



Studies on quaternary X_2 base CIS thin films for the optoelectronic devices

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Abstract: Nanocrystalline quaternary $CuIn(S,Se)_2$ in the form of thin films is prepared by a simple and inexpensive chemical bath deposition technique. As deposited nanocrystalline quaternary thin films have been characterized by XRD, FESEM, EDAX, TEM, and UV spectroscopy. Nanocrystalline quaternary $CuIn(S,Se)_2$ thin films with appropriate band gap energy have been attracting a great deal of attention because of their potential applications in optoelectronic devices. The results are discussed and interpreted.

Keywords: Nanocrystalline quaternary $CuIn(S,Se)_2$, chemical bath deposition technique, Analytical techniques.

1. INTRODUCTION:

The polycrystalline chalcogenide semiconductors play an important role in solar cell due to their favorable electrical and optical properties. Among the chalcogenide semiconductors, $CuIn(S,Se)_2$ is one of such type materials, which is an important materials for the development of various modern technologies of solid state devices such as solar cells, light emitting diode, detector etc.[1] Nanosphere semiconductors have potential applications in many technical fields [2]. The growth of ternary semiconductors thin films has been studied very extensively in the recent years, since these films play an important role in the fabrication of solar cells due to their favorable electrical and optical properties [3]. It is of great technological interest that $CuIn(S,Se)_2$ thin films have been used as a wideband gap window material in heterojunction solar cell and in photoconductive devices.

CIS-based quaternary compounds like $CuIn(Se,S)_2$, $Cu(In,Ga)Se_2$, $Cu(In, Al)Se_2$, $Cu(In, Ga)S_2$ are attracting great interest in recent research for optoelectronic and photovoltaic applications [4]. The chalcopyrite copper indium sulfur selenide compounds $CuIn(Se,S)_2$, (CISSe) are highly absorbing materials (10^{-5} cm^{-1} near the band edge) that can be used in the fabrication of thin film solar cells owing to their direct band gap, which lies in the range of 1.05–1.67 eV, which is close to the optimal value for embracing the solar spectrum[5].

In order to obtain Copper indium sulphoselenide films, there are several deposition methods like Single-Bath Electro deposition,[6] electro deposition [7] among this technique chemical bath deposition (CBD) method has attracted much attention since it is confirmed as a simple and promising technique to obtain device quality films. CBD is a simple which is also used to deposit the semiconductor on photovoltaic device. The CBD method appears suitable for large area industrial process because it is the least expensive and a low temperature method. Another advantage of the CBD technique is its ability to deposit very thin films (50 nm) in a conformal manner on a rough substrate surface. The rate of growth in CBD is controllable by pH, temperature, time of deposition and the relative concentrations of the reactants in the bath solution [8, 9]. In recent years, major attention has been given to the investigation of electrical and optical properties of $CuIn(S,Se)_2$ thin films.

In this work, Copper indium sulphoselenide thin films were prepared by chemical bath deposition technique. Phase purity and surface morphology properties were studied using X-ray diffractogram (XRD) and Field Emission Scanning Electron Microscope (FESEM). Chemical composition was studied using energy dispersive spectrophotometer (EDAX). Optical band gap property was investigated using UV-Spectroscopy. Microstructural characterization at high magnifications was carried out using a transmission electron microscope (TEM). This work reports the effect of Cu/In composition on structural, surface morphology, micro structural, and optical properties of these thin films.



2 Experimental details:

2.1 Preparation of Nanosphere CuIn(S,Se)₂ Thin Films

The physical properties of the chemical deposition of CuIn(S,Se)₂ films are dependent upon the growth parameters such as the bath temperature, the relative concentrations of the various reactants in the solution the pH value and the type of substrate. The starting materials used were cupric chloride, indium trichloride, sodium sulphides, elemental selenium, and thiourea. The chemical bath deposition technique was used to deposit the thin films of CuIn(S,Se)₂ on glass substrate. For the deposition of CuIn(S,Se)₂ thin films a well cleaned glass substrate was immersed vertically in the solution and temperature of bath maintained at 60 °C for 1 to 3 hours.

