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PHYSICS

Properties of $CuIn_{1-x}Ga_xSe_2$ Thin Films

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Abstract. Polycrystalline $CuIn_{1-x}Ga_xSe_2$ thin films have been fabricated. Some physical properties such as lattice parameters, crystal structure and microstructure of $CuIn_{1-x}Ga_xSe_2$ were determined using X-ray diffractomety and scaning electron microscopy. X-ray diffraction analysis showed that the films with $x \leq 0.5$ have a chalcopyrite structure and the films with $x \geq 0.5$ have a zinc blende structure. The lattice parameters were found to vary linearly with composition over a wide range from $x = 0$ to $x = 1.0$. The variation of lattice parameters with composition was found to obey Vegard's law. The variation of the c/a with composition was also linear. The quality of a wide range of $Cu\,In_{1-x}Ga_xSe_2$ thin film absorbers from CuInSe to CuGaSe was evaluated by Photoluminescence (PL) measurements.

1. Introduction

Thin film solar cell technology offers the best hope for obtaining photo voltaic devices with low price and reasonable efficiency One of the most promising thin film materials in this respect is $CuInGaSe_2$ (1). $CuInSe_2$ and $CuInGaSe_2$ based thin film solar cells have demonstrated better efficiencies in recent years (2,3)

Conversion efficiencies exceeding 15% were achieved by several groups (4,6). Both the band gap and lattice constant of $CuInGaSe_2$ thin film absorbers can be adjusted by changing the relative amounts of one or more additional elements from group III (Ga) and group VI (S) (6,7). It has been noted that determination of the important parameter namely the band gap, revealed somewhat different values and different empirical formulae [8-11].

Some physical properties of $Cu\,In_{1-x}Ga_xSe_2$ thin films of various composition prepared by varying Ga content have already been studied (7,12). In this paper, we present structural (crystal structure, microstructure) and photoluminescence properties of $CuIn_{1-x}Ga_xSe_2$ thin films by varying Ga content, x, We have also investigaed variation in the band gap with composition.

2. Experimental Methods

The $Cu\ In_{1-x}\ Ga_x\ Se_2$ films were fabricated by the simultaneous vacuum evaporation of the compound constituents in elemental form on Molybdenum coated alumina substrates. The substrate temperature was kept constant at about 550 °C.

Films of different Ga content or composition index can be made by changing only the evaporation rates of the appropriate sources (13,14). The films generally had a total thickness of approximately 3 µm. X-ray diffractometry was used to determine the lattice and the structure of $Cu\ In\ Ga\ Se_2$ films. This was done using a SIEMENS D5000 with Cu K_α radiation of average wavelength $1.54056A^0$. It was operated with target voltage and current of 30 KV and 20 MA, respectively. The diffraction patterns were recorded from $2\ \theta = 20^0$ to $2\ \theta = 80^0$. The surface topography was investigated using scanning electron microscopy (SEM) on model JxA-733 (JEOL).Photoluminescence (PL) data were taken at 8.2 k using ($\lambda = 514.5$ m) emission of 30 mw argon laser incident light.

3. Results and Discussion

3.1 Structural and lattice parameters properties

Figure 1 shows the typical XRD patterns of the $Cu\ In_{1-x}Ga_x\ Se_2$ films with $x = 0.37$ and 0.82 on the Mo-coated glass respectively. The diffraction peaks corresponding to (110) , (202) and (114) planes which are shown in the pattern of the $CuIn_{0.63}\ Ga_{0.37}\ Se_2$ film are not observed in that of the $Cu\ In_{0.18}\ Ga_{0.82}Se_2$ film due to the different diffraction structure of the films. The $CuIn_{0.18}\ Ga_{0.82}\ Se_2$ film has a zinc blende type structure owing to the diffraction peaks, corresponding to (111) , (220) and (311) planes were observed while a sample with $x \leq 0.5$ was found to possess halcopyrite structure. Table 1 gives the interplanar spacing, relative intensities and indices of some main diffraction peaks of the samples which revealed the chalcopyrite structure and the cubic structure.

The cubic structure is characterized by one lattic parameter "a", while the chalcopyrite structure is characterized by two lattice parameters "a" and "c".

