Preparation and Characterisation of Electrodeposited Cu (In, Ga) Se_2 Thin Film Solar Cells

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Abstract: *The copper indium gallium selenide (CIGS) thin film solar cell can be prepared by electrodeposition, chemical bath deposition and annealing technique. The as deposited films are crystalline in nature. The crystallinity increases further by annealing the thin film. The XRD analysis indicate the prominent peak of Cu(In,Ga)Se_2 (112) at 28.27^0. The resistivity of CIGS thin film is found to be 0.8915 Ω-cm. The solid state properties of window materials CdS are carried out by XRD, XPS & SEM. The as deposited films are stoichiometric in nature with Cd/S ratio equal to 1.1:1. The grains are spherical, well connected and no effect of charge are observed. The XRD spectra of CIGS solar cell show the prominent peak of CdS (002) and CIGS (112). Some minor peaks are observed due to Ga_2O_3, $CuSeO_4$ and $GaCl_3$. The performance of the CIGS solar cell are carried out and it is observed that the open circuit voltage, short circuit current density, fill factor and efficiency of CIGS solar cell are found to be 550 mV, 13mA/cm^2, 0.45 and 13% respectively.*

Key Words: *Electrodeposition, Absorption coefficient, Band gap, Interface, Resistivity.*

1. Introduction

The copper indium selenide and copper indium gallium selenide are direct band gap semi conducting material. The Cu (In,Ga)Se_2 film is formed by introducing gallium as the impurity to $CuInSe_2$ film. Due to introduction of the impurities the band gap of the material changes from 1.04 eV to 1.18 eV which is near to optimum.

A number of workers have developed the CIGS thin film by various methods like vacuum evaporation process, molecular beam epitaxy, selenization, electrodeposition processes etc. The vacuum evaporation process (Nakada, 2000; Ard, et. al. 2000; Lundberg, et. al. 2000; Sterner, et. al. 2000) requires very pure (99.999%) starting material. Due to high purity of the material the fabrication cost of the device is very high.

The CIGS thin film can be developed by molecular beam epitaxy process (Hahn, et. al. 2005; Nakada and Kunioka 1999; Tseng, et al. 1996) are grown epitaxially which is equivalent to single crystal. But it requires very high purity (99.999999%) working material.

The CIGS thin film can also be prepared by selenization process (Kushiya, et. al. 1996). In this process the CIGS thin film is prepared in two steps (i) development of In/(Cu-Ga) alloy precursor layers (ii) selenization of the In/(Cu-Ga) films to form Cu(In,Ga)Se_2 film. These films are porous i.e. full of pin holes, pits, cracks etc. Also it is difficult to control the excess of toxic and poisonous gas arising out of selenization.

To avoid the above problems, we have developed the CIGS thin film by low cost electrodeposition method (Hermann, et. al. 2000; Bhattacharya, et. al. 2000; Kampmann, et. al. 2000). In this method there is problem of stoichiometry control of the elements. To deposit all the four elements at a potential, some complexing agents are introduced. To complete the CIGS solar cell, the window material CdS is deposited over the Cu(In,Ga)Se_2 thin film by chemical bath deposition. The deposition of CdS film over Cu(In,Ga)Se_2 forms Mo/Cu(In,Ga)Se_2/CdS stacked layer. The stacked layer is annealed in air at 400^{0}C to form CIGS solar cell.

2. Experimental Procedure

2.1 Development of Cu (In,Ga)Se_2 thin films

The copper indium gallium selenide thin films were electroplated on molybdenum substrate at 80°C in an aqueous medium. The electrolyte was prepared by taking AR grade 9.3x10^{-3}M $CuCl_2$, 2.4x10^{-2}M KI, 8.2x10^{-3}M TEA, 2.7x10^{-2}M Na-Citrate, 1.8x10^{-2}M SeO_2, 1.4x10^{-3}M $InCl_3$, 1.6x10^{-2}M EDTA and 1.42x10^{-3}M $GaCl_3$ in 40ml of distilled water. The electroplating was carried out on polished molybdenum cathode under potentiostatic condition using EG&G

scanning potentiostat galvanostat model 362. During the electrodeposition the electrolyte was moderately stirred. The deposition duration was 10 minutes and deposition potential was kept at –0.70V (SCE). The graphite plate was kept as counter electrode.

