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Study of a growth instability of γ-In_2Se_3

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γ-In_2Se_3 thin film are deposited for various substrate temperatures in the range of 523–673 K. This study shows that at 573 and 673 K the thin films are well crystallized with grains aligned along the *c* axis. Between these temperatures, a domain of instability appears where the γ-In_2Se_3 thin films have a randomly orientation and the *c*-lattice parameter increases. The presence of the metastable phase κ-In_2Se_3, during the growth, can explain the existence of this domain of instability. The insertion of Zn during the preparation process allows us to stabilize the phase κ at room temperature which confirms our hypothesis that the presence of κ-In_2Se_3 perturbs the crystallization of γ-In_2Se_3. The increase of the *c*-lattice parameter can be explain by the fact that κ-In_2Se_3 has a larger unit cell than γ-In_2Se_3 or by a competition during the growth between the grains of both phases which could generate constraints along the *c* axis. During the cooling, the κ phase disappears in favor of the γ phase. [DOI: 10.1063/1.1622117]

I. INTRODUCTION

Among the binary chalcogenide alloys of the type III_2–VI_3, In_2Se_3 is one of the most studied compounds for its photovoltaic application. The results were rather confusing because of the existence of numerous phases and the absence of well defined naming. Now there are three relatively well known phases α, β, and γ. The α phase, composed by four polytypic terms, crystallizes in layer structure and is metastable at room temperature but stable at temperature higher than 823 K. β-In_2Se_3, obtained by heating α-In_2Se_3, is metastable but some authors have stabilized this phase at room temperature by adding Sb.[1] It has never been observed in thin film form. γ-In_2Se_3 appears as the stable phase at room temperature and crystallizes in a defect wurtzite like structure.[2–4] Indeed the crystal structure of the γ-In_2Se_3, like most of III_2–VI_3 compounds, is based on the tetrahedral bonding structure. Moreover in order to satisfy the octet rule for sp^3 hybridization, one third of cation sites are vacant.[5,6] Such structural vacancies behave as one atomic species and should be arranged in screw form along *c* axis (VOSF phase).[4] Finally, we can notice that some authors have reported the existence of a δ phase at very high temperature (973 K). The existence of this phase is discussed and it could be a product of dissociation of In_2Se_3. Likforman *et al.*[7] summarized previous works and proposed the following phase diagram:

$$\underbrace{\alpha \xleftrightarrow{473\ \mathrm{K}} \beta}_{\text{metastable}} \xrightarrow{623\ \mathrm{K}} \underbrace{\gamma \xleftrightarrow{823\ \mathrm{K}} \alpha}_{\text{stable}}$$

Only with stable phases, this diagram becomes:

$$\gamma \overset{823\ \mathrm{K}}{\leftrightarrow} \alpha$$

Recently a phase, κ-In_2Se_3, has been discovered.[8,9] Although the conditions of deposition are similar to that of the γ phase, Zn doping is necessary to obtain and stabilize κ-In_2Se_3 thin films at room temperature.[8–10] Moreover κ-In_2Se_3 has a flakelike structure, whereas γ-In_2Se_3 has a columnar structure. Crystallographic parameters of the different phases are summarized in Table I.

In this article, we report the existence of a domain of instability in the growth of γ-In_2Se_3 thin films prepared by co-evaporation. We first describe, in Sec. II, the experimental procedure. In Sec. III, we present the results and discuss about this a domain of instability which can be generated by the presence of κ-In_2Se_3 during the growth of the γ-In_2Se_3 thin films.

II. EXPERIMENTAL PROCEDURE

In the present work, thin films of γ-In_2Se_3 are deposited by co-evaporation in a vacuum chamber from elemental sources with resistively heated tungsten (In) and molybdenum (Se) crucibles. Pressure during deposition is about 1×10^{-5} mbar. Evaporation rate of indium, measured with a hf quartz oscillator, is 1.2 Å/s while that of selenium is about 12–15 Å/s in order to maintain a high partial pressure of Se. As it was shown the Se/In ratio of about 10 allows us to grow γ-In_2Se_3 thin films.[11] Soda lime glass substrates are heated by an infrared source. The temperature of the substrates (T_s) was determined by a thermocouple (type *K*) on the deposition side. Variable heating power was supplied to keep the temperature constant during all the process. The temperature range investigated is 523–673 K. The structural characterizations of the γ-In_2Se_3 thin films were performed using a Siemens D5000 diffractometer and a JEOL 6400 scanning electron microscopy (SEM). The composition of the films was determined using a JEOL 5800 electron microprobe analysis (EMPA).

