Rheotaxial growth of $CuInSe_2$ thin films

M. Varela, E. Bertran, A. Lousa, J. Esteve, and J. L. Morenza
Universitat de Barcelona, Departament de Física Aplicada i Electrònica, Avinguda Diagonal 645, 08028-Barcelona, Spain

(Received 14 April 1986; accepted 12 October 1986)

$CuInSe_2$ thin films were deposited onto glass and liquid-indium-coated glass substrates by coevaporation of copper, indium, and selenium. The morphology, composition, and crystalline properties have been studied in relation to the deposition process parameters. The deposition rate and the grain size are higher in films grown on liquid indium than on glass and depend on the indium film thickness. Films grown on indium do not show the same crystalline phases of films grown on glass, and in order to obtain films free of spurious phases the Cu fluxes must be increased.

I. INTRODUCTION

The efficiency of thin-film solar cells depends to a large extent on the crystalline grain size.[1] The increase of this can be obtained through the optimization of the deposition process parameters (growth temperature and growth rate) and film recrystallization through heat treatment processes after the deposition. An alternative technique is the growth of thin films on a liquid-metallic layer, or rheotaxy.[2] The large grain sizes obtained with this technique are due to the high mobility of the impinging atoms on the liquid surface. In previous studies[3,4] we have demonstrated the feasibility of growing continuous liquid-indium films onto glass and metal-coated glass substrates, and the suitability of these films for the rheotaxial growth of semiconductors.[5] In this work we report the rheotaxial growth of $CuInSe_2$ thin films on liquid-indium-coated glass substrates.

II. EXPERIMENTAL

The $CuInSe_2$ thin films were deposited by coevaporation under a pressure of 10^{-4} Pa, from three different sources, each one consisting of a cylindrical graphite crucible heated by a tantalum filament, and with a proportional integral differential (PID) temperature control system. The cells were 20 cm from the substrate and were tilted 10° from the normal to the substrate. The source temperature ranges were 1100–1250 °C for Cu, 930–1100 °C for In, and 240–330 °C for Se.

The films were deposited in each evaporation onto three glass slides held at different temperatures in the 175–350 °C range. Prior to the $CuInSe_2$ film deposition a continuous liquid-indium film 100 nm thick was deposited onto one-half of the glass substrate with a growth rate of 0.1 nm/s, the other half of the substrate being covered with a shutter. Next the shutter was fully opened and the $CuInSe_2$ films were deposited onto the indium film and onto the uncoated glass. In order to study the influence of the indium film thickness, a deposition of $CuInSe_2$ on a stepped indium film with thicknesses between 10 and 100 nm was performed.

The film thicknesses were determined by the Tolansky method and also through the cross-section micrographs of the films. The composition was obtained with the electron microprobe (EDAX/ECON 711), the morphology was studied with the scanning electron microscope (Philips PSEM 500), and the crystalline structure was determined from the x-ray diffraction spectra obtained with a Bragg–Brentano diffractometer (Philips PW1130) using the Cu $K\alpha$ line.

III. RESULTS AND DISCUSSION

A. Morphology

Table I shows the composition, thickness, grain size, and deposition process parameters of the obtained films. The thickness of the rheotaxial films is much higher than that of the films deposited on glass. The thickness of the rheotaxial films increases with increasing indium layer thickness and approaches saturation at higher thicknesses (Fig. 1). This indicates a larger deposition rate of the rheotaxial films that must be attributed to a higher sticking coefficient of the impinging atoms onto the indium layer.

