Preparation of homogeneous $Cu(InGa)Se_2$ films by selenization of metal precursors in H_2Se atmosphere

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Homogeneous single phase $Cu(InGa)Se_2$ films with Ga/(In+Ga)=0.25–0.75 were formed by reacting Cu–Ga–In precursor films in H_2Se followed by an anneal in Ar. X-ray diffraction and Auger analysis show that the metal precursors reacted only in H_2Se were multiphase films having a layered $CuInSe_2/CuGaSe_2$ structure. Solar cells made with the multiphase films have properties similar to $CuInSe_2$ devices. Cells made with the annealed single phase films behave like $Cu(InGa)Se_2$ devices with the band gap expected for the precursor composition. © *1995 American Institute of Physics.*

$CuInSe_2$ and related compounds with higher band gap are promising candidates for absorber layers in thin-film solar cells. Efficiencies exceeding 16% have been reported for cells based on $Cu(InGa)Se_2$.[1,2] To date the most successful methods for preparing $CuInSe_2$ and its alloys are multisource elemental evaporation and selenization of thin-film metallic precursors in a H_2Se atmosphere. While the former, due to its versatility and good control of the film growth, has been the method of choice for basic research, selenization may be more appropriate for large scale industrial production. However, with this method, problems have been encountered in the attempt to widen the $CuInSe_2$ band gap by adding Ga.[3] While adhesion of the film and open circuit voltage of the cell were improved, most of the Ga was found near the back contact and no significant increase of the band gap in the active region of the absorber was observed. In this letter, we report the preparation of homogeneous, single phase $Cu(InGa)Se_2$ films by reacting Cu–Ga–In precursors in H_2Se followed by an *in situ* annealing in an inert atmosphere. Characterization data and solar cell results are presented for multiphase (as-selenized films) as well as single phase annealed films.

Metal precursor films were deposited in the sequence Cu–Ga–In at room temperature onto Mo coated soda lime glass substrates by dc magnetron sputtering.[4] The Cu thickness was chosen to be 250 nm and the thicknesses of Ga and In layers were adjusted to yield a Cu/(In+Ga) ratio of ~ 0.9. Precursor films with Ga/(Ga+In) ratios of 0, 0.25, 0.5, 0.75, and 1.0 were prepared. The films were selenized in a flowing $H_2Se/Ar/O_2$ mixture for 90 min after a 10 min ramp to the chosen substrate temperature.[5] A substrate temperature of 410 °C was used with the Cu–In precursor while the films containing Ga were reacted at 450 °C. Postreaction heat treatments for 60–90 min were carried out *in situ* in an Ar atmosphere at 500 and 600 °C for the films with different Ga/(Ga+In) ratios, followed by a second exposure to the gas mixture containing H_2Se to compensate a possible Se loss at the films surface. The structure of the absorber layers was examined by x-ray diffraction (XRD) and their composition was determined by energy dispersive x-ray spectroscopy (EDS) and Auger depth profiles.

Heterojunctions were formed by chemical bath deposition of a 50 nm thick CdS buffer layer and a double layer (high resistivity/low resistivity) of rf sputtered ZnO:Al.[6] Ni front contacts were evaporated through a shadow mask. No antireflection coatings were used. The solar cells were characterized by current–voltage and spectral response measurements. Estimations of the parameters of minority carrier transport and the band gap of the absorber were derived from the long wavelength cutoff of the spectral response.[7] Capacitance was measured with a 100 kHz/50 mV excitation under ambient light.