2.2 Development of CdS film on Cu(In,Ga)Se_2 film

The electrolyte for deposition of CdS film was prepared by taking $2x10^{-2}$M $CdCl_2$ and $6.67x10^{-2}$M NH_4Cl. The ammonia solution was introduced in the electrolyte to fix the pH around 8. The deposition was carried out at 80±1°C under continuous stirring. The freshly prepared Cu (In,Ga)Se_2 film was washed with distilled water and dried. The dried Cu(In,Ga)Se_2 was dipped in the electrolyte and the $1.43x10^{-1}$M thiourea was introduced in the electrolyte. The duration of deposition was 5 minutes. After deposition a stacked layer of Mo/Cu (In,Ga)Se_2/CdS was formed.

2.3 Preparation of CIGS thin film solar cell

The stacked layer of Mo/Cu (In,Ga)Se_2/CdS was formed. The stacked layer was annealed in air at 400^0C to form CIGS solar cells.

2.4 Structural analysis

The X-ray diffraction analysis of Cu (In,Ga)Se_2 films were recorded on a Rigaku Automated Powder X-ray Diffractometer model D/Max 2100 using CuKa radiation.

2.5 Compositional analysis

The compositional analysis of the CdS films were carried out using an ESCALAB mark Ï X-ray photo electron spectroscopy (V.G. Scientific Ltd., U.K). X-ray photo electron spectroscopy (XPS) analysis was carried out using an AlKá (hõ = 1486.6 eV) source and a concentric hemispherical analyzer with a resolution of 0.8 eV. All the measured binding energies were referred to the Au 4f 7/2 peak located at 83.8± 0.1eV. The base pressure in the analysis chamber was $1x10^{-9}$ torr. Carbon (C 1s) at 284.6 eV was taken as the internal standard for as received samples and all the peak positions in all the samples were normalized with respect to it. An argon ion gun operating at 4 kV and 10 iA was used for cleaning and profiling the films. Elements identities were established first by a survey scan. Accurate compositional analysis was subsequently carried out by repeatedly scanning the peak over a narrow energy range.

2.6 Photoresponse of CIGS solar cells

The photoresponse of CIGS solar cells was examined on the illumination set up. The intensity of the incident ray was measured by lux meter model LUX 1. The panel meters were connected in series and parallel respectively to the circuit for the measurement of voltage and current.

3. Results and Discussions

3.1 XRD analysis of CIGS thin film

Fig. 1 shows the XRD spectra of Cu (In,Ga)Se_2 thin film annealed at 340°C. The prominent peak of Cu (In, Ga)Se_2 (112) is observed at 28.27°. Due to annealing of the film, some mixed peaks are also observed. The other peaks are due to Ga_2O_3, $CuSeO_4$, and $GaCl_3$. The compounds are mainly of copper, gallium and selenium. This clearly indicates that some free elements are there and when it is annealed at 340°C it forms compounds of different phases.

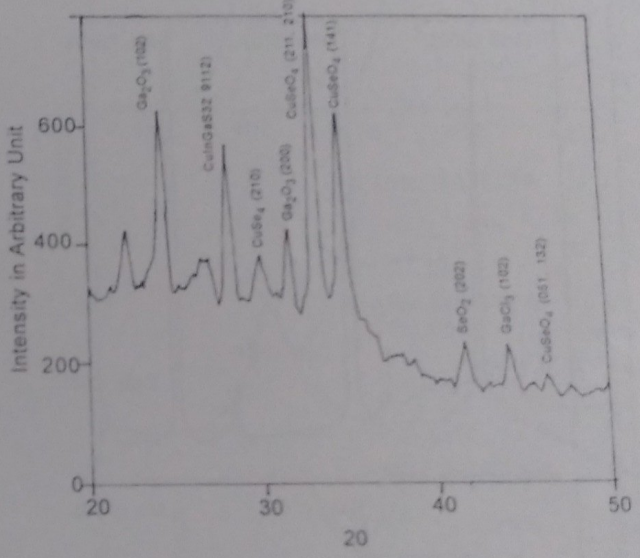

Fig. 1. XRD spectra of Cu (In, Ga) Se_2 thin film annealed at 340^0C.

