

ABSTRACT

Thin film solar cells which belong to the second generation of photovoltaic devices are made up of amorphous silicon or non-silicon materials such as Cadmium Telluride (CdTe), Gallium Arsenide (GaAs), Indium Phosphide (InP), Copper Indium Selenide (CIS), Copper Indium Gallium Selenide (CIGS) and Copper Zinc Tin Sulphide (CZTS). These solar cells are made up of layers which are of few microns thick. CZTS, a quaternary semiconducting material has been investigated for photovoltaic applications for the last two decades. Researchers replaced Indium and Gallium with Zinc and Tin in the CIGS structure and formed CZTS exhibiting Kesterite structure. Moreover, CZTS has advantages like high absorption coefficient of 10^4 cm^{-1} and energy band gap of 1.45 eV, which makes it a suitable absorber layer material for thin film solar cells.

CZTS absorber layer thin films were deposited using RF magnetron sputtering on soda lime glass substrates (SLG) using CuS, SnS and ZnS sputtering targets (99.99% pure, Cathay Advanced Materials, China) in six different stacking sequences. Initially, deposition of individual binary layers viz., CuS, ZnS and SnS onto soda lime glass substrates was carried out using the respective sulphur based binary targets. Each and every layer has been studied separately to ascertain their feasibility of stacking to form a single absorber layer. Subsequently, the three-sulphur based binary layers were stacked in six sequences as follows, CuS/ ZnS/ SnS, ZnS/ CuS/ SnS, CuS/ SnS/ ZnS, ZnS/ SnS/ CuS, SnS/ ZnS/ CuS and SnS/ CuS/ ZnS. CZTS thin films prepared using this arrangement were studied for composition and structure using XPS, XRD and Raman, respectively. From the XPS results, it was observed that the films prepared with the stacking sequence – SLG/ CuS/ ZnS/ SnS was near to stoichiometry and the XRD measurements carried out revealed the formation of kesterite structure. Subsequent experiments and trials were carried out using this optimized stacking order.

In order to promote the sulphur content in the films, post-deposition sulphurisation was carried out at 350°C on a quartz boat placed inside a tubular furnace, which was evacuated to 1×10^{-3} mbar using a rotary pump. Hydrogen sulphide (H_2S) gas was purged into the chamber for 1 hr and the furnace temperature was raised to 350°C. The tubular furnace was then cooled and vented with N_2 gas to remove the toxic residues.

The properties of the sulphurized CZTS thin films were studied in detail. X-Ray diffraction results revealed the formation of CZTS kesterite phase $\langle 112 \rangle$ orientation with other secondary peaks. Further, on sulphurization, the intensity of CZTS kesterite peak was observed to be prominent and the presence of secondary phase SnS peak was also found. To substantiate the formation of CZTS, the samples were analysed using Raman spectroscopy. The low energy vibrational modes of CZTS were noticed at 330 cm^{-1} and 337 cm^{-1} , with the presence of SnS secondary phases. The Raman spectra of the sulphurised CZTS films showed formation of kesterite CZTS phase with ternary $CuSnS_3$ (CTS) in monoclinic and cubic phases.

XPS has been used to study the elemental composition and oxidation state of the sulphurized samples prepared using the stacking order – SLG/ CuS/ ZnS/ SnS. The as - deposited CZTS films contained an elemental composition of Cu: 21.2%, Zn: 12.5%, Sn: 10%, S: 45%. The sulphurised CZTS thin films exhibited elemental composition as Cu: 22%, Zn: 12.65%, Sn: 14.8%, S: 46.3%. The comparison between the as - deposited and sulphurised samples revealed that the sulphurised samples had improved elemental properties in terms of stoichiometry.

FESEM and HRTEM images revealed smooth morphology of the as-deposited films with some pin holes in the samples annealed at higher temperatures. However, pin holes were not observed in those samples which were sulphurized. SAED pattern acquired from the HRTEM analysis were in agreement with XRD results. AFM images revealed large island like grains for the as-deposited

samples and they reduced as the samples were sulphurised and resulted in an optimal roughness of 12.8 nm. Electronic parameters such as Ionization energy, electron affinity and electronic band gap were determined as 5.9 eV, 5.4 eV and 1.45 eV respectively. The values were calculated from the UPS results.

Optical parameters such as transmittance, absorbance and band gap were measured for all the prepared samples. The band gap value for the sulphurised CZTS sample was around 1.43 eV.

A comparative study on the electrical properties of as-deposited and sulphurised CZTS was performed. Effect of temperature on resistivity revealed that as temperature increased, the resistivity decreased which indicate the semiconducting nature of CZTS thin film. The activation energy for the sulphurised CZTS thin films was calculated using the Arrhenius plot. Hall-effect measurements indicated the p-type nature of the CZTS thin film and the carrier concentration was found to be 4.9×10^{17} cm.

Cadmium Sulphide - CdS thin films have been prepared using vacuum based hot-wall deposition technique rather than the conventionally used chemical bath deposition. CdS powder (Sigma Aldrich, 99.9% pure) was loaded into the hot- wall setup which was placed in vacuum. The CdS powder was sublimated into thin films from the hot- wall setup within 60 seconds. The as-deposited films were annealed to 250 °C.

XRD studies revealed the formation of hexagonal CdS phase along $\langle 002 \rangle$ direction. The intensity of $\langle 002 \rangle$ phase improved on annealing. Raman spectroscopy results were in accordance with the XRD results. FESEM showed the surface to be uniform devoid of any cracks. HRTEM images indicated uniform surface orientation of the CdS thin films. SAED pattern acquired also substantiated the formation of hexagonal CdS phase along $\langle 002 \rangle$ direction.

The XPS survey spectrum confirmed the presence of Cd and S. The elemental composition obtained from the XPS results showed Cd: 50% and

S: 49%. AFM results showed that the surface roughness (rms value) of CdS thin film is about 4.47 nm. Optical microscopy images showed uniform surface of CdS thin films. UV-Vis-NIR spectroscopic analysis showed that CdS thin films exhibited a band gap of 2.42 eV which is optimum for a buffer layer in thin film solar cells. Hall effect measurements indicated n-type conductivity for the CdS thin films.

Gallium doped zinc oxide thin films for window layer / transparent conducting layer was deposited using RF Magnetron Sputtering system on soda lime glass substrates. Its low resistance and high transparency make its suitable as a window layer in thin film solar cells. Two inch GZO sputtering target (99.99%) from Cathay Advanced Materials, China was used for the deposition. The substrate temperature was maintained at 400°C. The distance between GZO target and the substrate was 15 cm. Argon gas was used for sputtering.

XRD studies revealed the formation of hexagonal <002> phase of GZO along with <102> of the ZnO phase. The XPS survey spectrum of GZO thin films showed the presence of Ga, Zn, O and C. Elemental composition of Ga: 15.5% and ZnO: 83% were found to be optimum. The UV-Vis-NIR spectroscopy studies revealed that GZO exhibited a band gap of 3.55 eV. The hall effect measurement revealed the n type nature of GZO thin films.

A thin film solar cell with the structure SLG/ Mo/ CZTS/ CdS/ GZO/ Al was fabricated. Initially, Mo thin film was coated onto SLG by RF Magnetron Sputtering. The optimized CZTS absorber layer was sputtered onto the Mo layer, followed by sulphurisation. CdS buffer layer was then evaporated onto the CZTS layer using hot-wall deposition technique. Finally, GZO was sputtered onto CdS buffer layer using RF magnetron sputtering. The final CZTS solar cell was tested using a solar simulator under 1.5 AM of radiation and the efficiency and short circuit were measured.