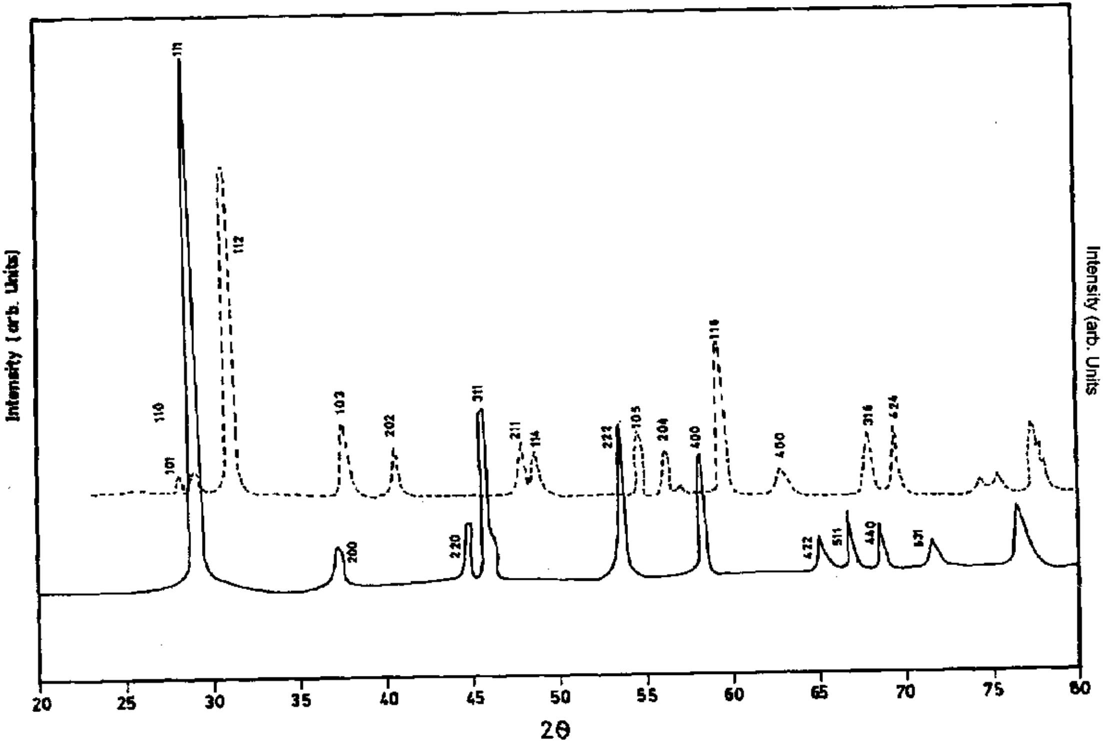


Fig. 1. X-Ray diffraction patterns of the (a) Cu In Ga Se and (b) Cu In Ga Se films on the Mo-coated glases. All of _____ a, ——

Table 1. X-ray diffraction data of $CuIn_{1-x}Ga_xSe_2$ films

x = 0.37			x = 0.82		
hkl	**d (A^0)**	I/I_0	**hkl**	**d (A^0)**	I/I_0
101	3.524	1.53	111	3.3194	100.00
110	3.4348	3.70	200	2.5459	7.03
112	3.1807	100.00	220	2.5111	2.49
103	2.5244	14.29	311	2.3751	2.58
202	2.3564	4.72	222	2.0826	13.03
211	2.0683	17.96	400	2.0348	32.42
114	1.7286	8.79	422	1.7362	28.37
105	1.6803	7.62	511	1.6001	22.06
204	1.6552	2.83	440	1.5110	3.02
116	1.5927	21.07	531	1.4390	4.93
400	1.503	2.96			
316	1.3981	8.53			
424	1.3981	8.63			

The measured variation in a and c with composition is given in Table 2, together with the type of structure. The variation in a and c with composition (x) is shown in Figure 2. where the squares and triangles refer the chalcopyrite and cubic phase material respectively. Both the lattice constants, a and c, linearly decrease with increasing the Ga content, x. This is because an In atom gets substituted for a similar Ga atom. As indicated by the XRD patterns of all the $CuIn_{1-x}Ga_xSe_2$ films, the $CuIn_{1-}Ga_xSe_2$ films have chalcopyrite structure when $x < 0.5$ and zinc blende structure when $x > 0.5$. Hence, the transition from chalcopyrite to cubic structure occurred at $x \approx 0.5$. This is in accordance with other results reported by Negami et al. [15] and Miguel et al. [16] Negami et al [15] reported that the $Cu(In_{1-x}Ga_x)_3Se_5$ films with $x \leq 0.5$ have an ordered vacancy chalcopyrite and the films with $x \geq 0.5$ have a zinc blende structure.