3.2 Resistivity of the CIGS thin film

The resistivity of the CIGS thin films is measured by using the formula.

$$\rho_0 = (V/I)\ 2\pi S$$

Where V = applied voltage (mV)

I = applied current (mA)

S = distance between the probes.

The resistivity of the CIGS thin film is determined by $\rho = \rho_0 / \rho_7$, where ρ_7 is the correction factor. The typical value of the resistivity ρ of the film is observed to be 0.8915 Ω- cm.

3.3 Carrier concentration and Hall coefficient of the CIGS thin film

The Hall coefficient and carrier concentration of the CIGS thin film are determined by Hall Effect set up. The value of Hall coefficient and the carrier concentration are determined by the graph and it is found to be 1.689×10^{-9} V-cm/Amp-Orested and 1.24×10^{18} carriers/cm^3.

3.4 XRD analysis of CdS film

Fig. 2(a) and 2(b) show the XRD pattern of as deposited and annealed CdS film at 400^0C in air. A prominent peak of (002) and weak peaks of CdS (102), (201) and (203) are observed. The prominent peak of (002) clearly indicates the cubic and hexagonal phase of the film. The hexagonal phases of the film annealed at 400^0C are good for device applications.

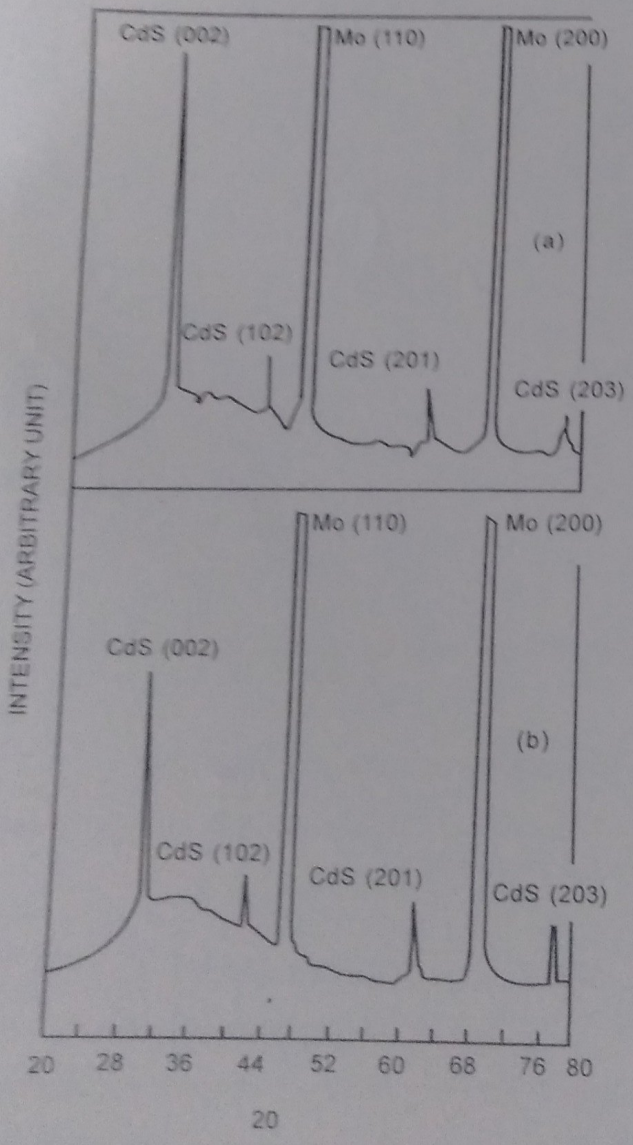

Fig. 2(a): XRD spectra of as deposited CdS film on molybdenum substrate and 2(b): XRD spectra of CdS film on molybdenum substrate annealed at 400°C in air.

