Influence of GaSe deposition temperature on the structural properties and in-depth compositional features of two-step grown Cu(In,Ga)Se₂ thin films

F. D. DEJENE, V. ALBERTS
Department of Physics, Rand Afrikaans University, PO Box 524, Johannesburg, South Africa
E-mail: valberts@mail.uden.edu

In this study, Cu(In,Ga)Se₂ thin films were prepared by a classical two-stage growth process, which involved the selenization of thermally evaporated InSe/Cu/GaSe precursors. During the precursor-formation step the InSe and Cu were always deposited at 200 °C, while the GaSe layers were deposited at temperatures between 200 °C and 400 °C. The respective precursors were simultaneously selenized under identical conditions in elemental Se vapor. In cases where the GaSe layers were deposited at low temperatures around 200 °C, X-ray fluorescence (XRF) analysis revealed a large variation in element concentration with sample depth after selenization. In correspondence, X-ray diffraction (XRD) studies revealed the presence of separate CuInSe₂ and CuGaSe₂ phases in these specific samples. Optimum structural properties were obtained when the GaSe films were deposited at 300 °C, followed by selenization. In general, these films were uniform and dense and XRD studies revealed single-phase Cu(In,Ga)Se₂ material. Even more importantly, XRF analysis revealed a remarkable improvement in in-depth compositional uniformity when the GaSe films were deposited at or above 300 °C. An increase in GaSe deposition temperature to 400 °C, however, resulted in a deterioration in the structural features of the Cu(In,Ga)Se₂ thin films. In contradiction with other reports, these results indicated that the in-depth composition uniformity and especially the Ga diffusion profile in two-step grown Cu(In,Ga)Se₂ thin films can be controlled. The crucial factor influencing the depth profile of these films is the GaSe deposition temperature during the precursor formation step.

© 2003 Kluwer Academic Publishers

1. Introduction
Polycrystalline CuInSe₂ (CIS) thin films and its related quartenary compounds, such as Cu(In,Ga)Se₂ or CuIn(S,Se)₂, are promising materials for photovoltaic applications. Recently, the development of CIS and related compounds has made rapid progress and conversion efficiencies above 18% have been achieved on a laboratory scale [1]. The chalcopyrite absorber materials of these high-efficiency laboratory-scale devices are generally produced by a single-stage growth technique in which all the elements (i.e., Cu, In, Ga, and Se) are co-evaporated from individual sources [2, 3].

In terms of large-scale applications, one of the most promising growth techniques is based on the two-stage deposition processes in which Cu-In-(Ga) alloys are deposited, followed by selenization and/or sulfurization using H₂Se and/or H₂S gases, Se and/or S vapors [4, 5]. However, the efficiencies of Cu(In,Ga)Se₂/CdS/ZnO solar cell devices in which the absorbers are produced by two-step growth processes are significantly lower than those in which co-evaporated absorbers are used. A significant problem related to two-step growth processes is the reported segregation of Ga towards the Mo back contact, irrespective of the position of GaSe in the precursor stack. This reported uncontrolled segregation of Ga results in separate CuInSe₂ and CuGaSe₂ phases and hence in inferior film quality [6].

In this study, the structural features and in-depth compositional uniformity of Cu(In,Ga)Se₂ thin films were investigated. The selenization conditions in elemental selenium vapor, the deposition order of the precursor stacks as well as the bulk composition of the respective films were kept constant during this study. The GaSe deposition temperature was varied in order to study its influence on the material quality of the Cu(In,Ga)Se₂ thin films. The quality of the respective thin films was evaluated and compared in terms of morphological features, formation of crystalline phases and in-depth compositional uniformity.
2. Experimental details

2.1. Absorber formation

All films were deposited on Mo-coated soda-lime glass substrates. The Mo back contact was about 1 μm thick and was deposited by electron beam evaporation. Selenium-containing InSe/Cu/GaSe precursors were prepared by the sequential thermal evaporation of the respective elements from three separate graphite heaters. The temperatures of the graphite heaters were carefully controlled in order to maintain growth rates around 0.1 nm s⁻¹. The thicknesses of the individual layers (1500 nm InSe/200 nm Cu/200 nm GaSe) were measured with a quartz crystal monitor and the deposition pressure was maintained at 10⁻⁴ Pa. The substrate temperature during InSe and Cu deposition was always maintained at 200 °C, while it was varied between 200 °C and 400 °C during the GaSe deposition step.

In the second step of the process, these stacked layers were reacted in vacuum to elemental Se vapor at 550 °C for 60 min. The substrate temperature was raised in 10 min from ambient temperature to 550 °C. In order to ensure a uniform Se vapor flux during the selenization process, a stainless steel effusion cell was used. The temperature of the effusion cell was increased in to 10 min from ambient temperature to 330 °C.