Table 2. Variation of lattice parameters with the Ga content, x

Composition n	**Structure**		**Lattice constant (A^0)**		c/a
x	Zinc Blende	Chalcopyrite	a	c	
1.00	Zinc blende	-	5.62	-	-
0.82	Zinc blende	-	5.543	-	-
0.58	Zinc blende	-	5.5971	-	-
0.45	-	Chalcopyrite	5.635	11.2582	1.9954
0.37	-	"	5.6451	11.2827	2.00012
0.28	-	"	5.6526	11.3434	2.0067
0.00	-	"	5.75	11.45	2.01

The c/a ratios were calculated and are also presented in table 2. Such ratios fall in the range of 2.02-1.992. This is also shown in Fig. 3. The variation is linear and may be expressed as;

$$c/a = 1.992 + 0.05\,x$$

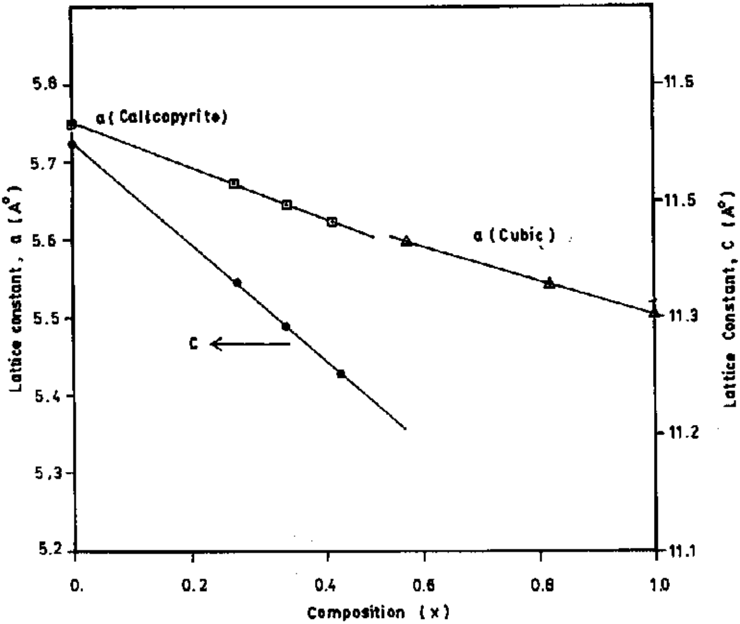


Fig. 2. Lattice parameters 'a' and 'c' as a function of composition (x).

Similar results for the lattice parameters have been found by Negami et al. [15] and Nishitani et al. [5]. They observed that the lattice parameters increased linearly with compositions. The variation in lattice parameter with composition would thus appear to obey Vegard's law. The dependence of lattice parameters "a" and "c" on composition has been found to obey an empirical relationship of the form

1) $a = 5.75 - 0.33\,x$
$c = 11.45 - 0.40\,x$

for Chalcopyrite structure with $x < 0.5$ where x is the mole fraction

2) $a = 5.62 - 0.1\,x$

for zincblende structure with $x => 0.5$

The data is very similar to the result reported by Al- Bassam et al. (17,18).