3.5 XPS Analysis of CdS Film

The X-ray photoelectron spectra of the as deposited and annealed at 400^0C of the CdS films are shown in figs. 3(a) and 3(b) respectively. The surface scan clearly indicates the presence of elements carbon (C 1s), oxygen (O 1s), sulphur (S 2p) and cadmium (Cd 3d) at the surface of the film. The presence of oxygen in the film is due to handling of the film in air and the carbon is due to standard of the instruments. It is observed in the XPS spectra, (not shown in the figure) both in the case of unannealed and annealed films, that as the sputtering time increases the traces of oxygen and carbon decreases.

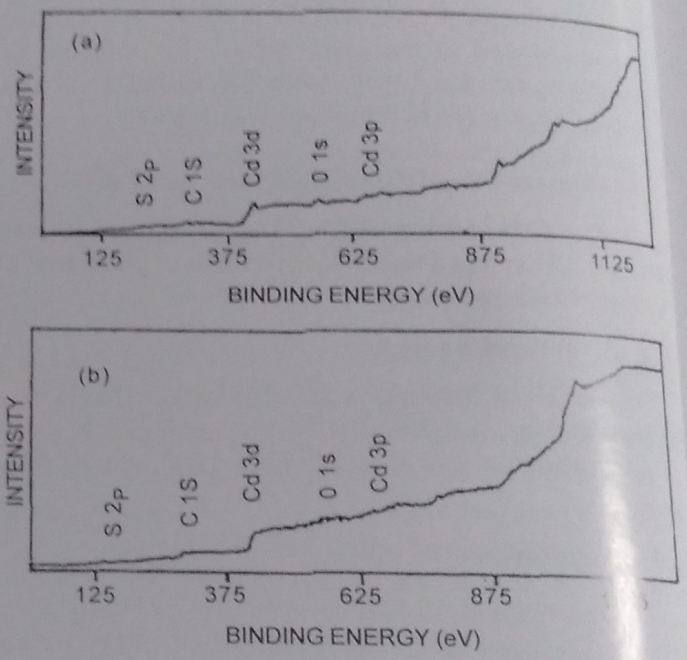

Fig. 3(a): XPS survey spectrum of as deposited CdS film on molybdenum substrate and 3(b): XPS survey spectrum of CdS film on molybdenum substrate annealed at 400°C in air.

Fig. 4(a) and 4(b) show the depth profile of the as deposited and annealed CdS films respectively and clearly show in both cases that the ratio of Cd and S are equal to 1.1:1 in the bulk. But in case of annealed films there is further loss of sulphur at the surface due to which the ratio changes from 1.1 to 1.25.

The variation of binding energy of photoelectron the elements with sputtering duration, provide information on the existence of their chemical environments. Fig. 5(a) & 5(b) and 6(a) & 6(b) show the narrow scan XPS spectra of Cd 3d and S 2p peaks after various sputtering duration in case of as deposited and annealed CdS films respectively.

