In situ investigation on selenization kinetics of Cu–In precursor using time-resolved, high temperature X-ray diffraction

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Abstract

In situ high-temperature X-ray diffraction was used to investigate the reaction mechanism and kinetics of \(\alpha\)-CuInSe\(_2\) formation from Cu–In precursors during selenization. The precursor films were deposited in a migration-enhanced molecular beam epitaxial reactor on Mo-coated thin glass substrates. During the selenization, the formation of CuSe was observed, followed by its transformation to CuSe\(_2\) at higher temperature. The formation of \(\alpha\)-CuInSe\(_2\) was initiated at a temperature between 250 and 300 °C. Additionally, the production of MoSe\(_2\) was clearly detected at temperatures above 440 °C. The reaction kinetics were analyzed using both the Avrami and parabolic rate models to estimate diffusion-limited activation energies of 124 (±19) and 100 (±14) kJ/mol, respectively.

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1. Introduction

Chalcopyrite \(\alpha\)-CuInSe\(_2\) and its alloys with Ga or S are very promising absorber materials for high-efficiency thin film solar cells. The commonly used techniques for CuInSe\(_2\) layer formation are co-deposition of elements [1], rapid thermal processing (RTP) of stacked or co-deposited Cu/In/Se precursors [2,3], and selenization of metallic precursors in H\(_2\)Se or Se vapor [1,4]. A systematic study of the equilibrium pathways, reaction mechanisms, and kinetics for the formation of Cu(In\(_x\)Ga\(_{1−x}\))Se\(_2\) (CIGS) and its subternaries (i.e., CuInSe\(_2\) and CuGaSe\(_2\)) would assist the selection and development of a cost-effective and high-performance CIGS growth process. While there have been several studies on the mechanism for forming CuInSe\(_2\), the detailed reaction pathways and kinetics are not yet fully understood.

To date, most studies on the mechanism of CuInSe\(_2\) formation by selenization of metallic precursors have been performed using ex situ methods [5–7], and thus providing limited kinetic information. Bekker et al. [6] compared the growth kinetics of three different selenization processes using different selenium sources, including a H\(_2\)Se/Ar gas mixture at atmospheric pressure, a Se pellet under Ar flow at atmospheric pressure, and Se vapor in vacuum (~10\(^{-6}\) mbar). According to their study, the H\(_2\)Se/Ar treated samples were superior to other selenization approaches in terms of morphological features and compositional uniformity. Adurodiya et al. [7] investigated CuInSe\(_2\) formation by a two-temperature Se vapor selenization of co-sputtered Cu–In precursor films within a partially closed graphite container. These studies suggested the following reaction mechanism: Cu\(_{11}\)In\(_9\) + CuIn\(_3\) + Se → CuSe + In\(_2\)Se\(_3\) [low-temperature step] → CuInSe\(_2\) + Se\(_2\)(g) [high-temperature step]. Recently, in situ study of the selenization of Cu–In thin films was reported by Kurdesau et al. [8]. By in situ resistivity measurements during the Se vapor selenization of Cu–In film in a quartz...
tube reactor, they suggested the following reaction path according to reaction time at 400 °C: Cu11In9 → In2Se3; Cu → CuInSe2.

In this paper, the reaction pathways and kinetics for α-CuInSe2 formation by the selenization of Cu–In/Mo/glass precursors using Se overpressure are investigated using in situ time-resolved, high-temperature X-ray diffraction (HT-XRD).

2. Experimental procedure

Time-resolved, in situ HT-XRD was used to investigate phase formation and disappearance during selenization of Cu–In/Mo/glass precursors. The HT-XRD system consists of a PANalytical X’Pert Pro MPD θ/θ X-ray diffractometer equipped with an Anton Paar XRK-900 furnace and an X’Celerator solid-state detector. The Cu–In/Mo/glass precursor was prepared in a migration-enhanced molecular beam epitaxial (MEE) deposition system under ultra-high vacuum conditions (10−7−10−9 Torr). Since molybdenum is widely used as a back-contact material in CIS-based solar cells, elemental Cu and In were co-deposited on the Mo-coated, sodium-free thin glass (Corning 7059; 0.4 mm thickness) without heating the substrate to minimize the reaction between Cu and In. Selenium powder was placed in wells on the HT-XRD sample holder adjacent to the precursor film. The sample holder containing the selenium source and precursor film was covered with aluminum foil with a thickness of 18(±2) μm and fixed to the holder with a Ni wire to minimize Se vapor loss. The sample temperature was calibrated from a determination of the lattice expansion of silver powder dispersed on an identical Mo-coated glass substrate. The silver lattice parameters could be converted to accurate sample temperature based on the equation of linear thermal expansion as a function of temperature suggested by Touloukian et al. [9].

