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Characteristics Of Nanostructured $CuInS_2$ Thin Film By Spray Pyrolysis Method

J.Tamil Illakkiya[1], P.Usha Rajalakshmi[1], Rachel Oommen[1]*

Department of Physics, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore-641 043, India

Abstract : $CuInS_2$ is a chalcogenide ternary semiconductor, an efficient absorber material for solar cell application. In the present work, $CuInS_2$ thin film (Cu/In=0.5) have deposited on pre-heated glass substrate at a growth temperature of 350˚C by cost-effective spray pyrolysis technique. The as-deposited film was annealed in vacuum at 200˚C for 1 hour. The effect of vacuum annealing on structural, optical and electrical properties of CIS thin has been investigated. Chalcopyrite structure of CIS film was confirmed by XRD analysis. Non-stoichiometric behaviour was observed by EDAX measurement demonstrating the presence of additional phases in CIS film. The absorption co-efficient of the sprayed $CuInS_2$ film was found to be in the order of 10^4 cm^{-1} and the optical bandgap varies from 1.47 eV to 1.51 eV for as-deposited and annealed film respectively. Photoluminescence analysis reveals that the emission was mainly due to donor-acceptor pair transitions. The resistivity of CIS film varies extensively with annealing temperature.

Keywords: $CuInS_2$ thin film, spray pyrolysis, structural, optical and electrical study.

Introduction

A pioneering energy system based on renewable and solar energy sources have drawn more consideration due to the rise in energy consumption and ecological concern. In this regard, the development of photovoltaic system as an alternative energy conversion has become a vital role. The advance of nanocrystalline chalcopyrite absorber layer for thin film photovoltaic cells has inward significant interest to contribute as the next generation of photovoltaic devices[1]. Copper Indium sulfide ($CuInS_2$) thin film is one of the most promising absorber material for solar cell applications with absorption co-efficient ($10^5 cm^{-1}$), exceptional insensitivity to radiation damage or impurity and optimum bandgap of 1.5eV which is perfectly matches with solar spectrum[2,3]. $CuInS_2$ thin film offers the outlook of low production cost with few microns of thickness can absorb majority of the incident light energy higher than the bandgap of the material[4]. Furthermore, it does not contain any toxic constituents as Se or Ga atoms. It was found that increase in the efficiency of solar cells based on chalcopyrite semiconducting materials was mainly attributed by post annealing treatment in air or oxygen[5].

Various methods have been developed for the fabrication of $CuInS_2$ thin film such as aerosol jet deposition[6], chemical bath deposition[7], chemical vapour deposition[8], co-evaporation[9], electrodeposition[10], paste coating method[11], SILAR method[12], spray pyrolysis[13,14], sputtering[15]. Among these techniques, spray pyrolysis is an attractive method for the deposition of thin film in large area production which is useful for solar cell applications. Flexibility of this method is to make it suitable for depositing thin film of compound semiconductors.

In the present work, $CuInS_2$ thin film was deposited by novel technique called nebulized spray pyrolysis. The as-deposited film was annealed in vacuum at 200˚C for 1 hour. The structural, optical, compositional and electrical properties of as-deposited and annealed film were analyzed using various characterization techniques.

Experimental Details

$CuInS_2$ (CIS) thin film was deposited on a glass substrate by an aqueous solution of $CuCl_2$, $InCl_3$ and $CS(NH_2)_2$. In the present study, the copper/indium molar ratio in the solution was Cu/In=0.56 and sulfur/copper ratio ration in the solution S/Cu=7.0. The surplus amount of thiourea was required in the final solution since it avoids the precipitation of metallic hydroxides and sulfides because it forms complexes with copper and Indium ions[16]. CIS thin film was deposited by nebulized spray pyrolysis technique. In this technique, a nebulizer has been used instead of atomizer in the standard spray pyrolysis unit. The solution was sprayed on pre-heated glass substrate ($25x25x1mm^3$) at a constant growth temperature of 350˚C using compressed air as a carrier gas at a pressure of 1 bar. The volume of the precursor solution of 56 ml was sprayed at a flow rate of 0.7ml/min with substrate to nozzle distance of 5cm respectively to obtain homogeneous CIS thin film. Post deposited treatments as thermal treatment in vacuum atmosphere at a temperature of 200˚C for 1 hour was made. The thickness of deposited film was determined by mass-difference method and was found to be 1.3136 µm.

