

# CONTROL OF COMPOSITION IN CO-EVAPORATED $\text{Cu}(\text{InGa})(\text{SeS})_2$ THIN FILMS

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## ABSTRACT

$\text{Cu}(\text{InGa})(\text{SeS})_2$  thin films have been prepared using multi source thermal co-evaporation. The incorporation of the volatile chalcogen species Se and S into the films depends on the fluxes of the evaporated species during growth and the relative  $[\text{Cu}]/[\text{In+Ga}]$  and  $[\text{Ga}]/[\text{In+Ga}]$  compositions. The dependence of the relative Se and S incorporation in  $\text{Cu}(\text{InGa})(\text{SeS})_2$  on the substrate temperature is characterized with various  $[\text{S}]/[\text{Se+S}]$  flux rate ratios for substrate temperatures of 300, 450, and 550°C. The relative chalcogen incorporation is the same at 450 – 550°C for both Cu-excess and Cu-deficient growth. However, at 300°C the relative  $[\text{S}]/[\text{Se+S}]$  incorporation changes. The chalcogen incorporation is compared to predictions from equilibrium thermodynamics and to an empirical kinetic model. Deposition processes with sequential layers including Cu-excess and Cu-poor fluxes have inhomogeneous composition and microstructural models for these processes are proposed.

## INTRODUCTION

Control of the composition of  $\text{Cu}(\text{InGa})(\text{SeS})_2$  films is a critical issue for their development as the absorber layers in wide bandgap devices. Previously, we reported that the  $[\text{S}]/[\text{S+Se}]$  ratio of co-evaporated  $\text{Cu}(\text{InGa})(\text{SeS})_2$  thin films depends on the fluxes of the evaporated species during growth and the relative  $[\text{Cu}]/[\text{In+Ga}]$  and  $[\text{Ga}]/[\text{In+Ga}]$  compositions [1]. Deposition with a uniform flux-time profile under Cu-deficient conditions,  $[\text{Cu}]/[\text{In+Ga}] < 1$ , leads to preferential incorporation of Se relative to the vapor flux. With excess Cu,  $[\text{Cu}]/[\text{In+Ga}] > 1$ , S is preferentially incorporated and the resulting  $[\text{S}]/[\text{Se+S}]$  ratio in the film depends on the relative In and Ga concentration.

In this work, the dependence of the relative Se and S incorporation in  $\text{Cu}(\text{InGa})(\text{SeS})_2$  on the substrate temperature is characterized with various  $[\text{S}]/[\text{Se+S}]$  flux rate ratios for deposition substrate temperatures ( $T_{\text{SS}}$ ) of 300°C, 450°C, and 550°C. The chalcogen incorporation will be compared to predictions from equilibrium thermodynamics and to a kinetic model. Different two and three stage sequential processes are sometimes implemented to control film properties and improve device performance. The implications of changes in chalcogen incorporation on composition control in sequential deposition processes is addressed.

## EXPERIMENT

$\text{Cu}(\text{InGa})(\text{SeS})_2$  films were prepared on Mo-coated soda lime glass substrates by the thermal co-evaporation of the five elements [2] with  $T_{\text{SS}} = 300^\circ\text{C}$ ,  $450^\circ\text{C}$ , and  $550^\circ\text{C}$ . Films were deposited with uniform flux-time profiles and sequential processes incorporating layers with Cu-excess and Cu-poor or Cu-free fluxes and compositions. All films were  $\sim 2 \mu\text{m}$  thick. Effusion rates were determined from the measured mass loss of the elements and the effective effusion duration. Flux ratios at the growing films were assumed to be the same as the ratios of the effusion rates since the effusion sources for Cu, In, and Ga and for Se and S had identical geometries. For analyses, as-grown and KCN etched (0.5 M, at  $55^\circ\text{C}$  for 1 min) samples were used. Films were characterized by EDS, measured with 20 kV accelerating voltage to determine composition of the top  $\sim 1 \mu\text{m}$ , and glancing incidence x-ray diffraction (GIXRD).