In the scanning electron microscope the rheotaxial $CuInSe_2$ films appear to be uniform without conglomerates or indium droplets. The films are polycrystalline with grain sizes in the 0.1–0.2 μm range for films grown on glass and in the 0.3–2 μm range for rheotaxial films (Table I). Figure 2 shows scanning electron micrographs of the two types of film. The higher grain size of the rheotaxial films is due to the larger mobility of the impinging atoms on the liquid surface which gives rise to a lower nuclei density and higher island size during the film growth. The larger thickness of the rheotaxial films can also contribute to the higher grain size, but this effect must be much lower than that of the indium-liquid film because in films 1–2 μm thick grown on glass, the grain size is always rather lower than 1 μm.[6]

Figure 3 represents the grain size as a function of the deposition temperature for films grown onto indium films of the same thickness. It can be observed that the grain size increases when the deposition temperature increases. This dependence is typical of polycrystalline thin films and is related with the higher mobility of the impinging particles on the substrate during the nucleation process.[7] The grain size, for a fixed deposition temperature, increases when the thickness of the indium layer increases (Fig. 4), but for thicknesses below 20 nm the grain size is similar to that of films grown on glass.

TABLE I. Technological parameters, composition, thickness, and grain size of $CuInSe_2$ thin films.

Sample	Substrate	Substrate temperature (°C)	Thickness In film (nm)	Thickness $CuInSe_2$ film (μm)	Composition (at. %) Cu	In	Se	Grain size (μm)
22T1	glass	250	···	0.4	28.5	20.4	51.1	0.1
22T1 R	indium	250	100	1.5	21.0	27.6	51.4	1.3
22T3	glass	176	···	0.4	28.5	18.0	53.5	0.1
22T3 R	indium	176	100	2.0	22.9	26.1	51.0	1.2
25T1	glass	350	···	0.4	24.8	22.4	52.8	0.2
25T1 R	indium	350	100	1.6	20.2	26.2	53.6	1.8
25T2	glass	300	···	0.4	24.4	23.2	52.4	0.2
25T2 R	indium	300	100	1.6	20.9	25.1	54.0	1.5
32T1	glass	350	···	1.1	···	···	···	0.3
32T1 R1	indium	350	10	1.3	···	···	···	0.3
32T1 R2	indium	350	20	1.8	···	···	···	0.3
32T1 R3	indium	350	40	2.4	···	···	···	0.5
32T1 R4	indium	350	70	3.0	···	···	···	0.8
32T1 R5	indium	350	100	3.0	···	···	···	1.0

It is to be noted that the cross-section micrographs of the rheotaxial films do not present the predeposited indium layer, even when this was 100 nm thick. Therefore, the indium layer is incorporated into the semiconductor film during the growth process.

B. Composition

The films grown on glass show compositions near stoichiometry, but the rheotaxial films have very different compositions (Table I). All these films show an increase of In concentration and, in proportion, a decrease of Cu concentration.

The increase of In concentration could be due to the indium incorporation from the liquid layer in the semiconductor film, in agreement with the disappearance of the indium layer. For the rheotaxial films, the study through electron probe microanalysis of the composition homogeneity in depth, shows a high In concentration near the substrate that decreases when the electron beam spot moves away from this. This inhomogeneity of the films can be explained in terms of two phenomena: the indium incorporation from the liquid

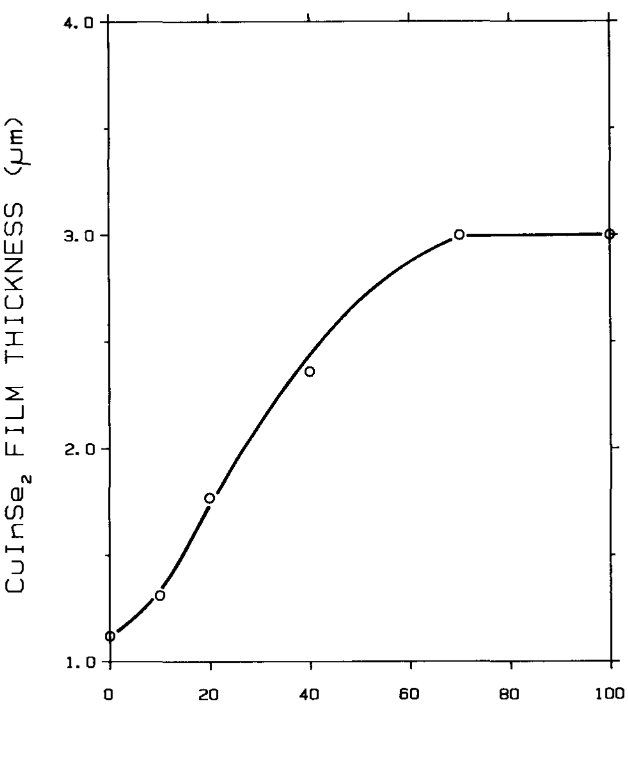

FIG. 1. Dependence of $CuInSe_2$ film thickness on indium film thickness (substrate temperature: 350 °C).

