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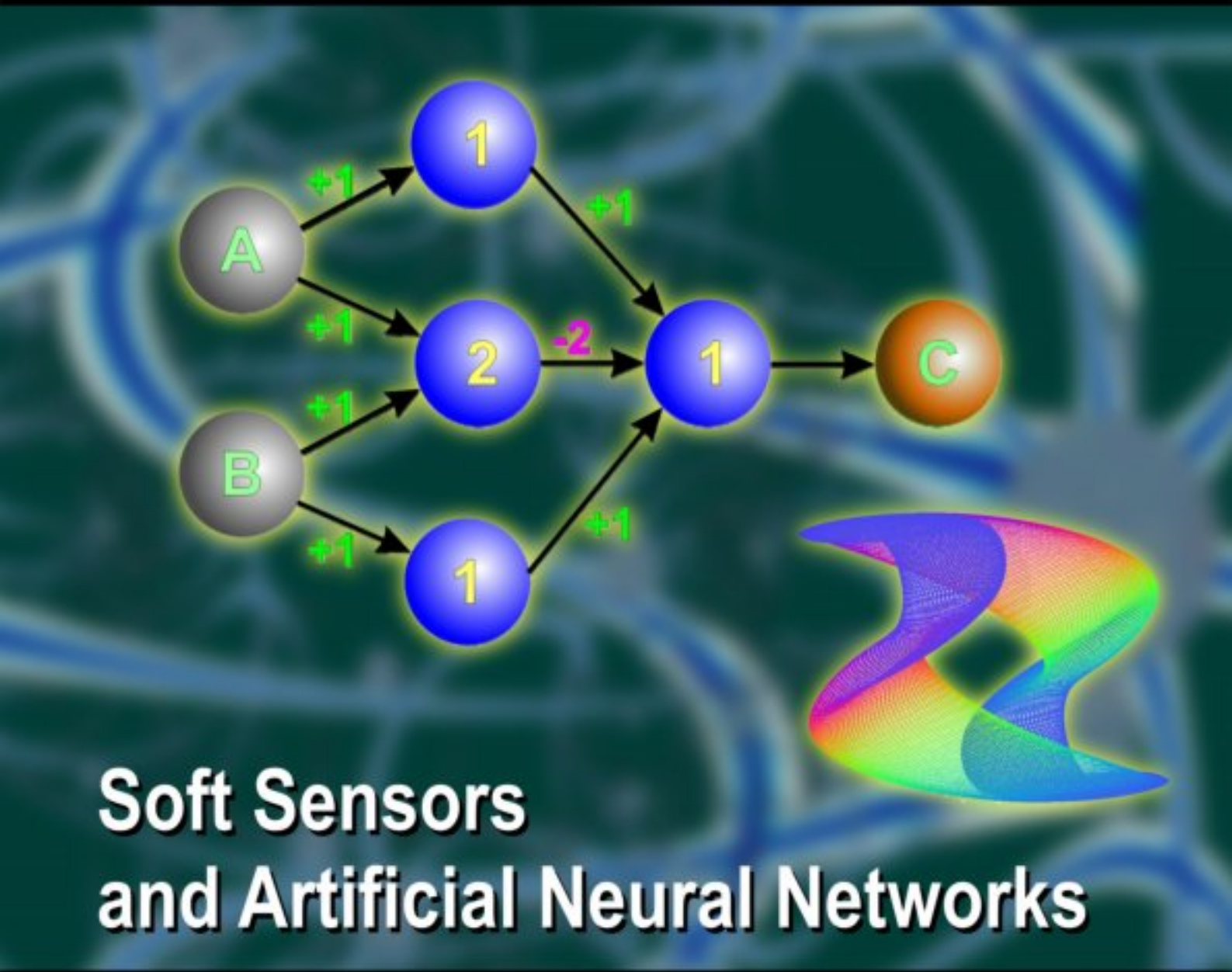

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General Editor: professor Nikolay V. Kirianaki, phone: +380 322 762971, e-mail: ifsa@sensorsportal.com
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Structural and Optical Properties of Chemical Bath Deposited $CuIn(S,Se)_2$ Thin Films

R.H. BARI, L.A. PATIL*
Materials Research Lab, P.G. Dept. of Physics, Pratap College,
Amalner 425 401, India
*Corresponding author: E-mail: rameshbari24@yahoo.com

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Abstract: Thin films of $CuIn(S, Se)_2$ have been prepared by chemical bath deposition technique at 60^o C on glass substrate. The deposition parameters such as pH, temperature and time have been optimized. All films were characterized by X-ray diffraction (XRD), Scanning electron microscopy (SEM), Energy dispersive X-ray analysis (EDAX), and Absorption spectroscopy. The morphology of the $CuIn(S, Se)_2$ was found to be nonstoichiometric. The set of films having different elemental compositions was prepared by varying Cu/In ratio from 1.86 to 12.15 (at %). The films with band gap energies varying from 1.15 eV to 1.54 eV were synthesized by varying composition.

