

EFFECT OF REDUCED DEPOSITION TEMPERATURE, TIME, AND THICKNESS ON Cu(InGa)Se₂ FILMS AND DEVICES

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ABSTRACT

This paper will address the ability to reduce process costs for multisource evaporation of Cu(InGa)Se₂ by reducing the deposition temperature and film thickness and increasing the deposition rate. Substrate temperature (T_{ss}) is varied from 600 to 350°C using fixed elemental fluxes. The grain size decreases over the entire range but Na incorporation from the soda lime glass substrate doesn't change. Solar cell efficiency decreases slowly for 550 to 400°C. At T_{ss} below 400°C there is a change in composition attributed to a change in the re-evaporation of In and Ga species in the growing film. Device performance is shown to be unaffected by reducing the film thickness from 2.5 to less than 1.5 μm . Finally, a kinetic reaction model is presented for the growth of CuInSe₂ by multisource elemental evaporation which provides quantitative predictions of the time to grow CuInSe₂ films as a function of substrate temperature and delivery rate.

INTRODUCTION

There are many technical issues which need to be addressed to effectively enable the transfer of Cu(InGa)Se₂ deposition and device fabrication technology from the laboratory to manufacturing scale. In general, these issues provide means to reduce thin film semiconductor process costs. Shorter deposition time, with reduced film thickness and increased deposition rate, is a primary means to lower costs by increasing throughput and can enable reduced size of the deposition zone in an in-line process. For films deposited by multisource evaporation the deposition time will depend on the delivery rate to the substrate and the film growth rate. Understanding the effect of delivery rate and temperature on the film growth requires the quantitative knowledge of the reaction chemistry and kinetics.

Thinner absorber films reduce the total amount of material used and allow faster process throughput. The minimum thickness of the Cu(InGa)Se₂ absorber layer may be determined by the nucleation of the film to form a continuous layer. From a device perspective, the minimum thickness is limited by the optical absorption coefficient of the Cu(InGa)Se₂ or the ability to incorporate optical confinement. If the absorber layer becomes too thin, so that the minority carrier diffusion length becomes comparable to the thickness, then V_{oc} may be reduced by back surface recombination at the Mo/Cu(InGa)Se₂ interface.

Soda lime glass has been used as the substrate for most high efficiency Cu(InGa)Se₂ solar cells but often deforms at the substrate temperatures used for these

devices. Additional effort and cost to control this for a large area deposition would be difficult for a manufacturing process. With lower substrate temperature (T_{ss}) alternative substrate materials, like a flexible polymer web, can be utilized. In addition, lower T_{ss} can lower processing costs by reducing thermally induced stress on the substrate, allowing faster heat-up and cool-down, and decreasing the heat load and stress on the entire deposition system.

This paper will address the need to improve process throughput by reducing the Cu(InGa)Se₂ thickness and increasing the deposition rate, and the effect of reducing deposition temperature. Baseline processes for Cu(InGa)Se₂ deposition by multisource elemental evaporation and solar cell fabrication are defined. All other deposition parameters are then held fixed to determine the effects of varying either the substrate temperature or, by changing the deposition time, film thickness. Characterization of the resulting Cu(InGa)Se₂ films and their device behavior will be presented. Finally, a chemical reaction model for the growth and kinetics of CuInSe₂ is presented to evaluate the effect of substrate temperature and delivery rate of elemental species to the substrate and to predict the minimum times to form the film.

EXPERIMENTAL PROCEDURES

Cu(InGa)Se₂ films were deposited by thermal evaporation from four elemental sources. Details of the deposition, film characterization, and device fabrication are described in Ref. 1. The baseline deposition process in this work is the same as described in Ref. 1 but with the T_{ss} maintained constant through the entire deposition. The films are deposited with a Cu-rich first layer, deposited in 32 min., and followed continuously by an In-Ga-Se second layer deposited in 12 min. The fluxes of Ga and In are constant through the deposition time so there is no grading of the bandgap. This results in ~2.5 μm thick films with $Ga/(In+Ga) = 0.3$ which gives a bandgap ~ 1.2 eV.

To study the effect of substrate temperatures, Cu(InGa)Se₂ films were deposited with T_{ss} from 600 to 350°C, maintaining fixed source effusion rates and deposition times. To study varying thicknesses, films were deposited with constant effusion rates and T_{ss} , and only the times adjusted.

The film thickness was determined by the mass gain after deposition and the films were characterized by scanning electron microscope (SEM) images, energy dispersive x-ray spectroscopy (EDS), x-ray diffraction (XRD). Secondary ion mass spectroscopy (SIMS) measurements were performed at NREL.