The crystal structure of the sprayed films was determined by X-pert pro PANalytical X-ray difractrometer with monochromatic Cu Kα radiation. The elemental composition of the film was analyzed by energy dispersive X-ray analysis-EDAX (VEGA3, Tescan). The optical properties of the films were examined using UV-VIS spectrophotometer (V-670, JASCO) and spectroflurometer (FluoroLog, Horiba) were used for the studies on optical properties. The activation energy and resistivity of the thin film was determined by four probe method.

Results and Discussion

Structural analysis

X-ray diffraction technique has been employed to identify the crystalline property of CIS thin film. Figure 1 shows the XRD pattern of as-deposited and annealed CIS film. The characteristics peak of as-deposited CIS film of 2θ value at 28.10˚, 46.5˚, 55.0˚ corresponding to $CuInS_2$ planes (1 1 2), (2 2 0), (1 1 6) with preferential orientation along (1 1 2) plane indicated the formation of $CuInS_2$ with chalcopyrite phase[17]. Lattice parameters of CIS film with a=b=5.52Å and c=11.0 Å which was in good agreement with a= b=5.523 Å and c=11.133 Å (JCPDS file No. 75-0106). The annealed CIS film contains secondary phase of In_2S_3 and Cu_2S phase in which the planes were well matched with JCPDS card no. 73-1366 and JCPDS card no.26-1116 respectively. It was found that the annealing environment and temperature can affect the formation of impurity phases such as Cu_2S and In_2S_3 in $CuInS_2$ thin film[18]. Better crystallinity was observed for annealed CIS film. The broadening of XRD peak suggested that grain size was on nanometer scale. The grain size was calculated by Scherer's equation, $D=0.9\lambda/\beta \cos\theta$ where λ, β and θ are wavelength of the X-ray used, full width half maximum (FWHM) of the peak and Bragg angle respectively. The grain size of the CIS (as-deposited and annealed) film were calculated and found to be 12nm and 40nm corresponding to the prominent (1 1 2) peak.

Compositional analysis

The elemental composition of $CuInS_2$ thin film was determined from EDAX analysis was shown in table 1. The EDAX spectrum (Figure 2) showed the intense peak of Cu, In, S indicating the composition of Cu, In and S were present in the CIS film. The present analysis showed that the deposited film was found to be non-stoichiometric in nature. The concentration of Indium was higher than the stoichiometric value attributed that Copper/Indium ratio (Cu/In=0.51) was lower than the expected value[19]. It may be concluded that the deposited film was In-rich CIS film. No traces of carbon were detected in EDS analysis.

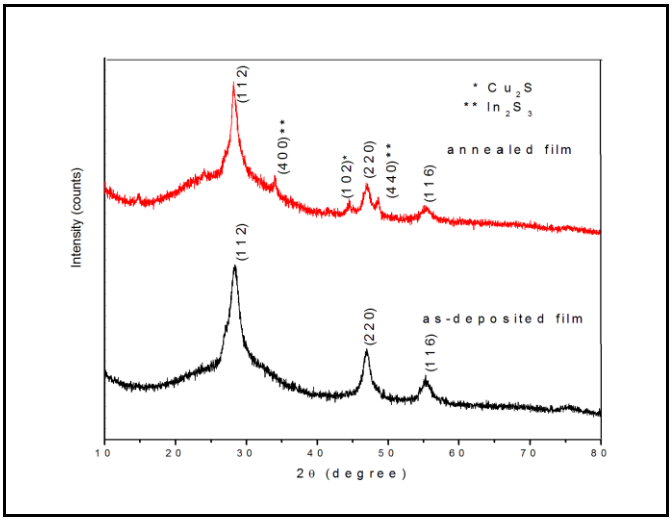


Figure 1. X-ray pattern of $CuInS_2$ thin film

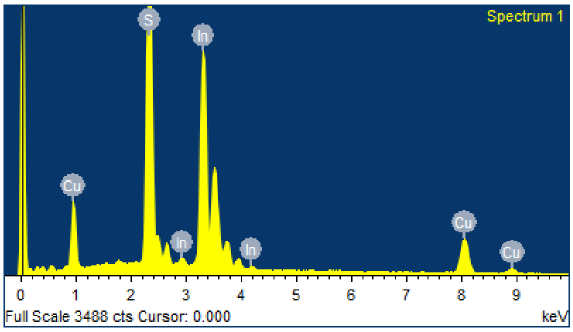


Figure 2. EDAX spectrum of CIS thin film

Table 1: Elemental composition of $CuInS_2$thin film

Elements	Weight %	Atomic %
Cu	16.09	15.70
n	55.95	30.22
S	27.97	54.09

Optical properties

The variation of transmittance with wavelength of light incident on the material has been recorded by UV-VIS spectrophotometer in wavelength range of 300 – 1200nm. The optical transmittance has great impact on annealing temperature. Improved transmittance property in the visible region was observed for as-deposited CIS film as shown in figure 3. The absorption edge was blue shifted for annealed film which in turn increases in the bandgap owing to nanostructure/impurities present in CIS film.

