

Stoichiometry control over a wide composition range of sputtered $\text{CuGa}_x\text{In}_{(1-x)}\text{Se}_2$

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Films of $\text{CuGa}_x\text{In}_{(1-x)}\text{Se}_2$ (CGIS) have been grown by rf sputtering from stoichiometric single targets with different Ga/In ratios. Adjusting growth temperature and argon pressure we are able to deposit films with a wide range of Cu contents: From CGIS Cu-poor (16 at. %) to Cu_2Se . Reevaporation of $(\text{Ga},\text{In})_2\text{Se}_3$ binaries is observed when substrate temperature is increased at a constant argon pressure (20 mTorr). An increase in Ar pressure from 5 to 150 mTorr at a growth temperature of 450 °C, produces a decrease in Cu atomic percentage from 24% to 16% due to a preferential diffusion of Cu sputtered atoms in the plasma. The relevant film properties of the analyzed films are found to be ruled by the Cu content. Graded composition absorbers with adequate physical properties for the fabrication of photovoltaic devices are grown with a proper choice of growth parameters.

I-III-VI₂ semiconductors have a great potential as absorbing materials in photovoltaic devices for terrestrial applications. High efficiency solar cells with a chalcopyrite absorber have been already grown by thermal evaporation.^{1,2} Chalcopyrite absorbers resulting in efficient solar cells are fabricated by means of the bilayer approach.² This scheme includes a Cu-rich bottom layer that ensures a large grain size and low resistivity (good ohmic contact with Mo) and a copper-poor top layer to achieve good quality interface properties and a slightly Cu-poor bulk composition, which is compulsory to obtain an efficient device.

Sputtering, an industrially more convenient technique than evaporation has not been widely studied. Previous results of rf sputtering of chalcopyrite compounds pointed out the difficulty to regulate film stoichiometry and morphology from a single target.³ In this letter, we show that a careful control of production conditions can yield, in a reproducible way, $\text{CuGa}_x\text{In}_{(1-x)}\text{Se}_2$ (CGIS) films of a wide range of compositions, enabling us to grow layers with graded compositions from a single target.

Target preparation of three different compositions ($x=0.25, 0.5$, and 0.75) was conducted as described elsewhere.³ Films were grown from a commercial rf sputtering system on 7059 and sodalime glass uncoated and Mo coated. Substrates were glued to the substrate holder with In to ensure temperature uniformity and good thermal contact. The production parameters used were as follows: Ar pressure (p_{Ar}): 5–200 mTorr; rf power: 50–100 W; target to substrate distance: 2–6 cm; growth temperature (T_G): 300–700 °C.

Film structure was determined by x-ray diffraction in a Siemens D-5000 diffractometer, optical properties (transmittance and reflectance) were measured from 400 to 2500 nm in a Perkin-Elmer Lambda 9 spectrophotometer with an integrating sphere, resistivity by the Van de Pauw method on 1 cm² samples morphology was evaluated in a scanning electron microscope (SEM) and composition was obtained by energy dispersive spectroscopy (EDS). The latter was performed on 1- μm -thick films, deposited on 2- μm Mo-coated glasses. The analysis was carried out in a JEOL 6400 SEM

operating with a beam energy of 20 keV in an area of 0.5 mm². As a standard $\text{Cu}(\text{Ga},\text{In})\text{Se}_2$ thin films calibrated by electron probe microanalysis were used. Measurements were repeated until the error was lower than 0.5 at. % The absorption coefficient and the refractive index were obtained analyzing the optical measurements by the method described in Ref. 4, the energy band gap was deduced from α^2 vs $h\nu$ plots. Only results from the $X=0.25$ target are presented, similar results were obtained from the other two targets.

Films of very different compositions can be grown from the same target as shown in Fig. 1, where a ternary phase diagram where Ga and In content have been included in the same axis is presented. Changing p_{Ar} and T_G in the ranges stated below, films with different compositions can be grown. Analogously to coevaporation, film composition fits the binary tieline from Cu_2Se to $(\text{In},\text{Ga})_2\text{Se}_3$. When sputter-

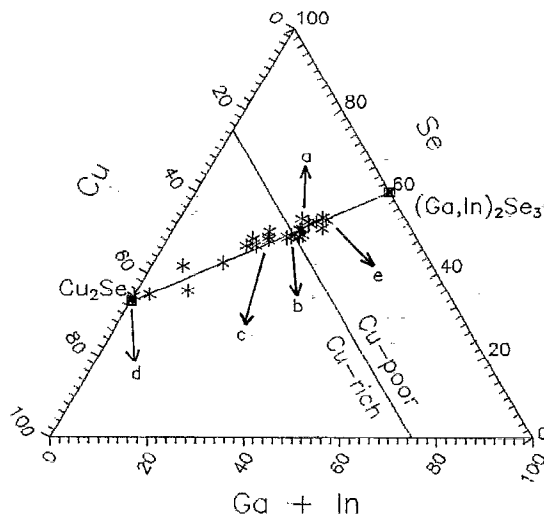


FIG. 1. Phase diagram of $\text{CuGa}_x\text{In}_{(1-x)}\text{Se}_2$ rf sputtered at different p_{Ar} and T_G . Properties of the a, b, c, d, and e films are listed in Table I.

