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Chemical Bath Deposited $Cuins_2$ Thin Films and Their Characterization

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ABSTRACT

Chemical bath deposition (CBD) technique has been used for the deposition of $cuins_2$ film on glass slide at very high temperature in alkaline medium. The deposited film showed both chalcopyrite and wurtzite structure. The values of lattice constants are quite close to the reported values. The grain size determined by Scherrer's formula was 22.8 nm. Morphological study showed that film surface is uniform and smooth. The band gap calculated was 2ev higher than bulk $cuins_2$. PL study showed strong emission peak in IR region.

Keywords: $Cuins_2$, CBD, XRD, Thin Film, Chalcopyrite

I. INTRODUCTION

Since last two decades' ternary chalcopyrite materials have drawn attention because they can be used to develop photovoltaic system as an alternative energy source. For high efficiency thin film solar cells $cuins_2$ is drawing attention due to its direct band gap of 1.53ev and high absorption coefficient of $10^5 cm^{-1}$[1]. $Cuins_2$ is having three crystal structure namely.

chalcopyrite (CH) (b) zincblende and (c) wurtzite (WZ) [2]. For the synthesis of films of CIS different methods were reported such as three sources molecular beam epitaxy [3], successive ionic layer absorption and reaction (SILAR) method[4], co-evaporation [5], reactive sputtering [6], electrodeposition [7], spray pyrolysis[8], chemical bath deposition[9]etc. This paper reported the thin film of $cuins_2$ synthesized by using the simplest and inexpensive CBD technique. The technique involves large area deposition, minimum material wastage, controlled process parameters and deposition at room temperature [10].

II. MATERIALS AND METHODS

The copper indium di sulphide ($cuins_2$) thin film was synthesised on microscopic glass slides by CBD technique. Before use glass slide substrate was cleaned several times with detergent and then washed with acetone and deionised water. The cleaned glass slide was dipped vertically in a liquid bath containing $cucl_2.2H_2O$ (0.5M), $incl_3$ (0.5M) and thiourea. TEA and ammonia (25%) were added as complexing agent and maintaining the ph of the liquid bath respectively. The solution was stirred for 10min to prepare homogeneous solution. The ph of the solution bath was ~9.5. The bath temperature was maintained at 80^0C. The deposition time was of 1hr. After 60min of time film was removed from the bath and washed using deionised water and kept for dry. The deposition occurs because of precipitation followed by condensation. The film thickness was measured by using gravimetric method. Panalytical X-ray diffractometer with cukα (1.540^0A) was used for XRD. Optical absorption spectrum was recorded by Elico

SL 210 double beam UV-VIS spectrophotometer. For recording PL sample was excited at 450nm.

III. RESULTS AND DISCUSSION

In Figure 1 the XRD of $CuInS_2$ film is shown. The as deposited film consists of peaks of both chalcopyrite (tetragonal) and wurtzite (WZ) phase of $CuInS_2$.The peaks at $2\theta = 27.8^0$and 31.9^0 are of chalcopyrite $CuInS_2$ (JCPDS-98-065-6271) and at $2\theta = 27.8^0$ and 29.5^0 are of wurtzite $CuInS_2$. Also, one peak at $2\theta = 22.4^0$ corresponds to $Cu_{1.8}S_1$. Peaks at $2\theta = 44.9^0$, 48.5^0 and 56.4^0 corresponds to In_1S_1 (JCPDS-98-008-1341). Also, few peaks appear for Cu_9In_4 (JCPDS-98-010-6556). The film is having multiphase and crystalline in nature. It shows polytypism structure [11]. The XRD data with observed and reported values of lattice constants are

Shown in Table 1. The values of constants a, c is coming close to the reported values. The grain size (D) is calculated by using Sherrer's formula [1].

D value(^{0}A)		Relative Intensities		Hkl	Lattice constant(^{0}A)	
O bs.	1. eported	2. bs.	3. eported	4.	5. bs.	6. Reported
a. $CuInS_2$ at 80^{0}C						
3.958	3.927		35.7 c=13.74	64.4 c =13.6		$(012)_h Cu_{1.8}S_1$
3.400	3.383		100 a=3.92	75 a =3.90		$(010)_w CuInS_2$
3.197	3.194		12 =11.12	100 c =11.10		$(112)_{ch} CuInS_2$ c
3.197 c = 6.4	3.214 c =6.42		12	52		$(002)_w CuInS_2$
3.020	2.994		56.7 c = 6.6	100 c =6.42		$(011)_w CuInS_2$
2.796	2.776		46.9 a = 5.58	5.7 a =5.52		$(004)_{ch} CuInS_2$

