ФІЗИКА І ХІМІЯ ТВЕРДОГО ТІЛА
Т. 5, № 4 (2004) С. 35-37

PHYSICS AND CHEMISTRY OF SOLID STATE
V. 5, № 1 (2004) P. 35-37

UDC 539.219.4

ISSN 1729-4428

S.N. Grigorov, V.M. Kosevich, S.M. Kosmachev, A.V. Taran

Crystallization of the Amorphous Indium Selenide Films during Annealing

National Technical University, "Kharkiv Polytechnical institute"
21, Frunze Str., Kharkiv, 61002, Ukraine, (0572) 400-092, sngrigorov@kpi.kharkov.ua

The article presents the TEM investigation of phase composition and structure of indium selenide thin films, deposited onto a glass and KCl surfaces at room temperature. Crystallization of amorphous films and phase transformations in such films took place during annealing in vacuum chamber at different temperatures as well as during annealing in situ.

Keywords: cooper chalkopyrite $CuInSe_2$(CIS), indium selenide (In_2Se_3), solar cell, layer, composition, evaporation, electron microscopy, film structure.

Стаття поступила до редакції 19.05.2003; прийнята до друку 23.10.2003.

I. Introduction

$CuInSe_2$(CIS) is one of the basic materials for highly efficient solar cells and used as the main absorber layer [1-4]. It was revealed that devices based on such compound exhibit high conversion efficiencies exceeding 18%. There are a great variety of methods to produce CIS. Method of sequential deposition of In_2Se_3 and Cu is among them. At present special attention is paid to the development of low temperature methods that allowed avoiding losses of costly materials. It should be noticed, that one of the main factors in solar cell production is the control of phase formations that impacts directly on electrical properties and efficiency of solar cells.

With sequential method of CIS growth it is important to know what kind of structural and phase transformations occurs during the preparation of the first, in our case In_2Se_3 layer. However, the preparation of In_2Se_3 thin films with homogeneous structure and stoichiometric composition for the following deposition of copper involves some difficulties. It was revealed that the large-crystalline In_2Se_3 thin films were formed at high substrate temperatures (550-600^{o}C) [5-6]. It is known that In_2Se_3 evaporates as In_2Se and Se_2 vapors. Therefore, due to decomposition processes it is impossible to obtain In_2Se_3 thin films at the temperatures below 100^{o}C. With additional Se from a separate elemental Se source and annealing at high temperatures, the resulting films are closer to the In_2Se_3 composition. Single phase In_2Se_3 thin films were prepared in [7], after annealing of films deposited at room temperature. The low-temperature α-In_2Se_3 modification was formed after annealing at 180^{o}C during 2 hours, whereas the high-temperature β-In_2Se_3 modification was formed after annealing at 350^{o}C for 7-8 hours. Cubic and monoclinic modifications were also observed in the film. Up to now, the crystalline structure of such films hasn't been investigated.

In the review paper we present the transmission electron microscopy study of phase composition and structure of In_2Se_3 thin films with the aim to obtain optimal conditions for the preparation of such films with perfect morphology for the following deposition of copper and formation of $CuInSe_2$ films.

II. Experimental

In_2Se_3 compound with a purity at 99,999% was evaporated in a vacuum $5\cdot10^{-3}$Pa onto glass and KCl substrates at room temperature. The film thickness was about 50 nm. Next, the obtained amorphous samples were annealed in a vacuum for 0,5 hour at T_{sub} = 100, 200, 300 and 400^{o}C on KCl and glass substrates and at 500^{o}C only on a glass substrate. The phase composition and structure were investigated by transmission electron microscopy (TEM).

