Effect of synthesis parameters on the optical and structural properties of CuGaSe$_2$ thin films

E. Romero$^{a,*}$, J. Clavijo$^{b}$, J.S. Oyola$^{b}$, and G. Gordillo$^{a}$

$^a$Departamento de Física, Universidad Nacional de Colombia, Bogotá, Colombia.
$^b$Universidad de la Amazonía, Florencia, Caquetá, Colombia.

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CuGaSe$_2$ (CGS) thin films grown on soda-lime and boro-silicate glass substrates by a chemical reaction of the precursor species, which were sequentially evaporated in a two stage process, were studied through spectral transmittance and x-ray diffraction (XRD) measurements, in order to investigate the effect of the substrate temperature and the selenium flow on the optical constants (refractive index $n$, absorption coefficient $\alpha$ and optical gap $E_g$) and on the structural properties (phase, crystalline structure and lattice parameters). Using the experimental measurements and computational tools that allow us simulating theoretically the transmittance and XRD spectra, the optical constants and the crystallographic parameters of the CGS films were calculated. These results showed that the mentioned synthesis parameters significantly affect the optical constants as well as the crystallographic properties of the CGS films.

Keywords: Optical and structural properties; thin films; X-Ray diffraction; solar cells.

1. Introduction

Wide-band gap chalcopyrite solar cells based on CuIn$_{1-x}$Ga$_x$Se$_2$ (CIGS) are sought for their high voltage and low current output [1, 2]. This type of electrical characteristics should, in principle, significantly reduce resistive losses in the device. Another area of interest for such wide-gap materials is the fabrication of tandem solar cells where these CIGS absorbers can be used for the top cell in either a mechanically stacked or monolithically grown structure.

The NREL group has reported that the optimum band-gaps for a series-connected two junction tandem cell are 1.72 eV for the top cell and 1.44 eV for the bottom cell [3]. These band-gaps are ideally matched to CuGaSe$_2$ (CGS) ($E_g$=1.68 eV) and Cu(In$_{0.7}$Ga$_{0.3}$)Se$_2$ ($E_g$=1.15 eV) solar cells. However, it is a well-known fact that cells made from a CIGS alloy with $x$>0.3 do not benefit from the increased band-gap because they are dominated by bulk recombination whenever their composition is Cu-poor [4].

This paper reports the improvements we have achieved in the CGS properties through careful choice of growth parameters. We selected as substrates for the experiment traditional soda-lime glass and alternative 7059 corning glass. These alternative substrates allowed us to explore higher processing temperatures (>600°C). Another variable of interest in this study, in addition to higher processing temperatures, is the Se overpressure during film growth.

2. Experimental

The CIGS films were grown by selenization of the precursors, which are evaporated sequentially using a system constituted by an evaporation chamber connected to a vacuum system working at pressures of about 10$^{-6}$ Torr, three boats (used to evaporate Se, 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 substrate temperature is controlled with a programmable PID controller (Eurotherm 900C).

Since the reproducibility of the selenium flux is easy to achieve by controlling the evaporation temperature of Se, the CIGS films were grown keeping constant the Se- evaporation temperature using a PID controller. However, the Se-flux determined through the deposition rate reported by the thickness monitor was correlated with the Se-evaporation temperature. Fig. 1 shows the deposition rate of Se as a function of the evaporation temperature of Se.

The deposition of the CGS films was accomplished in two stages:
In the first stage a Ga\textsubscript{x}Se\textsubscript{y} layer is grown by simultaneous evaporation of Ga and Se, keeping the substrate temperature at 30°C. During this stage the Se flux is kept around 16 Å/s and the flux of Ga at a value of about 4 Å/s.

In the second stage the substrate temperature is elevated to values ranging from 500 to 630°C and Cu is evaporated in a Se environment. During this stage the Se flux was varied between 3 and 40 Å/s and the flux of Cu was kept at a value of about 3 Å/s. Table I lists the deposition parameters and the variation range used to perform the parameter study.

The elemental evaporated metal flux and the substrate temperature profile that led to CGS films with good properties for solar cells fabrication is shown in Fig. 2.

The transmittance measurements were carried out with a VIS - IR Oriel spectrophotometer and the morphological characterization was performed using a PSI AFM microscope. The XRD measurements were performed using the Cu K\textalpha\ radiation of a Shimadzu-6000 diffraction-meter.

### Table I. List of deposition parameters and variation ranges used to perform the parameter study

<table>
<thead>
<tr>
<th>Deposition parameters</th>
<th>1\textsuperscript{st} stage</th>
<th>2\textsuperscript{nd} stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flux of Ga (Å/s)</td>
<td>4</td>
<td>-</td>
</tr>
<tr>
<td>Flux of Cu (Å/s)</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>Flux of Se (Å/s)</td>
<td>2 - 40</td>
<td>2 - 40</td>
</tr>
<tr>
<td>Substrate temperature (°C)</td>
<td>300</td>
<td>450 - 680</td>
</tr>
<tr>
<td>Evaporated mass of Ga (gr)</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>Evaporated mass of Cu (gr)</td>
<td>-</td>
<td>0.2</td>
</tr>
</tbody>
</table>
3. Results and discussion

3.1. Optical characterization

Figures 3 and 4 show the effect of the Se flux and the substrate temperature on the transmission spectra of CGS films deposited in two stages on soda-lime and boron-silicate glass substrates, respectively.