Keywords: Thin films, $CuIn(S,Se)_2$; Deposition parameter; Composition; Grain size; Band gap energy

1. Introduction

Polycrystalline $CuInSe_2$ thin films (with energy band gap=1.04eV) are one of the most widely used materials for solar cell application. The feasibility of alloying $CuInSe_2$ with either Ga or S has enabled the production of quaternary $Cu(In,Ga)Se_2$ or $CuIn(S,Se)_2$ with energy gap varying from 1.04 to 1.68 eV. Significant improvement in the open circuit voltage was attained in $Cu(In,Ga)Se_2$ due to the increased energy band gap, thus leading to the achievement of solar cell efficiency of about 18% [1].

A number of thin film growth technologies such as spray Pyrolysis [2,3], electrodeposition [4-6], RF sputtering [7, 8], chemical vapor deposition technique [9] etc. have been investigated for the fabrication of $CuInSe_2$ and related thin film compounds.

Chemical bath deposition is well known, simpler and cheaper. It is reported [10-12] that the $CuInSe_2$ films have been prepared by chemical bath deposition technique.

Efforts are made in present article to synthesize $CuIn(S,Se)_2$ thin films, by varying chemical composition, having band gap energies varying from 1.15 to 1.54 eV.

2. Experimental Procedure

The solution growth technique was used to deposit the films of $CuIn(S,Se)_2$. The starting materials used were cupric chloride, indium trichloride, sodium sulphides, elemental selenium, and thiourea. TEA was used as a complexing agent. Sodium hydroxide and ammonia solution were used to adjust pH of the reaction mixture and to increase the film adherence. To obtain good quality films time, temperature of deposition and pH of the solution were optimized, to be 60 min, 60^{o}C and 10 respectively.

The process involves the reaction of Cu^+, In^{3+}, S^{2-} and Se^{2-} ions in demonized water solution. Elemental selenium (99.95%) was dissolved in an aqueous solution of sodium sulphite (pH > 9) at 90^{o}C to form a partial unstable Na_2SeSO_3 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 Na_2SeSO_3 was added. In the solution, unstable Na_2SeSO_3 yields Se^{2-} and SO_3^{2-} ions. Sulphite ions reduce $Cu(NH_3)_4^{2+}$ and generate Cu^+ ions. The temperature of solution was held at 60^{o}C for about 2 h and uniform films of $CuIn(S, Se)_2$ were obtained on glass substrates. Films were annealed in air at 350^{o}C.

Structural characterization of the films was carried out with RIGAKU X-ray diffractometer system using CuKα radiation with wavelength 1.5418 Å. The optical absorption of the films was measured using Hitachi 330 UV-VIS spectrophotometer. The scanning electron microscopic studies were carried out using the JEOL,JSM-6360A SEM. Elemental analysis was carried out with an EDAX using energy dispersive spectrometer (EDS). The results were quantitated by ZAP standardless correction. An AFM Nanoscope digital instrument with a silicon nitride cantilever was used to probe different portions of the film surface in 'contact mode AFM'.

3. Results and Discussion

3.1 Structural Analysis

Figure 1 shows the diffractogram of the sample 6 scanned in the 2θ range of 20-80^o. The XRD peaks are approximately matching with standard ASTM data indicating the non-stoichiometric CISS $\{CuIn(S,Se)_2\}$. The XRD patterns of films reveal that CISS films are polycrystalline in nature. The grain size was calculated from XRD pattern using Scherrer's formula. It is estimated to be 151 nm.