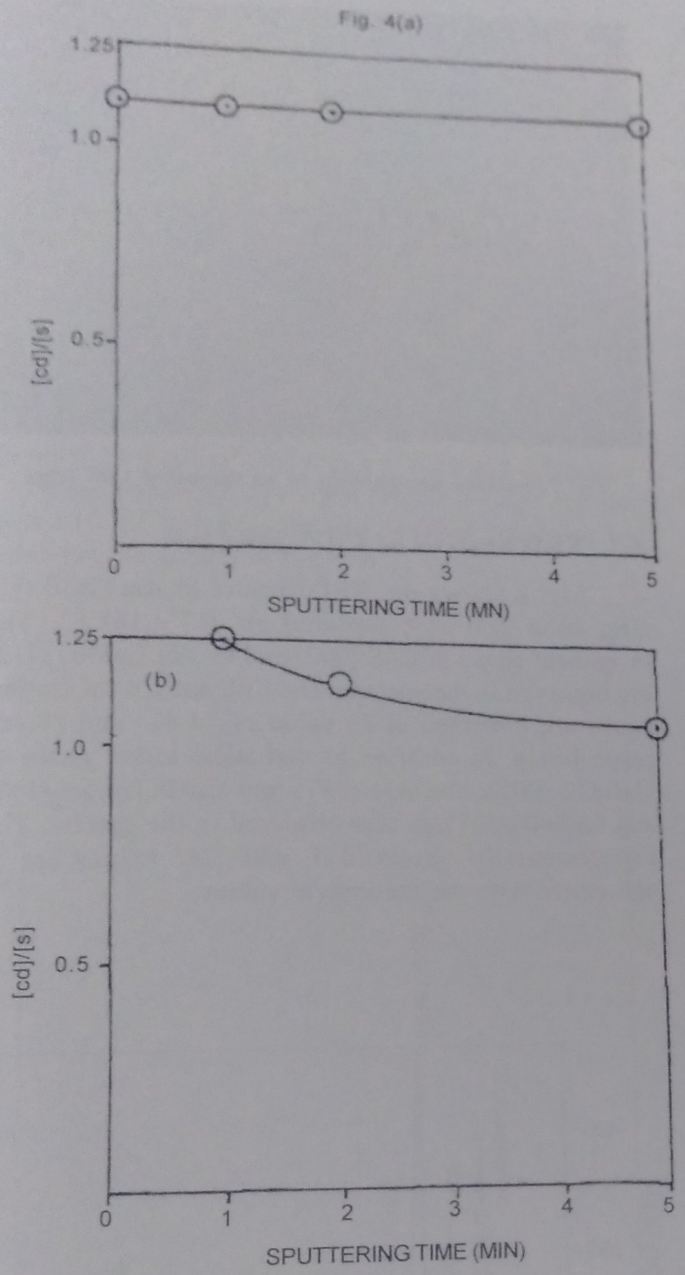

Fig. 4(a): The variation of Cd/S ratio with sputtering time for as deposited CdS films and 4(b): the variation of Cd/S ratio with sputtering time for CdS film annealed at 400°C in air.

