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Characterization of polycrystalline Cu(In,Ga)Te_2 thin films prepared by pulsed laser deposition

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Abstract

Thin films of the chalcopyrite compound $CuGa_XIn_{1-X}Te_2$ ($0 \le X \le 1$) have been prepared by pulsed laser deposition (PLD) of prereacted material onto glass substrates. The structural and optical properties of these films have been investigated using the techniques of X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX), Rutherford back scattering (RBS), transmittance (T), reflectance (R). Electrical characterization was performed using Hall and resistivity measurements, using the Van der Pauw technique at 300 K. The composition of the laser-deposited films was found to closely match that of the target materials and the XRD showed them to be single phase with the chalcopyrite structure and a preferred orientation along the (112) plane. The spectral dependence of the refractive index n and absorption coefficient α of the Cu(In,Ga)Te_2 thin films were determined using rigorous expressions for transmission and reflection in an air/film/substrate/air multilayer system. The $CuGa_XIn_{1-X}Te_2$ films had optical absorption coefficients of order 10^4 cm^{-1} and the energy gaps observed in these films increased from 0.96 to 1.32 eV with increasing Ga content.

Keywords: Pulsed laser deposition; Chalcopyrite thin films; Optical properties; Electrical properties

1. Introduction

$CuInTe_2$ and $CuGaTe_2$ ternary compounds are direct band gap semiconductors crystallizing in the chalcopyrite structure. They are the nearest electronic and chemical analogies of $A^{II}B^{VI}$ binary compounds [1,2]. Their band gaps are $E_g = 0.96$ eV ($CuInTe_2$) and $E_g =$ 1.35 eV ($CuGaTe_2$) [3–8]. These values are well adapted to the solar spectrum and taking into consideration the high absorption coefficients of these materials they are very attractive for a wide variety of optoelectronic device applications and thin film solar cells [1,2]. The fabrication and study of physical properties of these thin films have been reported by many authors [1–7]. Meanwhile, to the best of our knowledge there have only been a few published reports on thin films of the quaternary compounds $CuGa_XIn_{1-X}Te_2$ prepared by flash evaporation [4,5]. The quaternary mixed materials offer the advantage of tailoring suitable values of lat-

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tice parameters and energy band gap via the proper choice of composition. A better understanding of such properties would be useful for the fabrication of materials with optimized parameters for optoelectronic devices.

Pulsed laser deposition (PLD) has been shown to be a suitable method for fabrication of thin films of complex semiconductors due to its high energy flux [8–11]. In this paper we describe the fabrication and investigation of $CuGa_X In_{1-X}Te_2$ $(0 \le X \le 1)$ thin films prepared using the PLD technique, with $Cu(Ga,In)Te_2$ crystals used as targets. The structural, electrical and optical properties of the deposited films were studied and will be discussed. The lattice parameters, resistivity and energy gaps of films ranging in composition from $CuInTe_2$ to $CuGaTe_2$ have been determined and a relation between composition and energy gaps has been found.

2. Experimental details

The synthesis of $CuGa_X In_{1-X}Te_2$ solid solutions was performed from stoichiometric mixtures of the elements in evacuated quartz ampoules using the two-temperature method and directed crystallization of melt [12]. The $CuGa_X In_{1-X}Te_2$ state diagram allowed optimization of the synthesis. The bulk composition and homogeneity of the ternary compounds and solid solutions were investigated by chemical, X-ray diffraction (XRD), optical and differential thermal analyses [13,14]. Single phase chalcopyrite structure is observed in the resulting compounds. The target materials were 15 mm in diameter, cut from as-received alloys. The $CuGa_X In_{1-X}Te_2$ thin films were then prepared on Corning glass substrates by PLD using a Nd:YAG laser operated at a wavelength of 1.06 μm with a pulse duration of 10^{-3} s [8,15,16]. Substrate temperatures (T_S) in the range of 450–480°C were used with a target-to-substrate distance of 5–10 cm. Laser pulses at a repetition rate of 3×10^{-2} Hz were incident at an angle of 45° on the target, over the surface of which the partly focused laser beam was scanned. By changing the high voltage between 2.3 and 2.5 kV on the laser, the laser energy was varied from 150 to 200 J/pulse. The laser spot size on the target was measured to be 3×5 mm^2. The films were deposited at a residual pressure of approximately 10^{-5} torr. Typical deposition rates were $(2–4) \times 10^5$ Å/s and the thickness of the films was 300–1000 nm (20–50 laser pulses), measured with a surface profile measuring apparatus.