The process involves the reaction of Cu⁺, In³⁺, S²⁻ and Se²⁻ ions in demonized water solution. Elemental selenium (99.95%) was dissolved in an aqueous solution of sodium sulphite (pH > 9) at 90o C to form a partial unstable Na₂SeSO₃ compound. In order to prepare the films, the tetraamine copper was mixed with complex ion of indium and citrate. To this solution, mixture of thiourea and Na₂SeSO₃ was added. In the solution, unstable Na₂SeSO₃ yields Se²⁻ and SO₃²⁻ ions. Sulphite ions reduce Cu(NH₃)₄²⁺ and generate Cu⁺ ions. The temperature of solution was held at 60° C for about 2 h and uniform films of CuIn (S, Se) ₂ were obtained on glass substrates [8].

Finally, the substrates then washed with distilled water and annealed at temperature 225 °C for 10 minute. In order to obtain good quality of thin films, following parameter were adjust such as deposition time, temperature of deposition, pH of the solution is adjust by addition of liquid ammonia drop in the prepared solution. The optimum value of time, temperature and pH were tabulated in Table 1.

Table (1): Optimum parameter to obtain CuIn(S,Se)₂ thin films

Deposition Parameter	Optimum value / item
Deposition time	70 min.
pH	9
Concentration of precursor Cupric chloride, indium trichloride, sodium sulphides, elemental selenium, and thiourea	0.1 M
Solvent	Deionized water
Deposition temperature	60 °C
Annealed temperature	225 °C

3. Characterizations, Results and Discussion:

3.1 Structural properties

➤ X-ray diffraction

The phase purity of the film was analyzed with X-ray diffractogram (Miniflex Model, Rigaku, Japan) using CuK α radiation with a wavelength of 1.542 Å. The structural characterization is very important in explaining structural, micro structural and electrical properties of CuIn(S,Se)₂ thin films. The X-ray diffraction patterns were recorded from 20 to 80° as shown in Fig (1).

The sharp diffraction peaks additionally indicated high sample purity. There is no shift of the diffraction line position for the nanocomposites thin film samples. The broad diffraction peaks indicates the nanocrystalline nature of the component crystal in nanosphere. The observed peaks (+) (112), (200)/(004), and (204)/ (220) are match with standard JCPDS data of CuIn(S,Se)₂. One additional peak for (533) plane was observed for Cu₂S(*) phase respectively. It may be form due to combination of Cu, In, S and Se material.

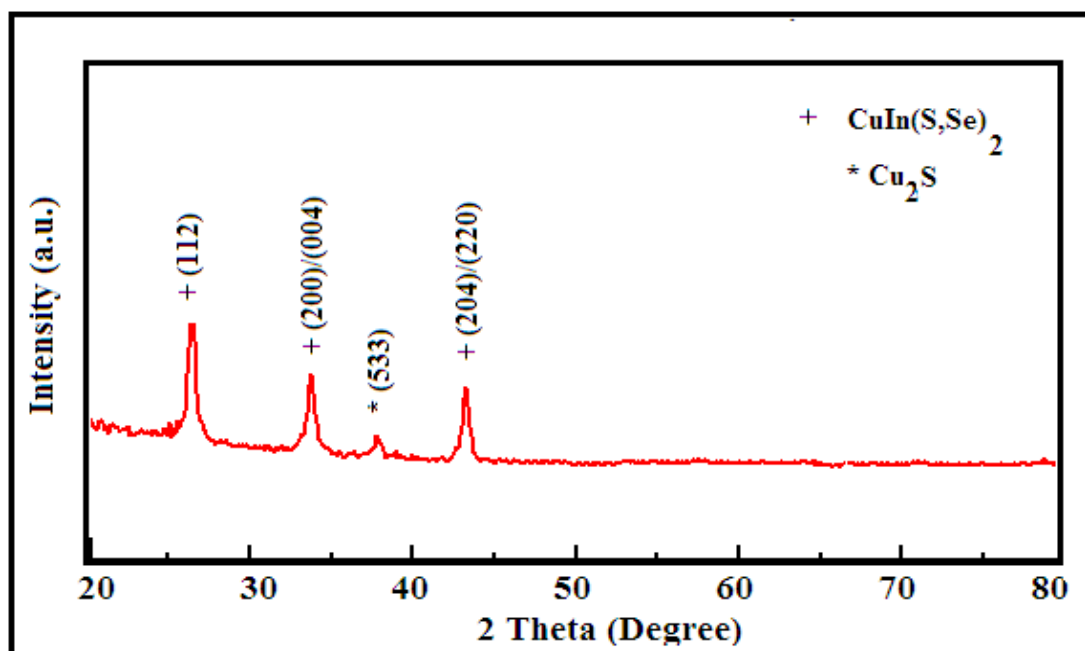


Figure (1): X-ray diffractogram of CuIn(S,Se)_2 thin film.