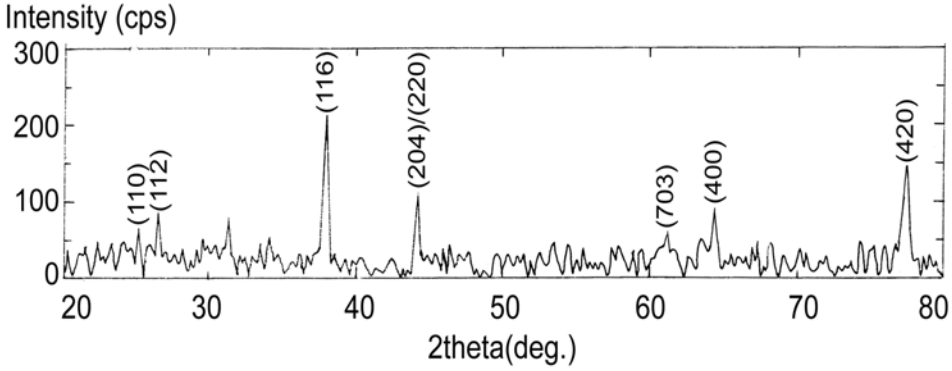


Fig. 1. XRD of the sample.

3.2 Elemental Analysis by EDAX

The quantitative elemental analysis of the as prepared films was carried out at room temperature. Table 1 shows the elemental composition of the films from EDAX. 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 1 that the films are nonstoichiometric in nature. The elemental composition of sample 6 is nearest to stoichiometry. It is clear from Table 1 that at % of In and S go on increasing and at % of Cu and Se go on decreasing.

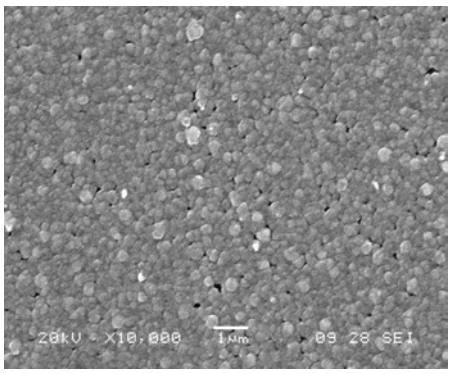
Table 1. Elemental composition of Cu In $(S, Se)_2$ films.

Sample No.	Cu wt%	In wt%	S wt%	Se wt%	Cu at%	In at%	S at%	Se at%	Cu/In (at %)
1	49.31	7.33	3.02	40.33	53.71	4.42	6.52	35.35	12.15
2	45.79	8.23	3.15	42.82	50.30	5.01	6.85	37.85	10.04
3	42.49	13.04	3.32	41.15	47.53	8.07	7.36	37.04	5.88
4	43.24	18.15	5.26	33.35	47.76	11.10	11.51	29.64	4.30
5	40.57	24.3	8.34	26.79	44.05	14.60	17.95	23.40	3.01
6	32.53	31.48	7.83	28.17	36.91	19.77	17.60	25.72	1.86

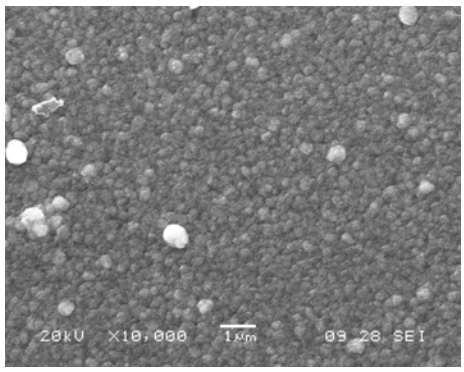
3.3 Microstructure using SEM

Figure.2 show the SEM images of the samples representing surface morphology of as synthesized copper indium sulphoselenide films with different Cu/In ratios. The average particle sizes obtained from the SEM images are tabulated in the Table 2.

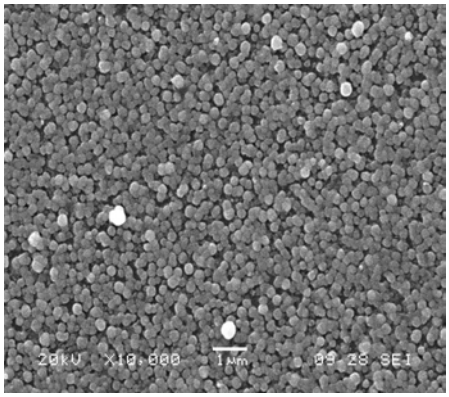
All SEM images show the spherical particles. These particles could be expected to consist of nanostructured grains with grain sizes less than 100 nm. The average particle size goes on increasing with the increase of Cu/In ratio i.e. with the increase of at % of Cu in the film composition. It could be expected that larger the at % of Cu faster would be the chemical activity and larger would be the grain growth.