The selenization of Cu–In and Cu–Ga precursor films resulted in single phase $CuInSe_2$ and $CuGaSe_2$, respectively. However, the selenization of the Cu–Ga–In precursors re-

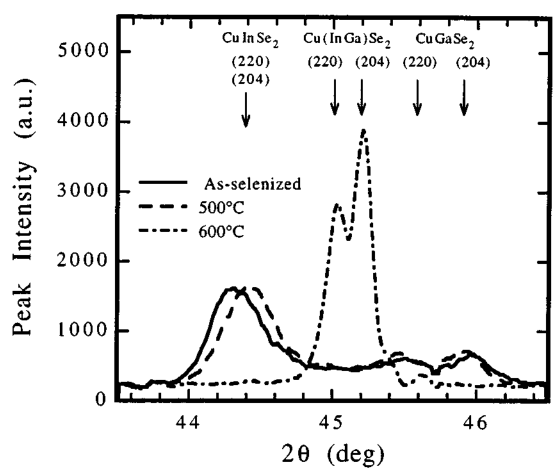

FIG. 1. X-ray diffraction spectra of (220) and (204) reflections of as-selenized and heat treated $Cu(InGa)Se_2$ films with Ga/(Ga+In)≈0.5.

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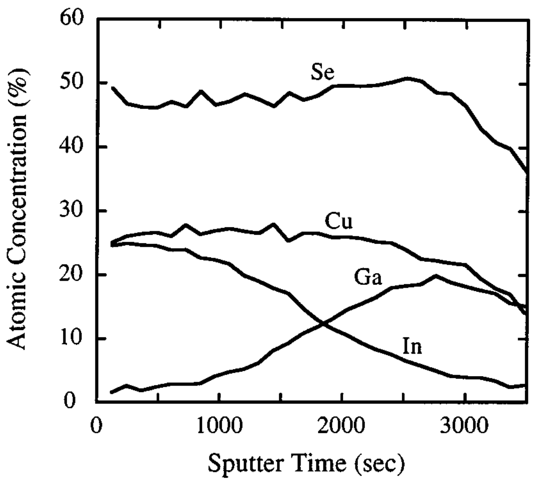

FIG. 2. Auger depth profile of an as-selenized $Cu(InGa)Se_2$ films with a Ga/(Ga+In)≈0.5.

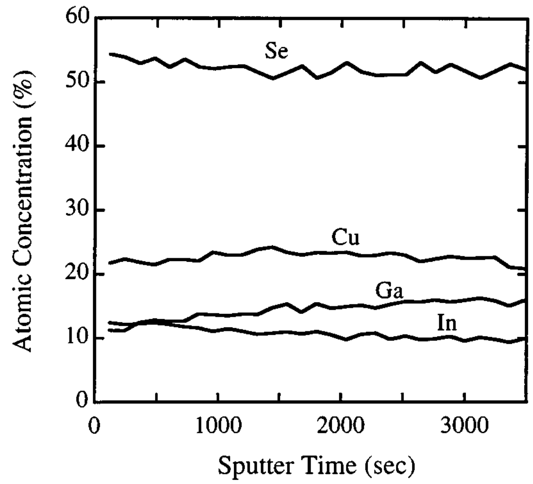

FIG. 3. Auger depth profile of an annealed (60 min, 600 °C in Ar) $Cu(InGa)Se_2$ film with a Ga/(Ga+In)≈0.5.

sulted in a film containing $CuInSe_2$ and $CuGaSe_2$ with little intermixing. The x-ray spectrum of the (220) and (204) reflections from the film with Ga/(In+Ga)≈0.5 is shown in Fig. 1. The as-selenized film showed distinct peaks corresponding to phases close to $CuInSe_2$ and $CuGaSe_2$. Even though $CuInSe_2$ and $CuGaSe_2$ are miscible at all concentrations, there is little $Cu(InGa)Se_2$ evident in the spectrum. The Auger depth profile of this film shown in Fig. 2 indicates that the film had a layered structure with $CuGaSe_2$ near the back and $CuInSe_2$ at the surface.

XRD spectra after the *in situ* Ar atmosphere anneals at 500 and 600 °C are also shown in Fig. 1. After the 500 °C anneal, the film still retained the two phase structure of the as-selenized film. The 600 °C anneal, however, converted the film to single phase $Cu(InGa)Se_2$. The Auger depth profile in this case is shown in Fig. 3 and confirms that the Ga and In are more homogeneously distributed. Similar behavior was observed for the films with Ga/(In+Ga)≈0.25. However, the film with Ga/(In+Ga)≈0.75 was converted to single phase after the 500 °C anneal. Since the homogenization occurred at a lower temperature it is assumed that interdiffusion of In and Ga is faster in films with greater Ga content.