3. Results and discussion

The overall atomic composition ([Cu]/[In] = 1.0) of Cu–In/Mo/glass as-deposited precursor film was determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) and its phase constitution (Cu2In, CuIn and In) was identified by both θ–2θ and grazing incident X-ray diffraction (GIXD), as shown in Fig. 1. The thicknesses of the Mo layer (~0.3 μm), Cu–In film (~0.6 μm), and selenized CuInSe2 film (~2 μm) were measured by SEM images of cleaved samples, as shown in Fig. 2. The matrix-island structure on the surface of the as-grown precursor is apparent in the SEM surface images and the islands were identified as an indium-rich or nearly pure indium phase by GIXD and electron probe micro-analysis (EPMA), as presented in Table 1.

During the selenization of Cu–In/Mo/glass by temperature ramp annealing (~20 °C/min), the formation of CuSe and its transformation to CuSe2, and then CuSe2 to CuInSe2 were observed from ~230 to 300 °C as shown in Figs. 3(a) and (b). The formation of CuInSe2 was initiated at a temperature between 250 and 300 °C. Additionally, the production of MoSe2, accompanied by a rapid decrease of Mo (1 1 0) reflection intensity, was clearly detected at temperatures above 440 °C, and only after the production of CuInSe2 was complete. In another experiment in which an insufficient amount of Se powder was placed in the well, the intensity of the CuInSe2 reflection kept increasing without producing MoSe2 even after 440 °C, which demonstrates the formation of CuInSe2 is preferred to that of MoSe2. These results are consistent with a simple equilibrium analysis of possible reaction pathways. Using values for the Gibbs energy of the components [10–12], the Gibbs energy changes for standard reactions for Mo reduction of CuInSe2 to produce either the elements or Cu2Se, given below, are all positive and thus consistent with preferred formation of CuInSe2.

\[ \text{CuInSe}_2(s) + \text{Mo}(s) \leftrightarrow \text{MoSe}_2(s) + \text{Cu}(s) + \text{In}(l), \]
\[ \Delta G^0_{f}^{200 \degree C} = 89.8 \text{ and } \Delta G^0_{f}^{500 \degree C} = 104 \text{ kJ/mol}, \]

(1)

\[ \text{2CuInSe}_2(s) + \text{Mo}(s) \leftrightarrow \text{MoSe}_2(s) + \text{Cu}_2\text{Se}(s) + 2\text{In}(l) + \text{Se}(l), \]
\[ \Delta G^0_{f}^{200 \degree C} = 236 \text{ and } \Delta G^0_{f}^{500 \degree C} = 249 \text{ kJ/mol}. \]

(2)

This result suggests that monitoring the presence of MoSe2 can be used for detecting complete formation of an absorber layer and perhaps a simple I–V characteristic can be used. There have been a few reports about MoSe2 formation and its contribution to the performance of CIGS solar cells. Wada et al. [13] reported that the (1 1 0) and (1 1 1) reflections of MoSe2 in CIGS/Mo absorbers deposited by a typical three-stage process were detected by XRD and the CIGS/Mo hetero-contact including the MoSe2 layer would be a favorable ohmic-type while the CIGS/Mo without MoSe2 layer exhibits a Schottky-type contact.
Isothermal annealing at selected temperatures between 260 and 330 °C was then performed for kinetic analysis using selected reaction models. A sample scan is shown in Fig. 4 for annealing at 280 °C. The 2θ scan range (20–30°) for the isothermal experiments was selected since the major reflection for the product CuInSe₂ (1 1 2) lies within this range. To complete the reaction, the temperature was elevated to 500 °C after each run and then maintained for about 12 min until only the α-CuInSe₂ phase remained as evident by a constant peak intensity. The fractional reactions of product CuInSe₂ phase were estimated using the normalized α-CuInSe₂ (1 1 2) peak area assuming that the maximum peak area represents complete reaction.