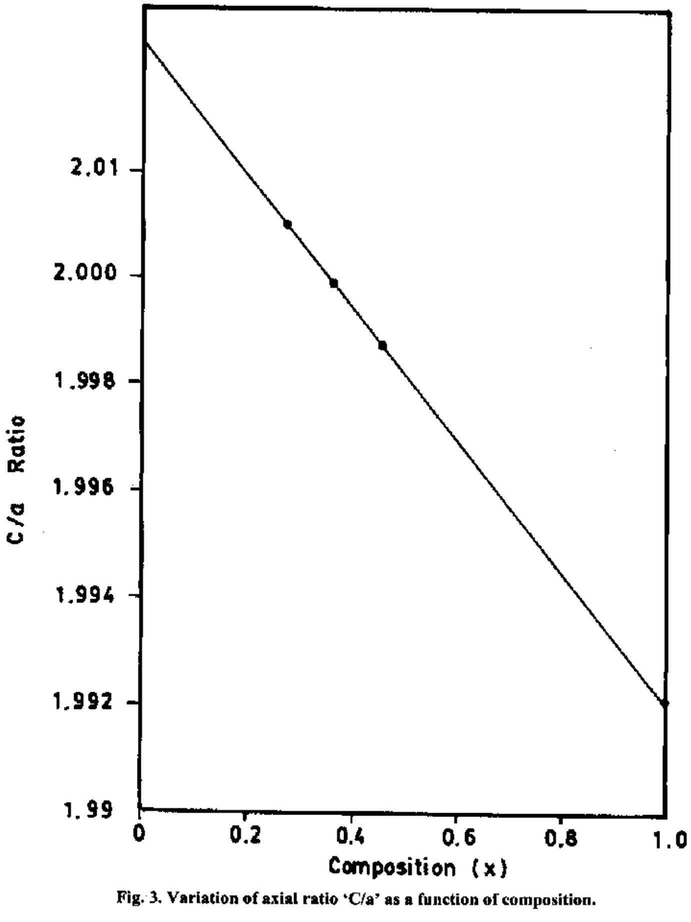
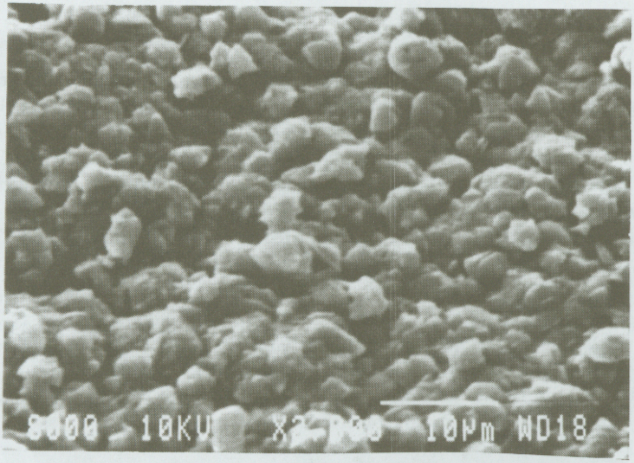
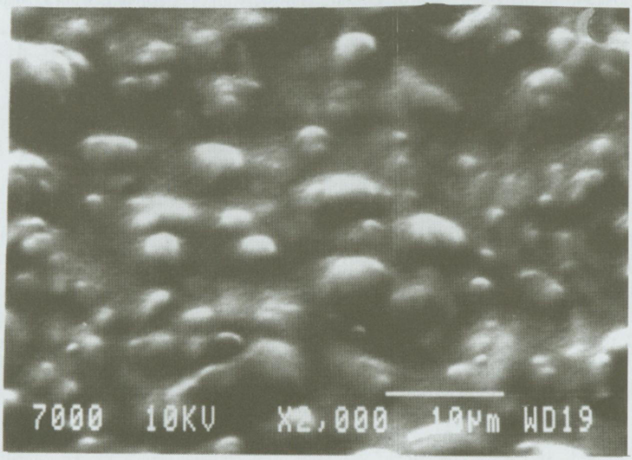


Fig. 3. Variation of axial ratio 'C/a' as a function of composition.

The scanning electron micrographic analysis of $CuIn_{1-x}Ga_xSe_2$ films with composition with $x = 0.37$ and $x = 0.82$ are shown in Fig. 4. The films had very rough surfaces. The grain size of 2.44 µm was observed with $x = 0.37$ while the grain size increased to 5.66 µm for $x = 0.82$. This is in a good agreement with other results reported by Araya et al. (19) and Pal et al. (20).



x = 0.37



x = 0.82

Fig. 4. Surface morphology of $CuIn_{1-x}Ga_xSe_2$ film at 2000 magnification. The white line represents 10 um.