The Cu(InGa)Se₂ films were deposited on soda lime glass substrates with a sputtered 1 μm thick Mo layer. Complete solar cells were fabricated [1] with the chemical bath deposition of ~ 30 nm CdS followed by rf sputtered ZnO:Al with thickness 0.5 μm and sheet resistance 20 /sq. A Ni/Al grid and 125 nm MgF₂ anti-reflection layer were deposited by electron beam evaporation. Cells were delineated by mechanical scribing to give areas ~0.5 cm². Devices were characterized by current-voltage (J-V) measurements at 28°C under 100 mW/cm² AM1.5 illumination.

RESULTS

Substrate Temperature

Cu(InGa)Se₂ films were deposited at varying T_{ss} with fixed effusion rates that were determined to give films of composition Cu/(In+Ga) 0.9 and Ga/(In+Ga) 0.3 when T_{ss} = 600°C. This required the total concentration of metals to be delivered to the substrate with ratios Cu/(In+Ga) 0.6 and Ga/(In+Ga) 0.3. The difference in the relative Cu and In compositions can be attributed to the re-evaporation of In and Ga from the surface of the growing film. The In and Ga form volatile intermediate binary species while no volatile Cu-Se species are formed [2]. The compositions of films deposited with T_{ss} varying from 600 to 350°C are plotted in Fig. 1. The composition is independent of T_{ss} except for T_{ss} = 400°C when the ratio Cu/(In+Ga) decreases. At T_{ss} = 350°C, the Cu/(In+Ga) ratio is comparable to that delivered to the substrate during growth. The relative Ga content of the films remains unchanged which suggests that films lose Ga and In at similar rates. The temperature dependence of the composition will, in general, depend on Cu/(In+Ga) flux ratio [3] and the Se flux.

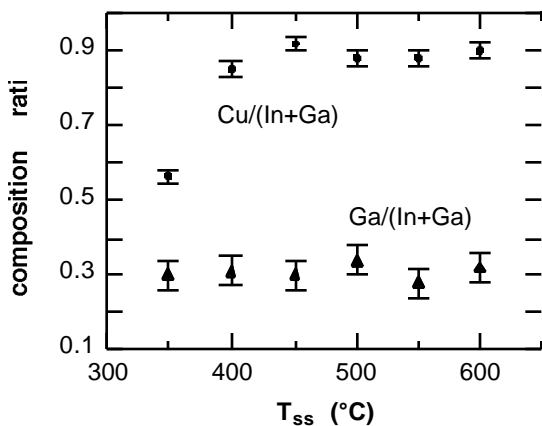


Fig. 1. The T_{ss} dependence of the composition ratios Cu/(In+Ga) and Ga/(In+Ga).

SEM micrographs show that the grain structure of the Cu(InGa)Se₂ films changes dramatically as T_{ss} changes. The cross sectional micrographs in Fig. 2 show columnar grains at T_{ss} = 600°C with typical grain size 1.5 -

2 μm. But the grains become smaller as T_{ss} decreases and for T_{ss} = 450°C it appears that single grains do not grow continuously from the Mo to the top surface. In this case, current in a working device clearly would need to cross several grain boundaries. XRD measurements did not reveal any significant differences in the film orientation or compositional distribution at different substrate temperatures. There is no peak broadening, indicating that the grain size at the lowest T_{ss} is still greater than ~ 300 nm.

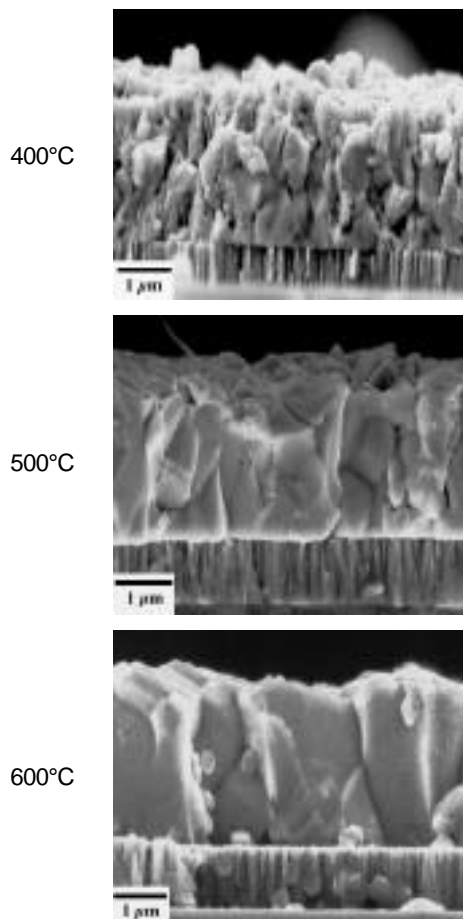


Fig. 2. Cross-sectional micrographs of Cu(InGa)Se₂ films deposited at different T_{ss}.

While the film deposited at T_{ss} = 600°C has the largest grains, the soda lime glass in this case is well above its softening point during the deposition which resulted in a curved substrate.

