OPEN ACCESS INTERNATIONAL JOURNAL OF SCIENCE & ENGINEERING

GROWTH AND CHARACTERIZATION OF CuInSe$_2$ THIN FILMS

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Abstract: **The present article reports about synthesis of copper indium di-selenide (CuInSe$_2$) thin films by large area depositing, user friendly and cost effective solution growth technique at room temperature on glass substrate. These as deposited thin films are characterized for physicochemical as well as optoelectronic properties using X-ray diffraction (XRD), energy dispersive X-ray spectrum analysis (EDAX), scanning electron microscopy (SEM), UV-Vis absorption spectra and I-V studies under dark and illumination conditions. From XRD pattern (112), (220) and (312) planes are obtained confirming the CuInSe$_2$ phase formation, the elemental composition is confirmed from the observed elemental proportion in EDAX spectra. Uneven distribution of granular, spherical, hazy particulates is observed in SEM images. The UV-Vis absorption spectrum shows an absorption peak centered at approximately 380 nm confirming the exciton induced charge transfer process. Electrical properties measured from the I-V response shows semiconducting behavior of CuInSe$_2$ films with an average charge mobility of around 260 cm^2 Vs^{-1}.**

Keywords – *CuInSe$_2$ thin film, Physicochemical and optoelectronic properties, Exciton induced charge transfer.*

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I INTRODUCTION

CuInSe$_2$ materials have attracted considerable interest of researchers due to wide variety of applications, ranging from electronics, catalysts to sensor arising from their unique or improved properties, which are primarily determined by size, composition and electronic structure [1] [3]. CuInSe$_2$ being direct band gap materials is highly investigated for its application in solar cell along with the other buffer layer materials like CdS, CdSe etc. The heterojunction configuration of CuInSe$_2$ thin film has so far yielded almost 13 % conversion efficiency when synthesized using sophisticated techniques. Literature survey represents several methods such as physical and chemical for the synthesis of CuInSe$_2$ thin films such as sputtering [2], high vacuum evaporation, electro-deposition, spray pyrolysis [4] [6] etc., however, most of these techniques are sophisticated and usually require high processing temperature, vacuum etc. this will naturally increase the cost of production and processing too, hence to reduce the production cost and use user friendly, large area depositing technique we have followed chemical synthesis method [7]. The surface morphology, composition and interface are the main properties which are responsible for high yielding of conversion efficiency. The surface morphology and composition are the main major properties which can be controlled and optimized in chemical synthesis method, although very few reports are available showing the use of chemical synthesis method for preparation of CuInSe$_2$ thin films in combination with other buffer layer but all those reveals confirmed controlled synthesis of heterojunction thin films while rarely a literature may be available mentioning about synthesis of CuInSe$_2$ thin films alone on substrate at room temperature [8] [9].

Hence considering the advantages of chemical synthesis method we have deposited the CuInSe$_2$ thin films by cost effective chemical bath deposition method at room temperature on glass substrate and characterized its physicochemical and optoelectronic properties.

II EXPERIMENTAL DETAILS

CuInSe$_2$ thin films have been prepared by simple chemical bath deposition method using chemical ingredients Indium Chloride (InCl$_3$) 99.99%, Selenium powder, Copper Chloride (CuCl$_2$) 99.99% procured from Aldrich Chemical Co. and anhydrous ethylene diamine of Merck Chemical Co. In a typical synthesis process, InCl$_3$ and CuCl$_2$ were added to 20 ml of ethylene diamine and heated at ~160ºC for more than 5hr with constant stirring; selenium (Se) powder was added into 120 ml of ethylene diamine and heated at ~200ºC

with magnetic stirrer for more than 5 hr. These mixtures of $InCl_3$ and $CuCl_3$ solution were then mixed with Se solution and allowed to cool on a substrate to settle as $CuInSe_2$ thin films, upon completion of reaction, the solution was allowed to cool naturally at room temperature. These thin films are then washed with distilled water and absolute ethanol to remove the excessively attached by-products. These as deposited thin films of $CuInSe_2$ were then characterized for structural, compositional, morphological, optical and electrical properties.

The structural analysis was performed using X-ray diffraction (XRD) patterns obtained from the films recorded on Bruker AXS, German (D8 Advanced) diffractometer in the scanning range 20-60° (2θ) using Cu Kα radiations with wavelength of 1.5405 Å. The compositional and surface morphology analysis of thin films probed from energy dispersive X-ray (EDAX) facility attached scanning electron microscopy (SEM) instrument JOEL-JSM-5600. The optical properties of the films studied in absorbance mode in 300-1000 nm range using UV-Vis spectrophotometer Perkin Elmer Lamda-25. The electrical properties were performed on Lab-Equip I-V measurement setup 2004 interfaced with computer.

