SnO$_2$, this technique can be extended to the in situ monitoring of diffusion with temperature.

6.4 Conclusion

The spray pyrolysis technique is again used for the preparations of SnO$_2$ film. SnO$_2$ films are optically transparent and good electrical conductors. They are widely used as electrode material in several optoelectronic devices. An alcoholic solution (0.9M) of SnCl$_2\cdot$5H$_2$O is used for this purpose. Very low resistivity (30 ohm-cm) films were obtained at a substrate temperature 450°C. It has a very good optical transmission.

The bilayer structure fabricated using the SnO$_2$ film is CdS/SnO$_2$. These bilayer films are prepared by spray pyrolysis. At first SnO$_2$ film is prepared over glass substrate at 450°C and then CdS film is prepared at 300°C over the SnO$_2$ film. The ellipsometric studies of CdS/SnO$_2$ interface show that the structure is very stable and has very narrow interface. Since this bilayer is widely used in thin film solar cells the stability of CdS/SnO$_2$ interface is very important. This interface is stable for thin film system annealed at very high temperature (300°C). A detailed study using correct optical model is required to make final conclusion.
Part II.

CdS/CuInSe₂ bilayer thin films.

6.5 Introduction.

CuInSe₂ has proved to be a very effective absorber material for thin film solar cell [25,26]. Development of highly efficient CuInSe₂ based solar cells and modules requires an understanding of the mechanism which controls the photovoltaic performance. Analysis of interlayer diffusion between the films that form the pn junction is also an important study for the characterization of solar cells. Chemically prepared CdS and CuInSe₂ films are becoming more and more attractive due to its low cost of production and simplicity of operation. It is important also due to the fact that films having large area can be deposited. Chemical bath deposition (CBD) technique is used for the production of semiconducting thin films like CdS, CuInSe₂ etc. This technique (CBD) was first used in 1946 to prepare PbS films [30]. A large number of groups have reported the preparation of CdS by CBD [31-38]. The resistivity of these films is very high [36,37]. Basol et al have reported that this is due to the near stoichiometric nature of the film prepared by CBD [37]. It is also reported that CdS film prepared by CBD techniques is intrinsic in nature [36].

CuInSe₂ films is prepared by different techniques [39-42]. Recently CBD is used for the CuInSe₂ film preparation [43-46]. Minimum lattice mismatch between CdS and CuInSe₂ (only 1.6%) and favourable electron affinity difference (0.1eV) [23] are the attractive aspects of these materials. The p-type CuInSe₂ film forms pn junction with n-type CdS film and latter acts as a window layer [25,26]. CuInSe₂ based single junction thin film solar cells have shown efficiency as
high as 15% [25]. In this work we have fabricated a bilayer Cds/CulnSe₂ structure over glass substrate by CBD and interlayer diffusion taking place in the bilayer structure due to heating is studied using VASE.

6.6 Chemical bath deposition.

CBD is growth from liquid by ion-by-ion condensation of different ions of the compound on the substrate from an aqueous basic medium. According to the solubility product (SP) principle, in a saturated solution of weakly soluble compound the product of the molar concentration of its ions called ionic product (IP) is a constant at a given temperature. If IP exceeds SP precipitation occurs. Spontaneous precipitation is to be eliminated to form a thin film by controlled ion-by-ion reaction. This can be achieved by using a fairly stable complex of the metal ions. The concentration of metal ions are controlled by adding appropriate complexing agents in correct concentration [27].

6.61 Cds Thin Film.

CBD deposition of Cds films was initiated by Mokrushin and Tkachev in 1961 [35]. In this technique triethanolamine (TEA) is used as the complexing agent as reported by Mondel et al [38]. Detailed description of present technique is given in [31,33]. The attraction of work based on TEA is that good quality film is obtained at room temperature. The Cd²⁺ ions are present in the form of a complex species [Cd(TEA)]²⁺ in solution, the dissociation of which causes the release of Cd²⁺ ions and the formation of film by reaction with S²⁻ ions from thiourea in a basic media with pH > 10 [33]. The relevant chemical equation is

\[
(Cd(TEA))^2+ + 2SC(NH₂)₂ + 2OH^- \rightarrow CdS + TEA + OC(NH₂)₂ + H₂O
\]

Measured quantity of CdCl₂ solution (1N) was mixed
with TEA, followed by the addition of ammonia solution. pH of the solution is maintained above 10 and measured quantity of thiourea is added to the mixture. Substrates were kept vertically in the solution for CdS deposition. About 1500 nm thick CdS film is deposited on glass substrate and 50 nm thick CdS is deposited over CuInSe₂ film by CBD.

