Chalcopyrite $CuGa_xIn_{1-x}Se_2$ semiconducting thin films produced by radio frequency sputtering

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(Received 13 November 1991; accepted for publication 30 January 1992)

$CuGa_xIn_{1-x}Se_2$ thin films have been deposited by rf sputtering from three targets with different (Ga,In) content ($x = 0.25$, $x = 0.5$, and $x = 0.75$). A structural, compositional, optical, and electrical study has been carried out for films grown at substrates temperatures higher than 350 °C. We have successfully obtained chalcopyrite single phase stoichiometric films. Very sharp absorption edges are obtained, with band gaps of 1.12, 1.35, and 1.51 eV for $x = 0$, $x = 0.5$, and $x = 0.75$, respectively.

I-III-VI_2 chalcopyrite compound semiconductors have a great potential in photovoltaic devices, both in single heterojunction and in tandem structures.[1] We have successfully produced thin films of single phase chalcopyrite $CuInSe_2$ (Refs. 2,3) and $CuGaSe_2$ (Refs. 4,5) by radio frequency (rf) sputtering. In this letter, we present first results on the preparation and characterization of rf sputtered $CuGa_xIn_{1-x}Se_2$. This compound has been already grown by other techniques,[6] but, to our knowledge, no reports on sputtered $CuGa_xIn_{1-x}Se_2$ have been published. The variation of the x value will allow us to tailor the properties of the films in order to obtain high efficiency photovoltaic devices.

Target preparation was done as follows: We synthesized 2% Se-rich $CuGa_xIn_{1-x}Se_2$ of three different Ga content ($x = 0.25$, 0.50, and 0.75) by a method similar to the one already used for the preparation of $CuInSe_2$ and $CuGaSe_2$ targets.[3,4] After the synthesis, we reduced the resulting ingots to powder of grain size lower than 40 μm and analyzed it by means of an x-ray diffractometer. The powder diffractometer data for the three different compositions (Table I) show, in all cases, single phase chalcopyrite structure. Then we cold pressed the powder in the form of 2" diam pellets.

We grew $CuGa_xIn_{1-x}Se_2$ thin films from a commercial rf sputtering system (GCA Vacuum Industries) on Al_2O_3 and quartz substrates with an Ar pressure of 20 mTorr, a target voltage of 1300 V and a target to substrate distance of 5 cm. Growth temperature was always higher than 350 °C.

We characterized the resulting thin films compositionally (energy dispersive spectrometry analysis), structurally, optically, and electrically. All the films were Cu poor with Ga, In, and Se contents near the stoichiometric composition. In Table II we show the x-ray diffraction (XRD) pattern results of a representative film from each target grown upon Al_2O_3 substrates. In Fig. 1, we show the unit cell parameters, c and a of the tetragonal structure, deduced from the peak position, for both the targets and the thin films. In this figure we have also included the corresponding values for $CuInSe_2$ and $CuGaSe_2$.[2,5] We obtained single phase chalcopyrite films only at very high growth temperatures. As it is known, the alloying of $CuInSe_2$ with Ga has two main consequences from a structural point of view:[7] (i) A lowering of the intensity in the superlattice chalcopyrite reflections [(101), (103), (211), (105,213), (301)] due to the similar value of the atomic scattering factor of Cu and Ga and (ii) a distortion of the tetragonal structure ($c/a < 2$) when the Ga/In ratio is higher than 1. Due to this distortion the (220)-(204) and (116)-(312) doublets are split.

For $x = 0.25$ all the superlattice reflections of the ordered chalcopyrite structure are clearly identified in both the target powder (Table I) and the thin film (Table II).

TABLE I. Powder diffractometer data for the three different targets for 2θ values ranging from 10° to 60°.

	$CuGa_{0.25}In_{0.75}Se_2$		$CuGa_{0.5}In_{0.5}Se_2$		$CuGa_{0.75}In_{0.25}Se_2$	
hkl	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0
101	5.142	3	5.056	2	5.056	2
112	3.295	100	3.272	100	3.254	100
103	3.162	3	···	···	···	···
211	2.493	4	2.478	3	···	···
213 105	2.118	3	···	···	···	···
220 204	2.023	54	2.005	43	1.997 1.987	23 35
301	1.878	2	···	···	···	···
312 116	1.725	28	1.712	21	1.703 1.687	20 8

TABLE II. Diffractometer data for single phase chalcopyrite thin films of the three compositions for 2ϑ values ranging from 10° to 60°.

	$CuGa_{0.25}In_{0.75}Se_2$		$CuGa_{0.5}In_{0.5}Se_2$		$CuGa_{0.75}In_{0.25}Se_2$	
hkl	*d*	I/I_0	*d*	I/I_0	*d*	I/I_0
101	5.195	3	5.060	1	...	...
112	3.315	100	3.291	100	3.257	100
103	3.182	2	...	...	...	...
211	2.501	2	...	...	...	...
213 105	2.128	1	...	...	...	...
220	2.028	23	2.015	11	1.999	5
204					1.989	7
301	1.885	1	...	...	...	...
312	1.732	16	1.717	4	1.706	7
116					1.688	3