III RESULTS AND DISCUSSION

Figure 1 represents the XRD pattern obtained from the $CuInSe_2$ thin films used for structural and materials identification, from figure it can be observed that three prominent peaks identified as plane (112), (220) and (312) being due to $CuInSe_2$ chalcopyrite tetragonal crystal structure [10] with lattice constants of 0.5936 nm and 1.0784 nm for a and c respectively, which are in good agreement with the standard JCPDS card 40-1487. In addition, no peaks of other impurities were detected, indicating the high phase purity of $CuInSe_2$ thin films. The average crystallite size calculated using Debye Scherer formula was found to be ~30 nm.
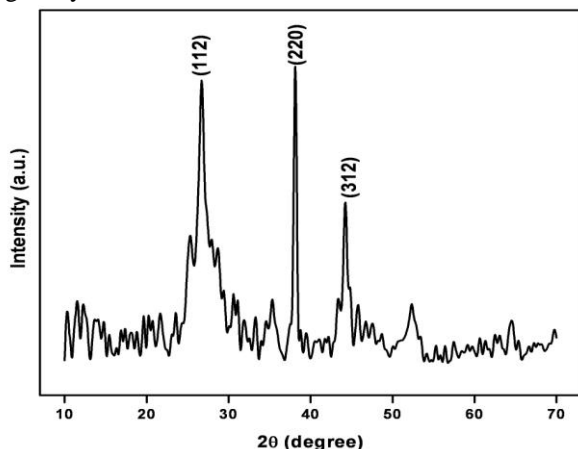

Figure 1 XRD pattern obtained from the as deposited CuInSe₂ thin films grown by soft chemical route at room temperature

Elemental compositions of the thin films were determined using energy dispersive X-ray spectra analysis (EDAX) as shown in figure 2. EDAX shows identical values that confirms the compositional uniformity of the sample with an observation of peak for Cu, in and Se along with peaks for C, O, Si and Cl which may have been caused due to the presence of glass substrate. The elemental atomic composition observed were 15.31%, 16.90% and 67.79% for Cu, in and Se respectively.
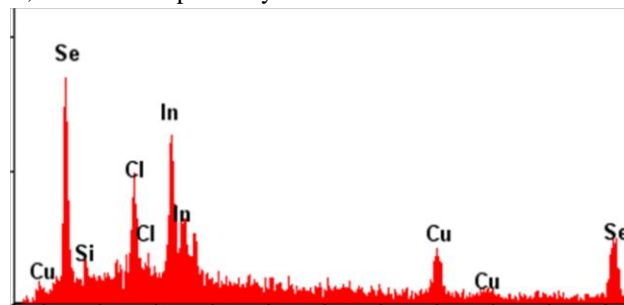

Figure 2 EDAX spectra obtained from the as deposited CuInSe₂ thin films

Figure 3 represents the scanning electron microscopy (SEM) images of $CuInSe_2$ thin films showing irregular, hazy and granular particles distributed over the substrate surface. These rough, irregular shapes of $CuInSe_2$ surface may be helpful in optoelectronic applications specifically surface based sensor mechanism. Thin films of $CuInSe_2$ are always used as an absorber layer for high-efficiency photovoltaic p-n junction solar cells, thus, understanding the optical properties related to the electronic transitions and surface region has been considered to be crucial.
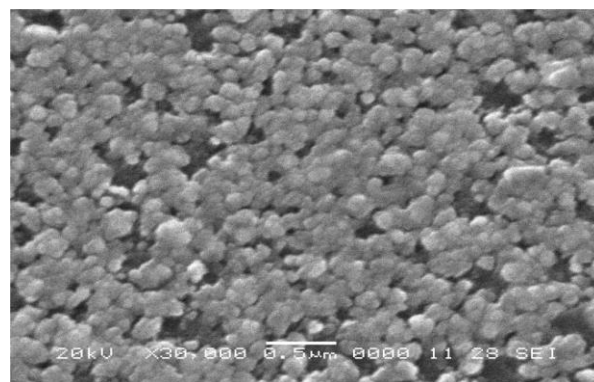