6.612 CuInSe₂ Thin Film

CuInSe₂ thin film is prepared by CBD along with various other techniques [39-42]. In the earlier CBD process TEA was used for complexing copper ions [43-45]. In this case the reaction mixture was maintained at elevated temperature and the pH of the solution is ~10. In the present technique citrate is used as the common complexing agent for Cu and In ions and deposition is made possible at room temperature by controlling the pH of the solution, as reported by Vidyadharan et al [46].

Thin films of CuInSe₂ were prepared by CBD from a deposition mixture containing aqueous solutions of copper sulfate, trisodium citrate, sodium selenosulphate and InCl₃. Sodium selenosulphate was prepared by dissolving elemental selenium in an aqueous solution of sodium sulfite maintained at a temperature of 90°C and pH>9. The solution was then cooled and filtered. A known quantity of copper sulfate solution (0.2M) mixed with trisodium citrate (0.1M) was added to known quantity of selenosulphate (0.1M). InCl₃ was dissolved in citric acid and this was added to the above mentioned mixture drop by drop. The solution was thoroughly mixed and taken in a 50 ml beaker. The pH value of the solution was adjusted to be ~8. Ion-by-ion condensation on the clean glass substrate takes place slowly due to the homogeneous precipitation of ions. Uniform film of thickness 80 nm was obtained in a single dipping. Films of any desired thickness can be obtained by repeated dipping [46].
6.7 Measurement.

The CdS/CuInSe₂ bilayer thin films were annealed at different temperatures in the range 100-300°C as described in earlier sections. VASE is used for the measurement of CuInSe₂ thin film and CdS/CuInSe₂ bilayer thin films and also for the study of effect of annealing (details of VASE analysis is given in chapters 2 and 3). The ellipsometric calculation of CuInSe₂ films were done in the wavelength range 470-650 nm. The VASE analysis of bilayer thin films was done in the sensitive region wavelength and angle of incidence as given in the section 3.43.

6.8 Results and discussion.

The Figs. 6.21 and 6.22 give the refractive index of CuInSe₂ films calculated using ellipsometry in the range of wavelength 470 to 650 nm. The calculated values of n and k are used for further analysis of CdS/CuInSe₂ bilayer thin film. The thickness of 'thin' CuInSe₂ film is measured by ellipsometry and it is ~85 nm for single dip. A second dip of this film into a fresh solution makes the thickness ~180 nm. Gravimetric technique using microbalance is also used for verifying this thickness measurement.

CBD deposition of CdS on glass substrate gives a very thick (~1.5 µ) film even at single dip. But the CdS film deposited on CuInSe₂ by the same technique has a thickness of ~50 nm. This shows that initial growth rate of CdS on CuInSe₂ is very slow. In the present study a bilayer film system with CuInSe₂ film of thickness ~250 nm and CdS film with thickness ~50 nm is used. For the ellipsometric analysis of CdS/CuInSe₂/glass system different optical models were applied. Glass is eliminated from all models, because the high absorption of CuInSe₂ hides glass from probe beam. Therefore CuInSe₂ is treated as substrate material. The results of
Fig. 6.21 Variation of \textit{imag} part (k) of refractive index of CuInSe$_2$ thin film prepared by CBD technique.

Fig. 6.22 Variation of \textit{real} part (n) of refractive index of CuInSe$_2$ thin film prepared by CBD technique.
Cds/CuInSe₂ system is given in Table 6.21, which contain VASE analysis of two optical models viz.,

Model (a). air/Cds/CuInSe₂,
Model (b). air/Cds/(Cds+CuInSe₂)/CuInSe₂.