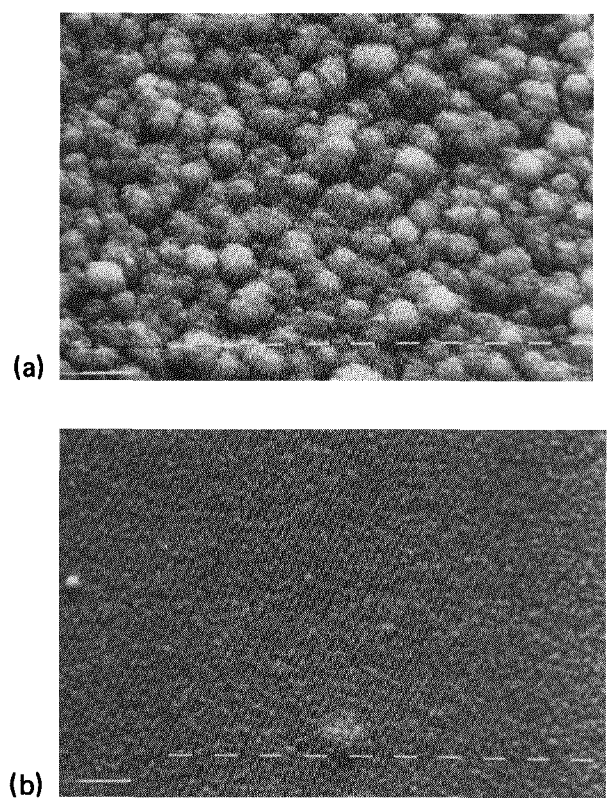

FIG. 2. Scanning electron micrographs (scale bars, 1 μm) of $CuInSe_2$ films grown on (a) an indium liquid film and (b) uncoated glass.

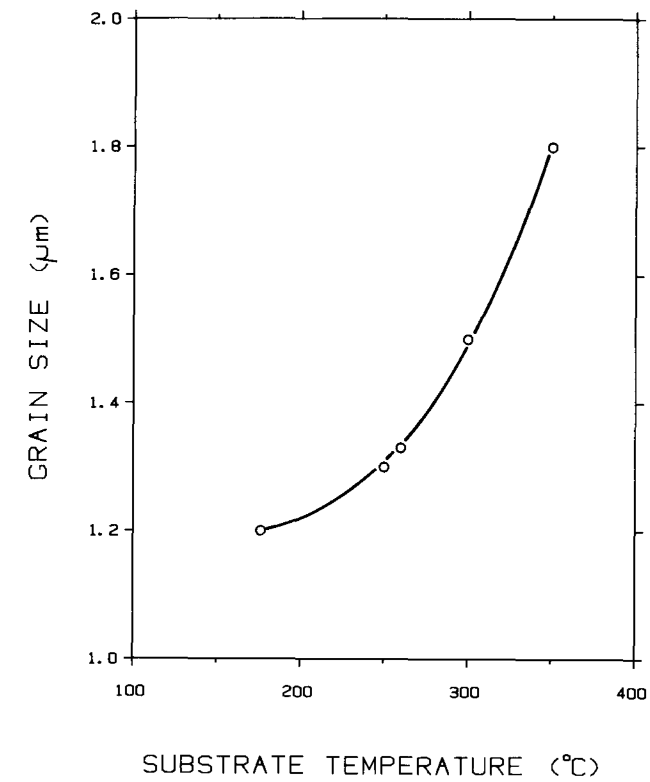

FIG. 3. Dependence of the grain size on the substrate temperature (indium film thickness: 100 nm).

