# Phase Identification and AES Depth Profile Analysis of $Cu(In,Ga)Se_2$ Thin Films

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Received on 8 December, 2005

This work presents results related with phase identification and study of the homogeneity in the chemical composition of $Cu(In,Ga)Se_2$ (CIGS) thin films grown by a chemical reaction of the precursor species evaporated sequentially on a soda-lime glass substrate, in a two or three-stage process. For that, the CIGS samples were characterized through X-ray diffraction (XRD) and Auger Electron Spectroscopy (AES) depth profile measurements, respectively. The presence of secondary phases growing superficially was identified through small angle XRD measurements. Theoretical simulation of the XRD spectra, carried out with the help of the PowderCell package, confirmed this result. The results showed that the deposition conditions affect the homogeneity of the chemical composition of the CIGS films, as well as the phase in which these films grow. In general, the samples grown in a two stage process present a mixture of the $Cu(In,Ga)Se_2$ phase with the secondary $In_2Se_3$ and $Cu_2Se$ phases, whereas, the films grown in a three stage process do it, mainly, in the $Cu(In,Ga)Se_2$ phase with a tetragonal (chalcopyrite type) structure and better homogeneity. CIGS films with characteristics like those found for the three stage samples, have demonstrated good properties for its use as absorber layers in thin film solar cells.

Keywords: CIGS; Solar cells; XRD; AES

## I. INTRODUCTION

$CuIn_{1-x}Ga_xSe_2$ (CIGS) is the most widely investigated material for thin film solar cells applications. The result of an extensive research on this material is the achievement of over 19% efficiency by the co-evaporation of Cu, In, Ga and Se [1,2]. Several other techniques, such as sputtering, selenization and electro-deposition, have been used for the fabrication of CIGS thin films, but these techniques film quality is inferior to the one attained by co-evaporation. The co-evaporation technique can be either a simultaneous evaporation of Cu, In, Ga and Se elements or a sequential three stage evaporation of Ga-In-Se, Cu-Se, and Ga-In-Se [3].

The published pseudo-binary $In_2Se_3$-$Cu_2Se$ phase diagram [4,5] suggests that Cu-rich ([Cu]¿[In]) compositions will exist in equilibrium as a two-phase mixture of CIGS and $Cu_2Se$. Any excess $Cu_xSe$ can be detrimental to device performance due to its highly conductive nature. Therefore, the $Cu_xSe$ is generally consumed by depositing Cu-poor material in the later stages in order to shift the composition toward single-phase, Cu-poor CIGS [6].

For this investigation we chose to explore an approach to CIGS formation through a chemical reaction of the precursor species, co-evaporated sequentially in two and three-stage processes respectively. In the first stage of the deposition, we co-deposited In and Ga, together with Se onto a soda-lime glass substrate at a temperature $T_s$ of $300^o$ C. The obtained films were of the composition $(In_x,Ga_{1-x})_2Se_3$. These precursors were subsequently exposed (in a second stage) to a flux of Cu and Se at a substrate temperature of $600^o$ C to form CIGS. XRD measurements indicated that the obtained films contain a mixture of the $Cu(In,Ga)Se_2$ phase and the secondary $In_2Se_3$ and $Cu_2Se$ phases. Finally, in the $3^{rd}$ stage, In and Ga (10% of the amount deposited in the 1st stage) was co-deposited with Se at $T_s$ = 600 $^o$C in order to convert any $Cu_2Se$ to CIGS, and to construct a surface with less Cu than the bulk. These assumptions were verified by XRD and AES depth profile measurements.

## II. EXPERIMENTAL

The CIGS films we studied in this work were prepared by co-evaporation of the precursors using a deposition system constituted by: a evaporation chamber connected to a vacuum system which allows working at pressures of about $10^{-6}$ Torr, three boats (for the evaporation of Se, In+Ga and Cu respectively) and a thickness monitor (Maxtec TM-400) with a quartz crystal as sensor which was used for measuring the flux of the evaporated elements.

The elemental evaporated metal fluxes and the substrate temperature profile that we used to fabricate the CIGS films are shown in Fig 1. The substrate temperature was controlled with a programmable PID controller (Eurotherm 900C).

The deposition was accomplished in two or three stages:

The first stage, done at a substrate temperature of 300 $^o$C, forms an $(In,Ga)_xSe_y$ precursor layer containing ∼90% of the total In and Ga needed to grow the overall CIGS film. During this stage the Se flux is kept around 16 Å/s and the flux of In+Ga at a value of about 5 Å/s.