The average crystallite size of CuIn(S,Se)_2 thin film samples were calculated by using the Scherrer formula,

$$D = 0.9\lambda/\beta\cos\theta \text{ ----- (1)}$$

Where, D = Average crystallite size

λ = X-ray wavelength (1.542 Å)

β = FWHM of the peak

θ = Diffraction peak position.

The average crystallite size was calculated around in the range of 19 nm respectively.

3.2 Quantitative Elemental Analysis (EDAX)

The EDAX measurement has been carried out to obtain element compositional and combining information of the CuIn(S,Se)_2 thin film. The quantitative elemental analysis of the as prepared films was carried out at room temperature.

Table 2 depicts the elemental composition of the thin films from EDAX spectra. It indicate that the formation of CuIn(S,Se)_2 thin films. Theoretically expected stoichiometric composition of CuIn(S,Se)_2 (in terms of at %) is: Cu =25, In = 25, Se = 25, S=25. It is clear from Table 2 that the films are nonstoichiometric formation [9].

Table (2): Quantitative elemental analysis as prepared CuIn(S,Se)_2 thin films.

Sample No.	At %				Cu/In at %	Wt %				Cu/In wt %
	Cu	In	S	Se		Cu	In	S	Se	
G1	38.45	9.13	37.98	14.4	4.21	39.42	11.70	35.40	13.48	3.36
G2	39.69	10.61	34.44	14.26	3.75	35.69	12.44	39.61	12.26	2.86
G3	36.45	11.76	34.68	17.11	3.09	29.67	10.46	34.67	25.2	2.83
G4	31.33	10.61	36.40	21.66	2.95	27.41	11.69	29.99	30.91	2.34
G5	29.67	11.54	34.59	24.20	2.57	24.69	13.52	31.42	30.37	1.82
G6	22.28	16.33	31.43	30.07	1.35	20.13	16.69	29.11	12.42	1.20