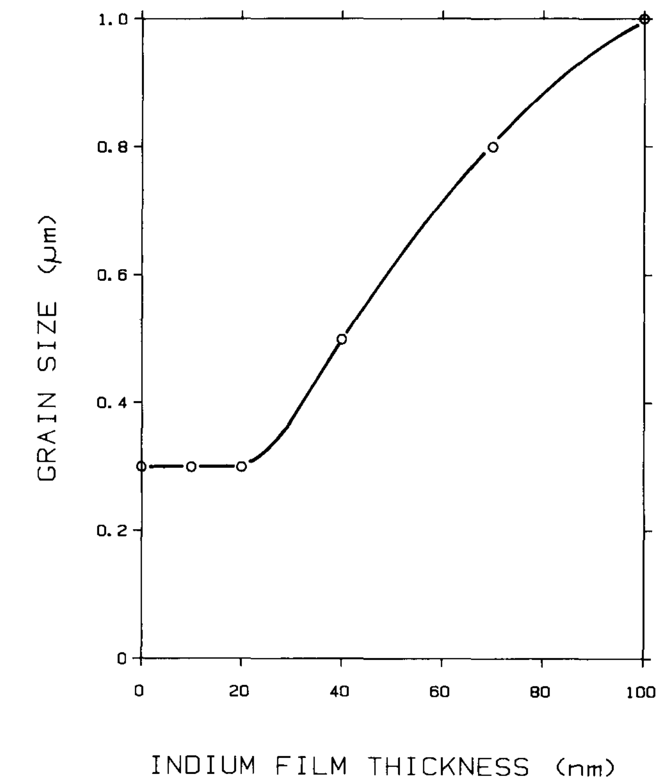

FIG. 4. Dependence of the grain size on the indium film thickness (substrate temperature: 350 °C).

layer into the growing $CuInSe_2$ film at the first stages of deposition, and the In diffusion inwards the $CuInSe_2$ film during its growth.

Nevertheless the amount of In in the liquid layer (100 nm thick) is not enough to explain the observed excess of this element in the $CuInSe_2$ film, which has a much larger thickness. Then this fact must be attributed to the different values of the increase of the sticking coefficient of indium, copper, and selenium on liquid indium with respect to bare glass, that are higher for indium.

C. Crystalline structure

Figure 5 shows the evolution of the x-ray diffraction spectra with the growth temperature for films simultaneously grown on liquid indium and on glass. The spectra indicate

