X-RAY DIFFRACTION ANALYSIS OF R.T.P PROCESSED Cu/In/Se STACKED THIN LAYERS

H. Galindo, A.B. Vincent, J.M. Martín, Dora Gómez de Anderez, F. Camillo*, M. Donat * and L.D. Laude+.

Facultad de Ciencias, Universidad de los Andes, Mérida, Venezuela
*: IUTEC- Región Capital, Caracas, Venezuela
+: Université de l'Etat, Faculté des Sciences, Mons, Belgium

Abstract

Stacked layers of Cu/In/Se have been processed by Rapid Thermal Processing (RTP) via strong incoherent light. The x-ray diffraction analysis indicates that a chalcopyrite structure is present in the processed films when using a particular set of the RTP parameters. Their influence was the investigated and found that these must be well controlled in order to avoid unwanted secondary phases or strong segregations.
Keywords: Copper - indium - diselenide thin films.

Resumen:

Capas superpuestas de Cu/In/Se se procesaron por tratamiento térmico rápido (RTP) por medio de una luz fuerte e incoherente. Los análisis de difracción de rayos x indican que la estructura tipo calcopirita se presentó, en algunos casos, con parámetros de RTP particulares. Se investigó la influencia de éstos, encontrándose que pueden ser controlados para evitar la formación de fases secundarias no deseables o segregaciones fuertes.

INTRODUCTION

It has been established that the ternary $CuInSe_2$ is one of the most promising candidates for solar cell fabrication [1]. The preparation of thin films of this compound in large areas, with optimum optical and electrical characteristics, is still an open issue. There are several proposed techniques for this [2]. With the laser induced synthesis (LIS) technique [3], stacked elemental layers are processed via an argon laser beam at medium power, achieving good films of this ternary compound. Extrapolating this process, we have developed in our laboratory a rapid thermal processing (RTP) system [2]. Similar attempts are reported elsewhere [4-6]

We publish in this report the x-ray analysis carried out on the obtained compounds processed with this method.

EXPERIMENTAL

Films with 250 nm thickness were formed by evaporation, in a chamber at 10^{-6} torr, of Copper, Indium and Selenium layers in a stoichiometric proportion of 1:1:2 on Corning 7059 glass substrates. The obtained films were subsequently treated on an apparatus, which simulates the effect of a commercial rapid thermal processor (RTP) controlled with a PC microcomputer.

After a previous work [2], we were able to refine the process and could obtain better films prepared in the 260 to 290°C range. Analysis of these films was carried out by x-ray diffraction. Each x-ray spectrum was recorded using a Philips equipment with a 2θ range from 20° to 100° with the CuKα line operated at 40 kV.

The structural parameters such as crystalline phase, preferred orientation and crystallite size were determined.

RESULTS

Figure 1 shows the x-ray diffraction patterns obtained with the specimens treated during 60 seconds at several temperatures.

Analysis of these spectra indicates that: 1) at 260°C the $CuInSe_2$ compound was formed in

the sphalerite phase; 2) at 290°C we can observe the presence of new peaks corresponding to diffractions of the chalcopyrite lattice planes (103) and (211), which clearly indicates the formation of the $CuInSe_2$ in that phase; 3) the obtained value for c/a is 2.0260, which is in reasonable agreement with reported values [7]; 4) these spectra also show a peak, with a d-spacing of 2.91 A, which correspond to the In_2O_3 compound.

We summarize, in table I, the relevant data of the sample obtained at 290°C along with theoretical reported values [8].

The Scherrer equation was used to calculate the crystallite size from a single diffraction peak (Table II). This crystallite size, of a same phase, increases with temperature, but decreases again at 290°C when the chalcopyrite phase is formed.