The spectral dependence of absorption co-efficient affects the solar conversion efficiency[4]. Absorption co-efficient (α) was found to be in order of 10^4 cm^{-1} in the UV and visible region (300-800nm) for as-deposited and annealed film. The bandgap of CIS thin film can be obtained from hν versus $(\alpha h\nu)^2$ which was shown in figure 5. The optical bandgap E_g of the as-deposited and annealed film ranges from 1.47eV to 1.51eV respectively. The bandgap energy increases with increase in annealing temperature which may be due to secondary phases such as Cu_2S and In_2S_3 were present in annealed film[20].

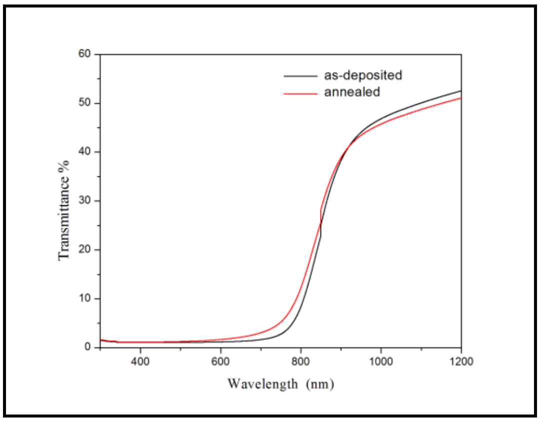


Figure 3: Transmittance spectrum of as-deposited and annealed film

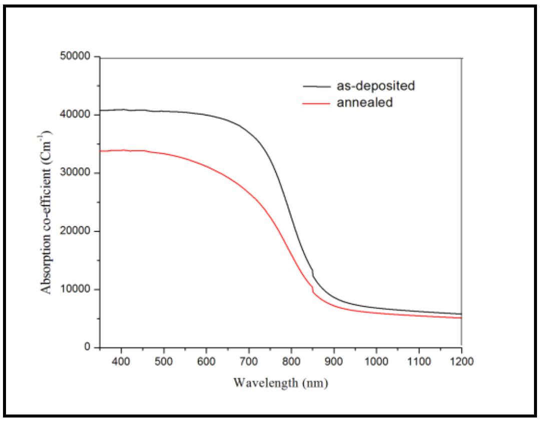


Figure 4: absorption co-efficient as a function of wavelength of CIS film

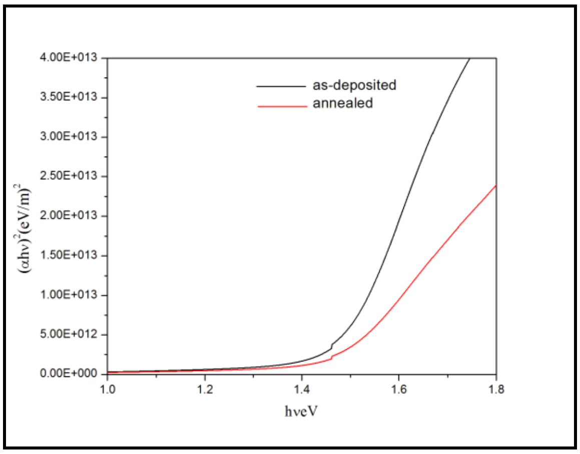


Figure 5. Optical bandgap of as-deposited and annealed CIS film

Photoluminescence property

Figure 6. shows the film exhibited luminescence in visible region excited at 400 nm. The luminescence related to $CuInS_2$ has been initiated from defects and non-stoichiometric nature of the material. The as-deposited and annealed CIS film revealed the emission peak was observed at 450nm with blue emission. The broadening of the emission peak was attributed to high concentration of defects and non-equilibrium process of the film deposited[21]. The characteristic peak has assigned to Donor-acceptor (DAP) pair transition sulfur vacancy or Indium vacancy or Cu on in site[22]. The appeared emission was related to defect state increasing at the growth of crystallites are due to deformation in crystallinity/large vacancies[23]. The photoluminescence intensity drastically decreased upon annealing which may be due to rising in the number of surface state densities.