3.3. Surface Morphology Study

➤ Field Emission Scanning Electron Microscope

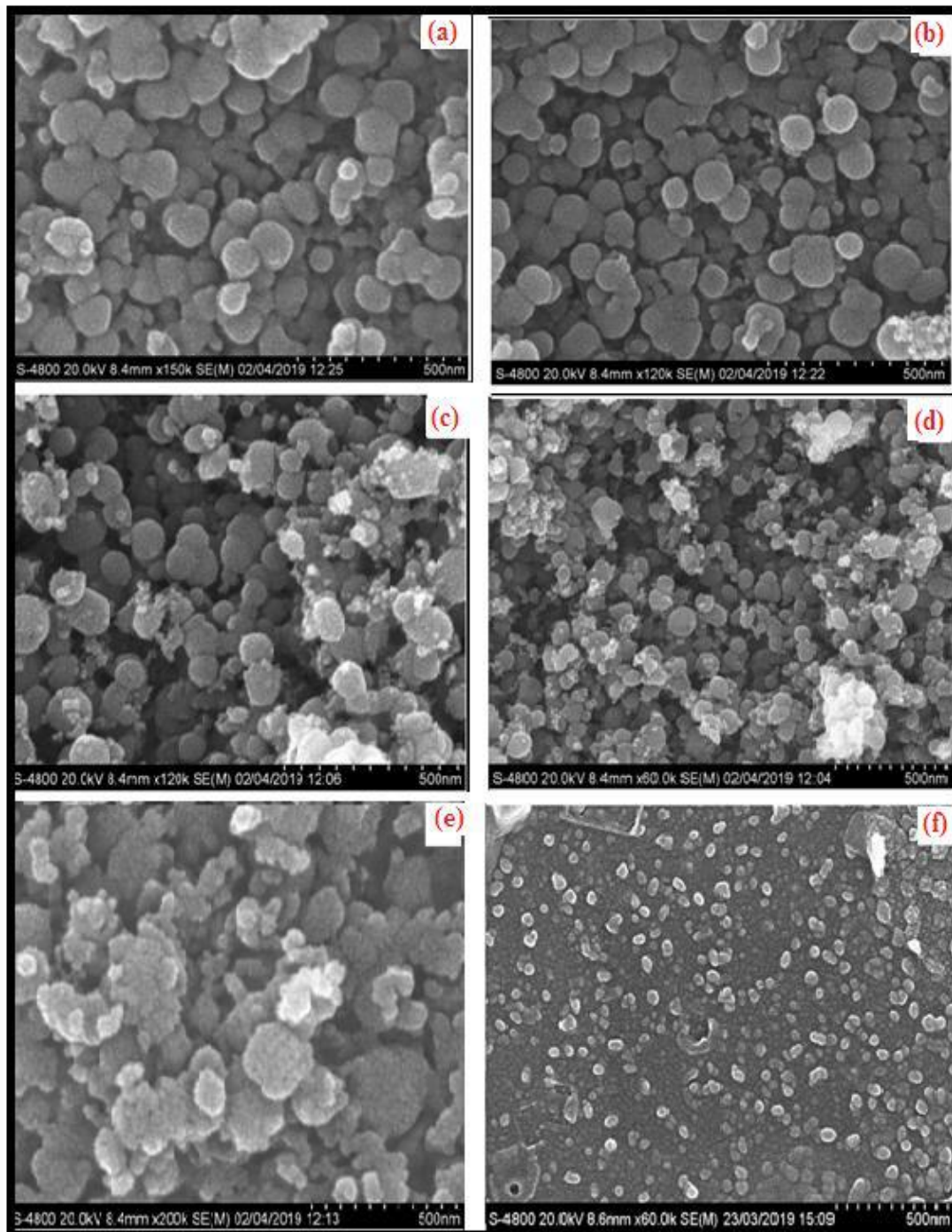


Figure (2): (a), (b), (c), (d), (e) and (f) shows FE-SEM images of CuIn(S,Se)_2 thin film for sample G1, G2, G3, G4, G5 and G6.

The surface morphology of the prepared film was analyzed using a field emission scanning electron microscope coupled with energy dispersive X-ray analysis (EDAX) (FE-SEM, JEOL. JED 6300). FESEM images of CuIn(S,Se)_2 thin films were investigated in Fig (2). Field Emission Scanning electron microscope resolves nanoparticle associated with the film even at high magnification of “20E+3”. Fig (2) (a), (b), (c),(d),(e) and (f) shows the sphere formation of the particle for CuIn(S,Se)_2 thin film. Fig. (2) represents that the resulting particles are almost spherical in shape.

In Fig. (2) (a) shows agglomerations of the grains with low at ratio of Cu/In. While in Fig. 2 (b-f) shows well appear to be sphere grain morphology. No cracks can be found, which is beneficial for its photovoltaic applications. The films were crystalline in nature.

Grain size were found to be in the range of 23 to 46 nm respectively. It is observed that the grain size decreases with increase in Cu/In ratio, the films are obtained has a nanosphere like structure as Cu/In ratio composition, so it may be useful for photovoltaic applications [10-15].

3.4 Microstructural properties using TEM, SAED and HRTEM

The crystallinity and morphology of nanocomposite samples were examined using TEM. Fig. 3 (a-b) represents the TEM image of the thin film sample G5 images at different magnification scale. The particles were uniformly distributed on film surface. The morphology of the particles is as spherical in shape.