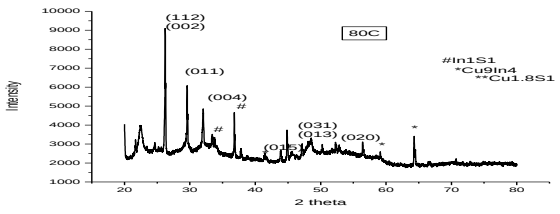

Figure 1. XRD of $CuInS_2$ thin film

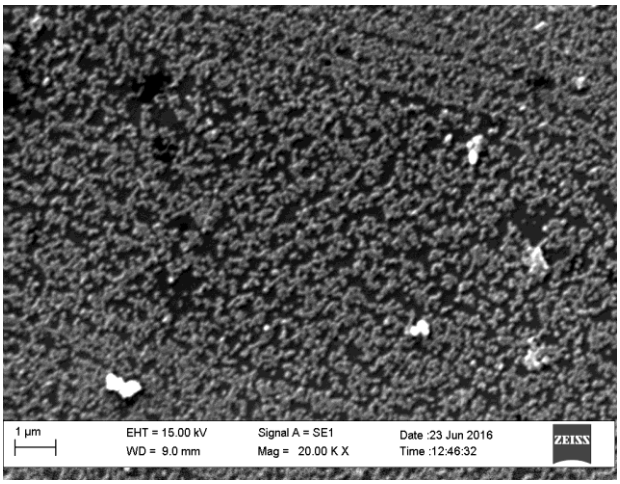

Figure 2. SEM images of $CuInS_2$ thin film

$$D = \frac{K\lambda}{\beta_{1/2}\cos\theta} \quad \text{----------(i)}$$

where 'λ' is the wavelength of X-rays and 'θ' the Bragg's angle (in radian), K is a constant and nearly equals to ~0.9. $B_{1/2}$ is the full width at half-maximum (FWHM).The average grain size of the sample is found to be 22.8 nm.

Table1. XRD data of $CuInS_2$ film (deposition time = 60 min; temperature of deposition = 80°C).

In Figure 2 semof $CuInS_2$ film is shown at 20KX magnification. The film surface is smooth and uniform. It consists of small grains of 100 nm size. M. Krunks et al. [13] reported that isolated grains are seen in copper rich films, inter connected grains are observed in indium rich film and stoichiometric films are smooth consisting of fine grains. On the basis of this we can easily predict that the morphology of the CIS film is stoichiometric.

The optical studies are essential to get information about electronic band structures, localized states; optical transitions etc. The optical absorption spectra recorded at 300nm-1100nm range is depicted in Figure3. It shows that thin film of $CuInS_2$ is having absorption in the IR region with absorption periphery between600-700nm.

The optical absorption coefficient α is related to the optical band gap E_g by the relation

$$\alpha = \frac{c\,(h\nu - Eg)^{1/2}}{h\nu} \quad \text{.....ii}$$

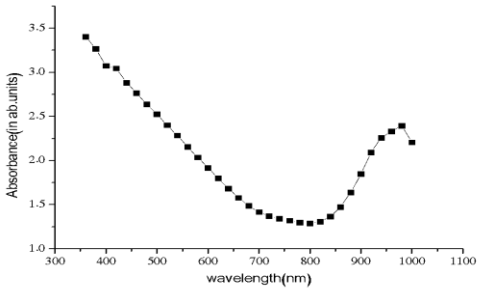

Figure 3. Absorption spectra of cuins2 thin film

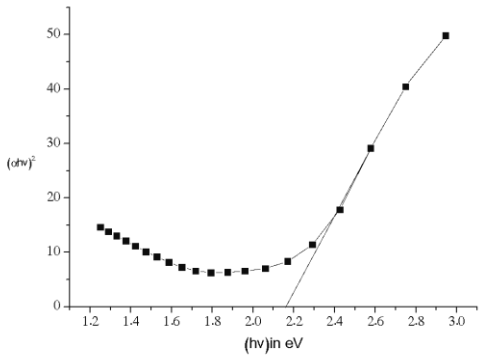

Figure 4. Plot of $(\alpha h\nu)^2$ and (hν)of cuins2 thin film

Where c is a constant [14]. Thus, the extrapolation of nonlinear plot between $(\alpha h\nu)^2$ and (hν) gives the value of band gap of cuins2 thin film as it is a direct band gap material[15-17]. Plot between $(\alpha h\nu)^2$ and (hν) is drawn in Figure 4.The band gap of the film obtained is 2.19 ev which is higher than bulk cuins2 (1.53ev).It showed about 0.66ev blue shift in comparison to bulk cuins2. This increase in the band gap can be associated to smaller particle size which affirms formation of nanostructure.Figure5 shows the PL spectra of cuins2 thin film excited at 450 nm. The emission is basically allied with defects which are emerged during the crystal growth. It is related to deformation of crystallinity due to dislocations and vacancies. The photoluminescence process is a charge transfer process, since the photoluminescence emission associated with the combination of electron from the conduction band, holes in the valence band and change of the near-band-edge as reported by peng et al.2000[18]; zhao et al.2008[19] in their paper. A strong emission peak is obtained in 676nm (Red band emission) in the IR region corresponding to 1.83ev that has 360 mev red shift compared to 2.19ev. This type of red shift may be due to presence of defect levels in cuins2 crystal structure [20].

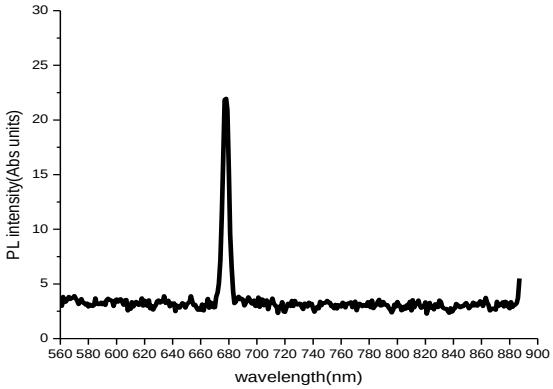

Figure 5. PL emission spectra of cuins2 thin film

IV. CONCLUSIONS

The simple chemical bath deposited cuins2 thin film has been prepared successfully. The film deposition was carried out with simple instruments. The structural study of cuins2 thin film showed both chalcopyrite and wurtzite structure. The calculated values of lattice constants are matching with the reported value. The grain size calculated from XRD is 22.8nm.The SEM micrograph showed that the film is adherent to the surface and it is uniform. No agglomerations were seen. Nano size grains of about 100nm are observed. Higher optical band gap of 2.19ev confirms the formation of nanocrystalline film. PL spectra confirm the formation of large number of defect states or secondary phases.

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