The bulk compositions were determined by energy dispersive X-ray (EDX) measurements and the results verified using Rutherford back scattering (RBS), employing a 2-MeV He beam from a Van de Graaff generator. The phases and crystallographic structure of the films were investigated by X-ray diffraction (XRD) using Cu K_α radiation. The observed phases were determined by comparing the *d*-spacing with Joint Committee on Powder Diffraction Standard (JCPDS) data files. The lattice parameters were determined by the X-ray powder calculation program APX-63. The surface morphology was observed using scanning electron microscopy (SEM). Hall and resistivity measurements were carried out on the films using the Van der Pauw method and silver paint for ohmic contacts. The optical transmission and reflection spectra were measured in the range of 400–2500 nm, enabling determination of the absorption coefficient α, refractive index n and energy gap E_g as a function of composition.

3. Results and discussion

The EDX results for the bulk analysis of the thin films with $CuGa_X In_{1-X}Te_2$ ($X = 0.0$, 0.2, 0.4, 0.8 and 1.0) as evaporants are shown in Table 1 and demonstrate that the tellurium content is generally below that of the target material. This is likely to be due to the reduced sticking coefficient of tellurium atoms at the substrate temperatures employed. The gallium/indium ratios of the target materials are, however, seen to be faithfully reproduced in the thin films. The apparently high copper content in the laser-deposited films is in reality due to a deficiency of tellurium. A high copper content is indicative of the formation of indium/tellurium binaries. These have significant partial vapor pressure at high temperatures and will be removed from the system before they can be deposited on the substrate. It should be noted that in compounds with

Table 1
EDX bulk composition analysis data for PLD-deposited $CuGa_X In_{1-X}Te_2$ films

Target X, mole fraction	T_S, °C	Cu, At.%	Ga, At.%	In, At.%	Te, At.%	Film X, mole fraction	Cu/(Ga + In)	(Cu + Ga + In)/Te
0.0	470	26.515	–	24.781	48.704	0.00	1.06	1.05
0.2	480	27.099	3.809	25.399	43.689	0.13	0.93	1.28
0.4	480	27.609	9.801	18.204	44.387	0.35	0.98	1.25
0.8	480	30.067	19.014	6.910	44.009	0.74	1.15	1.27
1.0	480	28.109	22.965	–	48.926	1.00	1.22	1.04

$X = 0.2$, 0.4 and 0.8 the concentration ratio (Cu + Ga + In)/Te is higher than the aimed composition of the target. These results show that laser-deposited $CuGa_XIn_{1-X}Te_2$ thin films are off-stoichiometry. The films are tellurium poor, but also copper-rich in some cases. According to the phase diagram for these chalcopyrites, samples with such concentrations may present a mixture of several phases in the films, consisting of Cu–Te binaries in addition to the majority chalcopyrite phase.

The EDX data were compared to results from an RBS study, which can provide accurate results for the composition of the surface. The RBS results show a good correlation between the surface composition of the films and that of the target and indicate a good degree of uniformity in the $CuGa_XIn_{1-X}Te_2$ thin films [8,15]. An apparent discrepancy between the composition results from RBS and EDX is observed. It may be explained by the fact that RBS analysis gives accurate information about the surface layers of the films, whereas the EDX technique gives results which are an average over the full film thickness including the initial nucleation layers. The RBS data are thus less likely to be affected by the initial stages of thin film growth. The required distribution between the component elements and structure of $CuGa_XIn_{1-X}Te_2$ is only likely to be established in the later stages of film growth, i.e. after initial nucleation (possibly associated with the formation of secondary phases) on the substrate has been completed. It should be noted that RBS analysis showed the presence on the surface of very thin off-stoichiometry films ($d = 40$–80 Å) with composition close to Cu–Te binaries.