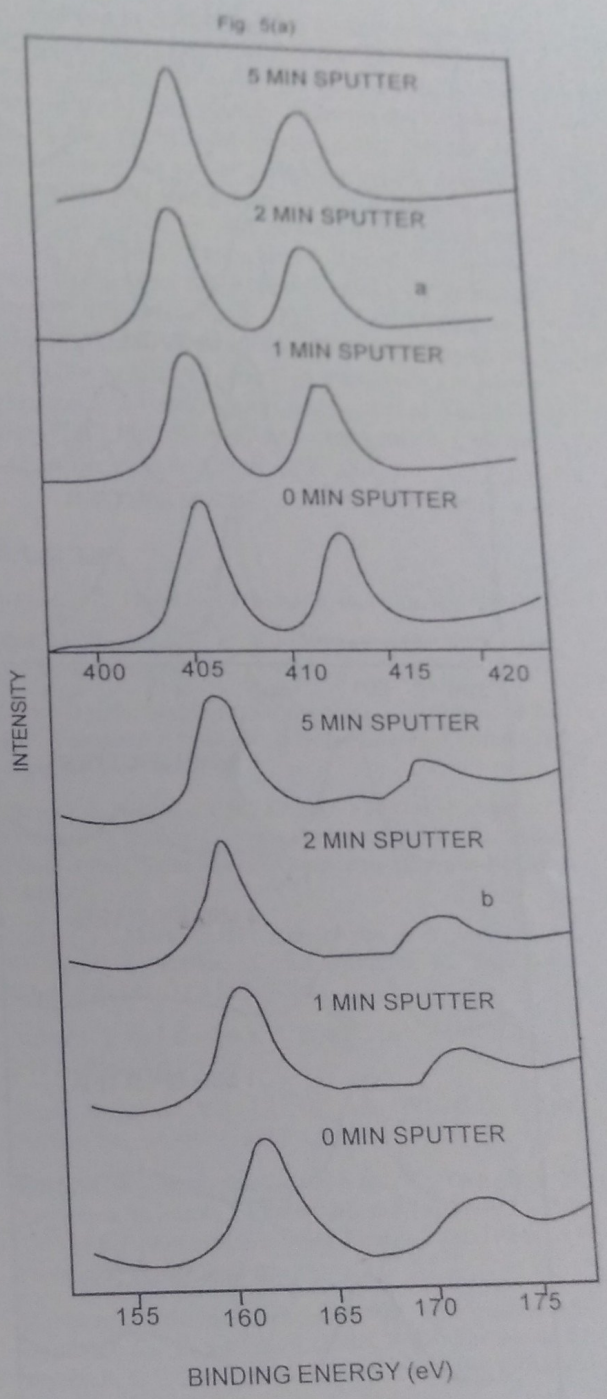

Fig. 5(a): A comparison of narrow scan peaks of Cd 3d at various sputtering durations for as deposited CdS film and 5(b): a comparison of narrow scan peaks of S 2p at various sputtering durations for as deposited CdS film.

3.6 Surface morphology of CdS film

The surface morphology of the as deposited CdS film is shown in fig. 7. It is observed from the photograph that grains are spherical and well connected to each other. No effects of pin holes and cracks are observed. Charging is also not observed in the film.

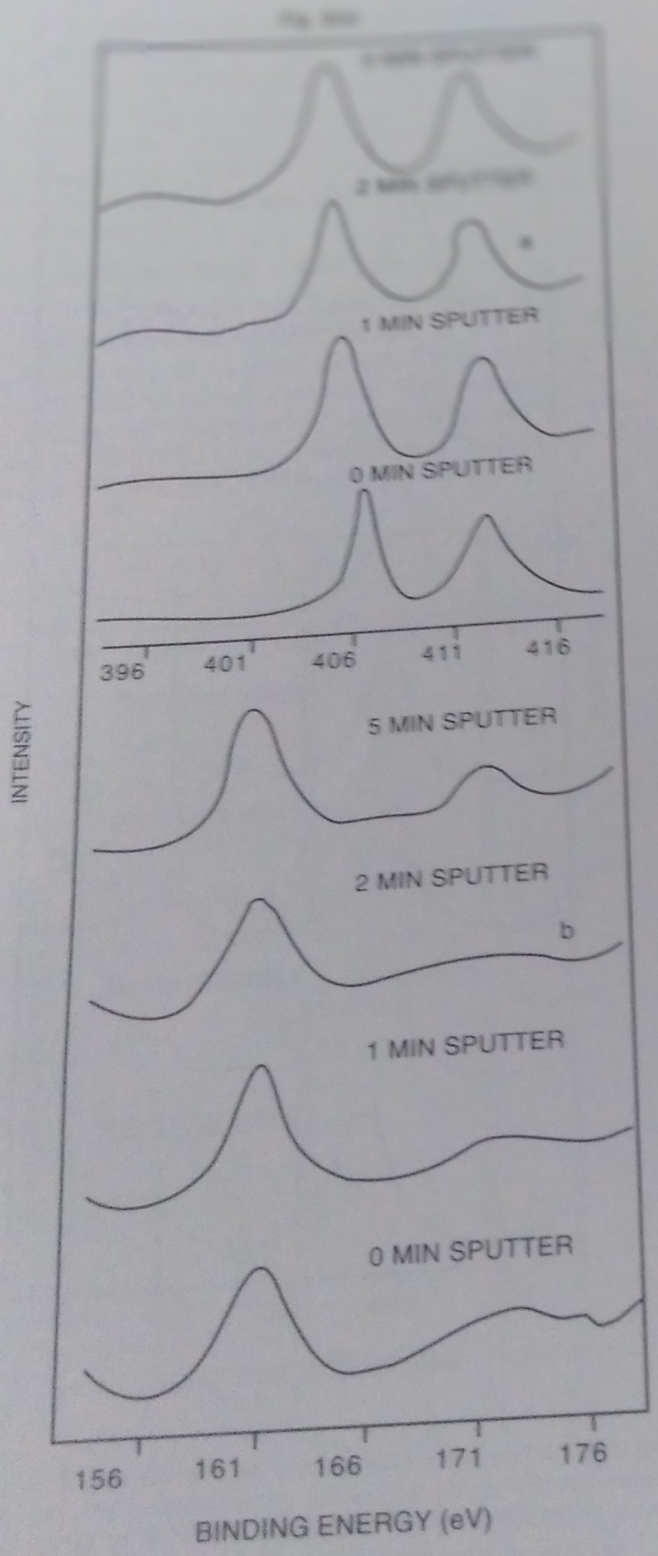

Fig. 6(a): A comparison of narrow scan peaks of Cd 3d at various sputtering durations for CdS film annealed at 400°C in air and 6(b): a comparison of narrow scan peaks of S 2p at various sputtering durations for CdS film annealed at 400°C in air.