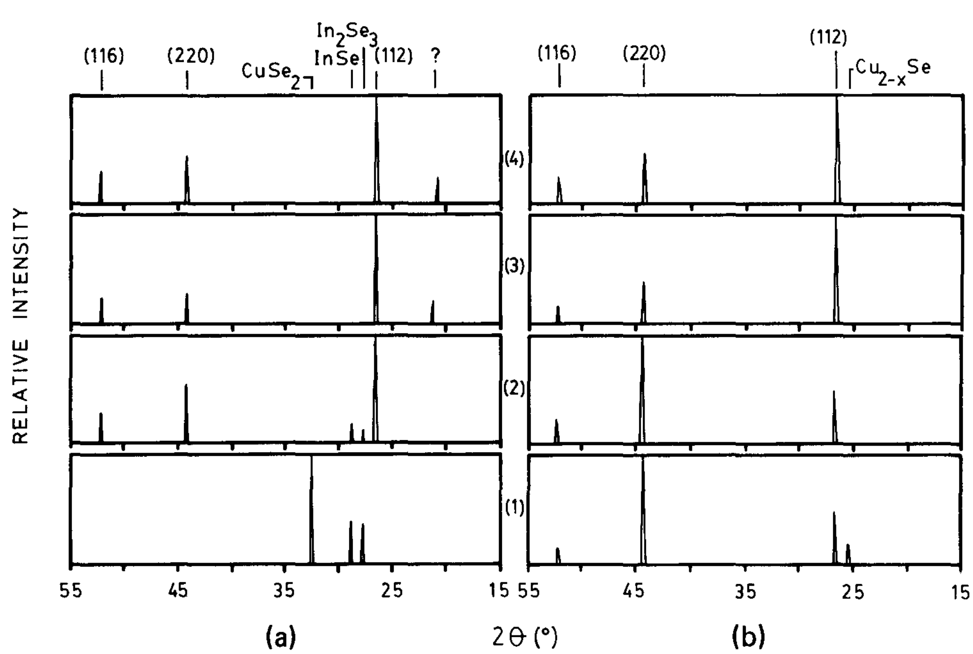

FIG. 5. X-ray diffraction spectra of films simultaneously grown on (a) liquid indium and (b) glass at various substrate temperatures: (1) 176, (2) 250, (3) 300, and (4) 350 °C.

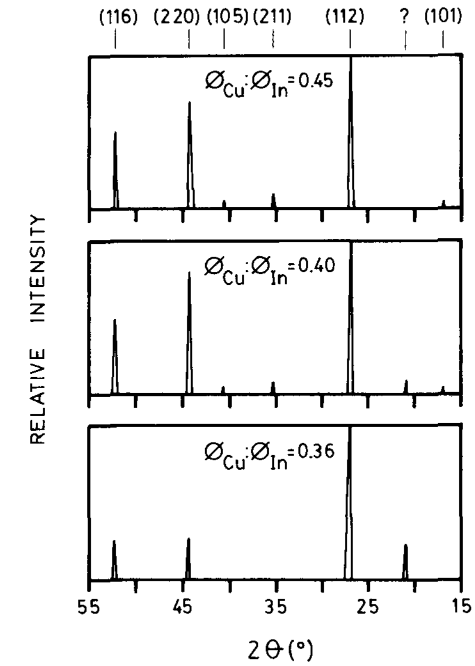

FIG. 6. Evolution of the x-ray diffraction spectra with the Cu–In flux ratios (substrate temperature: 300 °C).

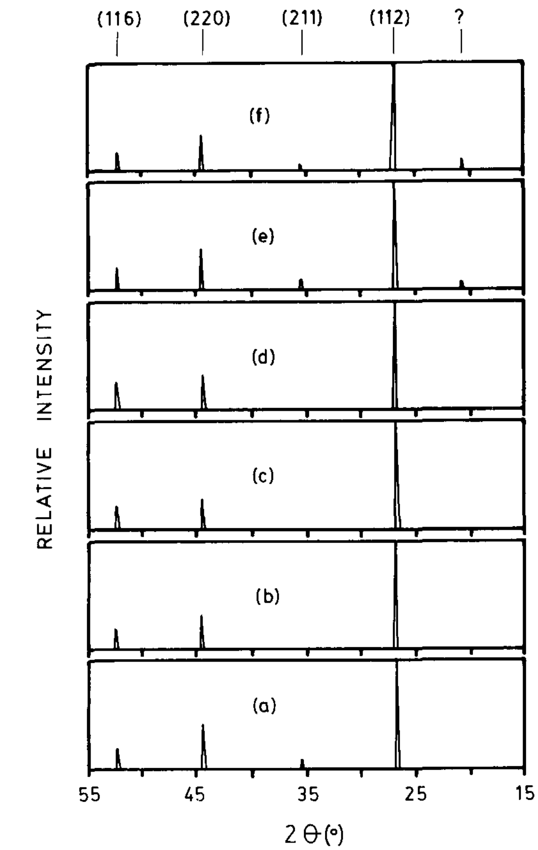

FIG. 7. Evolution of the x-ray diffraction spectra with the liquid-indium film thickness: (a) 0, (b) 10, (c) 20, (d) 40, (e) 70, and (f) 100 nm.

that films grown on glass are constituted by the crystalline phases of $CuInSe_2$ (probably sphalerite because the characteristic peaks of chalcopyrite do not appear) and only in the film grown at the lower temperature does an additional low-intensity peak attributed to Cu_{2-x} Se appear.