The reaction kinetics in terms of an activation energy and reaction order were estimated using two solid-state reaction models, the “Avrami” and “parabolic rate” models [14–16]. The Avrami model analysis is a widely used method for the preliminary identification of the growth rate law. In this model the transformation kinetics under isothermal reaction are described by

\[ \alpha = 1 - \exp[-(kt)^n] \], (3)

where \( \alpha \) is the fractional reaction, \( k \) the first-order kinetic rate constant, \( n \) the Avrami exponent, and \( t \) is time. This analysis has been advocated by Hulbert [16], who showed that the Avrami exponent can vary between 0.5 and 1.5 in the case of one-dimensional, diffusion-controlled reactions. The value of \( n \) is close to 0.5 if the nucleation is instantaneous, and close to 1.5 if the nucleation rate is finite and constant throughout the reaction. For our experimental data, the \( n \) values over the entire temperature range, except at the highest temperature 330 °C (\( n = 0.3 \)) studied, are between 0.6 and 0.8, suggesting the Avrami model is appropriate for this reacting system below 330 °C as shown in Fig. 5. The low value of the estimated Avrami exponents also suggests that the nucleation of α-CuInSe₂ occurs so rapidly that the nucleation time is nearly zero. The Arrhenius equation

\[ k = A \exp\left(\frac{-E_a}{RT}\right) \] (5)

was used to estimate the apparent activation energy \( E_a \) for α-CuInSe₂ formation by selenization of Cu-In/Mo/glass precursor films. An activation energy of 124 (±19) kJ/mol was estimated from the Arrhenius plot shown in Fig. 5. Note that the sample annealed at 330 °C showed a different reaction behavior than those annealed at lower temperatures and thus was not used to obtain this estimate.
The simple parabolic rate model \([14–16]\) is another widely used one that was developed based on reaction between two solid materials with planar surfaces. As the reaction proceeds, further reaction is limited by diffusion across the product layer to form more product layer at one of the interfaces of the two reactants. Assuming a uni-directional process (i.e., planar growth front), the reaction kinetics of the parabolic model is described by

\[ a^2 \sim k_p t, \]  

where \(a\) is the fractional reaction, \(k_p\) is the parabolic rate constant incorporating the diffusion coefficient of the migrating species, and \(t\) is time. Fig. 6 shows the plot of \(a^2\) vs. \(t\) for the same data set as used previously for the Avrami model analysis. The parabolic rate model also provides a good fit to the data over the entire isothermal experiment range (260–330 °C). An activation energy of 100 ± 14 kJ/mol estimated from the Arrhenius plot, and again the 330 °C datum was excluded. Based on the results of these two models, the formation of \(\alpha\)-CuInSe\(_2\) from selenization of Cu–In/Mo/glass precursor films apparently follows a one-dimensional diffusion-controlled reaction with a nucleation and subsequent growth sequence. The process likely involves the rapid nucleation of CIS at the interface and formation of a thin and planar \(\alpha\)-CuInSe\(_2\) layer on top.
of the Cu–In films, which serves to limit reactant diffusion and thus formation of α-CuInSe$_2$.

4. Conclusions

High-temperature X-ray diffraction was used to follow the reaction pathways and kinetics of α-CuInSe$_2$ formation. During the selenization of Cu–In/Mo/glass precursor structure by temperature ramp annealing, the formation of CuSe and its transformation to CuSe$_2$, and then CuSe$_2$ to CuInSe$_2$ were observed in the temperature range ~230–300 °C. Interestingly, in a temperature ramp experiment, MoSe$_2$ was observed, accompanied by a rapid decrease of Mo (110) peak height, only after the production of CuInSe$_2$ was complete. Furthermore, all samples finished with an anneal at 500 °C showed XRD evidence of MoSe$_2$ formation. The α-CuInSe$_2$ formation by the selenization of Cu–In/Mo/glass precursors could be described by a one-dimensional diffusion-controlled reaction process. For this reaction, the activation energies of 124±7 and 100±14 kJ/mol were estimated with the Avrami and parabolic rate models, respectively. Both of these values for the activation energy are between the value for CuInSe$_2$ formation from a CuSe/InSe bilayer precursor (66 kJ/mol) and the value for CuInSe$_2$ formation from a CuSe/In$_2$Se$_3$ bilayer precursor (162±5 kJ/mol) estimated from similar hot-stage XRD studies [14,15].

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