It is observed in Fig. 3 that the decrease of both, the Se flux and the substrate temperature, leads to a decrease of the transmittance, especially at λ values close to the cut-off wavelength. This behavior seems to be caused by absorption through states within the energy band gap associated to native defects (vacancies and antisite defects) [5]. Absorption via extended states associated to tail bands could be another possible cause of the transmittance decrease observed when the Se-flux and/or the substrate temperature decrease. Therefore, to get CGS films with low density of states associated to native defects or to tail bands, it is recommendable to prepare them, under Se-overpressure and high substrate temperature conditions. Similar results were reported elsewhere [6].

The optical constants (refractive index \( n \), absorption coefficient \( \alpha \) and optical gap \( E_g \)) were determined using the transmission spectrum and calculations based on a procedure described in detail in reference [7].

Figure 5 shows typical curves of \( n \) vs. \( \lambda \), \( \alpha \) vs. \( \lambda \) and \((\alpha h\nu)^2\) vs. \( h\nu \), obtained for CGS films deposited on soda-lime and boron-silicate glass substrates. From the results shown in Fig. 5, the following facts can be remarked:

- The refractive index of the CGS films grown on boron-silicate glass substrate is greater than that of the films deposited on soda-lime glass substrates. This behavior could be attributed to the fact that the CGS films grown on boron-silicate glass present, generally, an electrical conductivity greater than the other CGS films, taking into account that the refractive index can be expressed by the relation, \( n = \frac{4\pi\sigma}{c} \alpha \) [8].

- The absorption coefficient of the CGS films grown on both types of substrates is greater than \( 10^4 \) cm\(^{-1}\), indi-
cating that these films are adequate as absorber layers in thin film solar cells.

- The linear behavior of the $(\alpha h\nu)^2$ vs. $h\nu$ curves indicates that the CGS thin films have a direct energy band gap. Using the relation $(\alpha h\nu)^2 = A(E_g - h\nu)$, which is valid for this type of materials, $E_g$ values of 1.68 and 1.76 eV were found for the CGS films deposited on soda-lime glass and boron-silicate glass substrates respectively.

3.2. Structural characterization

The effect of the Se-flux and the substrate temperature on the structural properties of the CGS films was also studied through XRD measurements. Figures 6 and 7 show typical XRD spectra of CGS films deposited under different Se-flux and substrate temperature conditions, on soda-lime and boron-silicate glass substrates, respectively.

The XRD measurements indicate that the CGS films grow with a chalcopyrite type structure and, in general, independently of the substrate type used, the CGS films deposited at low Se-flux (atomic flux ratio of anion to cation < 2.5) and low substrate temperature (< 550°C) grow with a preferential orientation along the (112) plane. The increase of the Se-flux and/or the substrate temperature leads to the growth of more randomly oriented CGS films.

The data regarding structure and lattice constants associated to the CuGaSe$_2$ phases, which are listed in the Table II, were obtained using the data reported in the JCPDS data base for these types of compounds.

3.3. Morphological characterization

The CGS films were characterized through AFM measurements in order to determine the effect of the Se flux, substrate temperature and type of glass substrate on the morphology. Figure 8 shows typical AFM images of CGS films deposited on soda-lime and boron-silicate glass substrates, under different substrate temperatures and Se-flux. It is clear from these results that the deposition conditions and substrate type significantly affect the films’ morphology.

Table III lists the average values of the grain size and roughness of the CGS films deposited on soda-lime and boron-silicate glass substrates, as functions of the Se-flux and substrate temperature, respectively.

**Figure 8.** AFM images indicating the influence of the substrate temperature and Se-flux on the morphology of CGS thin films deposited a) on soda-lime and b) on boron-silicate glass substrate.
TABLE III. Variation of the roughness and average grain size of the CGS films deposited on soda-lime and boron-silicate glass substrates, as functions of the Se-flux and substrate temperature.

<table>
<thead>
<tr>
<th>Se-flux (Å/s)</th>
<th>Rms rough. (nm)</th>
<th>Grain size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Soda-lime</td>
<td>Boro-silicate</td>
</tr>
<tr>
<td>8</td>
<td>71.0</td>
<td>79.2</td>
</tr>
<tr>
<td>21</td>
<td>52.2</td>
<td>50.4</td>
</tr>
<tr>
<td>40</td>
<td>36.7</td>
<td>26.5</td>
</tr>
<tr>
<td>Se-overpress.</td>
<td>Rms rough (nm)</td>
<td>Grain size (µm)</td>
</tr>
<tr>
<td>500</td>
<td>24.5</td>
<td>0.30</td>
</tr>
<tr>
<td>550</td>
<td>13.6</td>
<td>0.15</td>
</tr>
<tr>
<td>580</td>
<td>11.5</td>
<td>0.11</td>
</tr>
</tbody>
</table>

It is observed that the grain size of the CGS films increases by increasing the Se-flux, whereas the roughness decreases when the Se-flux is increased. On the other hand, it was found that the increase of the substrate temperature leads to a decrease of both, the average roughness and the average grain size. It was also found that the grain size and roughness of the CGS films deposited on soda-lime glass substrates are greater than those of the films deposited on boron-silicate substrates. Until now, we have not investigated the causes of this behavior.

4. Conclusions

CuGaSe₂ thin films with adequate properties to be used as absorber layer in the top solar cell of tandem structures were grown through two stage processes. Characterizations carried out using spectrophotometry measurements as well as XRD and AFM measurements have revealed that the substrate type as well as the substrate temperature and Se-overpressures significantly affect the optical, structural and morphological properties. In general, the films grown at higher substrate temperatures and under Se-overpressures present better properties to be used as absorber layer in solar cells.

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