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TABLE I. Crystallographic parameters of the different phases of In_2Se_3.

Phase	System	a_h (Å)	c_h (Å)
α	Hexagonal ($n=1,2$)[a]	4.02 ± 0.02	$n\times9.56$
	Trigonal ($n=3,4$)[a]		
β	Hexagonal[a]	4.01	19.22
	Trigonal[a]		28.33
γ	Hexagonal[b]	7.1286 ± 0.0005	19.382 ± 0.002
κ	Hexagonal[c]	8.09 ± 0.005	19.85

[a]See Ref. 7.
[b]See Ref. 3.
[c]See Ref. 9.

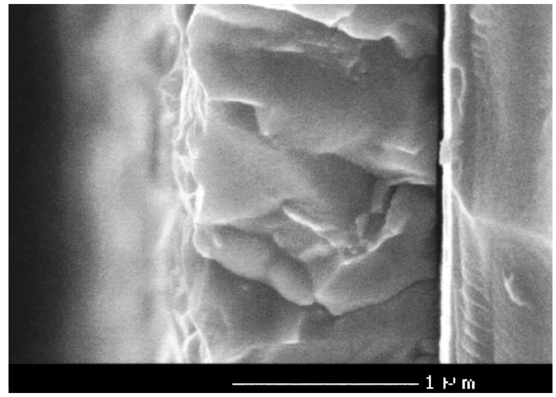

FIG. 2. SEM photography of a cross section of γ-In_2Se_3 thin film deposited at 573 K.

III. RESULTS AND DISCUSSION

The EMPA shows that all the films, obtained in the temperature range investigated, are nearly stoichiometrics with 60 ± 1.5 at. % of Se and 40 ± 1.2 at. % for In. Typical x-ray diffraction patterns are shown in Fig. 1. We notice immediately that for the lowest temperature used, the films present two phases. Indeed, in addition to γ-In_2Se_3 peaks, some peaks of In_4Se_3 and InSe are visible, respectively, at 523 and 548 K. At 573 K, the diagram presents only the (006) peak and its higher order peak (0012) which indicates that the grain are aligned along the c axis. Moreover the full width at half maximum is about 0.18°, which indicates that the size of the grains, following the c axis, is superior to 150 nm.[12] This observation is confirmed by Fig. 2, which shows SEM photography of a cross section of γ-In_2Se_3 thin film deposited at 573 K. The film is homogeneous and the size of grains is equal to the thickness of the layer. Between 598 and 648 K, the x-ray diagrams presented in Fig. 1 show several peaks but no preferential orientation is visible. At 673 K, the diagram again shows preferential orientation along the c axis even if some small peaks with mixed indices are visible. Another significant difference between diffraction patterns of γ-In_2Se_3 deposited at 573 and at 673 K and the others is the intensity of the peaks. When the grains are aligned along the c axis, the peaks intensity, for the same film thickness, is about 2 orders magnitude greater than when no preferential orientation is visible. Bindu and Sudha Kartha have reported a similar phenomenon. With a different deposition process, they have observed an alternation of well crystallized γ-In_2Se_3 thin films and amorphous In_2Se_3 phases.[13]

Figure 3 shows different diffraction patterns of four γ-In_2Se_3 thin films deposited in the same conditions. The pressure is 1×10^{-5} mbar and the substrate temperature is