In the second stage, the substrate temperature is elevated at $600^o$ C and Cu is evaporated in a Se environment. During this stage the Se flux is kept at 16 Å/s and the flux of Cu at a value of about 4 Å/s.

In the third stage, the remaining 10% of In and Ga is evaporated in a Se environment to get the Cu-poor CIGS film.

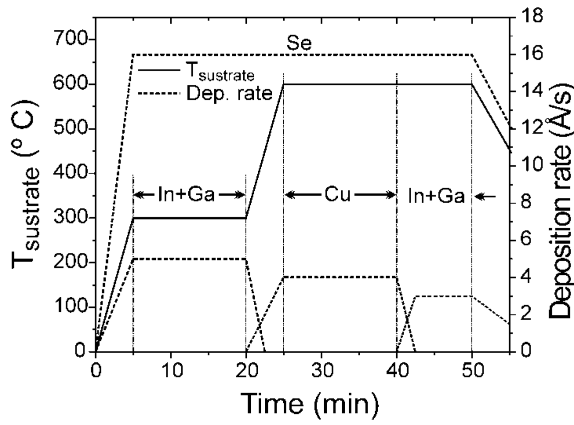


FIG. 1: Metal fluxes used to fabricate the CIGS films. Included in the figure is the substrate temperature profile used during the film growth.

$CuIn_{1-x}Ga_xSe_2$ thin films with chemical compositions varying between x=0 ($CuInSe_2$) and x=1 ($CuGaSe_2$) were prepared varying the amount (in mols) of Ga evaporated during the film growth and keeping constant the total of Cu, In and Ga needed to form the overall CIGS film.

The XRD measurements were carried out with a Diffractometer Shimadzu-6000 and the AES measurements were performed using a Perkin-Elmer ESCA/SAM system, model 560. The Ga content was determined using the DPSV (differential pulsed stripping voltametry) method [7].

## III. RESULTS AND DISCUSSION

### A. Structural characterization

The CIGS films were characterized through XRD measurements in order to investigate the effect of the preparation conditions on the phase and crystallographic properties. In Fig. 2 are depicted typical XRD patterns corresponding to $CuIn_{1-x}Ga_xSe_2$ thin films prepared en two and three stages, with three different chemical compositions (x=0, x=0.25 and x=1). In table I are reported data of crystalline structure and lattice constants corresponding to the phases identified in the studied CIGS samples. The phase identification was attained using the PDF-2004 data base and theoretical simulations of the XRD spectra with the help of the PowderCell package.

From the XRD measurements, the following facts can be remarked:

Depending on the precursor elements used, the films deposited by co-evaporation grow predominantly in the phases $CuInSe_2$ (CIS), $CuGaSe_2$ (CGS) or $Cu(In,Ga)Se_2$ (CIGS) with tetragonal structure (chalcopyrite type). However, secondary phases of $In_2Se_3$-hexagonal and $Cu_2Se$-cubic were identified, which are not desirable because they affect negatively the performance of the device. In CIGS films grown in three stages, the secondary phases tend to disappear indicating that, during the third stage, the $In_2Se_3$ and $Cu_2Se$ phases are reconverted partially or totally into the predominant chalcopyrite phase.

TABLE I. Phases identified in the studied CIGS samples and corresponding crystalline structure and lattice constants.

| Sample | Lattice Constants | | | | |
|---|---|---|---|---|---|
| | Tetragonal structure $CuIn_{1-x}Ga_xSe_2$ | | Hexagonal structure $In_2Se_3$ | | Cubic structure $Cu_2Se$ |
| | a | C | a | c | A |
| CGS-2 Stages | 5.6148 | 10.9616 | - | - | 5.7049 |
| CIGS-2 Stages | 5.6538 | 11.0627 | 7.5703 | 9.4610 | 5.7049 |
| | 5.6952 | 11.1673 | | | |
| CIS-2 Stages | 5.7752 | 11.5310 | - | - | 5.7049 |
| CGS-3 Stages | 5.6128 | 10.8940 | - | - | 5.7049 |
| CIGS-3 Stages | 5.7586 | 11.5196 | - | - | 5.7049 |
| CIS-3 Stages | 5.7782 | 11.5440 | - | - | |

Most films based on free of Ga ternary compounds (CIS), did not exhibit reflections associated to secondary phases, independently if they were fabricated in two or three stages.