3.2 Band gap from photoluminescence

The PL peak positions obtained from these thin films were scattered in a wide range of wavelength from about 1115 nm (1.11 ev) for CuInSe [CIS] to around 770 nm (1.61 ev) for CuGaSe [CGS]. The dominant PL peak position of CuInGaSe [CIGS] thin films showed a tendency to shift towards a shorter wave length by adding Ga into CIS thin films as shown in Figs. 5 and 6. The variation in band gap with composition was determined for these films from PL spectra. The results are given in Table 3.
The band gap Eg(x) in ternary alloys of the form $A_x B_{1-x} C$ is often found to follow a quadratic relationship of the form [2],:

$$Eg\ (x) = Eg\ (A) + [\ Eg\ (B) - Eg\ (A) - b]_x + bx^2 \qquad \text{..................(1)}$$

where Eg (A) and Eg (B) are the band gaps of the binary compounds, AC and BC respectively and b is the bowing parameters. The band gap range for Cu In_{1-x} Ga Se_2 change from 1.11 to 1.61 eV at room temperature and was found to allow relationship of the form of Eqn. (1). Thus at room temperature ;

$$Eg\ (x) = 1.11 + 0.4\ x + 0.1\ 1x^2$$

Table 3. Variation in the energy gap of Cu In_{1-x} Ga_x Se_2 with composition as from PL determined spectra

Composition (x)	Wavelength (nm)	Energy gap (ev)
1.00	770	1.61
0.82	823	1.505
0.58	900	1.376
0.45	946	1.31
0.37	975	1.272
0.28	1008	1.229
0.0	1115	1.11

This is in accordance with results reported by Kushiya etal [6]. They determined the quality of a wide range of CuInGaSe thin film absorbers from CuInSe to CuGaSe as evaluated by PL measurements. Based upon the analysis of PL spectra, peak positions and the effects of annealing in air, it was suggested that In_{cu} antisite donor defects might have been replaced with Ga_{cu} antisite donor defects increasing the fractional Ga contents in the CIGS thin films [6]. Also our values are in closer agreement with those of Ciszek etal [11] than with the earlier data of Paorici etal. [9].

4. Conclusion

Polycrystalline Cu In_{1-x} Ga_x Se_2 thin films have been fabricated and studied with "x" value from 0.1 to 1.0. X-ray diffraction analysis showed that the films, with $x \leq 0.5$ have a chalcopyrite structure and the films with $x \geq 0.5$ have zinc blende structure. The lattice parameters (both a and c) were found to show a linear dependence with composition. The dependence of the lattice parameters of a and c on composition can be expressed as:

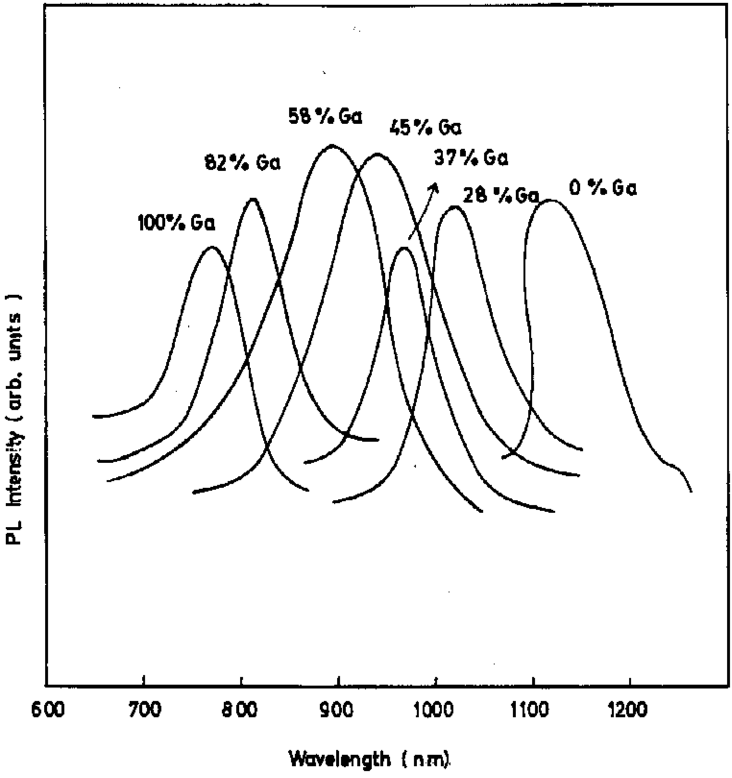


Fig. 5. PL Spectra of Cu In_{1-x} Ga_x Se_2 thin films with different Ga contents.