Cu(InGa)Se₂ have been shown to contain significant levels of Na impurities when deposited on soda lime glass substrates [4]. The Na is incorporated into the Cu(InGa)Se₂ by diffusion and is therefore expected to be temperature dependent. Depth profiles of the Na content measured by SIMS are shown at different T_{ss} in Fig. 3. The Cu and Mo levels for T_{ss} = 500°C are shown for reference to indicate the position of the Cu(InGa)Se₂/Mo interface. The

Na level varies by relatively little from 400 to 600°C and is actually highest for the lowest T_{ss} , though diffusion of Na is expected to increase with increasing T_{ss} . This can be explained by Na diffusion along grain boundaries since there is a greater grain boundary density at the lower temperature.

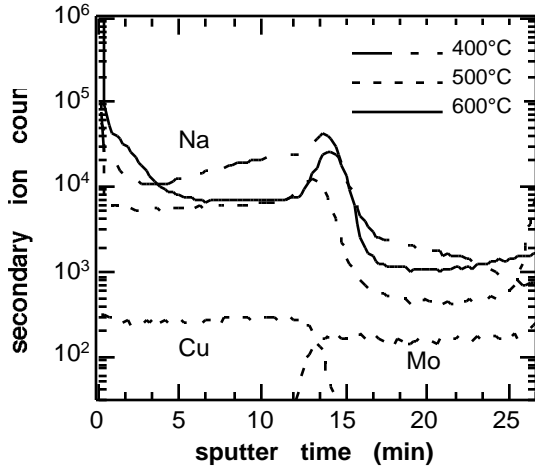


Fig. 3. SIMS profiles showing the Na content of Cu(InGa)Se₂ films deposited at different T_{ss} .

Finally, solar cells were fabricated with films deposited at varying T_{ss} and the J-V parameters are listed in Table 1. The efficiency (η) decreases slowly as T_{ss} decreases from 550°C, but is still 12.8% at 400°C. While there is some tradeoff in V_{oc} and J_{sc} which may be associated with variations in the Ga content and, therefore, bandgap of the Cu(InGa)Se₂, the biggest change is the fill factor. With $T_{ss} = 350^\circ\text{C}$ the Cu(InGa)Se₂ films with Cu/(In+Ga) 0.6 had $\eta = 7.0\%$, but a film deposited with the Cu effusion rate adjusted to give Cu/(In+Ga) 0.9 gave $\eta = 10.9\%$.

Thickness

Using the same effusion rates as above, the effect of thickness has been studied by changing the

Table 1. J-V parameters with varying substrate temperature.

T_{ss} (°C)	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	η (%)
600	0.596	31.2	67.4	12.5
550	0.583	34.3	71.8	14.4
500	0.606	32.5	70.0	13.8
450	0.605	32.6	68.4	13.5
400	0.606	32.5	64.8	12.8
350	0.557	23.2	54.2	7.0
350*	0.561	33.2	58.6	10.9

* Cu effusion rate adjusted to give Cu/(In+Ga) 0.9

deposition times with $T_{ss} = 450^\circ\text{C}$ to give films with thickness (d) ranging from 2.5 to 1.0 μm . The composition of these films was unchanged over the thickness range with all films having Cu/(In+Ga) 0.9 and Ga/(In+Ga) 0.3 and again, no difference in orientation or compositional distribution was observed by XRD.

Device results for different Cu(InGa)Se₂ thickness with this deposition process are shown in Table 2. With d 1.4 μm the devices have $\eta = 13\%$. There are no significant thickness related losses which might include effects of bulk series resistance or back surface recombination. For d = 1.0 μm , η decreases due to decreases in V_{oc} , J_{sc} , and FF. In addition, the J-V curves both in the dark and under illumination indicate an increased shunt conductance for the thinnest cells.

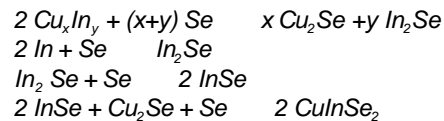
Table 2. J-V parameters with decreasing Cu(InGa)Se₂ thickness for films deposited at $T_{ss} = 450^\circ\text{C}$.

d \pm 0.2 (μm)	V_{oc} (mV)	J_{sc} (mA/cm ²)	FF (%)	η (%)
2.5	0.605	32.6	68.4	13.5
1.8	0.581	33.7	66.6	13.0
1.4	0.590	32.5	69.5	13.3
1.2	0.526	34.2	64.9	11.7
1.0	0.514	30.7	62.5	9.9

Growth Time

A chemical reaction analysis of the growth and kinetics of CuInSe₂ has been previously developed based on the species formed by the reaction of Cu/In precursors in H₂Se and Se vapor [5,6]. This required identification of the species present in the film versus time and at different reaction temperatures and quantitative determination of their concentrations by XRD and atomic absorption spectroscopy. This analysis has not been completed for the growth of CuGaSe₂ or Cu(InGa)Se₂ because of difficulty quantitatively measuring the elemental Ga and binary Ga selenide phases.