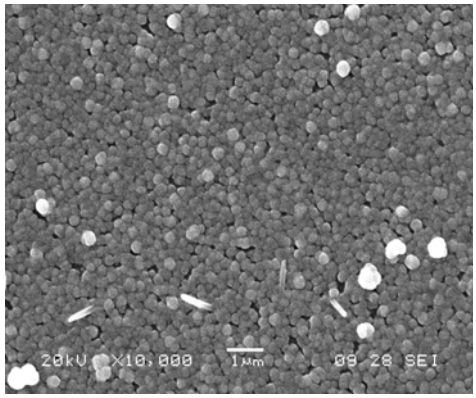
(a) Sample 1



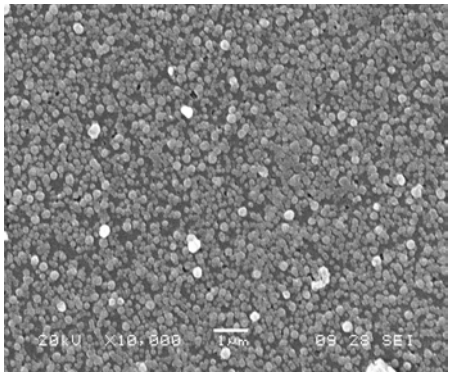
(b) Sample 2



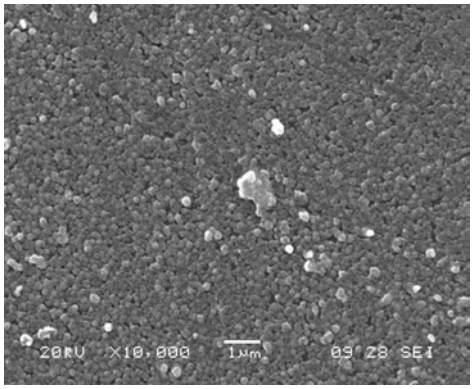
(c) Sample 3



(d) Sample 4



(e) Sample 5



(f) Sample 6

Fig. 2. SEM images of the samples.

Table 2. Dependence of grain size on Cu/In ratio.

Sample	Cu/In (at %)	Grain size (nm)
1	12.15	395
2	10.04	308
3	5.88	294
4	4.30	288
5	3.01	227
6	1.86	176

3.4. Surface Morphology

AFM has been proven to be a unique method to analyze the surface morphology of the films. Fig. 3 (a), (c) shows three dimensional (3D) and Fig (b), (d) shows two-dimensional (2D) images of sample 6. 2D images [Fig (b), Fig (d)] show that the film is covering well to the substrate surface. At the right hand side of the image, an intensity strip shown, which indicates the depth or height of the surface grains along z-axis. It is seen that the film has spherical grains of different diameters with some roughness. This roughness of the film is unavoidable, since particles are in spherical shapes, which shows semi-rounded hills on the upper surface.