The surface morphology of films deposited at different regimes have been investigated using scanning electron microscopy. It was determined that the quality of the film surface (structural defects) depends on the laser power level. These defects (droplets and rings) were formed by 'spitting' from the target material. 'Spitting' is one of the major problems of the pulsed laser evaporation process [17]. It occurs when the subsurface layer is superheated by excess radiation before the subsurface itself has reached the vapor phase. Particles 'ejected' from the target material can be entrapped inside the layer during the course of deposition and their presence aggravate the crystal structure of the thin films. This effect can be reduced by lowering the laser power level. At 10^6 W/cm^2 ejected particles cover more than 60% of the surface area and characteristic defects have the average size of 25 μm. At 5×10^5 W/cm^2, a condition used in previous studies, the particle size is reduced to 15 μm and the surface coverage is also lower. At 10^5 W/cm^2 the surface becomes featureless and the average size of the defects is less than 5 μm (Fig. 1). The droplets and rings do not significantly differ in chemical composition compared with the smooth areas according to microprobe results. It should be noted that the 'spitting' effect in PLD may be effectively reduced by changing the laser parameters and using targets with good homogeneity and high density [11]. Cross-sectional SEM images of thin films have two aspects: (1) uniform and clear columnar grains that facilitate current transport across the films; and (2) a rather densely packed microstructure free of pinholes and microcracks (Fig. 1 insert).

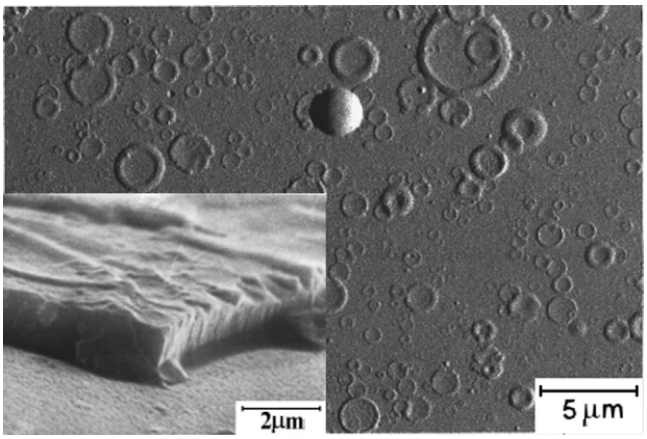

Fig. 1. Scanning electron micrographs of the surface morphology and cross-section structure (insert) of $CuInTe_2$ film prepared by PLD.

X-Ray diffraction measurements were performed to identify the structure and phases in the as-grown films [8,15,16]. The diffraction spectra of the powder target materials were also recorded for comparison. XRD peaks corresponding to diffraction from the planes of the chalcopyrite structure were observed, with no diffraction peaks from other phases (Fig. 2). The X-ray diffraction peaks for $2\Theta = 22.45°$ and $2\Theta = 27.38°$ are related to the film holder. As the gallium content increased, the (112) peak position of the $CuGa_XIn_{1-X}Te_2$ thin films along the 2Θ direction is observed to shift from the $CuInTe_2$ angle towards that of $CuGaTe_2$, as seen in Fig. 3. The spectra demonstrate that the films always grew with a $\langle 112 \rangle$ preferable orientation, i.e. parallel to the plane of the substrate. The full width at half maximum (FWHM) for the (112) diffraction peaks of thin films was observed to increase from 0.163° for $CuInTe_2$ to 0.272° for $CuGaTe_2$.

Table 2 shows the lattice parameters a and c of $CuGa_XIn_{1-X}Te_2$ thin films calculated using the X-ray powder calculation program APX-63 for all the XRD peaks observed in a full 2Θ scan. It is seen that the variation of the a and c lattice parameters vs. Ga composition (X) is virtually linear, following the usual Vegard's law behavior:

$$a = 6.192 - 0.185 \cdot X \text{ (Å)} \quad \text{and} \quad c = 12.354 - 0.362 \cdot X \text{ (Å)}$$

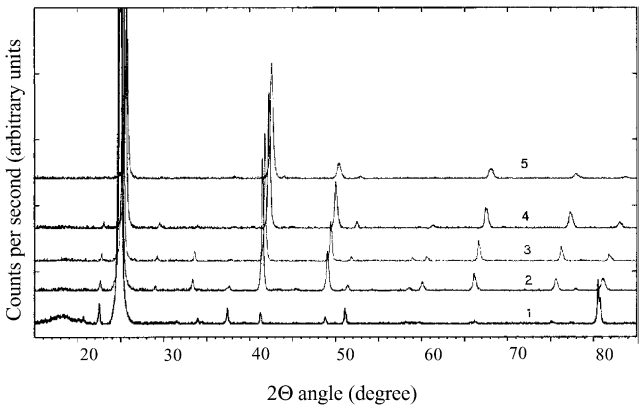

Fig. 2. X-Ray diffraction spectra of $CuGa_XIn_{1-X}Te_2$ thin films grown at $T_S = 480°C$. Traces 1–5 correspond to X-values of 0.00, 0.13, 0.35, 0.74, 1.00, respectively.