The VASE studies reveal that as prepared Cds/CuInSe₂ system has sharp boundaries between the two layers.

The heat treatment of Cds/CuInSe₂ solar cell is useful not only for the post fabrication device optimization but also for the information about the temperature stability of the cell [23]. The stability of this bilayer thin film, which forms the pn junction, is studied in the present work by annealing the Cds/CuInSe₂ film system at different temperatures in the range 100-300°C. The VASE studies show that the annealing at low temperature (100°C) does not affect the interface of Cds/CuInSe₂. But high temperature annealing (above 200°C) causes the degradation of the interface. Kazmerski et al also reported that the low temperature (60°C) annealing of Cds/CuInSe₂ cell does not affect the performance of the cell [23] as in the case of our studies.

In the case of high temperature annealed samples, the model (b) is found to be more suitable. This is due the diffusion of the materials from one layer into the other. The thickness of the interlayer at 200°C is ~17 nm and the volume fraction of CdS in this interlayer is 0.08 (8%). The annealing at 300°C causes further degradation of the bilayer i.e., the thickness of the interlayer increases to ~25 nm while the volume fraction of CdS increased to 0.12 (12%). This shows that the Cds/CuInSe₂ layer that forms pn junction is degraded due to high temperature treatment unless some precautionary measures are taken before forming the pn junction. Kazmerski et al have reported that the annealing of Cds/CuInSe₂ cell at 220°C causes 38% degradation in its efficiency [23]. This is due to the some physical changes in junction region. The AES studies also confirm the degradation of the cell due to
<table>
<thead>
<tr>
<th>Annealing temperature (°C)</th>
<th>Unbiased estimator value of optical models</th>
<th>Vol. fraction of CdS in mixed layer and its thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CdS/CIS</td>
<td>CdS/(CdS+CIS)/CIS</td>
</tr>
<tr>
<td>unannealed</td>
<td>0.0750</td>
<td>0.1321</td>
</tr>
<tr>
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<td>0.0857</td>
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<td>0.1050</td>
<td>0.0974</td>
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<td>300</td>
<td>0.1150</td>
<td>0.0816</td>
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</tbody>
</table>

Table 6.21 Results of VASE analysis of CdS/CuInSe₂/glass bilayer thin film system after annealing at different temperatures. The degradation of CdS/CuInSe₂ bilayer starts at 200°C.
annealing at 220°C and above. AES results also show that at 220°C S from CdS and Se from CuInSe₂ diffuse into the other layer and hence cause interlayer widening. Also at 400°C Cd diffuses into CuInSe₂ layer and this results in fatal failure of the cell [23]. These results are corroborating our observations on CdS/CuInSe₂ using a simple non-destructive technique.

6.7 conclusion.

CBD is also used for the preparation of CdS. CdCl₂ and thiourea solution complexed with triethanolamine (TEA) is used for the preparation of CdS film at room temperature. Ammonia solution is used to adjust the pH value above 10.

CBD technique is used for the preparation of CuInSe₂ films. Thin films of CuInSe₂ were prepared by CBD from a deposition solution containing aqueous solution of copper sulfate, trisodium citrate, sodium selenosulphate and indium chloride. The pH of the solution is adjusted to ~8 and the deposition takes place at room temperature itself.

The CdS/CuInSe₂ bilayer thin film is prepared by CBD technique. CuInSe₂ film is prepared over glass substrate by CBD as mentioned earlier. Next this CuInSe₂/glass structure is used for the preparation of CdS/CuInSe₂ bilayer films by the same technique CBD.

VASE results indicates that the as prepared samples have no interlayer between CdS and CuInSe₂. Again the VASE studies on annealed samples give a clue that annealing upto 100°C does not affect the interface. Annealing at temperature 200°C causes the formation of a thin interlayer of CdS and CuInSe₂ and at high temperature more and more material mix together and the thickness of interlayer is very high.
References.


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