In rheotaxial films, when the growth temperature is below 250 °C, there are only several binary compounds of Cu, In, and Se. For the growth temperature of 250 °C the characteristic peaks of $CuInSe_2$ appear, but several peaks of other In–Se phases still exist. The films grown at temperatures in excess of 250 °C show the peaks of $CuInSe_2$ and an unidentified peak of lower intensity at 21 °C with an interplanar spacing of 4.17 Å. It is to be noted that the films do not present In characteristic peaks in any case.

The unidentified peak, which does not appear in the films grown on glass, can be related with the incorporated indium in the rheotaxial films and could be due to other ternary compounds of Cu, In, and Se.[8–10]

In order to obtain $CuInSe_2$ films free of spurious phases, and taking into account the excess of indium in the rheotaxial films, we have tried to deposit films with Cu fluxes higher than those used to obtain stoichiometric $CuInSe_2$ films on glass. The diffraction spectra of the films show that when the Cu flux increases the relative intensity of the unidentified peak decreases until it disappears (Fig. 6), and the films have only $CuInSe_2$ peaks. Moreover, it is to be pointed out that the diffraction spectra of the films with the larger Cu–In flux ratios show the (211) characteristic peak of the $CuInSe_2$ chalcopyrite phase.

On the other hand, in order to study the influence of the indium layer on the unidentified peak we have analyzed the x-ray diffraction spectra of films with several thicknesses of the indium layer. Figure 7 shows the evolution of the spectra with the indium layer thickness. The unidentified peak only appears for thickness below 70 nm. Furthermore, it is to be noted that the (211) characteristic peak of $CuInSe_2$ chalcopyrite phase, which is present in the films grown on glass, disappears in the films grown on a thin layer of indium, but reappears together with the unidentified peak when the thickness is 70 nm or higher.

IV. CONCLUSION

Rheotaxy using a liquid-indium thin layer is a feasible technique for the growth of $CuInSe_2$ thin films with higher grain sizes and also higher deposition rates. The grain size shows an important dependence on the growth temperature and the indium layer thickness. The deposition rate, however, depends essentially on the indium layer thickness.

Rheotaxial films with only $CuInSe_2$ phases can be obtained by means of the increase of the Cu flux in relation to that used for films deposited on glass, or by means of the decrease of the indium-liquid layer thickness.

ACKNOWLEDGMENTS

The authors acknowledge the collaboration of the Service of Electron Microscopy and the Department of Crystallography and Mineralogy of Universitat de Barcelona. The work is included in program 2301 of the Institut d'Estudis Catalans and was financed by the Comisión Asesora de Investigación Cientifica y Técnica del Ministerio de Educación y Ciencia (Project No. 3967/79 and No. 1106/81).

[1]H. J. Hovel, in *Semiconductors and Semimetals* (Academic, New York, 1974), Vol. 11, p. 103.

[2]A. G. Milnes and D. L. Feucht, in *Proceedings of the 12th IEEE Photovoltaic Specialist Conference*, Baton Rouge, LA, 1976 (IEEE, New York, 1976), p. 997.

[3]A. Figueras, J. L. Morenza, J. Esteve, E. Bertran, and J. M. Codina, Thin Solid Films **103**, 51 (1983).

[4]E. Bertran, J. L. Morenza, J. Esteve, M. Varela, A. Figueras, and J. M. Tura, Thin Solid Films **129**, 103 (1985).

[5]J. L. Morenza, A. Figueras, M. Varela, J. Esteve, and J. M. Codina, Thin Solid Films **113**, 21 (1984).

[6]M. Varela, E. Bertran, J. Esteve, and J. L. Morenza, Thin Solid Films **130**, 155 (1985).

[7]K. L. Chopra, *Thin Film Phenomena* (McGraw–Hill, New York, 1969), p. 183.

[8]C. Djega-Mariadassou, R. Lesueur, J. Leloup, and J. H. Albany, Phys. Lett. A **65**, 455 (1978).

[9]C. Djega-Mariadassou, A. Rimsky, R. Lesueur, and J. H. Albany, Jpn. J. Appl. Phys. **19** (Suppl. 19–3), 89 (1980).

[10]H. Neumann, B. Schumann, E. Nowak, A. Tempel, and G. Kühn, Cryst. Res. Technol. **18**, 895 (1983).