Relative film compositions are specified by Y and X in  $\text{Cu}(\text{In}_{1-X}\text{Ga}_X)(\text{Se}_{1-Y}\text{S}_Y)_2$ , i.e.  $X \equiv [\text{Ga}]/[\text{In+Ga}]$  and  $Y \equiv [\text{S}]/[\text{S+Se}]$ . For Cu-deficient conditions, the films were grown with  $[\text{Cu}]/[\text{In+Ga}] = 0.7\sim 0.9$ , and for Cu-excess conditions  $[\text{Cu}]/[\text{In+Ga}] > 1.1$ . All films were grown using excess chalcogen species in the flux with  $[\text{S+Se}]/[\text{Cu+In+Ga}] \approx 10$ , and both flux rate ratios of  $[\text{S}]/[\text{Cu+In+Ga}]$  and  $[\text{Se}]/[\text{Cu+In+Ga}]$  were greater than unity throughout all experiments.

## RESULTS and DISCUSSION

### Chalcogen incorporation

Fig. 1 shows the relation between the concentration ratios of Y in the flux ( $Y_{\text{flux}}$ ) and in the film ( $Y_{\text{film}}$ ). There is a distinct change in  $Y_{\text{film}}$  for films grown with Cu poor composition (open symbols) to those with Cu-excess composition (closed symbols). Data for films with excess Cu were measured after a KCN etch to remove Cu-(SeS) and all films have  $[\text{Ga}]/[\text{In+Ga}] = 0.45 \pm 0.05$ . The solid lines are drawn using the general function:

$$\frac{Y_{\text{film}}}{1 - Y_{\text{film}}} = C \frac{Y_{\text{flux}}}{1 - Y_{\text{flux}}}, \quad (1)$$

where the relative concentrations of the chalcogen species in the flux and in the film are related with a constant C. Values of  $C > 1$  indicate preferential incorporation of S relative to Se and  $C < 1$  indicates preferential incorporation of Se.

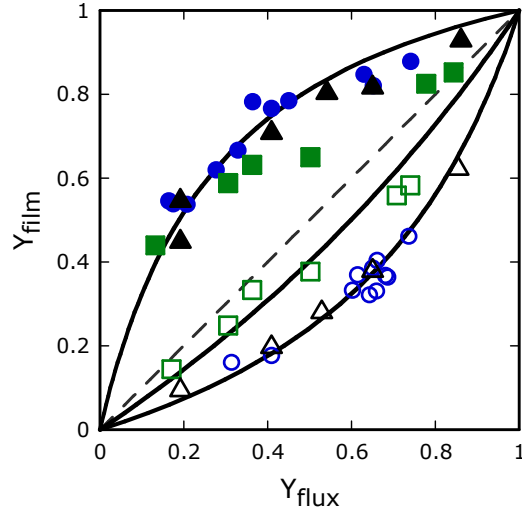


Fig. 1. Relation between  $Y_{\text{film}}$  and  $Y_{\text{flux}}$  in which the shape of the symbols corresponds to  $T_{\text{SS}}$  of 300°C (■, □) 450°C (▲, △), and 550°C, (●, ○). Open and closed symbols correspond to Cu-poor and Cu-excess deposition conditions, respectively.

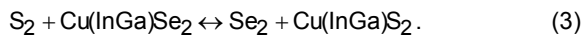
For films grown with Cu-poor flux, the preferred incorporation of the chalcogen shows good agreement with Eq. 1. At substrate temperatures of 450°C and 550°C, the films all fall on a single curve with  $C = 0.32$ . A fit of the data at 300°C gives  $C = 0.67$ . With Cu-excess growth, a line with  $C = 4.3$  fits the data at 450°C and 550°C. However, the films grown at 300°C with  $Y_{\text{flux}} > 0.3$  deviate from the line and the data cannot be fit with Eq. 1.

Eq. 1 can be derived with different models for film formation which consider relative kinetic and thermodynamic effects and give different meaning to the parameter  $C$ . For the kinetic model, relative rates of absorption and desorption, and reaction of the volatile Se and S species can be considered [3]. In this case, the constant  $C$  in Eq. 1 is a function of the sticking probabilities  $S$  and the molecular masses of the S and Se species as:

$$C \propto \left( \frac{S_{\text{S}}}{S_{\text{Se}}} \right) \left( \frac{M_{\text{Se}}}{M_{\text{S}}} \right)^{1/2}. \quad (2)$$

In this case  $C$  may vary with temperature.

