Solar cell fabrication and characterization

This chapter briefs all the fabrication steps and characterization techniques used for fabricating the complete solar cell structure and its characterization.

3.1 Substrates cleaning

Soda lime glass (SLG) is taken as the base substrate for fabricating the CZTS solar cell structure. The cleaning of substrate is done by first washing it in a soap solution and thoroughly rinsing in DI water. Substrates are then ultrasonically cleaned in acetone and methanol and at each step rinsed with DI water. Finally, substrates are exposed to dry nitrogen gas and used for the deposition.

3.2 Deposition of Mo layer

Mo has been reported as a preferred back contact material with CIGS and CZTS solar cell device structures. The solar cell processing starts with the deposition of Mo layer on soda lime glass substrate. The deposition is carried out using DC magnetron sputtering with Ar as a carrier gas and a 4 inch diameter Mo disc as a Mo source target for the present work. Typical base pressure and working pressure for deposition is kept at 9×10^{-6} mbar and 6×10^{-3} mbar, respectively. At first, single Mo layer deposition has been tried and it was observed that conductivity and adhesion of Mo film to the substrate improves with increasing deposition power and observations are in accordance with the previous reports [Takahashi, Pethe, Dhere, & Solar, 2010][Gordillo, Mesa, & Calder, 2006]. However, continuous sputtering at high power resulted in the formation of undesired flakes because of high sputter yield of Mo. At the same time, a single layer deposited Mo on SLG substrate at low sputter power does not show good adhesion to the substrate. To overcome this issue of adhesion, observed during single layer Mo deposition, and to have low resistivity a bilayer molybdenum deposition process is adopted [Scofield, Duda, Albin, Ballard, & Predecki, 1995][P. Huang et al., 2013]. At first Mo layer is deposited at high DC power of 500 W for 30 min and then power is reduced to 200 W and deposition is done for additional 1 hour. This process resulted about ~ 1 micron thick Mo films. XRD pattern of the deposited Mo on SLG substrate is shown in **Figure 3.1 (a)**. It is observed that (110) diffraction peak is the most intense, suggesting highly textured Mo along (110) and all other observed peaks are in agreement with ICDD pdf # 042-1120. The surface and the cross sectional images of the deposited Mo film on SLG substrate are shown in **Figure 3.1 (b)**. A dense microstructure is observed in the surface SEM image of the bilayer deposited Mo film with columnar growth of Mo as seen in the cross sectional image. In this bilayer deposition process, adhesion is taken care by the first Mo layer which is deposited at high sputter power and the second Mo layer deposited at low sputter power, makes whole film less resistive and free from surface Mo flakes.
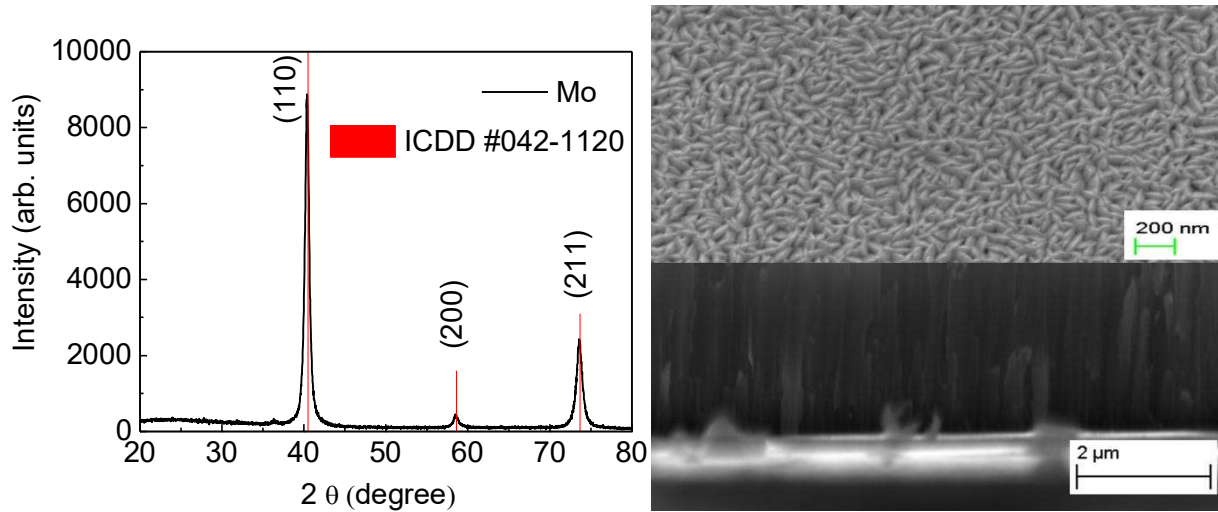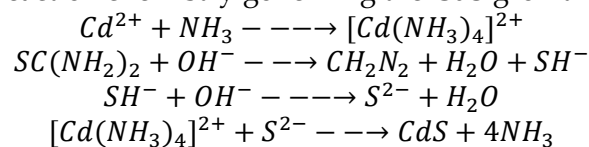
Figure 3.1 (a) XRD micrograph of Mo deposited on SLG substrate (b) Surface and cross sectional image of Mo film deposited on SLG substrate