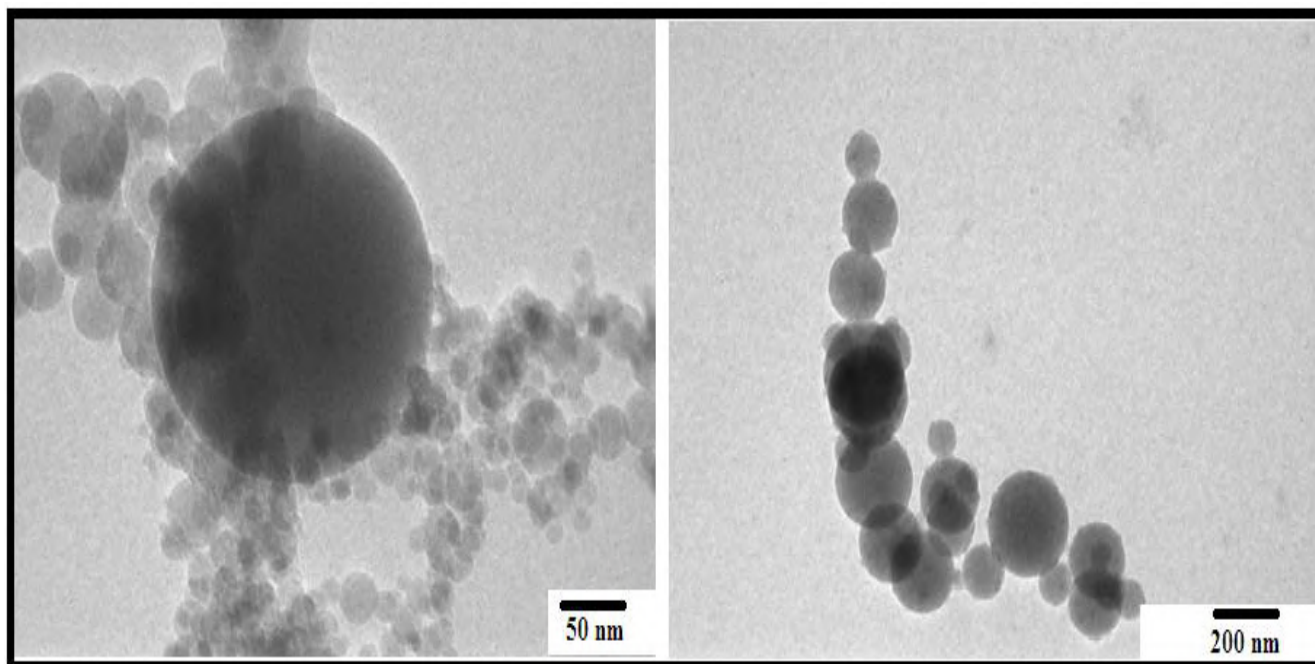


Figure 3 (a-b): TEM images of porous nanosphere $\text{CuIn}(\text{S,Se})_2$ for the sample G5 (Using different magnification scale).

To obtain the TEM images, we used sample G5. We scratched the film surface and mixed the powder with ethanol. The powder was then held using a copper grid and the agglomerated particles were then observed using a transmission electron microscope.

The difference in size can be due to the measurement method as FESEM constructs an image based on the field emission scattered electron profile, while TEM gives an electron-transmission-based image. The microstructure property of prepared nanosphere $\text{CuIn}(\text{S,Se})_2$ thin films was further characterized by SAED pattern. Fig.3 (a) shows a high resolution transmission electron micrograph image of porous nanosphere $\text{CuIn}(\text{S,Se})_2$ thin film.

3.5. Optical Properties Using UV-Spectroscopy

The study of optical properties of $\text{CuIn}(\text{S,Se})_2$ thin films is having special implication in the field of science, technology and industry for developing new optical devices. Optical absorption study provides useful information which is helpful to analyze band gap of thin film which are directly related to particle size. As we know that band gap of thin films is important for designing the photovoltaic cells [16].

The optical absorbance of the films was measured using UV-visible-2450 spectrophotometer at room temperature. Fig (6) shows the optical absorption spectra of nanosphere $\text{CuIn}(\text{S,Se})_2$ thin films were carried out in the wavelength (λ) of range 200-800 nm. The variation of absorbance with wavelength (λ) is as shown in Fig (4). The band gap energies of the samples were calculated from the absorption edges of the spectra. For the all samples it was shows that, gradual decrease in absorbance with the increase in wavelength.