Alternatively, a thermodynamic model can be considered according to the equilibrium between the chalcogen and  $\text{Cu}(\text{InGa})(\text{SeS})_2$  as follows:



The equilibrium constant  $K$  for this reaction is given by

$$K = \frac{[\text{Se}_2][\text{Cu}(\text{InGa})\text{S}_2]}{[\text{S}_2][\text{Cu}(\text{InGa})\text{Se}_2]}, \quad (4)$$

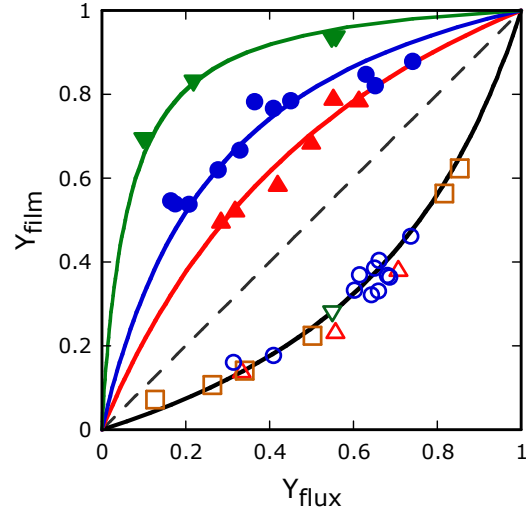


Fig. 2. Relation between the  $Y_{\text{film}}$  and  $Y_{\text{flux}}$  for different values of  $X$ . The shape of symbols correspond to  $X = 0$  (▲, △),  $X = 0.35 \pm 0.05$  (□),  $X = 0.55 \pm 0.05$  (●, ○), and  $X = 1$  (▼, ▽). The open and close symbols correspond to Cu-poor and Cu-excess deposition conditions.

where the reaction constant  $K$  is understood using the Gibbs free energy difference  $\Delta G$  as:

$$K = \exp(-\Delta G/kT). \quad (5)$$

Eq. 4 can be rewritten in the same form as Eq. 1 with  $K = C$ .

To consider the applicability of the kinetic and thermodynamic models, the composition dependence of the chalcogen incorporation must also be considered. Fig. 2 shows the influence of the relative Ga concentration on the relationship between  $Y_{\text{film}}$  and  $Y_{\text{flux}}$  [1]. The films were deposited at 550°C under Cu-poor and Cu-excess conditions with  $X = 0, 0.35, 0.55$ , or 1. As previously, films with excess Cu were measured after a KCN etch. The solid lines in Fig. 2 are fits of the data to Eq. 1 with a single value of  $C$  for the Cu-poor films and different values for the Cu-excess films corresponding to each value of  $X$ .

Dependence on  $X$  seems to follow the thermodynamic model. While complete free energy data covering the  $\text{Cu}(\text{InGa})(\text{SeS})_2$  alloy system is not available, trends from the literature can be considered [4,5,6,7]. In particular, sulfide compounds tend to have lower free energies to form the chalcopyrite than selenide compounds, while the energies of  $\text{S}_2$  and  $\text{Se}_2$  are similar. Furthermore, the Gibbs free energies of the Ga species are more negative than those of In. Therefore, the compositional dependencies of the chalcogen incorporation under Cu-excess growth conditions are consistent with the thermodynamic trends of the  $\text{Cu}(\text{InGa})(\text{SeS})_2$  system.

On the other hand, chalcogen incorporation independent of X and a preference for Se relative to S in the Cu-poor growth are consistent with the kinetics. A lower sticking probability of S relative to Se can be expected due to its higher vapor pressure.

Based on the above considerations, the temperature dependence in Fig. 1 can be addressed. From 450 to 550°C both Cu-poor and Cu-excess growth conditions follow the empirical relationship of Eq. 1 with a single value of C, as both the thermodynamic and kinetic behaviors become independent of temperature. However, as the temperature is reduced to 300°C, the change in C for the Cu-poor case suggests a different temperature dependence of the sticking probability. Deviation from the form of Eq. 1 in the Cu-excess case suggests that a different reaction model prevails. The difference between the Cu-excess and Cu-poor cases is assumed to be related to the presence of  $\text{Cu}_\alpha(\text{SeS})_\beta$  phases at the surface of the growing film in the Cu-excess case [8]. The temperature dependence then may be related to a  $\beta\text{-Cu}_{2-x}\text{Se} \leftrightarrow \gamma\text{-CuSe}$  phase transition at 380°C [9] or the melting temperature of CuS at 507°C [10].