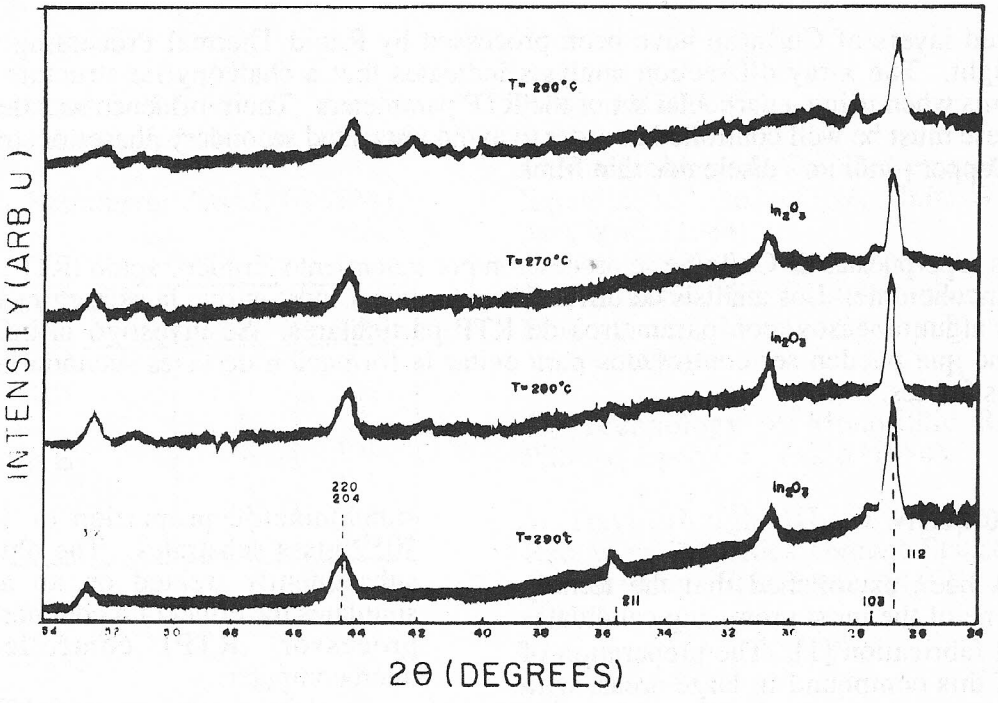

Figure. 1. X-Ray Diffraction patterns obtained with the specimens treated during 60 seconds at several temperatures.

Table I. X-Ray diffraction Data for a $CuInSe_2$. Thin film obtained at 290°C: d_{cal}=Calculated Theoretical Values from [8] and d_{obs}=Experimental Results from this Work.

h k l	d_{cal} (Å)	d_{obs} (Å)
1 1 2	3.34	3.3276
1 0 3	3.22	3.2322
2 1 1	2.52	2.5118
2 2 0/2 0 4	2.04	2.0490
1 1 6/3 1 2	1.743	1.7460

Table II . Crystalline Sizes

Treatment Temperatura (°C)	Crystallite size (L) (Å)
260	270
227	303
280	290
454	370

DISCUSSION

Our x-ray results for the samples synthetized with this RTP technique confirm these temperatures for thin film formation by other techniques [4, 9]. At these temperatures, interdiffusion of the atoms of the elemental constituents of the Cu/In/Se sand, wich is produced, giving place to the ternary semiconductor via solid-solid reactions, first in the sphalerite phase at 260°C and then in the chalcopyrite at 290°C.

In this work, the x-ray diffraction patterns allowed us to conclude that, at a low temperature formation, a disordered phase (or sphalerite) for $CuInSe_2$ was obtained, which only disappeared at a 290°C treatment when the chalcopyrite phase is formed.

The presence of $Cu_{2-x}Se$ phases is difficult to distinguish since the three prominent peaks of this phase are superimposed with those of the chalcopyrite structure. Nevertheless, the formation of those phases (similar to the $Cu_{2-x}Te$ case) [10] would seem to be the nucleation for the growth of the ternary compound.

Segregation of In_2O_3 is the result of film oxidation due to a poor vacuum in the RTP apparatus (10^{-3} torr). Processing of the film in an inert atmosphere may significantly reduce the oxide's admixture, since, as it is well known, presence of these oxides changes dramatically the electrical properties of the materials.

CONCLUSIONS

Layers of In/Cu/Se/, in 1:1:2 atomic proportion, thermally evaporated onto a glass substrate, were processed with RTP. X-ray diffraction data revealed that the compound was formed at 260°C in a sphalerite phase and, at 290°C, the chalcopyrite compound was obtained with some In_2O_3 segregation. Comparison of these results with previous ones shows us that computed control RTP permits better (higher) gradients at the beginning of the process, which reduces the formation of binary phases.

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