TABLE I. Composition, intensity ratio of 112 and 220+312 x-ray peak, resistivity, and band gap of samples produced at different Ar pressure and growth temperatures on 7059 glass.

Film No.	P_{Ar} (mTorr)	T_G (°C)	Cu (at. %)	Ga (at. %)	In (at. %)	Se (at. %)	$I_{112}/(I_{220}+I_{312})$	E_g (eV)	ρ (Ω cm)
a	20	400	23.2	4.97	21.2	50.6	6.7	1.12	2×10^4
b	20	550	25.7	4.86	20.4	49.0	23	1.13	7×10^1
c	20	600	30.3	3.87	18.0	47.8	4.5	1.13	10^{-2}
d	20	675	65.3	---	---	34.5	Cu_2Se	1.55	10^{-2}
e	150	450	16.5	5.2	25.4	52.9	3.4	1.12	1×10^5

ing CGIS at 20 mTorr, 50 W, and 400 °C, resulting films are slightly Cu poor (23% Cu at. %—film a in Table I) due to the faster thermalization of Cu-sputtered atoms in the plasma, what allows a preferential diffusion of Cu out of the substrate holder area. If growth temperature is increased, Cu content increases up to 675 °C where Cu_2Se films are obtained (film d in Table I). At this temperature (Ga,In) and Se binaries reevaporate from the substrate holder, as it is also observed in cosputtered CuInSe_2 films.⁵ On the other hand, when P_{Ar} is increased it is possible to obtain very In-rich films because of the preferential diffusion of Cu in the plasma. In fact, increasing P_{Ar} from 5 to 150 mTorr at $T_G=450$ °C, Cu atomic content changes from 24% to 16%. In Table I we list the composition and main properties of films grown at different T_0 and P_{Ar} . From Fig. 1 it is evident the role of binaries in the growth of chalcopyrite CGIS. Further evidence of the binary influence on the CGIS formation is in progress, and it will be published elsewhere.

Figure 2 shows SEM micrographies of films, a, b, c, and d, quoted in Table I. It is observed that morphology sharply changes with Cu content. Sample a, which is Cu poor, shows a very smooth and uniform appearance with small grains, this corresponds with the fact that Cu poor films have a shiny appearance. For a film with 25.7% Cu (sample b) morphology is very different, grain size is bigger, and voids appear on the film. When Cu content is further increased (higher than 29%), film texture is promoted and whiskers are observed (112 oriented crystallites, 1 μm wide and up to 100 μm long) (sample c). Finally, if Cu content increases above 40%, Cu_2Se crystallites are detected, as observed in sample d. This morphology change from smooth, shiny appearance

for Cu-poor films to granular for Cu-rich films, has been reported by other authors for coevaporated CGIS films.⁶

Figure 3 presents transmittance for films grown at $p_{Ar}=20$ mTorr and different Cu content. It is evident the evolution from Cu-poor CGIS films (sample a) with a well defined absorption edge and a band gap of 1.12 eV to Cu_2Se films with a band gap of 1.55 eV and a strong free carrier absorption (sample d). The reflectance spectrum of this sample shows a sharp increase in the near infrared also due to the pseudometallic behavior of Cu_2Se . Films with intermediate Cu content show the band gap of the CGIS and a strong sub-band-gap absorption, in agreement with the behavior observed on coevaporated slightly Cu-rich films.⁶

As observed on Table I film resistivity is strongly dependent on film Cu content. Films with a Cu content lower than 24.5% show a resistivity of $2 \times 10^4 \Omega$ cm, for higher Cu contents a sharp resistivity decrease is observed. For films with Cu contents higher than 30% resistivity is $10^{-2} \Omega$ cm. This abrupt change is due to the presence of Cu_2Se which determines the low resistivity in Cu-rich samples as it incorporates in the film forming a low resistance electrical path.⁷

X-ray diffraction (XRD) patterns reveal the presence of highly 112 oriented chalcopyrite tetragonal structure for films grown at temperatures above 400 °C. For lower temperatures only reflections corresponding to cubic sphalerite are found, not detecting the superlattice reflections originated by the ordering of the cation sublattice for Ga-poor films, and the (220,204) and (312,116) peak splitting for the Ga-rich films.³ For T_G above 600 °C, which corresponds to Cu contents above 30%, additional diffraction peaks are detected. These peaks appear in the same position for the films sputtered from all CGIS targets, not depending on the Ga/In

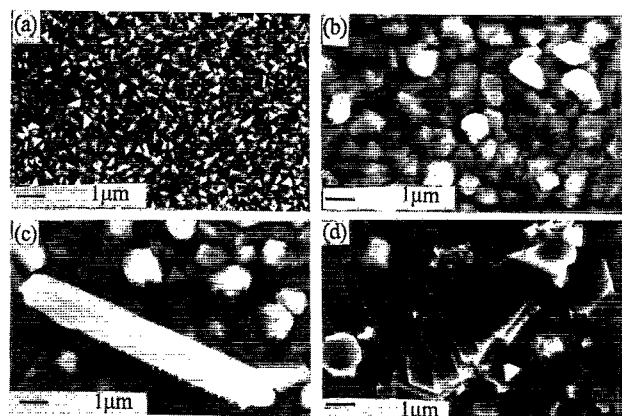


FIG. 2. SEM micrographies of films a, b, c, and d quoted on Table I.