Our results are in good agreement with those for bulk materials [13,18].

The mobility and carrier concentrations were determined from measurements of resistivity and Hall data on all samples. The films were all found to be p-type with resistivities in the range of 0.011–0.037 Ω cm. The Hall data gave hole concentrations and mobilities varying in the ranges (3.1–16) 10^{18} cm^{-3} and 14–91 cm^2 V^{-1} s^{-1}, respectively. Thermal treatment in vacuum did not produce changes in the electrical characteristics of the films. The electrical results for $CuGa_XIn_{1-X}Te_2$ thin films are summarized in Table 3

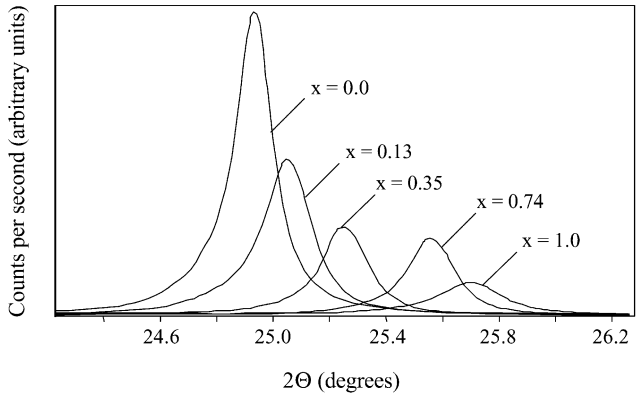

Fig. 3. XRD data showing the shift in the (112) peak position with increasing amounts of gallium in $CuGa_XIn_{1-X}Te_2$ thin films.

Table 2
The lattice parameters calculated for the $CuGa_XIn_{1-X}Te_2$ thin films

Films	a. Å	c. Å	c/a
$CuInTe_2$	6.192 (1)	12.354 (3)	1.995
$CuGa_{0.13}In_{0.87}Te_2$	6.154 (1)	12.305 (3)	1.999
$CuGa_{0.35}In_{0.65}Te_2$	6.144 (1)	12.214 (3)	1.997
$CuGa_{0.74}In_{0.26}Te_2$	6.044 (1)	12.052 (3)	1.994
$CuGaTe_2$	6.007 (1)	11.982 (3)	1.994

and are correlated with those for films prepared by flash evaporation [4,5].

The optical properties of the $CuGa_XIn_{1-X}Te_2$ thin films were characterized in order to investigate their application as the absorber material for solar cells. The refractive index n and absorption coefficient α of films were obtained by means of transmittance (T) and reflectivity (R) measurements. The optical properties were studied using rigorous expressions for the transmission and reflection in an air/film/glass substrate/air multilayer system. The solutions of these equations relative to this system are not unique. To be able to obtain a good n dispersion curve and, therefore, a correct absorption coefficient, we propose a simple modification of the equation for T and R through a factor called the coherence factor (CF) [19]. Because of the surface roughness and non-uniformity of n and α, the light rays that reflect internally in the interface between the substrate and film have a random difference in optical path. The CF accounts for this effect. This modification leads to an unambiguous and accurate determination of the optical properties of thin films for all wavelengths where the transmission is not negligible. Fig. 4 shows the dispersion curves of the refractive index n for the $CuGa_XIn_{1-X}Te_2$ thin films that were analyzed. For all samples normal dispersion is observed even for energies above the band gap and no clear correlation between refractive index and preparation conditions was found.