The reflections of the XRD pattern for the CIGS films prepared in two stages are shifted toward greater values of 2θ compared with the three stage films, probably because the chemical reaction occurred during the third stage induces changes in the Ga content of the CIGS films. On the other hand, it is observed that the peaks of the difractograms of the CIGS samples prepared in two stages are quite broad and asymmetric. This behaviour could be due to the existence of a mixture of phases caused by an incomplete chemical reaction. In an attempt to identify the possible mixed phases, the reflection (112) was de-convolutioned in Gaussian/Lorentzian curves. Fig. 3 compares the de-convolution of the (112) reflection for a two stage CIGS film with that of the same CIGS film prepared in three stages. It was found, through a theoretical simulation carried out with the PowderCell program, that the three reflections resulting from the de-convolution of the (112) reflection of the two stage samples could be associated to the (111) plane of the cubic $Cu_2Se$ phase and the two remaining reflections, to the (112) plane of the tetragonal $CuIn_{1-x}Ga_xSe2$-phase with two different Ga content (x=0.5 and x=0.76 respectively). It was found for three stage samples, that they grow predominantly in the tetragonal $CuIn_{1-x}Ga_xSe_2$-phase with a Ga content of about 15%. However, a small proportion of the $Cu_2Se$ phase was also identified in this type of samples.

The change in the chemical composition, observed in the CIGS films during the third stage, seems to be caused by diffusion of In (coming from the $In_2Se_3$ surface layer formed during the 2nd stage) into the bulk of the CIGS layer. Since $x = mols\ of\ Ga / mols\ of\ (In + Ga)$, this value is reduced by increasing the In content in the sample.

In table I are listed the phases identified in the studied simples and their corresponding crystalline structure and lattice constants.

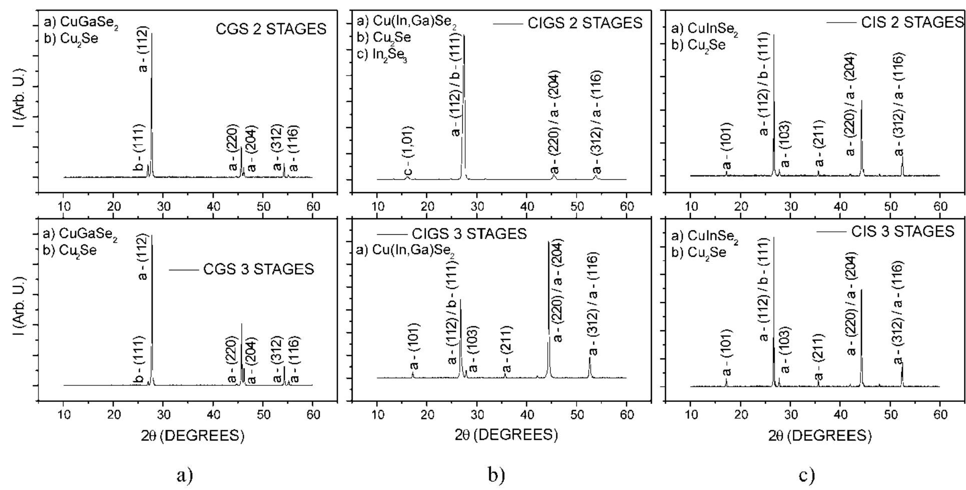


FIG. 2: XRD patterns of $CuIn_{1-X}Ga_XSe_2$ thin films fabricated by co-evaporation in two and three stages, with different Ga content a) x = 1.00; b) x = 0.25; c) x = 0.00.

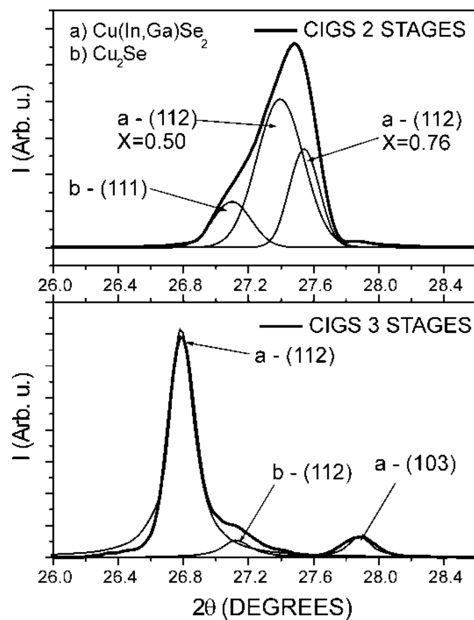


FIG. 3: De-convolution of the reflection (112) identified in CIGS films deposited by co-evaporation in two and three stages respectively.