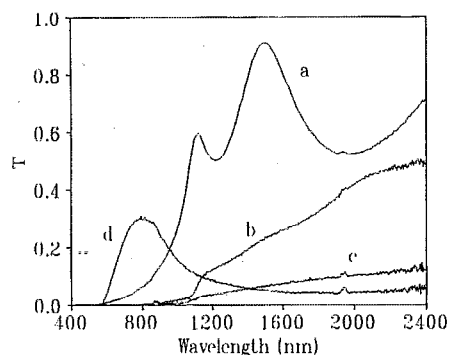


FIG. 3. Transmittance of films with different copper content (samples a, b, c, and d of Table I).

ratio, suggesting the presence of a (Cu,Se) binary. The XRD pattern of a film grown at 625 °C shows a mixture of tetragonal CGIS and Cu₂Se. This sample, with 53.7% of Copper, is formed by big Cu₂Se triangular grains 5-μm-long embedded in a CGIS matrix. However, XRD pattern show very weak peaks of Cu₂Se due to its low x-ray scattering power.⁸ Consequently, slightly Cu-rich films may have big quantities of Cu₂Se, although it is not detected by x-ray diffraction. Evidence of the presence of Cu₂Se in this film comes from the high sub-band-gap absorption observed on the optical transmittance spectrum and the low resistivity. Regardless of substrate and composition, films had a strong 112 orientation as we can see in Table I, where the $I_{112}/(I_{220}+I_{312})$ ratio has been quoted for all different films.

This flexibility on films production allows us to grow by rf sputtering with a single target graded composition absorbers, resembling the coevaporated bilayer films. In fact, we have already deposited compact films with bulk Cu content of 23.5% and columnar grains 3–4 μm wide. Details about bilayer and devices fabrication will be published elsewhere.

Summarizing, we have shown that modifying growth conditions uniform films can be grown with controlled composition in the Cu₂Se-(Ga,In)₂Se₃ binary tie line. When T_G is changed from 300 to 700 °C at $p_{Ar}=20$ mTorr, Cu content increases due to the re-evaporation of the Ga, In, and Se binaries. For the higher T_G , no indium is detected by EDS and the optical, structural, and electrical properties confirm

the presence of Cu₂Se. On the other hand, when p_{Ar} is increased from 5 to 150 mTorr, composition changes in the Cu-poor side from 24% to 16%. We have also seen that regardless of the production conditions, the main film characteristics are ruled by the Cu content. We have been able to tailor Cu content in a reproducible way in CGIS films grown by rf sputtering from a single target. These results show that it is possible to grow high quality absorbers for photovoltaic devices by a readily scalable technique as sputtering.

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¹ L. Stolt, J. Hedström, J. Kessler, M. Ruckh, K. Velthaus, and H. Schock, *Appl. Phys. Lett.* **62**, 597 (1993).

² K. W. Mitchell, C. Eberspacher, J. Ermer, and D. Pier, *Proceedings of the 20th IEEE Photovoltaic Specialist Conference* (IEEE, New York, 1988), p. 1384.

³ J. L. Hernández-Rojas, M. L. Lucía, I. Mártel, J. Santamaría, G. González-Díaz, and F. Sánchez-Quesada, *Appl. Phys. Lett.* **60**, 1875 (1992).

⁴ J. L. Hernández-Rojas, M. L. Lucía, I. Mártel, G. González-Díaz, J. Santamaría, and F. Sánchez-Quesada, *Appl. Opt.* **31**, 1606 (1992).

⁵ A. Rockett, T. C. Lommason, L. C. Yang, H. Talien, P. Campos, and J. A. Thornton, *Proceedings of the 20th IEEE Photovoltaic Specialist Conference* (IEEE, New York, 1989), p. 1505.

⁶ D. S. Albin, J. R. Tuttle, G. D. Mooney, J. J. Carapella, A. Duda, A. Mason, and R. Noufi, *Proceedings of the 21st IEEE Photovoltaic Specialist Conference* (IEEE, New York, 1990), p. 562.

⁷ J. R. Tuttle, D. S. Albin, and R. Noufi, *Sol. Cells* **30**, 21 (1991).

⁸ T. Walter and H. W. Shock, *Thin Solid Films* **224**, 74 (1993).