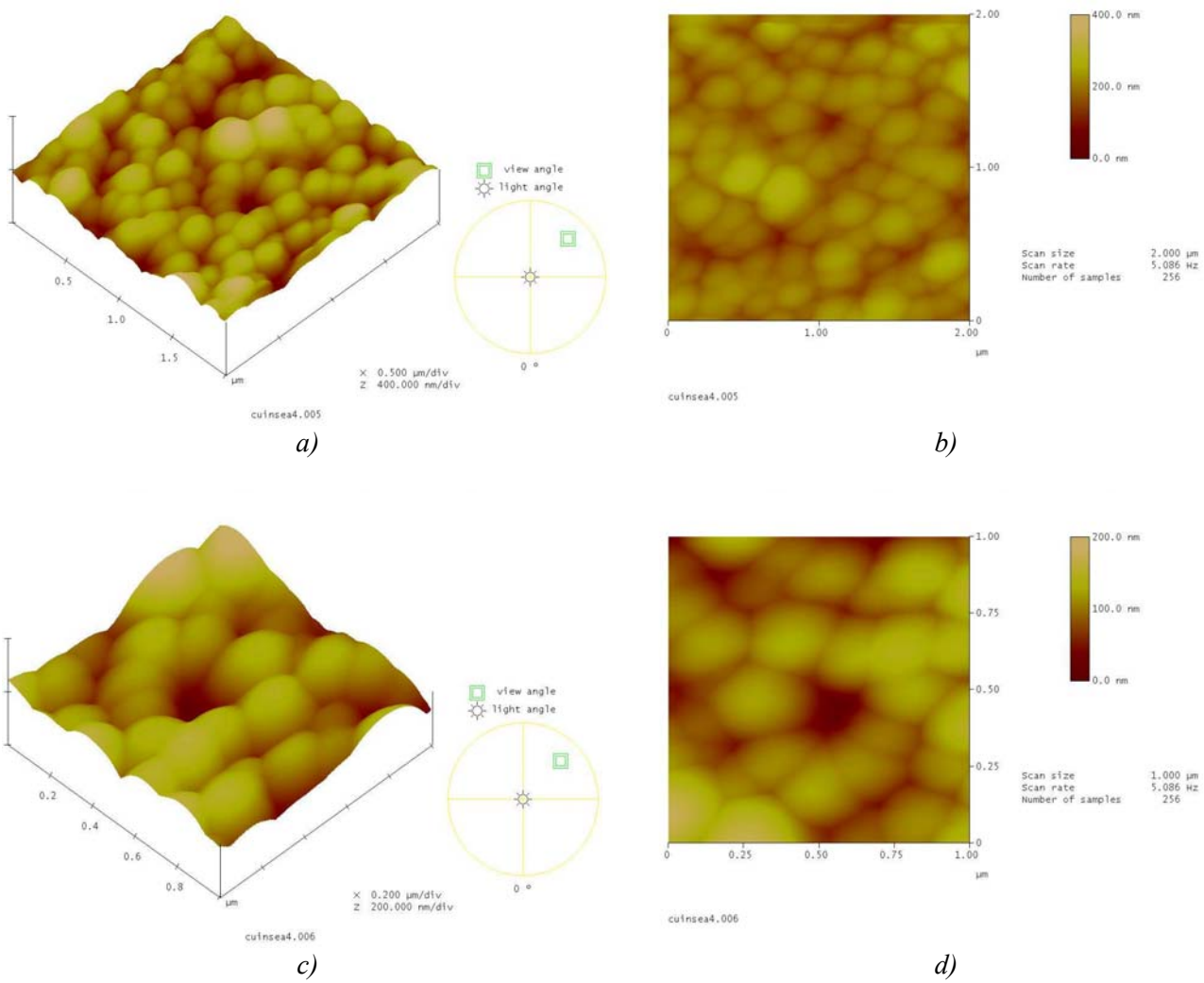


Fig. 3. (a), (b), (c), and (d) AFM pictures of the sample.

There was agglomeration of particles in most of the cases as evident from the 2D micrographs. The root mean square value of the surface roughness of the film (Rg_{AFM}) is calculated from number of scans at different areas of the film. It was observed that the surface roughness of the film is 23.46nm/1μm*1μm. It is reasonable to expect that the particles would have been made up of nanostructured grains as evidenced from X-ray observation.

The average particle size was observed to be 305 nm. This observation reveals that the film to be nanocrystalline in nature. The average particle sizes observed from SEM images and from AFM image are approximately equal.

3.5. Optical absorption

Optical absorption studies of $CuIn(S,Se)_2$ films were carried out in the wavelength (λ) range 400-1300 nm. The variation of absorbance with the wavelength (λ) is shown in Fig. 4. The band gap energies of the samples were calculated from the absorption edges of the spectra. Fig. 4 depicts the absorption spectra of the films.

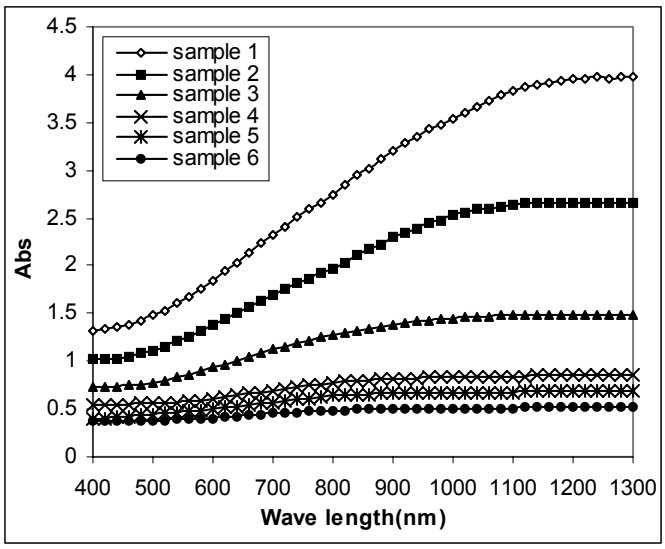


Fig. 4. The absorption spectra of the films.