3.3 Chemical bath deposition of CdS layer

CdS as an n type buffer layer has been a preferred choice with chalcogenide absorbers. It has also shown good hetero interface characteristics with CZTS absorber and is chosen as a buffer layer material for the CZTS solar cell architecture. However, there are certain issues such as toxicity of Cd and lower band gap of CdS ~2.4 eV possesses challenge towards green energy. Lower bandgap of CdS allow significant portion of the solar spectrum to be absorbed before reaching to the CZTS absorber layer. Even with very low thickness of CdS layer there is significant photon absorption in CdS which finally do not contribute to the current collected at the outer circuit. Other prominent buffer layer materials such as ZnS, Zn(OH)S, In_2S_3, FeS_2 etc. are also explored but their effect on the device performance is still under investigation.

Chemical bath deposition of CdS is a wet chemical process and is well established technique for both small to large scale manufacturing. CBD technique is preferred for the CdS deposition as it is a low cost and gives relatively good quality CdS films. However, after the deposition of CdS thin film. the whole bath solution suffers from the problem of waste disposal because of toxic Cd and ammonia in the bath solution. In terms of device performance, CBD technique for CdS deposition offers some advantages too over vacuum deposited CdS. In CBD-CdS growth over CZTS film, CZTS substrate is kept in an alkaline solution containing ammonia and Cd salt for some time, which allows etching of surface oxides prior to the CdS deposition [Erkan et al., 2015][Timmo et al., 2010]. Cd from CdS can also diffuse in CZTS forming donor antisites defect (Cd_{Cu}) by replacing Cu from the surface and can form buried p-n heterostructure as is observed with CIGS [T Nakada & Kunioka, 2013].

The procedure for the deposition of CdS is adopted from the literature [Doña, 1995][Mane & Lokhande, 2000]. In brief, chemical bath for the deposition consist of cadmium sulfate, thiourea and ammonium hydroxide (NH_4OH) in DI water at bath temperature of ~75 °C. At first 0.015 M $CdSO_4$ is taken in 200 ml of DI water kept at 200 °C with continuous stirring. 20 ml NH_4OH (28-30%NH_3) is then put into the reaction mixture which acts as a complexing agent for the Cd ions present in the solution. A substrate for the CdS deposition is then inserted vertically into the reaction bath keeping its front face facing the beaker wall where deposition is required. To start the reaction 10 ml of 0.15M thiourea aqueous solution is inserted drop wisely in the bath under continuous stirring. The reaction chemistry governing the CdS growth is described as below

$$Cd^{2+} + NH_3 ---\rightarrow [Cd(NH_3)_4]^{2+}$$
$$SC(NH_2)_2 + OH^- ---\rightarrow CH_2N_2 + H_2O + SH^-$$
$$SH^- + OH^- ---\rightarrow S^{2-} + H_2O$$
$$[Cd(NH_3)_4]^{2+} + S^{2-} --\rightarrow CdS + 4NH_3$$

