

Formation and Analysis of Graded $\text{CuIn}(\text{Se}_{1-y}\text{S}_y)_2$ Films

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Abstract

CuInSe_2 and CuInS_2 form a continuous solid solution in which the optical bandgap varies from 1.0 to 1.55 eV [1]. By reacting CuInSe_2 films in a flowing $\text{H}_2\text{S}/\text{Ar}$ atmosphere, the films can be completely converted to CuInS_2 or converted to a graded $\text{CuIn}(\text{Se}_{1-y}\text{S}_y)_2$ film, depending on processing conditions. A phenomenological model of the reaction/diffusion process is presented wherein H_2S reacts with CuInSe_2 at the surface to form CuInS_2 , releasing Se. The CuInS_2 and CuInSe_2 layers interdiffuse, resulting in a S/Se gradient in the structure. X-ray diffraction (112) line profiles of graded films are compositionally broadened due to continuously changing lattice parameters. The 3-dimensional sulfur distribution was calculated for measured grain size distribution using the formalism of Gilmer and Farrell and used to generate diffraction line profiles. These were fit to measured line profiles using bulk and grain boundary diffusion coefficients as fitting parameters, yielding diffusion coefficients and activation energies for bulk and grain boundary diffusion processes.

Keywords: Solar cells, thin films

1. Introduction

Alloy materials based on CuInSe_2 are potential absorber layers for wide bandgap, $E_g > 1.5$ V, heterojunction solar cells. High performance, wide bandgap, solar cells could: 1) improve module performance and reduce module cost; and 2) provide the wide bandgap device needed for 'next generation' monolithic tandem devices. Graded bandgaps could be used to improve V_{oc} of present generation devices by allowing incorporation of graded bandgap structure into the junction region; The Cu-In-Ga-Se-S chalcopyrite materials system, $\text{CuInSe}_2 \leftrightarrow \text{CuInS}_2 \leftrightarrow \text{CuGaSe}_2 \leftrightarrow \text{CuGaS}_2$, can be developed to yield bandgaps from 1.0 to 2.5 eV, since alloys of these compounds form continuous solid solutions. At present, substitution of Ga for In to form alloys has resulted in the highest performance devices, but at $\text{Ga}/(\text{Ga}+\text{In}) > 0.5$, with $E_g > 1.3$ eV, the device performance decreases [2]. Siemens Solar Industries utilizes a graded $\text{Cu}(\text{InGa})(\text{SeS})_2$ film structure where the junction region is alloyed with sulfur to increase V_{oc} , while the back contact region is alloyed with gallium [3].

In this paper, formation of $\text{CuIn}(\text{Se}_{1-y}\text{S}_y)_2$ alloy films is addressed with respect to formation of graded structures and providing a quantitative basis for characterizing the film formation process. The experimental approach consists of reacting CuInSe_2 films in flowing $\text{H}_2\text{S}/\text{Ar}$ atmosphere at 450°C to 525°C to convert films completely to CuInS_2 , or to produce graded $\text{CuIn}(\text{Se}_{1-y}\text{S}_y)_2$ alloy films. A model of the reaction/diffusion conversion process was developed and a method to quantitatively analyze the process is presented that predicts the compositional distribution of the converted films. The methodology is similar to that recently reported for analyzing CdS/CdTe thin-film couples [4].

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2. Experimental

The samples used for this study were 2 μm thick CuInSe_2 films deposited onto Mo coated soda lime glass by co-evaporation from elemental sources at a substrate temperature of 550°C. The composition of the films, determined by energy dispersive x-ray spectroscopy, was Cu = 25 at%, In = 25 at% and Se = 50 at%. A laminar flow thermal CVD reactor was used to react CuInSe_2 at atmospheric pressure. Samples were ramped to reaction temperature over a 10 minute interval in Ar atmosphere and held for 30 minutes before introducing H_2S . The gas composition was 2% H_2S in Ar and the total flow rate was 1320 sccm, giving a linear flow velocity of 76 cm/min. The samples were treated for a specified time and then pulled out of the hot zone. H_2S gas flow was simultaneously terminated and power was removed from the heating mantle. The system was then allowed to cool to room temperature under flowing argon and the substrate temperature dropped from 500°C to below 200°C within 2 minutes. In this way, CuInSe_2 samples were sulfurized at 450°C, 500°C and 525°C for 20, 40 and 60 minutes.