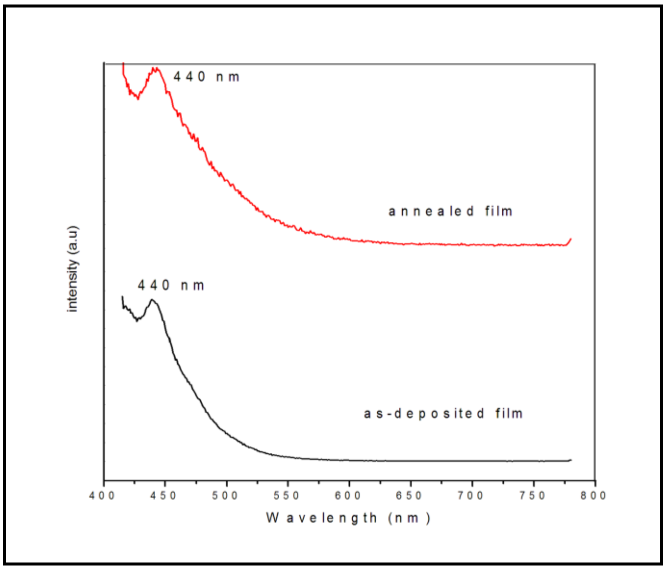
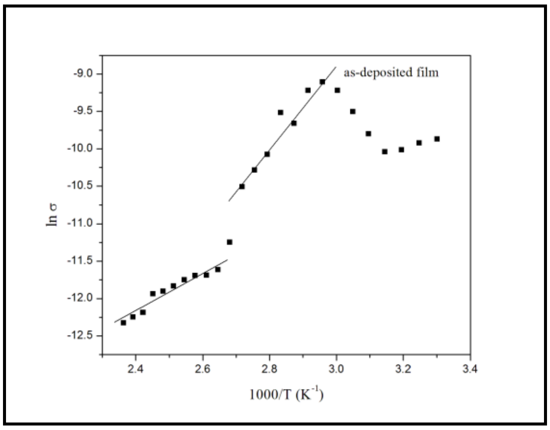


Figure.6 Photoluminescence spectra of CIS thin film

Electrical properties

The dc conductivity of as-deposited and annealed CIS film has been measured as a function of temperature range of 30˚C to 150˚C as shown in figure 7 and 8. The resistivity was higher for as-deposited film and it decreases with annealing temperature showed improvement in electrical properties and confirming the semiconducting behaviour. Non-linear variations were observed which includes discontinuous nature/impurity levels present in the film. The resistivity of as-deposited and annealed CIS film varied at 0.019 MΩ and 0.002MΩ at room temperature. The high resistivity of CIS film (in the order of $\sim 10^6 \Omega$) was associated with excess of Indium present in thin film which can be explained by nanocrystalline nature/defect states[16,24]. From the slope of the plots, the activation energy has been calculated and is found to be 0.5eV and 0.20eV for as-deposited and annealed CIS film respectively.



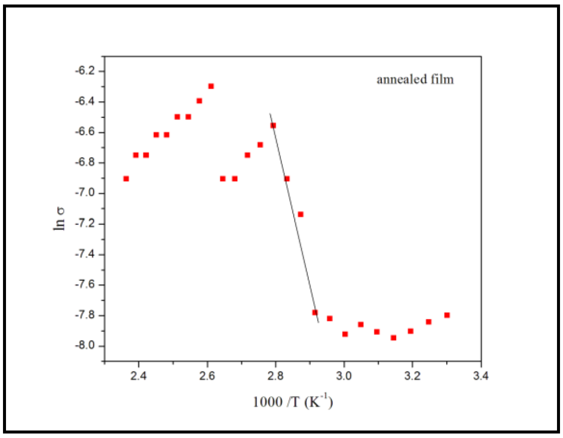


Figure7. Arrhenius plot of as-deposited CIS film

Figure 8. Arrhenius plot of annealed film

Conclusion

$CuInS_2$ thin film was successfully deposited by nebulized spray pyrolysis method by using $CuCl_2$, $InCl_3$ and $CS(NH_2)_2$ as precursor material at a growth temperature of 350˚C. Sprayed CIS film exhibited chalcopyrite structure with preferred orientation along (1 1 2) direction. The grain size of as-deposited and annealed film was in nanometer scale. Secondary phase of In_2S_3 and Cu_2S phase were present in annealed CIS film. From EDAX analysis, it was confirmed that the deposited film was In rich CIS film. High resistivity and poor crystallinity were observed due to nanostructured nature for CIS film. The absorption edge was blue shifted for annealed film which in turn increases the bandgap from 1.47eV to 1.51eV owing to nanostructure nature/impurities present in film. The activation energy of as-deposited and annealed film was obtained from Arrhenius plot and was found to be 0.5eV and 0.20eV respectively.

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