Device results for the solar cells made from films with the different Ga contents and anneal conditions are listed in Table I. Spectral response plots for the as-selenized and annealed films with Ga/(In+Ga)≈0.5 are shown in Fig. 4. The open circuit voltage (V_{oc}) and long wavelength cutoff of the spectral response of the as-selenized multiphase absorbers are similar to $CuInSe_2$ cells. The photovoltaic response is controlled by the more In rich, lower band gap phase close to the heterojunction. The second phase is separated from the active layer of the device and does not deteriorate the cell performance. Devices with the annealed single-phase films have increased V_{oc} and a shift in the spectral response cutoff consistent with the expected Ga/(In+Ga) for these films. Evaluation of the spectral response and capacitance for all cells suggests a narrow field zone and a good diffusion length of 0.6–1 μm. The long wavelength spectral response can be described with good accuracy by assuming a constant, direct band gap, i.e., there is no indication for a graded band gap.

In summary, we have shown that absorber films prepared by selenization of Cu–Ga–In precursor layers with H_2Se are inhomogeneous with a layered structure containing two phases with compositions close to $CuInSe_2$ and $CuGaSe_2$. Cell results and spectral response measurements are consistent with the In-rich phase at the top of the film and exhibit a comparable or better performance than cells on single phase $CuInSe_2$. An *in situ* anneal in Ar, immediately after the selenization, is shown to create homogeneous, single

TABLE I. Results on cells fabricated.

$\frac{Ga}{Ga+In}$	Anneal (°C)	Structure	Cu (at. %)	In (at. %)	Ga (at. %)	Se (at. %)	V_{oc} (V)	J_{sc} (mA/cm^2)	FF (%)	Eff (%)
0	⋯	$CuInSe_2$	23.9	25.0	⋯	51.1	0.44	39	66	11.2
0.25	⋯	Multiphase	22.3	14.0	2.9	50.8	0.46	39	58	10.4
0.25	500	Multiphase	22.7	22.5	2.6	52.2	0.45	38	68	11.5
0.25	600	Single phase	22.3	18.6	5.9	53.2	0.56	34	67	12.9
0.50	⋯	Multiphase	22.4	18.9	7.9	50.8	0.53	38	64	13.1
0.50	500	Multiphase	22.4	18.3	8.9	50.4	0.54	35	66	12.5
0.50	600	Single phase	22.3	12.8	13.2	51.7	0.59	30	60	10.5
0.75	600	Single phase	21.6	7.0	19.0	52.4	0.63	22	46	6.4

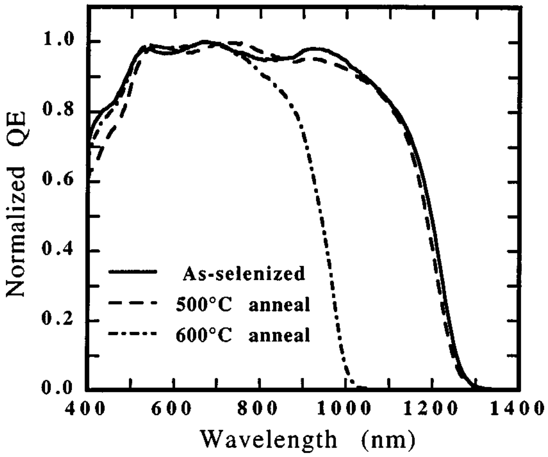

FIG. 4. Spectral response of devices made from an as-selenized and heat treated $Cu(InGa)Se_2$ films with Ga/(Ga+In)≈0.5.

phase films, even at high Ga content. Material and device measurements show that these films contain the same Ga/(In+Ga) composition as the starting precursors.

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