Film thickness and grain columnarity were analyzed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) of cross-sections. Film grain size and morphology was analyzed by surface atomic force microscopy (AFM) using a Digital Instruments model 3100 Nanoscope in tapping mode. Reacted CuInSe_2 films were etched to reveal grain boundaries using 1% Br_2 by mass in methanol at room temperature. The etch process removed approximately 0.25 μm from the surface of the films and revealed the grain boundaries. After etching, 10 x 10 μm areas were scanned in four random regions on each sample to provide a statistically significant sampling of > 400 grains on each sample. The features interpreted as grain boundaries were traced onto transparent film and the grains were categorized into discrete size bins, determined by averaging the major and minor axis of each grain. The resulting distributions were found to conform to a log normal distribution:

$$f(D) = \frac{1}{D \sqrt{2\sigma^2}} \exp \left(-\frac{(\ln(D) - \ln(D^*))^2}{2\sigma^2} \right) \quad (1)$$

where D is the grain bin diameter, D^* is the mean grain diameter and σ is the standard deviation. This is the commonly observed distribution for films with *normal*, or continuous, grain growth [5]. A typical AFM image, binned grain sizes and fitted distribution are shown in Fig. 1. For this film, the mean grain diameter was 0.6 μm , with a standard deviation of 0.6 μm . The distributions of all films examined in this work conformed to a similar function; it is important to note that grain shape, distributions, and film orientation were preserved throughout the reaction process.

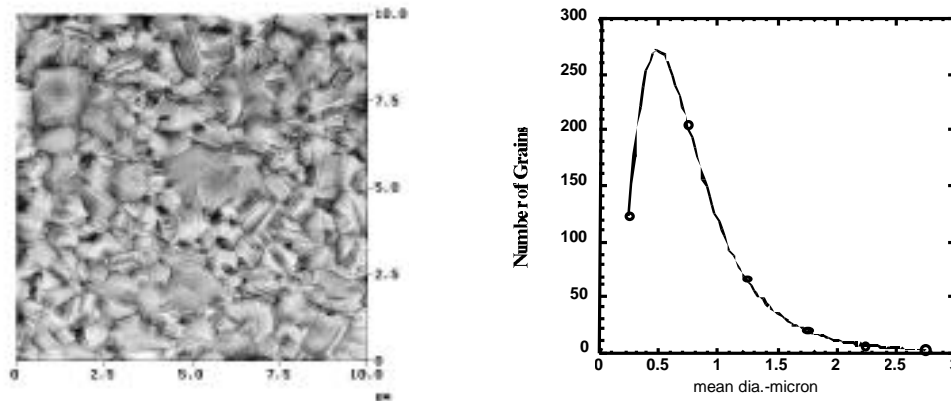
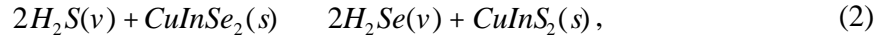


Fig. 1. Atomic force micrograph and grain size distribution of etched CuInSe_2 film.

XRD line profiles of the $\text{CuIn}(\text{Se}_{1-y}\text{S}_y)_2$ (112) reflection were measured using a Phillips/Norelco Bragg-Brentano focusing diffractometer with 35 kV Cu-k α radiation and a graphite crystal monochromator. Line profiles were acquired by step scanning in 0.01° intervals from 26.0 to 28.5° in 2θ . The x-ray diffraction data was smoothed and the $k=2$ component was stripped using the Rachinger correction. For comparison purposes, the backgrounds were removed, and the resulting profiles were normalized to equal area. Because the films were nominally the same thickness, had similar (112) texture, and since the (112) structure factor from CuInSe_2 to CuInS_2 varies by only ~15%, very little normalization was necessary.

3. Equilibrium Thermochemistry and Diffusion Model

The net chemical reaction of CuInSe_2 in H_2S gas is:



with free energy of reaction $G_{450^\circ\text{C}} = +12.86$ kcal/mol, taking into account gas and solid phase mixing enthalpy [6]. Note that the minimum chemical energy is attained by formation of the $\text{CuIn}(\text{Se}_{1-y}\text{S}_y)_2$ alloy, and the solid phase concentrations in Eq. 2 represent the molar fractions in the alloy. The equilibrium constant for the reaction is thus expressed:

$$k = \frac{[\text{CuInS}_2][\text{H}_2\text{Se}]^2}{[\text{CuInSe}_2][\text{H}_2\text{S}]^2} = \frac{1-x}{x} \frac{y}{1-y}, \quad \text{where} \quad (3)$$

$$x = \frac{[\text{H}_2\text{S}]}{[\text{H}_2\text{S}] + [\text{H}_2\text{Se}]} \quad \text{in the gas phase, and} \quad y = \frac{S}{\text{Se} + S} \quad \text{in the film.} \quad (4)$$

Thus, annealing a CuInSe_2 film in a closed system with H_2S gas, the equilibrium state will consist of a $\text{CuIn}(\text{Se}_{1-y}\text{S}_y)_2$ in a $\text{H}_2\text{S} + \text{H}_2\text{Se}$ atmosphere. The flowing reactor employed deviates from the closed system by constantly removing H_2Se while replenishing H_2S . The reaction rates to form CuInS_2 are assumed to be faster than solid state diffusion, resulting in formation of a CuInS_2 -rich surface layer, which acts as a constant diffusion source in a couple with CuInSe_2 . The process is modeled by assuming a pseudo-steady state with a surface reaction that continuously forms a CuInS_2 surface layer that provides a constant diffusion source. The CuInS_2 - CuInSe_2 diffusion couple is assumed to follow Fick's Law with S and Se species diffusing into bulk crystallites and along grain boundaries. The sulfur concentration of the surface layer, c_0 , depends on the kinetics of the surface reaction and the removal of Se from the gas phase. Thus, c_0 was a function of the $S/(S+\text{Se})$ ratio in the surface layer and was used as a fitting parameter in the analysis. Although the diffusion mechanism is not yet known, the treatment of diffusion does not rely on a particular mechanism, but rather all operating mechanisms are lumped into a species-independent effect described by net bulk, D , and a grain boundary, D_b , diffusion coefficients.