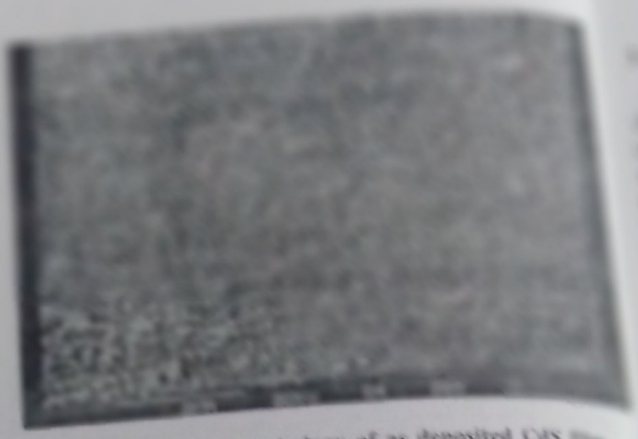

Fig. 7. Surface morphology of as deposited CdS film.

3.7 XRD analysis of CIGS solar cell

Fig. 8 shows the XRD spectra of the CIGS thin film solar cell electroplated at –0.7V (SCE). The prominent peaks of CdS (002) and Cu (In,Ga)Se_2 (112) are observed in the spectra. The CdS and Cu (In,Ga)Se_2 peaks are observed at 2è value of 24.82° and 28.16° respectively. In addition to that some minor peaks of $GaInO_3$ (002), $GaInO_3$ (311) and Cu(In,Ga)Se_2(112) and $CuSeO_4$(311)are also observed in the spectra. The experimentally observed'd' and '2è' values are in agreement with the theoretical values.

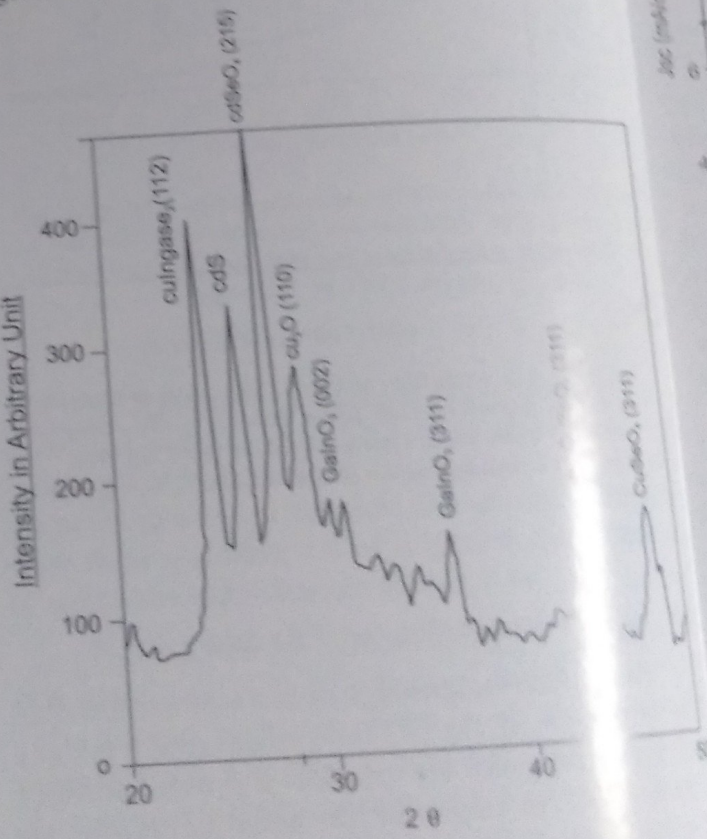

Fig. 8. XRD spectra of CIGS thin film solar cell electrodeposited at – 0.70V (SCE).