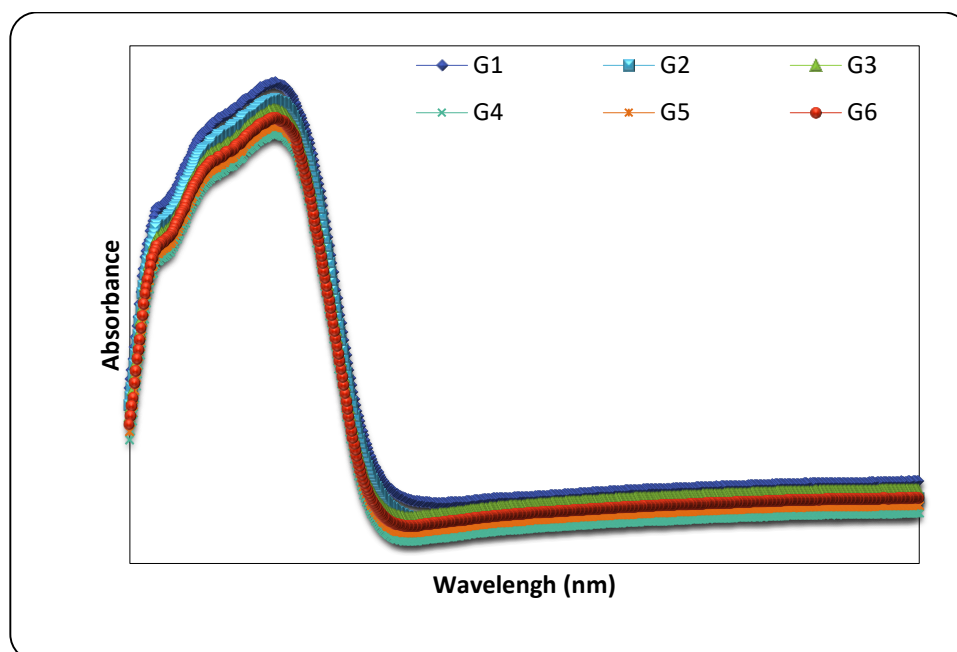


Figure (4): Variation of absorbance with the wavelength in nm for samples G1, G2, G3, G4, G5 and G6.

The slope drawn from the start of an absorption edge (the onset of absorbance) and horizontal tangent had drawn on absorption minimum and intercepted each other at some point. The effects of Cu/In composition on the band gap (E_g) values of the $\text{CuIn}(\text{S},\text{Se})_2$ films have been studied.

In order to obtain the band gap, the absorption coefficient (α) was calculated from the absorption data. Optical band gap energies of the samples were observed to be slightly varying from 1.54 to 2.24 eV [17].

Band gap energy was slightly larger as compared to reported band gap energy it may be formation of nanocrystalline nature of thin films. It is well known that a significant increase in the band gap energy is possible when the size of crystallites reaches the size of the quantum dots. It can be seen that the band gap varies with Cu/In ratio in a nonlinear way [18]. Thus these materials are having good scope to be used in solar cells.

Table (4): Measurement of Cu/In at% ratio, grain size and optical band gap energy.

Sample No.	Cu/In at% ratio	Average grain size from FESEM (nm)	Optical band gap from UV-VIS (eV)
G1	4.21	43	1.54
G2	3.75	39	1.76
G3	3.09	35	1.89
G4	2.95	29	1.97
G5	2.57	26	2.13
G6	1.35	23	2.24

It is also clear from Table 5.4, grain size decreases from 43 nm to 23 nm with increase in Cu/In at ratio while optical band gap energy goes on increasing with increase in Cu/In at ratio in the thin films. This may be due to the improvement in the crystallinity with increase in Cu/In at ratio which leads to minimum



It seen that from table 4, the slightly increase in the optical band gap energy of the films with increasing film in Cu/In at ratio can be attributed to the decrease in the grain size.

4. CONCLUSIONS:

Copper indium sulphoselenide ($\text{CuIn}(\text{S},\text{Se})_2$) films were deposited on to glass substrate by using simple chemical bath deposition technique. The deposition parameters were optimized to obtain good quality of ($\text{CuIn}(\text{S},\text{Se})_2$) thin films. The films obtained were uniform and had good adherence to the substrate. The structural investigation using XRD reveals that formation of $\text{CuIn}(\text{S},\text{Se})_2$ thin films. Surface morphology studies confirm that the as-prepared Copper indium sulphoselenide thin films were nanosphere structure. The elemental analysis of the films indicate that the films are nonstoichiometric. The values of band gap energy go on increasing with the decrease in Cu/In ratio. Large band gap energies, grain sizes estimated from XRD, FESEM, TEM and AFM observations support that the films would be nanostructured consisting of nanocrystalline grains. This study will have significant impact on the use of Copper indium sulphoselenide in optoelectronics devices.

5. Acknowledgements

The authors are thankful to Principal, Z. B. Patil Arts, Science and Commerce College, Dhule, for providing laboratory facilities for this work.

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