As soon as thiourea is inserted in the bath, reaction starts and the transparent bath starts becoming dark yellow in color as time progresses showing formation of CdS. We take deposited substrate out after 30 minutes of insertion and vigorously rinsed in DI water, followed by ultrasonication in DI water for few seconds to remove any residual surface impurities from the bath solution during CdS deposition. The CdS samples grown with this technique showed compact dense morphology with thickness of ~ 50 nm. The surface microstructure of such CdS deposited film is shown in **Figure 3.2 (a)**. The prepared CdS film shows granular structure without any voids/macro-defects over the entire surface. The film shows amorphous characteristics and no significant XRD peaks were observed in collected XRD pattern (not shown here). Transmittance spectrum of the prepared CdS, **Figure 3.2 (b),** shows high transmittance more than 80% for higher wavelength greater than the band gap (~ 2.42 eV) for CdS. This high transmittance is essential for a material to be an efficient buffer layer.
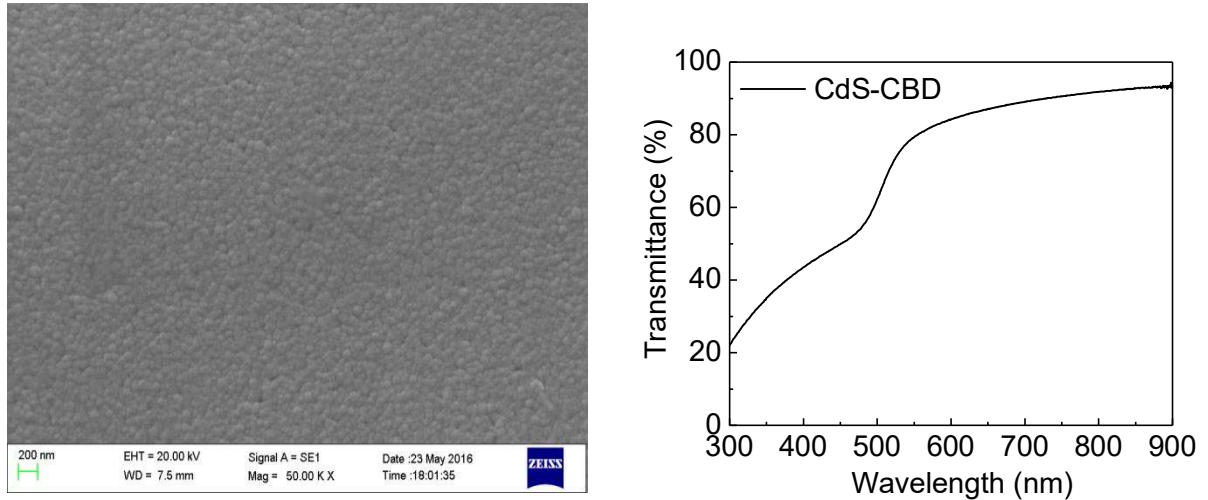

Figure 3.2 (a) Secondary electron microscopy (SEM) image and (b) Transmittance spectra of CBD deposited CdS thin film on glass substrate

3.4 RF/DC sputtering of i-ZnO/Al:ZnO layer

i-ZnO/Al:ZnO bilayer window is deposited on the top of CdS layer which serves as a transparent front contact to the solar cell. Al doped ZnO is considered as a transparent front contact material for solar cell application as it is nontoxic and uses cheap elements as compared to other metal e.g. In based transparent conductors. It also has high transmittance in the visible range and high conductivity comparable to the Indium tin oxide (ITO). At first highly resistive intrinsic ZnO of thickness ~ 80 ± 20 nm is deposited using RF-sputtering on the top of CdS. A 4 inch diameter ceramic ZnO target was pre-sputtered for 10 minutes to remove any target surface impurities. The deposition of i-ZnO thin film is carried out for one hour at 150 W RF power in presence of 10% O_2 + Ar gas mixture. Substrates are kept far about ~ 15 cm away from the target to insure that there is no heating of the substrate and no reverse etching of the deposited ZnO thin film. The oxygen vacancies in ZnO favor its n type semiconductor characteristics and thus, to ensure high resistivity of deposited i-ZnO deposition, the deposition is carried out in Ar+O_2 gas mixture. This deposition of i-ZnO prior to Al:ZnO assists in preventing the probable shunting path between top and bottom contacts. This intrinsic ZnO layer also restricts reverse etching of thin CdS buffer layer during the DC sputtering deposition of Al:ZnO. Aluminum doped ZnO (Al:ZnO/AZO) is deposited using DC sputtering of Al:ZnO (ZnO + 2 wt% Al_2O_3) target in argon gas plasma. Target to substrates distance are kept ~5 cm and deposition is done for 15 min to get conducting Al:ZnO thin film. The conductivity of deposited AZO thin film increases with increasing thickness of the layer but at the same time it deteriorates the transmittance property of the layer. As we have not deposited metallic contact