Table 3 shows the variation of optical band gap energy with Cu /In metal ratio. It is clear from the table that the values of band gap energy go on increasing with the decrease in Cu/In ratio and particle size.

Table 3. Dependence of band gap energies on Cu/In and In /(S+ Se) ratios.

Sample No.	Cu/In (at%)	S/Se (at%)	In/S+Se (at%)	Grain size (nm)	Band gap energy(eV)
1	12.15	0.184	0.11	395	1.15
2	10.04	0.181	0.12	308	1.22
3	5.88	0.198	0.18	294	1.38
4	4.30	0.388	0.27	288	1.42
5	3.01	0.767	0.35	227	1.48
6	1.86	0.684	0.45	176	1.54

4. Summary

Copper indium sulphoselenide films were deposited on to glass substrate by simple chemical bath deposition technique. The films obtained were uniform and had good adherence to the substrate. The EDAX 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. The structural characterization clearly indicates that the particles associated with the films are spherical. Large band gap energies, grain sizes estimated from XRD, SEM and AFM observations support that the films would be nanostructured consisting of nanocrystalline grains.

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References

[1]. T. Nakada and M .Mizutani. 18% Efficiency Cd free Cu(In,Ga)Se_2 thin film solar cells fabricated using chemical bath deposition (CBD)-ZzS buffer layers, *Jpn.J.Appl.Phys* 41 (2002). p. L165.

[2]. P. Agnihotri, P. Rajaram, R. Thangaraj, A. K Sharma, A. Raturi, Structural and optical properties of sprayed CuInSe2 films, *Thin Solid Films* 102 (1983) 291.

[3]. S Shirakata, Murakami Tomonori, Kariya Tetsuya and Isomura Shigehiro, Prepartion of $CuInSe_2$ thin films by chemical spray Pyrolysis, *J. Appl. Phys*. 35 (1996). p. 191-199.

[4]. G. Nealkanth, M. Dhere, C. Lourence, G Ramesh ,G. Dhere, Kazmerski, Composition and structure of $CuInSe_2$ thin films prepared by vacuum evaporation of the constituent elements, *Solar cells* 13 (1984). p.59-65.

[5]. R. Pal, K. Chattopadhyay, S. Chaudhari and A. Pal. Variation of trap state density and barrier height with Cu/In ratio in $CuInSe_2$ films, *Thin Solid Films* 247 (1994).p.8-14.

[6]. L. Thouin, J. Vedel, Electrodeposition and characterization of $CuInSe_2$ thin films, *J. Electrochem. Soc*.142(9) (1995).p.2996-3001.

[7]. F. Adurodija, J. Song, I. Asia, K. Yoon, Formation of $CuIn(Se, S)_2$ thin films by thermal diffusion of sulfur and selenium vapours into Cu-In alloy within closed graphite container, *Solar Energy Materials and Solar Cell.* 58 (1999). p.287-297.

[8]. Y. Uamanoto, T. Yamaguchi, Y. Demizu, T. Tananka, Formation and characterization of $CuIn(Se_{1-Y} S_y)_2$ thin films deposited by r.f. Sputtering, *Thin Solid Films,* 281/282 (1996). p.372-374.

[9]. M. Engelmann, B. McCandles, R..Birkmire, Formation and analysis of graded $CuIn(Se_{1-Y} S_y)_2$ films, *Thin Solid Films* 387 (2001).p.14-17.

[10].J. Garg , R. Sharma, K .Sharma, Characterization of p-$CuInSe_2$ for photovoltaics grown by a chemical deposition technique, *Thin Solid Films* 164 (1988).p. 269-273.

[11].K. Murali. Preparation and characterization of chemically deposited $CuInSe_2$, *Thin Solid Films* 167 (1988).p.L19-L22.

[12].G. Padam. Composition and structure of chemically deposited $CuInSe_2$, *Mat.Res.Bull* 22(6)(1987).p. 789-794.