Plots of absorption coefficient vs. photon energy for the films are shown in Fig. 5. The magnitude of the absorption coefficient above the fundamental band edge exceeds 10^4 cm^{-1} for all films. The tail of absorption in the low energy range may be connected with the presence of the thin layer of Cu–Te binaries. These values

Table 3
Electrical characteristics of the $CuGa_XIn_{1-X}Te_2$ films

$CuGa_XIn_{1-X}Te_2$ X, mole fraction	Thickness, nm	p 10^{-18} (cm^{-3})	μ (cm^2 V^{-1} s^{-1})	ρ 10^2 (Ω cm)
1.0	505	4.4–10	67–91	1.4–2.1
0.74	720	3.1–16	41–60	1.3–2.2
0.35	585	4.8–6.7	16–27	2.4–3.2
0.13	630	3.1–5.9	14–18	1.1–2.4
0.0	325	5.5–6.3	34–38	2.9–3.7

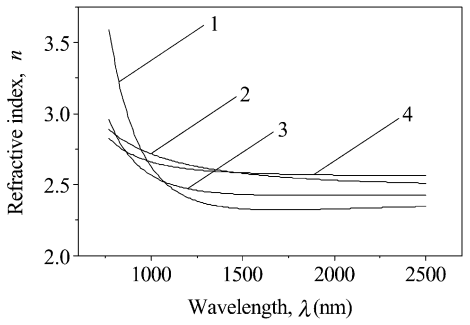

Fig. 4. Spectral dependence of the refractive index of $CuGa_XIn_{1-X}Te_2$ films. X, 1–0.13; 2–0.35; 3–0.74; 4–1.0.

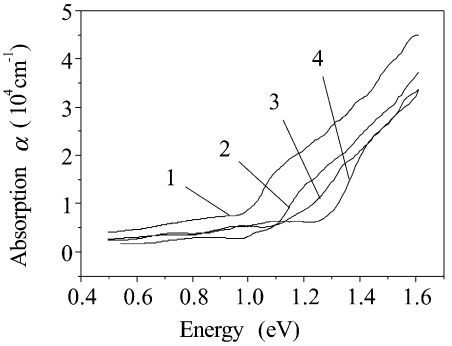

Fig. 5. Dependence of the absorption coefficient on photon energy for $CuGa_XIn_{1-X}Te_2$ thin films. X, 1–0.13; 2, 0.35; 3–0.74; 4–1.0.

are suitable for fabrication of thin film photovoltaic devices. The absorption coefficient curves show a well-defined edge near the forbidden gap for $CuGa_XIn_{1-X}Te_2$ films. For a fundamental allowed direct transition, the relationship between the absorption coefficient and the photon energy can be approximately expressed by

$$\alpha(h\nu) = A \cdot (h\nu - E_g)^{1/2},$$

where A is a constant and E_g is the energy gap. Therefore, the band gap of the thin films can be determined by linear extrapolation of a plot of α^2 vs. $h\nu$. The results obtained for the optical energy gaps of laser-deposited $CuGa_XIn_{1-X}Te_2$ thin films are summarized in Table 4. These values of the band gaps of laser-deposited $CuGa_XIn_{1-X}Te_2$ thin films are suitable for absorption of photons in the solar spectra. Similar results have been reported for bulk materials [14] and flash evaporated $CuGa_XIn_{1-X}Te_2$ films [4,5].

A correlation between the lattice parameters, energy gap and composition of films has been sought. It appears that an increase in the Ga concentration is associated with a decrease in the lattice parameter and an increase in the energy gap. No dependence on any composition parameters has been found for the electrical properties.

4. Conclusion

Thin films of the $CuGa_XIn_{1-X}Te_2$ system have been prepared by pulsed laser deposition. The films have compositions which closely match that of the target materials. X-Ray diffraction studies showed that the films were single phase with the chalcopyrite structure and a preferred orientation along the (112) plane. The lattice parameters were shown to vary linearly with the Ga content in the films. The samples always show p-type conductivity with resistivity in the $(1.1–3.7)\times 10^{-2}$ Ωcm range. The optical absorption coefficient of the thin films exceeds 10^4 cm^{-1} and the band gaps were found to increase from 0.96 to 1.32 eV with increasing Ga content. The electrical and optical characteristics of laser-deposited $CuGa_XIn_{1-X}Te_2$ films indicate their suitability for optoelectronic devices.

Table 4
Energy gaps estimated for the $CuGa_XIn_{1-X}Te_2$ thin films

Films	T_S, °C	E_g, eV
$CuInTe_2$	490	0.964
$CuGa_{0.13}In_{0.87}Te_2$	480	0.992
$CuGa_{0.35}In_{0.65}Te_2$	470	1.124
$CuGa_{0.74}In_{0.26}Te_2$	490	1.235
$CuGaTe_2$	480	1.315

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