grids to support current collection on the top of TCO layer, hence we opted for relatively thicker films to achieve both good electrical conductivity and transmittance at the same time. The observed thickness of AZO film after deposition is ~1 μm. The transitivity and resistivity are above 90%, **Figure 3.3**, and ~80±10 Ωcm, respectively for i-ZnO/Al:ZnO bilayer configuration, used for CZTS solar cells.
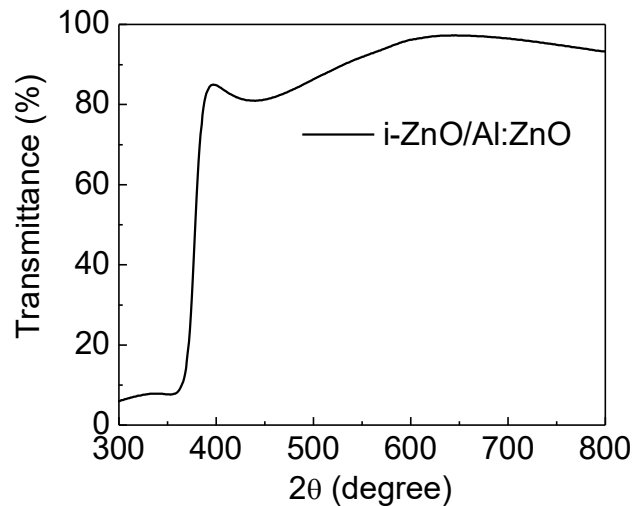

Figure 3.3 Transmittance spectra of i-ZnO/Al:ZnO bilayer deposited on glass substrate with corrected transmittance of glass substrate

3.5 Scribing

Once all the solar cell layers are sequentially deposited, the final cell of defined area has been scribed mechanically using sharp stainless surgical blade with hardness smaller than Mo so that it does not scratch the bottom Mo surface. Small cell area has been scribed to avoid the necessity of top metallic grid and to ensure efficient current collection.

3.6 Device structure

The complete device structure of deposited CZTS heterostructure solar cell is shown in **Figure 3.4**. This solar cell architecture Al:ZnO/i-ZnO/n-CdS/p-CZTS/Mo/SLG is mostly adopted from the CIGS solar cell structure due to their similar structure, optical and electronic properties.
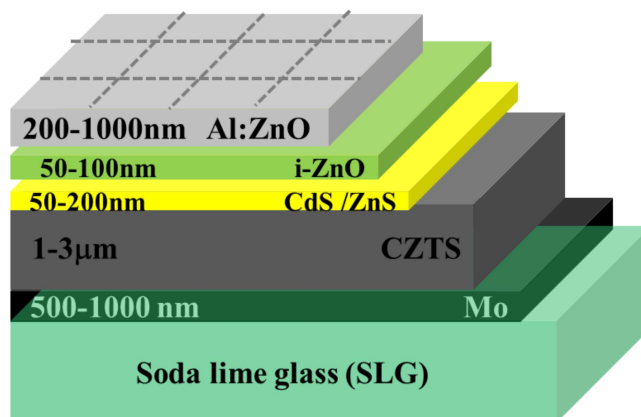

Figure 3.4 Schematic representation of complete device structure of CZTS solar cell, with representative layer thicknesses

Mo back contact layer of thickness 500-1000 nm has been sputter deposited on cleaned soda lime glass substrates. Soda lime glass has an advantage of providing Na diffusion through Mo inside CZTS bulk. This Na diffusion helps in improving the electrical properties enhancing the grain growth and defect passivation at the grain boundaries as observed in CIGS solar devices [Chiril et al., 2011][Nagaoka et al., 2014]. A drastic increase in conductivity of CZTS is observed due to increased hole concentration by forming antisite defects at Cu site by Na (Na_{Cu}) [Prabhakar & Jampana, 2011]. CZTS absorber layer has been deposited using sol gel technique followed by annealing at elevated temperature in presence of sulfur environment. On the top of CZTS absorber, a thin CdS layer is grown which is acting as an n type buffer layer. This CdS layer makes a heterojunction interface with absorber layer. On the top of CdS layer i-ZnO/Al:ZnO bilayer has been deposited, which serves as a transparent window to the solar spectrum and simultaneously serves as a conducting layer for front contact. No metallic grid contact has been made on the top of AZO layer and the fabricated solar cell structure is mechanically scribed into small area, **Figure 3.4**, to ensure proper collection of photo generated current at the outer circuit.