Figure 3 SEM images of chemical route synthesized CuInSe₂ thin films

Spectroscopic absorbance measurements of $CuInSe_2$ thin films shown in figure 4 which shows an absorption peaks at ~380 nm related to the band to band transitions and spin orbit splitting mechanism, variation in spin orbit interaction between Cu and Se of the $CuInSe_2$ is expected to be main cause for the observed absorption band edge [11] [12]. The p-d hybridization in $CuInSe_2$ might be considered responsible for spin-orbit interaction in the chalcopyrite $CuInSe_2$ thin

film, which can also be explained in terms of density of Cu 3d and Se 4p states. Nevertheless, the effect of this hybridization is clearly reflected in the energy band gap value of the CuInSe$_2$ thin film.
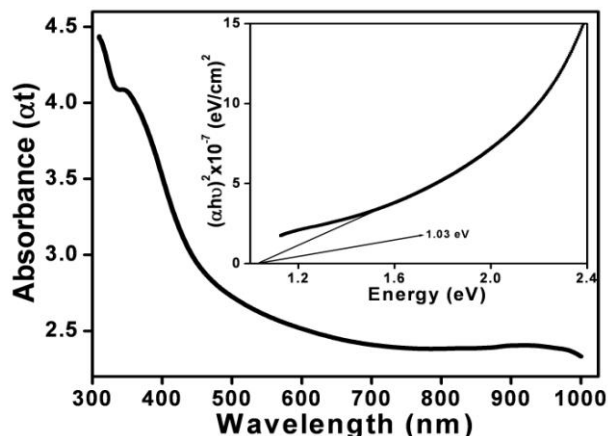

Figure 4 Optical absorbance spectra recorded for as deposited CuInSe$_2$ thin films Inset figure represents the energy band gap of CuInSe$_2$ thin films

Inset in figure 4 shows the plot of $(\alpha h\upsilon)^2$ verses hυ for calculation of energy band gap (Eg), confirming the energy band gap of 1.03 eV, attributed to the p-d interaction in Cu and Se ions in CuInSe$_2$ domains. According to the band theory and results available in literatures about the electronic transitions in the I-III-VI$_2$ group compound (CuInSe$_2$), The upper valence band is formed exclusively by p-d hybridization of Cu 3d and Se 4p, whereas In cations are not involved in band formation. The strength of d-p interaction depends inversely on the energy of separation between the Cu 3d orbital and Se 4p orbital. This repulsive interaction pushes the anti-bonding p-d states that constitute the valence band maxima (VBM) to higher energies. The VBM is composed of Cu 3d orbital that are hybridized with the Se 4p orbital, here the p-d interaction is expected to be balanced so this interaction would be balance the VBM as well as the conduction band minima (CBM).
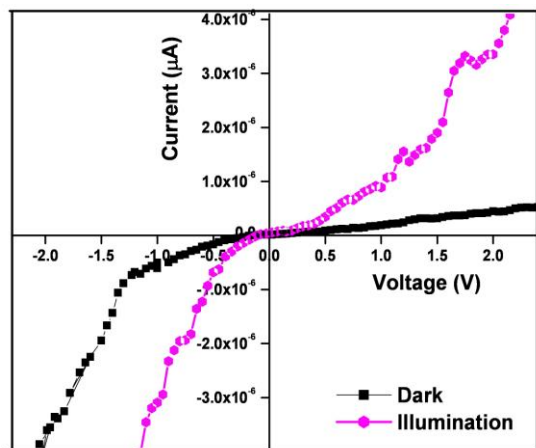

Figure 5 I-V characteristics obtained from as deposited CuInSe$_2$ thin films under dark and illumination conditions

Figure 5 shows plot of I-V characteristics obtained for CuInSe$_2$ thin films under dark and illumination to 100 mW/cm^2 light source. From figure it is clear that, under illumination condition the photocurrent in thin films improves. Observed electrical response can be co-related with observed crystallinity, surface and interface properties of the CuInSe$_2$ thin-films. In the CuInSe$_2$ thin films, the observed grains are expected to be the cause for the enhancement in electrical response by the phenomenon of grain boundary charge transportations [13-16]. Furthermore, the existence of electron hole separator in CuInSe$_2$ and the creation of cation poor surface result in increase in the density of negatively charged acceptors at the surface. Such charged surface defects might be responsible for surface reconstruction and lowering of valence band at the surface of these grains, restricting holes from entering inside it. So the re-arrangement at the grain surface might repel holes, thus, creating free charge zone at the grain surface leading to fast electron transport at the surface.

IV CONCLUSIONS

The ternary I-III-VI$_2$ semiconductor of CuInSe$_2$ thin films have been successfully synthesized using cost effective chemical route on glass substrate and subsequently characterized for physicochemical and optoelectronic properties. The planes (112), (220) and (312) observed from XRD pattern confirms formation of CuInSe$_2$ phase; the EDAX confirms expected and observed elemental compositions. The rough, hazy and irregular distribution of grains over substrate surface represents probable application in surface based phenomenon like sensor. The observed optical absorbance along with the energy band gap at 1.03 eV can be correlated to band to band transition and elemental spin orbit splitting phenomenon. The observed increase in electrical response under dark and illumination condition arising due to surface grain boundry phenomenon confirms the probable application in conductivity instruments like photovoltaic devices.

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