A cylindrical representation of $\text{CuInSe}_y\text{S}_{1-y}$ grains was adopted to model bulk and grain boundary diffusion. The 2-dimensional analytical solution developed by Gilmer and Farrell for polycrystalline films was employed using a constant diffusant source, reflecting back surface, and isolated grain boundaries [7]. Using measured grain size distributions and grain boundary width, estimated from TEM analysis to be $\sim 20\text{\AA}$, 3-dimensional $\text{CuIn}(\text{Se}_{1-y}\text{S}_y)_2$ alloy distributions were determined for individual grain sizes and integrated to generate compositionally broadened x-ray diffraction (112) line profiles. Line profiles were generated by convolution of the Pearson VII function with the volume fractional alloy distribution function obtained from the model and

corrected for absorption [8]. The modeled x-ray diffraction line profiles were regressed with measured profiles, using the bulk and grain boundary diffusion coefficients and surface source layer composition as the fitting parameters. The diffusion coefficients were determined at fixed temperature for times ranging from 20 to 60 minutes. The precise value of the grain boundary width is not critical to this analysis. This is because the grain boundary width and the grain boundary diffusion coefficient have an approximately multiplicative relationship. Details of the model will be presented in a forthcoming paper.

4. Results

Measured and modeled XRD (112) line profiles for CuInSe₂ films reacted at 500°C for 20, 40 and 60 minutes are shown in Fig. 2. There is a time-progressive shift of the profile towards the expected location of pure CuInS₂, and after 60 minutes the film composition approaches uniform CuInS₂. Determining the precise solid state source composition *a priori* would require detailed knowledge of the solid-vapor steady state in each case. AES analysis of the near-surface region of selected samples showed that the c_0 values used to fit modeled to measured XRD line profiles were within 10% of measured surface S/S+Se composition [9]. For reaction at 500°C, all treatment times yielded the same net bulk and grain boundary diffusion coefficients; $D = 3.0 \times 10^{-12}$ cm²/sec and $D_b = 3.0 \times 10^{-10}$ cm²/sec. Fitted diffusion coefficients and surface source compositions for the time-progressive data at 500°C and for selected times at different temperatures are listed in Table 1. Data for reactions at different temperatures from Table 1 yields the following estimates of the activation energy for net bulk and grain boundary diffusion coefficients: $E_D = 1.0$ eV and $E_{D_b} = 0.4$ eV.

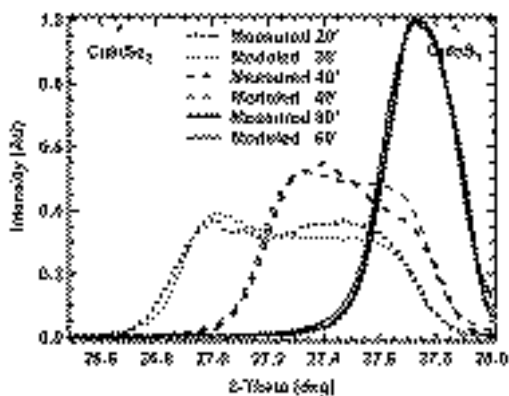


Fig. 2. Measured and modeled time progressive x-ray diffraction (112) line profiles for CuInSe₂ films reacted in H₂S at 500°C.

Table 1
Diffusion coefficients and surface source compositions.

Temp (C)	Time (min)	D (cm ² /sec.)	D _b (cm ² /sec.)	c ₀ S/(Se+S)
500	20	3.0x10 ⁻¹²	3.0x10 ⁻¹⁰	0.88
500	40	3.0x10 ⁻¹²	3.0x10 ⁻¹⁰	0.92
500	60	3.0x10 ⁻¹²	3.0x10 ⁻¹⁰	1
450	60	1.2x10 ⁻¹²	2.5x10 ⁻¹⁰	1
525	20	6.0x10 ⁻¹²	5.0x10 ⁻¹⁰	0.88

5. Conclusions

A method for making thin film $\text{CuIn}(\text{Se}_{1-y}\text{S}_y)_2$ with uniform or graded compositions has been developed and quantitatively analyzed. Estimates of the bulk and grain boundary diffusion coefficients can be used to generate 3-dimension composition maps of the films. If a $\text{H}_2\text{S}/\text{H}_2\text{Se}$ mixed gas composition is used during the annealing process, the S/Se composition of either a graded or uniform film can be controlled and used to tailor the bandgap of the material. This approach is being extended to the reaction CuGaSe_2 and CuInGeSe_2 films in H_2S with the eventual goal of producing $\text{CuInGa}(\text{SeS})_2$ with bandgap from 1.5 to 1.8 eV.

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