For $x = 0.50$ the two most intense superlattice chalcopyrite reflections [(101),(211)] are identified in the target powder (Table I), meanwhile in the thin film pattern only the (101) reflection is present (Table II). It has been shown[8] that the XRD pattern of $CuGa_{0.5}In_{0.5}Se_2$ powder only exhibits the most intense superlattice reflections with very low intensities. Furthermore, it is easily proved that the structure factor of the superlattice reflections decreases with the content in Ga due to the very similar values of the atomic scattering factor of Cu and Ga and the difference of this factor between Cu and In. Then the high Ga content and the strong preferential orientation of the film seem to be responsible for the absence of the superlattice reflections when $x \gg 0.5$. The presence of the (101) reflection is the only evidence of the chalcopyrite structure for this film, provided that the tetragonal distortion in $CuGa_{0.5}In_{0.5}Se_2$ ($c/a = 1.995$) does not allow the splitting of the (220)(204) and (116)(312) doublets. This nonsplitting is also evident in the XRD patterns of the target powder (Table I). For the highest Ga content ($x = 0.75$) we do not observe superlattice reflections. However, a tetragonal distortion of $c/a = 1.985$ allows the doublets splitting in both the powder (Table I) and the film (Table II), thus asserting the presence of the chalcopyrite structure for this composition of the alloy.[9]

Films grown at temperatures lower than 400 °C reveal, for the three targets, the presence of the disordered sphalerite structure. Similar results have been observed in evaporated thin films.[6]

By hot probe experiments we proved that all the films exhibit *p*-type conductivity. We measured the resistivity of the films by the Van der Pauw method with a square geometry. For the three compositions we observed an increase in the resistivity from 1 Ω cm for films grown at 70 °C to 10^5 Ω cm for films grown at 450 °C. This increase of the resistivity takes place in spite of the following: The nonvariation in the composition of the films with growth temperature and the fact that the scanning electron microscopy observations we performed showed a monotonous increase in the grain size of the films with growth temperature up to 0.5 μm. To clarify the meaning of this variation of the resistivity, we are now performing measurements of the electrical properties of the films at different specimen temperatures.

We performed the optical characterization measuring the transmittance and reflectance of films grown on quartz substrates with a Perkin-Elmer Lambda 9 Spectrophotom-

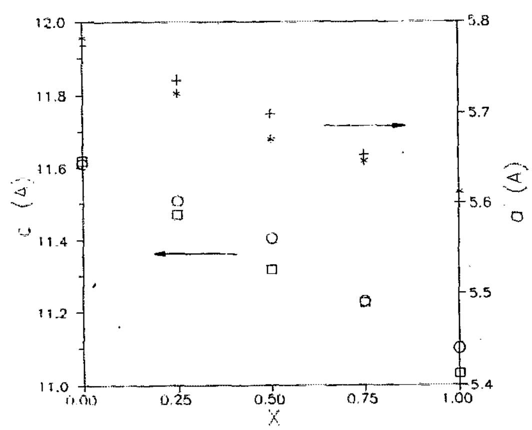

FIG. 1. Chalcopyrite unit cell parameters, *a* (+ : target powder; *: thin film) and *c* (O: target powder; □: thin film) vs Ga content deduced from the reflections in the XRD patterns. We also show these values for the corresponding ternary compounds.

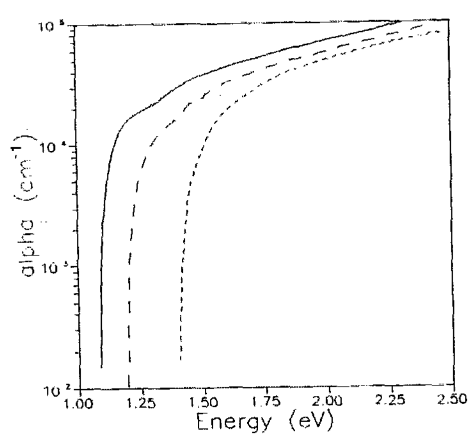

FIG. 2. Absorption coefficient vs photon energy for three different films of $CuGa_xIn_{1-x}Se_2$ (continuous line for $x = 0.25$, dashed line for $x = 0.50$, dotted line for $x = 0.75$).

eter. We obtained the values of the absorption coefficient by means of a calculation that takes into account the multiple reflection processes at the air–film, film–substrate, and substrate–air interfaces, and the different nonuniformities of the film.[10] In Fig. 2 we show the absorption coefficient for one representative film grown from each target at very high substrate temperatures. Well defined, sharp absorption edges are visible in the figure. By fitting $(\alpha h\nu)^2$ vs $h\nu$ we deduce that the fundamental band gap is allowed direct with values of 1.12, 1.35, and 1.51 eV for $x=0.25$, 0.5, and 0.75, respectively. These values are in good agreement with previous results for evaporated films.[6] The low absorption coefficient values at energies lower than the band gap are indicative of good stoichiometry and absence of secondary phases.[6] In the high absorption zone we can see a shoulder that indicates the presence of an additional optical transition, as it is usual in chalcopyrite compounds.[2,5,7]

In summary, we have made targets of single phase chalcopyrite $CuGa_xIn_{1-x}Se_2$ of three different Ga contents ($x=0.25$, 0.5, 0.75). From these targets we have grown thin films by rf sputtering on Al_2O_3 and quartz substrates. For growth temperatures higher than 400 °C we obtained single phase chalcopyrite films from all three targets. We deduced the unit cell parameters from the XRD patterns. The optical characterization has shown a well defined band edge with band gaps of 1.12, 1.35, and 1.51 eV for $x=0.25$, 0.5, and 0.75, respectively. All these characteristics are similar to those obtained on evaporated quaternary $CuGa_xIn_{1-x}Se_2$ thin films.

The authors would like to express their acknowledgments to S. Garcia-Martin (XRD facilities) and J. Carabe (Optical Measurement facilities).

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