3.8 Photoresponse of CIGS solar cells

The photoresponse of CIGS solar cells have been determind by tungsten halogen lamp. The visible region of the solar spectra is passed through the water filter which eliminates IR and UV region. The intensity of the allowed visible region is measured by the luxmeter. The intensity of the input light is fixed at 25mW/cm^2. The open circuit voltage , short circuit current density, fill factor and efficiency increases with the increase of the etching time. The optimum etching time is 10 seconds. Beyond 10 seconds the quality of performance of the device lower down. Fig.9 shows the J-V plot of the typical CIGS solar cell etched for 10 seconds. The open circuit voltage = 550mV, the short circuit current density = 13 mA/cm^2, fill factor = 0.45 and efficiency = 13% are observed. The open circuit voltage and the short circuit current density further improve by improving the quality of the film.

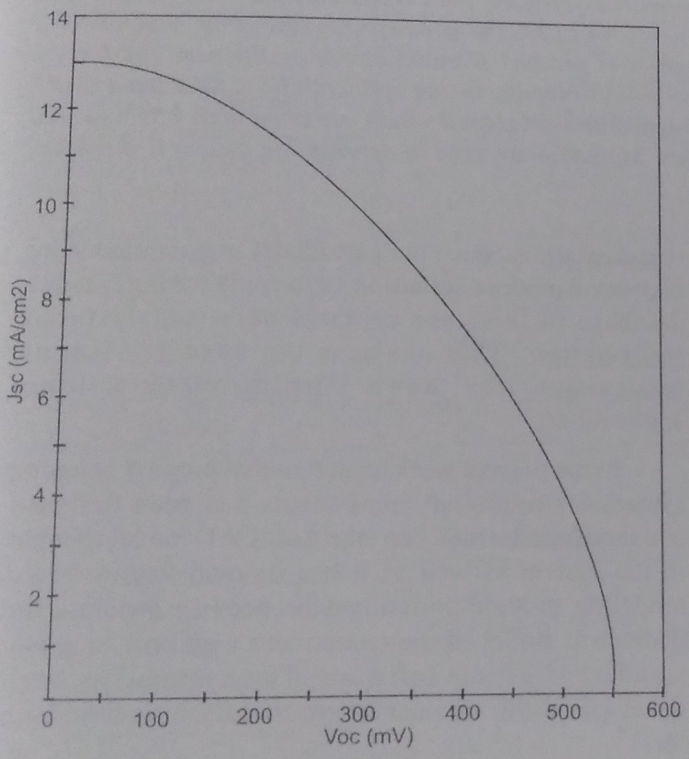

Fig. 9. J-V plot of the typical CIGS solar cell etched for 10 seconds.

4. Conclusions

The copper indium gallium selenide thin film can be developed by single step electrodeposition process. The problem of co-deposition of all the four elements is overcome by using the complexing agents. The deposition potential –0.7V (SCE) has been optimized for the deposition of Cu (In,Ga)Se_2 thin film. The structural analysis by XRD of the as deposited and then annealed at 340°C has been carried out. The sharpness of the peak in both the cases clearly indicates the crystalline nature of the material. Chalcopyrite structure of Cu(In,Ga)Se_2 (112) is observed in the spectra. In addition to that some minor peaks of In_2O_3, Ga_2O_3, $CuSeO_4$, and Ga_2O_3 are observed. The resistivity and carrier concentration of the as deposited films are observed to be 0.8915 Ω cm and 1.24×10^{18} carriers/cm^3 respectively. The XRD spectra of the CIGS solar cell clearly indicate the peaks of CdS (002) and Cu(In,Ga)Se_2 (112). In addition to that some minor peaks of $GaInO_3$, $CuSeO_4$ are also observed. The open circuit voltage = 550mV, short circuit current density = 13 mA/cm^2, fill factor = 0.45 and efficiency = 13% are observed in the case of CIGS solar cell.

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