1) a (zinc blende) = 5.62 - 0. 1x
2) a (chalcopyrite) = 5.75 - 0.33 x
c (chalcopyrite) = 11.45 - 0.4x

The band gaps were estimated from photo luminescece spectra. Thus the band gap energy at room temperature is given by:
$Eg(x) = 1.11 + 0.4x + 0.1x^2$.

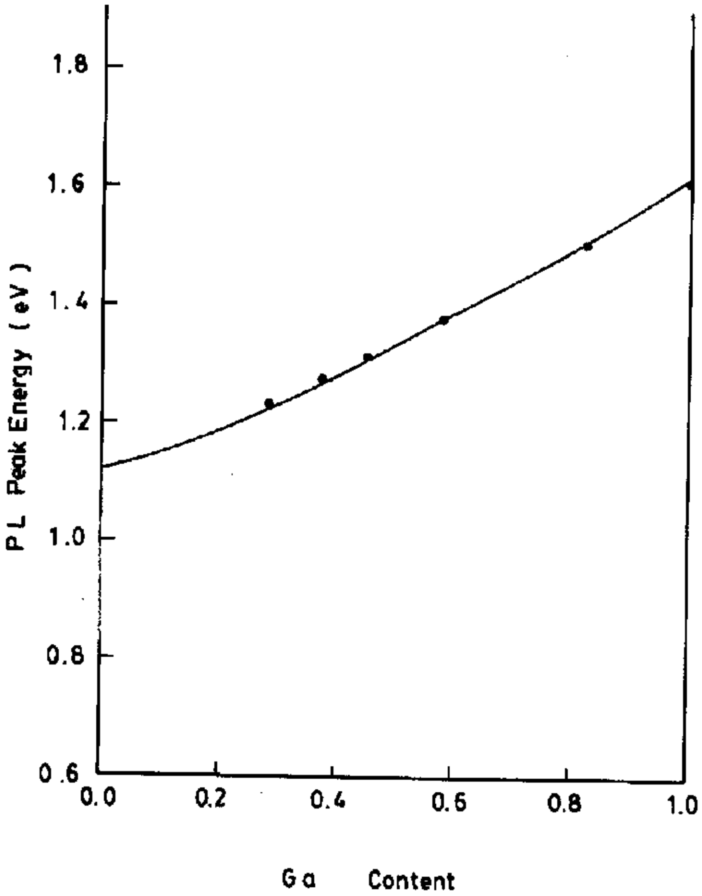


Fig. 6. Relationship between PL peak position and Ga content in Cu In_{1-x} Ga_x Se thin films.

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خواص الأغشية الرقيقة لــ $CuIn_{1-x}Ga_xSe_2$

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(استلم في ٨/٤/١٤١٨هـ، وقبل للنشر في ٢٠/١٠/١٤١٨هـ)

ملخص البحث. لقد جهز غشاء رقيق لخليط من CuIn1-xGaxSe2 عديد التبلور. وتم قياس بعض الخواص الفيزيائية مثل ثوابت الشبكية، التركيب البلّوري وبيانات الأشعة السينية باستخدام حيود الأشعة السينية. وضح تحليل حيود الأشعة السينية أن الأغشية الرقيقة التي لها التركيز (x0.5) يكون التركيب Chalcopyrite بينما الأغشية الرقيقة التركيز (x0.5) يكون التركيب Zinc blende. تتغير ثوابت الشبكية خطياً مع التركيز في مدى من x=0 إلى x=1.0.

التغير في ثوابت الشبكية مع التركيز تحقق قانون أفوجادرو. كما أن التغير للنسبة c/a مع التركيز يكون خطيا.

المدى الواسع لهذه النوعية من الأغشية الرقيقة الممتصة من CIS إلى CGS قدرت بواسطة القياسات الضوئية.