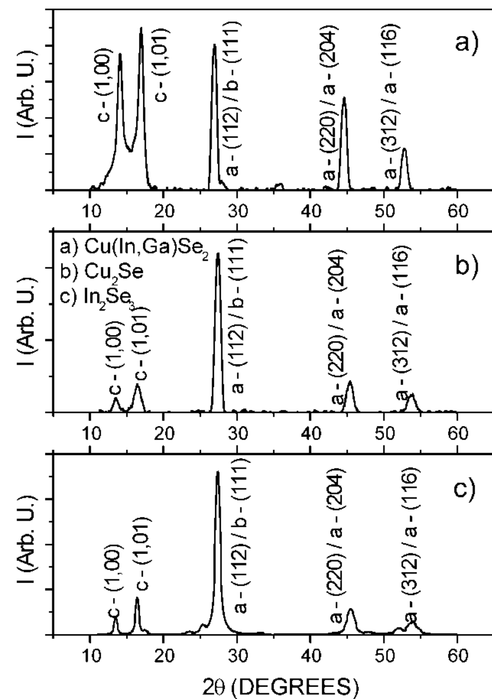


FIG. 4: Low angle XRD patterns corresponding to a $CuIn_{0.67}Ga_{0.33}Se_2$ thin film a) fabricated in two stages and b) fabricated in three stages. A theoretically simulated XRD pattern (of the sample fabricated in three stages) is also included (Fig. 4c).

In order to identify the phases growing predominantly near the surface of the CIGS films, XRD measurements were carried out keeping the x-rays incidence angle under 1.5 degrees. In this way, the reflections observed in the XRD pattern correspond predominantly to the surface phases. Fig 4 shows typical low angle XRD patterns obtained for CuIn0.67Ga0.33Se2 films fabricated in two and three stages.

These results show that the $Cu_2Se$ and $In_2Se_3$ phases identified in the CIGS films grow predominantly near the film surface. The CIGS films fabricated in two stages present thicker surface layers than the films fabricated in three stages. The theoretically simulated XRD pattern confirms the presence of the $Cu_2Se$ and $In_2Se_3$ surface phases.

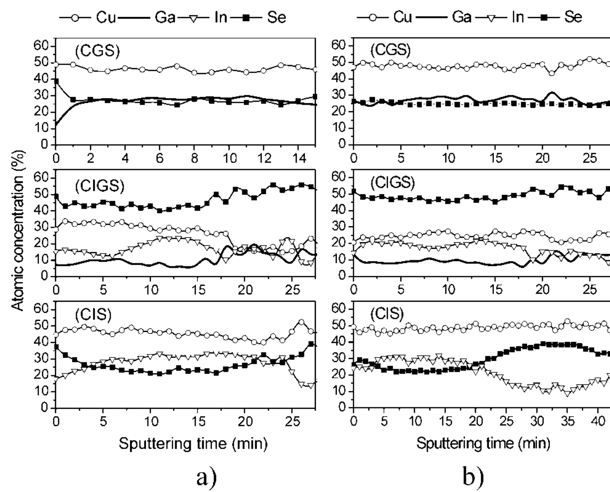


FIG. 5: AES depth profile of the films of Fig.2, deposited a) in two stages and b) in three stages.

## IV. AES DEPTH PROFILE ANALYSIS

Figure 5 compares the AES depth profile of CIS, CIGS and CGS films deposited in two stages vs those deposited in three stages. It is observed that the samples grown in two stages are Cu-rich near the film surface. This behaviour is not observed in films deposited in three stages. In this case, the Cu-content close to the top surface tend to be similar to that of the In+Ga. It is also observed that the chemical composition near the bottom is not significantly affected by the third stage. These results are in agreement with those obtained by the Low angle XRD measurements.

## V. CONCLUSION

Thin films of ternary and quaternary compounds based on Cu, In, Ga and Se, were deposited through a chemical reaction of the precursor species evaporated sequentially, in two and three stages . It was found that the films grow predominantly in the $CuIn_{1-x}Ga_XSe_2$ phase with chalcopyrite type tetragonal structure. However, secondary compounds corresponding to the cubic-$Cu_2Se$ and hexagonal- $In_2Se_3$phaseswere also identified. Through low angle XRD measurements it was found that the secondary phases grow near the film surface.

AES depth profile measurements indicated that the films deposited in two stages are Cu-rich near the film surface, whereas the samples grown in three stages are In-rich near the film surface. This result leads generally to an increase of the device efficiency.

**Acknowledgements**

This work was supported by DINAIN-Universidad Nacional de Colombia and Colciencias. The authors would like to thank Eng. Wilian Cauich for his assistance with the AES measurements.

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