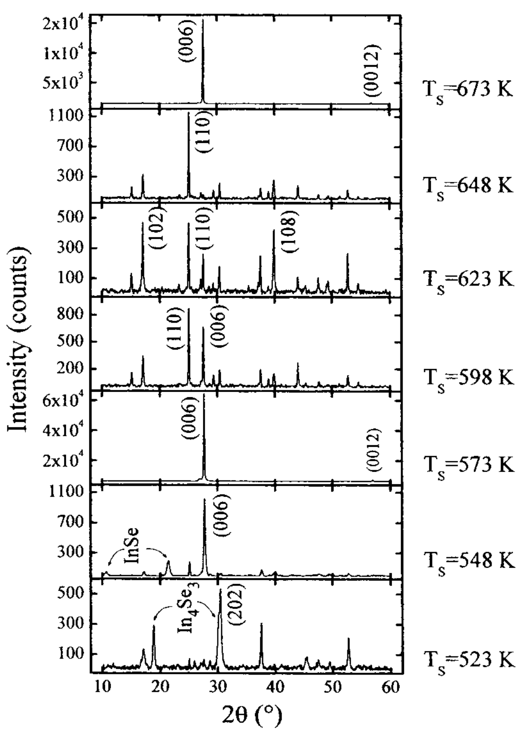

FIG. 1. X-ray diffraction diagrams taken with Cu $K\alpha$ radiation for γ-In_2Se_3 thin film deposited at substrate temperature varying from 523 to 673 K.

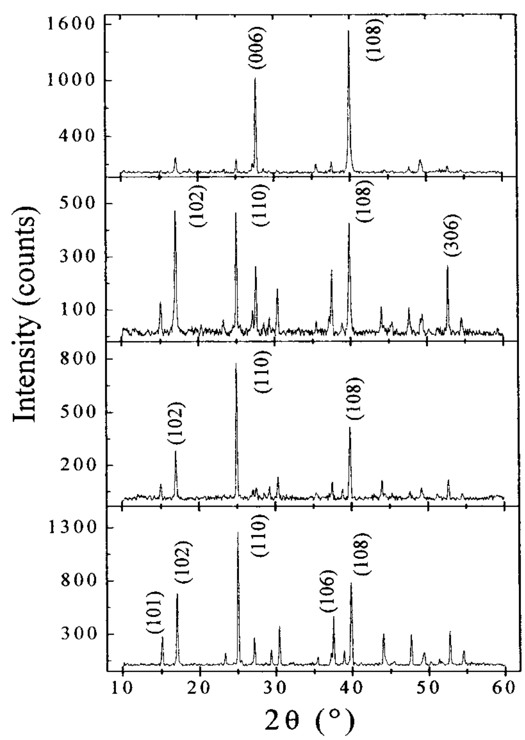

FIG. 3. X-ray diffraction diagrams taken with Cu $K\alpha$ radiation for γ-In_2Se_3 thin film deposited in the same conditions Pressure during deposition is about 2×10^{-3} Pa. Evaporation rate of indium is 1.2 Å/s while that of selenium is about 12–15 Å/s. Se/In ratio of about 10.

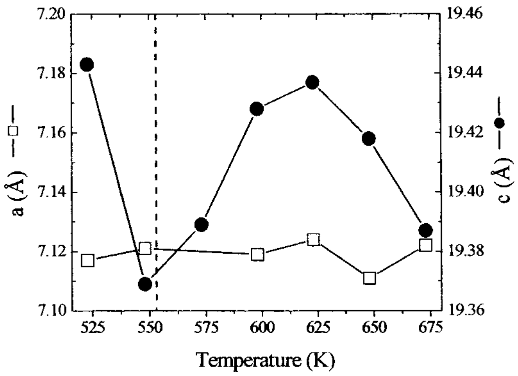

FIG. 4. Variation of the *a*- and *c*-lattice parameter of γ-In_2Se_3 thin film according to the substrate temperature. Below a temperature of 560 K, the samples are biphased.

623 K. The Se/In ratio is about 10 with an indium flux of 1.2 Å/s and a selenium flux of 15 Å/s. It can be clearly seen that no diffraction patterns are similar. The number of peaks and the intensity of these peaks are different for each diagram. The same observations are made for thin film deposited at 598 and 648 K. These results suggest that there is a domain of instability in the temperature range of 598–648 K.