### Sequential depositions

The differences in chalcogen incorporation have a significant impact on the compositional control in sequential deposition processes which include Cu-excess and Cu-poor or Cu-free layers. However, the characterization of sequential processes can help elucidate the growth process. Two different deposition sequences are described by the deposition rate of Cu relative to In+Ga as shown in Fig. 3: deposition with Cu-poor followed by Cu-excess fluxes, and with Cu-excess followed by Cu-free fluxes. Also shown in Fig. 3 is the change in composition ratio  $[\text{Cu}]/[\text{In+Ga}]$  of the growing films, i.e. the integral of deposition rate. During these sequential depositions the chalcogen flux was constant with  $Y_{\text{flux}} = 0.6$ , In and Ga fluxes were constant with  $X = 0.6$ , and substrate temperature was 550°C. These processes result in  $\text{Cu}(\text{InGa})(\text{SeS})_2$  films with non-homogeneous compositions depending on the growth history in accord with Fig. 2.

The compositions of films grown using the two processes for different times are shown in Fig. 4. The composition measurements of films with excess Cu are shown for both the as-deposited film and after a KCN etch. For the Cu-poor/Cu-excess process,  $Y_{\text{film}}$  remains unchanged after the Cu-flux is increased but  $[\text{Cu}]/[\text{In+Ga}]$  remains less than 1. As soon as the film contains excess Cu,  $Y_{\text{film}}$  increases. Thus, increased incorporation of S depends on Cu-rich film composition rather than just Cu-excess flux. After the KCN etch,  $Y_{\text{film}}$  is reduced indicating that the  $\text{Cu}_\alpha(\text{SeS})_\beta$  layer on the surface contains greater relative S content than the  $\text{Cu}(\text{InGa})(\text{SeS})_2$  but the composition of the underlying  $\text{Cu}(\text{InGa})(\text{SeS})_2$  film follows Fig. 2.

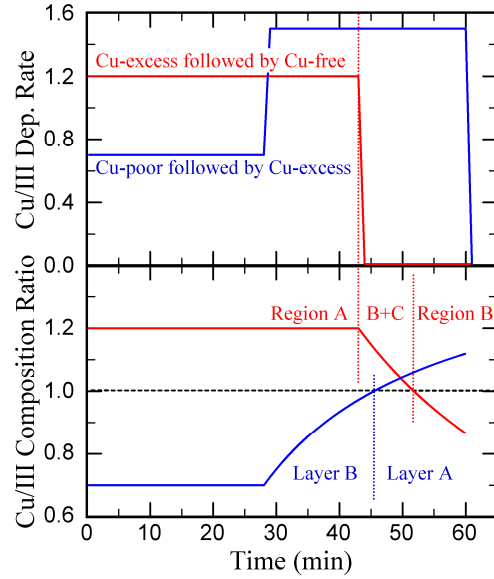


Fig. 3. Comparison of sequential deposition processes. The top shows the relative  $[\text{Cu}]/[\text{In+Ga}]$  deposition rate and the accumulated  $[\text{Cu}]/[\text{In+Ga}]$  composition versus time for each process is at the bottom.

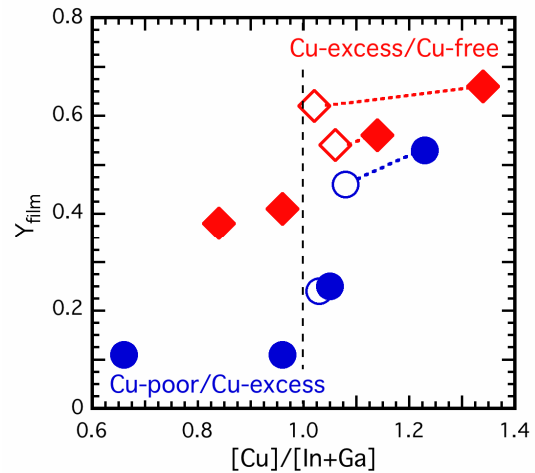


Fig. 4.  $Y_{\text{film}}$  as function of relative Cu composition for films grown with the Cu-excess/Cu free process (red) and Cu-poor/Cu-excess (blue) processes. Open symbols show the composition after a KCN etch of the sample connected by a dashed line.