2.2. Characterization

The surface morphologies and crystalline phases of the precursors and selenized films were examined by scanning electron microscopy (SEM) and X-ray diffraction (XRD), respectively. The in-depth compositional uniformity of the samples was determined by XRF intensity measurements of Kα1,2 lines as a function of sample depth; for this purpose the absorber layers were repeatedly etched in bromine methanol, followed by XRF Kα1,2 line intensity measurements. Chemical etching was conducted at room temperature and the samples were rinsed in water and blown dry with nitrogen before XRF measurements were conducted. The Kα1,2 scans were recorded with a sequential XRF wavelength dispersive spectrometer (SRS 3000, Bruker AXS, Rh-anode, 60 kV). More details about this characterization technique can be found in Klenk et al. [7].

3. Results

The conversion efficiencies of Cu(In,Ga)Se₂-based devices are critically influenced by the concentration and depth profile of Ga through the absorber layer. Absorber films produced by standard co-evaporation processes are known to contain a significant amount of Ga in the near-surface region, resulting in an increase in the band gap of the absorber film, and hence the open-circuit voltage of the completed devices. On the other hand, it is generally reported that it is difficult to incorporate appreciable amounts of Ga in the active region of a CIGS film formed by simple selenization processes of metallic precursors. Regardless of its location in the precursor stack, Ga has been observed to segregate to the back of the film and the resulting film is phase-segregated with CuGaSe₂ near the Mo electrode and CuInSe₂ at the film surface [6]. In this paper, these issues are addressed and optimum growth parameters were determined for the deposition of device-quality Cu(In,Ga)Se₂ thin films with uniform Ga depth profiles.

3.1. Structural properties of InSe/Cu/GaSe precursors and selenized films

Fig. 1 depicts the characteristic surface morphologies of InSe/Cu/GaSe precursors, deposited under the experimental conditions discussed in Section 2.1. It is important to keep in mind that while the InSe and Cu layers were in all cases deposited at 200 °C, the GaSe layers were deposited at (a) 200 °C, (b) 300 °C, and (c) 400 °C. It is well known that the final surface morphology of a specific sample is significantly influenced by the overall bulk composition of the film. Therefore, for the purpose of comparison, the films depicted in Fig. 1 had similar bulk compositional properties with Ga/(In + Ga) and Cu/(In + Ga) ratios of approximately 0.25 and 0.75, respectively. The observed variation in structural features is therefore directly related to the fact that the GaSe films were deposited at different substrate temperatures. In the case where the total structure was deposited at 200 °C, the InSe/Cu/GaSe precursor morphology was dominated by the presence of a high density of mostly rounded grains (Fig. 1(a)), covering almost the entire layer surface. Typical grain sizes varied between 0.5 and 1 μm. A similar structure was observed when the GaSe layers were deposited as at 300 °C (Fig. 1(b)) onto the InSe/Cu structures. In this case, however, the grain shapes appear to be more irregular and less dense. A further increase in the GaSe deposition temperature to 400 °C resulted in the formation of a completely different precursor alloy, composed mainly of large (1 to 3 μm) smooth-faced droplet-like crystallites in addition to other much smaller sub-micrometer grains in the background (Fig. 1(c)).

In Fig. 2 the XRD patterns from the respective precursor films are displayed. In all cases weak evidence of the Cu(In,Ga)Se₂ (CIGS) phase could be detected along with the expected binary-selenide phases. Strong evidence of InSe was detected in cases where the GaSe layers were deposited at 200 and 300 °C (Fig. 2(a) and (b)). In cases where the GaSe layers were deposited at temperatures around 400 °C (Fig. 2(c)), no evidence of InSe was detected, but relatively strong evidence of both GaSe and CuSe binary phases. The (1 1 2) preferred orientation of CIGS phase also became more prominent when the GaSe layers were deposited at 400 °C in the precursor structure, indicating the expected higher degree of interaction between the binary phases at higher substrate temperatures.

These precursor films were simultaneously reacted to elemental Se vapor at 550 °C for 60 min. The resulting surface morphologies are depicted in Fig. 3. XRF studies revealed virtually no variation in the bulk composition (i.e., Ga/(In + Ga) and Cu/(In + Ga) atomic ratios) of films after selenization. The influence of the precursor morphology on the structural features of the final selenized films is clearly evident, especially in cases where the GaSe layers were deposited at 400 °C during the precursor formation stage. A comparison of Figs. 1(c) and 3(c) reveals how the two distinct regions (i.e.