From the diffraction patterns of Fig. 1 and the software CELREF,[14] we have calculated the *a* and *c* lattice parameter. These values according to the substrate temperature are plotted in Fig. 4. First of all, we note that whatever the substrate temperature is, the value of *a* lattice parameter is constant, within experimental error, and equals 7.12 Å. This value is in good agreement with the literature.[2–4] The behavior of the *c*-lattice parameter is slightly different. For the lowest temperature used, i.e., 523 and 548 K, samples are not single phased. The presence of In_4Se_3 and InSe can disturb the crystallization along the *c* axis. At 573 K, when the thin film is well crystallized, the value of the *c*-lattice parameter is 19.39 Å, which is in a good agreement with the JCPDS card 40-1407. The value increases with the temperature to reach a maximum of 19.44 Å at 623 K and then decreases to return to its initial value, 19.39 Å, at 673 K. In the temperature range of 598–648 K, the grains not only have randomly orientation but also undergo constraints along the *c* axis which increase the value of the *c*-lattice parameter. We can exclude a disturbance due to thermal agitation during the deposition since the diffraction patterns and the value of the *c*-lattice parameter are identical at 573 and 673 K. The absence of parasite phases in the diffraction pattern implies that the constraints are exerted during the growth of the grains. This temperature range could thus promote the appearance of a metastable phase. During the growth of the grains, there would be a competition between the grains of the metastable phase and those of γ-In_2Se_3, which could generate constraints along the *c* axis. During the cooling, the metastable phase disappears in favor of γ phase. If we refer to the phase diagram proposed by Likforman *et al.*,[7] it is the β phase which should appear in the temperature range of the domain of instability but this phase is obtained only by heating the α phase and has never been observed in the thin film form. It is no very probable that the β phase is at the origin of the domain of instability. On the other hand κ-In_2Se_3 could be involved. Jasinki *et al.*[9] have obtained κ-In_2Se_3 by annealing at 523 K Zn doped In_2Se_3 thin films. This temperature corresponds, in our case, to the most significant variation of the *c*-lattice parameter.

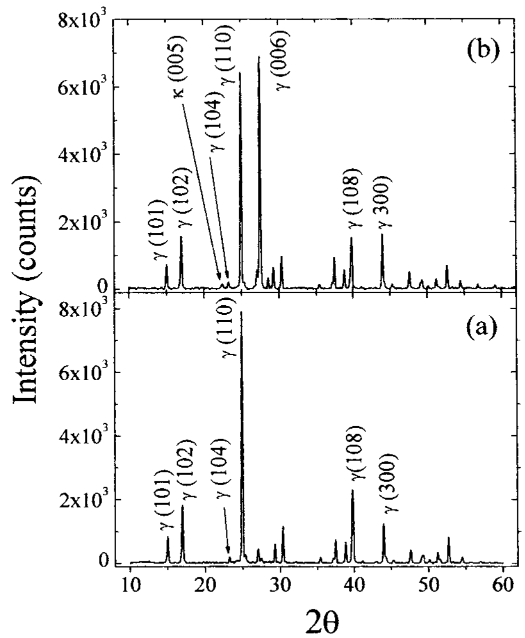

FIG. 5. X-ray diffraction diagrams of undopped γ-In_2Se_3 (a) and Zn dopped In_2Se_3 (b) elaborated in the same conditions. Concentration of Zn does not exceed 1 at. %.

As it was shown,[8–10] κ-In_2Se_3 is a metastable phase and Zn doping is needed to stabilize it at room temperature. In order to verify the presence of the κ phase during the growth of γ-In_2Se_3 thin films, Zn is added during the elaboration process to stabilize κ-In_2Se_3 at room temperature. The thin films have been deposited on soda lime glass substrate heated at 623 K. The concentration of Zn, deduced from the ratio of thicknesses measured by the hf quartz oscillator measurements, does not exceed 1 at. %. Figures 5(a) and 5(b) present x-ray diffraction patterns of Zn doped In_2Se_3 and undoped γ-In_2Se_3 synthesized in the same conditions. We notice that the Zn doped sample crystallizes in the γ-In_2Se_3 structure and its diffraction diagram presents, like that of undoped γ-In_2Se_3, several peaks. Nevertheless, a peak appears at $2\theta = 22.40°$ which is not referenced in the JCPDS card 40-1407 [Figs. 5(b) and 6(b)]. However the peak of the stronger intensity of the κ phase, (005), is located at 22.33°.[8,9] In absence of any contamination, confirmed by EMPA, this peak can be only attributed to the κ phase. So during the growth, in the temperature range of 598–648 K, in addition to the γ phase, some grains of the κ phase appear. In the absence of Zn, κ-In_2Se_3 is metastable and transforms into the γ phase during the cooling.[8–10] The increase of the *c*-lattice parameter of the γ phase can be explained by the competition, during the growth, between the grains of both phases which can generate constraints along the *c* axis. Moreover κ-In_2Se_3 has a larger unit cell than the γ phase which can also explain the increase of the *c*-lattice parameter of γ-In_2Se_3 when the κ phase transforms into the γ phase.