With the Cu-excess/Cu-free process, the films have  $[\text{Cu}]/[\text{In+Ga}] = 1.35$  at the end of the Cu-excess growth step but  $Y_{\text{film}}$  decreases as soon as the Cu flux is turned off. Relative S incorporation is reduced even while the overall film contains excess Cu. This indicates that growth with preferred Se incorporation depends only on the incident flux and not on the overall film composition.  $Y_{\text{film}}$  in this process continues to monotonically decrease as the

process continues and the film transitions to Cu-poor composition.

Figs. 5a and 5b show microstructural models of films prepared using these sequential depositions after completion according to Fig. 3. The detailed analysis and deconvolution of XRD measurements as a function of incident angle used to construct the models will be presented elsewhere [11]. For the Cu-poor/Cu-excess sequence, the film consists of two layers as shown in Fig. 5a. The Se-rich layer B is formed during Cu-poor deposition of the film. The S-rich top layer A is formed after the film composition changes from Cu-poor to Cu-excess. The film is vertically inhomogeneous and laterally homogeneous.

For Cu-excess/Cu-free deposition, three distinct XRD peaks, corresponding to different compositions, can be observed and the film consists of three regions as depicted in Fig. 5b. The S-rich region A is grown during the Cu-excess deposition step. Then region C is formed during growth with Cu-excess film composition and Cu-free flux using Cu, Se, and S from the  $Cu_{\alpha}(SeS)_{\beta}$  in addition to the arriving In, Ga, Se, and S species. At the same time region B with higher Se content grows when the arriving Cu-free flux reacts only with Cu diffusing from the underlying layers and continues when there is no excess Cu phase in the film. This microstructural picture including laterally as well as vertically segregated regions under these conditions is necessary to describe the different incident angle dependences of the three XRD peaks.

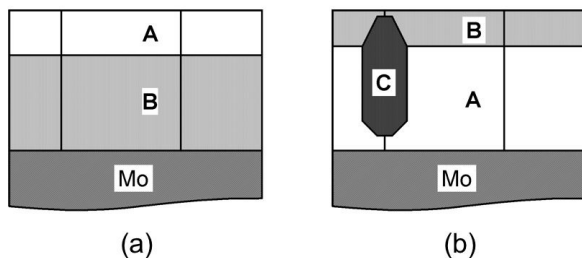


Fig. 5. Microstructure models of films prepared by deposition with (a) Cu-poor followed by Cu-excess fluxes and (b) Cu-excess followed by Cu-free fluxes. Regions A, B, and C correspond to Se-rich composition, S-rich composition, and converted S-rich regions, respectively and are formed during the deposition process as indicated in Fig. 3.

## SUMMARY AND CONCLUSION

The temperature and composition dependence of the incorporation of Se and S in the elemental co-evaporation of  $Cu(InGa)(SeS)_2$  has been studied. Deposition with a uniform flux-time profile under Cu-deficient conditions, i.e.  $[Cu]/[In+Ga] < 1$ , leads to preferential incorporation of Se relative to the vapor flux with no difference between 450 and 550°C. At 300°C the relative  $[S]/[Se+S]$  composition

changes although a simple relationship between  $Y_{film}$  and  $Y_{flux}$  is maintained. With excess Cu, i.e.  $[Cu]/[In+Ga] > 1$ , S is preferentially incorporated and, in this case, the resulting  $[S]/[Se+S]$  ratio in the film also depends on the relative In and Ga concentration. There is again no difference between 450 and 550°C but a change at 300°C.

From preliminary kinetic and thermodynamic considerations, it is suggested that the difference in temperature dependence between Cu-poor and Cu-excess grown conditions could be attributed to a difference in the reaction mechanisms determining the incorporation reaction of the chalcogens. Microstructural models formed by sequential process were proposed. The sequential process lead to both vertically and laterally non-homogeneous films.

With both uniform or sequential deposition processes, the empirical model provided by Eq. 1 provides a practical means to control film composition by control of the fluxes.

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