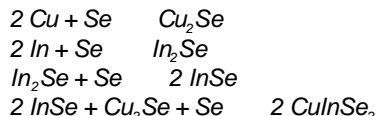
The reaction pathway leading to the formation of CuInSe₂ by selenization which was used to model the measured species concentrations was:



The rate constants and activation energies for each of these reactions were determined by fitting the concentrations to a detailed set of kinetic equations [6].

This analysis can be used to predict the growth of CuInSe₂ by three source elemental evaporation if modified to include a rate of delivery term for the elemental species. It is assumed that the reaction proceeds from elemental species, since the reaction time to form a Cu/In alloy is long, and that there is an unlimited continuous supply of Se. Finally, it is assumed there is no direct reaction of

$In + Cu + 2 Se \rightarrow 2 CuInSe_2$. since there was no evidence of this reaction in analysis of the selenization experiments. These assumptions and modifications lead to the following proposed reaction pathway for the multisource evaporation:



Using the rate constants and activation energies determined previously [6], this model was used to predict the time to form $CuInSe_2$ as a function of substrate temperature and delivery rate. This has been completed for 2 cases and the results are shown in Fig. 4 at $T_{ss} = 600, 500, \text{ and } 400^\circ\text{C}$. Case 1 models a process similar to that described above which deposits a $2 \mu\text{m}$ thick film with the Cu delivered to the substrate in 30 min. and the In delivered in 40 min. while maintaining a constant T_{ss} . Case 2 in Fig 4. shows the theoretical limiting case when the Cu and In are delivered instantaneously at time equal to zero. An intermediate case, with the metals delivered at 5 times the rate in case 1 was also calculated and the curves (not shown) fall in between cases 1 and 2 as expected. These $CuInSe_2$ formation curves provide quantitative predictions for film growth time as a function of delivery rate and substrate temperature.

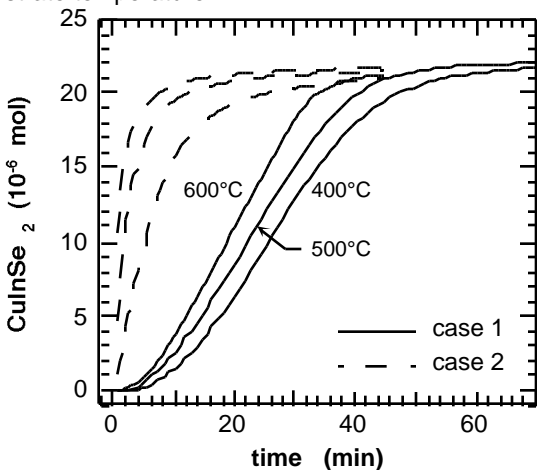


Fig. 4. Model predictions for the molar concentration of $CuInSe_2$ versus time for different T_{ss} and delivery rate (cases 1 and 2 defined in text).

DISCUSSION AND CONCLUSIONS

The $Cu(InGa)Se_2$ grain size decreases as T_{ss} decreases from 600 to 400°C but there is little change in the incorporation of Na from the glass substrate. The dependence of grain size with T_{ss} has been reported previously [7], and at high temperatures was attributed to the formation of copper selenide phases above $\sim 525^\circ\text{C}$ which act as a "flux" for grain growth in the Cu rich film [8]. However, the films in this work show an increasing grain size with increasing T_{ss} over the entire temperature range. There is only a small drop-off in device performance with

lower T_{ss} despite the decreasing grain size. The ability to fabricate cells with 13% at $T_{ss} = 450^\circ\text{C}$ allows flexibility in the choice of substrate materials and process design which can potentially lead to lower costs.

The absorber thickness can also be reduced to minimize materials use and deposition times. With the baseline process in this work there was no fall-off in device performance with the absorber layer thickness reduced to $\sim 1.5 \mu\text{m}$.

Increased growth rate and reduced thickness are critical means to increase throughput. Experimental verification of the effect of growth rate and time on device performance still need to be established, although, using a similar deposition process, a 13% cell efficiency with a deposition time of 10 min. was demonstrated in Ref. [9]. The kinetic reaction model presented here for $CuInSe_2$ film growth by elemental evaporation provides a quantitative prediction of the effect of T_{ss} and delivery rate on the film growth rate. This provides necessary information to design a manufacturing process and commercial scale deposition equipment. Experimental measurements of the concentrations of reaction species versus time in the growth of $CuInSe_2$ by evaporation are needed to provide the verification of the growth model and assumptions. This will require rapid substrate quenching to provide the necessary time resolution.

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