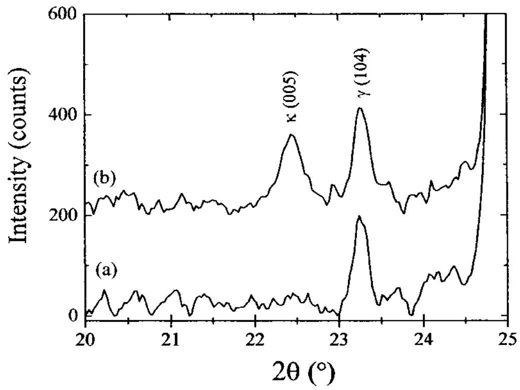

FIG. 6. Appearance of the diffraction peak (005) of the κ-In_2Se_3 phase in the x-ray diffraction pattern of the Zn dopped In_2Se_3 (b). (a) X-ray diffraction diagram of undoped γ-In_2Se_3 elaborated in the same conditions.

IV. CONCLUSIONS

In conclusion γ-In_2Se_3 thin films have been deposited for substrate temperature varying from 523 to 673 K. Whereas the films are well crystallized at 573 and 673 K, a domain of instability appears between these temperatures where the c-lattice parameter increases. The presence of the metastable phase κ-In_2Se_3 during the growth of the thin films has been shown by insertion of Zn during the deposition process. This range of temperature promotes the appearance of κ-In_2Se_3 in addition to γ-In_2Se_3. The increase of the c-lattice parameter can be explained by constraints generated by the presence of the two phases during the growth or by the transformation of the κ phase into the γ phase during the cooling. These results allow us to optimize the preparation conditions of γ-In_2Se_3 thin films used as an absorber layer in solar cells.

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[1] D. Eddike, A. Ramdani, G. Brun, J. C. Tedenac, and B. Liautard, Mater. Res. Bull. **33**, 519 (1998).
[2] A. Likforman and D. Carré, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **34**, 1 (1978).
[3] A. Pfitzner and H. D. Lutz, J. Solid State Chem. **124**, 305 (1996).
[4] J. Ye, S. Soeda, Y. Nakamura, and O. Nittono, Jpn. J. Appl. Phys., Part 1 **37**, 4264 (1998).
[5] P. C. Newman, J. Phys. Chem. Solids **23**, 19 (1962).
[6] P. C. Newman, J. Phys. Chem. Solids **24**, 45 (1963).
[7] A. Likforman, P. H. Fourcroy, M. Guittard, J. Flahaut, R. Poirier, and N. Szydlo, J. Solid State Chem. **33**, 91 (1980).
[8] C. de Groot and J. S. Moodera, J. Appl. Phys. **89**, 4336 (2001).
[9] J. Jasinky, W. Swider, J. Washburn, Z. Liliental-Weber, A. Chaiken, K. Nauka, G. A. Gibson, and C. C. Yang, Appl. Phys. Lett. **81**, 4356 (2002).
[10] A. Chaïken, K. Nauka, G. A. Gibson, H. Lee, C. C. Yang, J. Wu, J. W. Ager, K. M. Yu, and W. Walukiewicz, J. Appl. Phys. (to be published).
[11] T. Ohtsuka, K. Nakanishi, T. Okamoto, A. Yamada, M. Konagai, and U. Jahn, Jpn. J. Appl. Phys., Part 1 **40**, 509 (2001).
[12] Kaeble, *Handbook of X-ray* (McGraw–Hill, New York, 1967).
[13] K. Bindu, C. Sudha Kartha, K. P. Vijayakumar, T. Abe, and Y. Kashiwaba, Appl. Surf. Sci. **191**, 138 (2002).
[14] J. Laugier and B. Bochu, Celref ⟨http://www.inpg.fr/LMGP/lmgp_suite5.htm⟩