III. Results and discussion

The Fig. 1. presents the transmission electron micrograph of indium selenide film deposited onto KCl substrate at room temperature. The film has an amorphous structure. TEM micrograph of such structure revealed a dissimilar contrast in a form of rounded dark

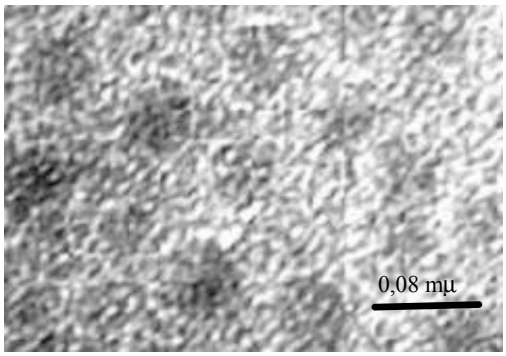

Fig. 1. TEM image of the amorphous In(Se) film deposited onto KCl substrate at room

spots (40 nm in diameter) that can be caused either by irregular film thickness or different distribution of Se and In elements in the film plane. The crystalline phase is formed after annealing at 100°C. Such crystallites are mainly incorporated near the dark spots. After in-situ annealing these crystallites reevaporate from the film leading to the formation of voids. Unfortunately, the micro-diffraction pattern contained only few reflections to identify the phases.

In films deposited onto a glass substrate, the crystalline phase was observed before the annealing procedure. We speculate that partial crystallization could start during separation of the film from the substrate (water temperature was about 70°C), because in the film grown on a glass substrate and annealed at 100°C, the amount of crystalline phase is lower than in the initial film. Electron-diffraction pattern from the initial film contains three sharply defined lines from the planes with d = 0,339, 0,204 and 0,175 nm. This new set of lines we couldn't attribute to any of known In(Se) compounds. But, it should be noted, that such lines fitted (accuracy 0,002 nm) with three intensive reflections of the InSe phase referred in [8] and with these that of the high-temperature β-In_2Se_3 phase, described in [9]. The crystalline phase disappears after annealing in a vacuum at 200°C. As a result, an amorphous film remains with the voids of 20 nm in size. Such porosity was revealed in the film and after the following annealing steps.

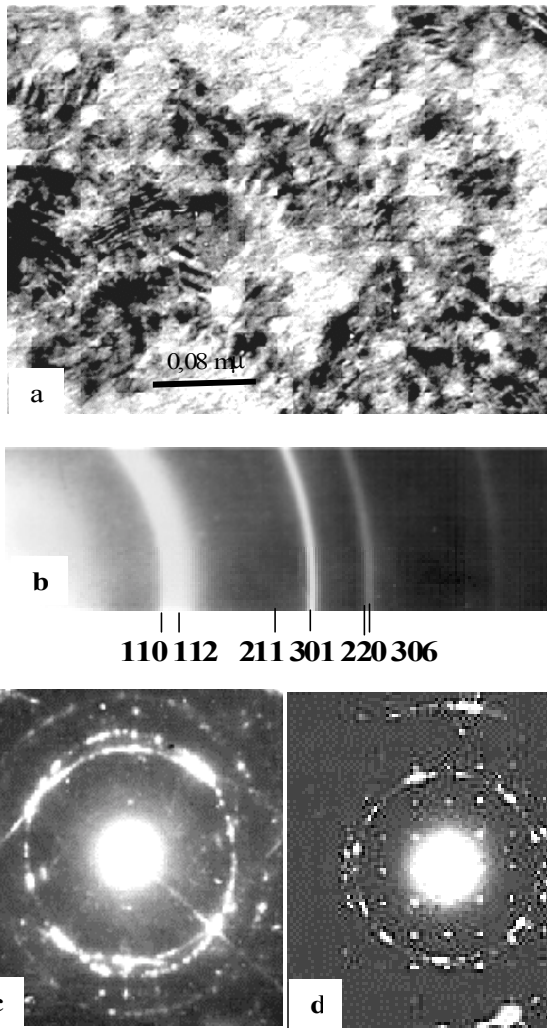

Fig. 2. TEM image (a), electron-diffraction pattern (b) and microdiffraction pattern (c) of In(Se) thin film after annealing at 500°C, and microdiffraction pattern (d) after additional exposure in air during 2 month.

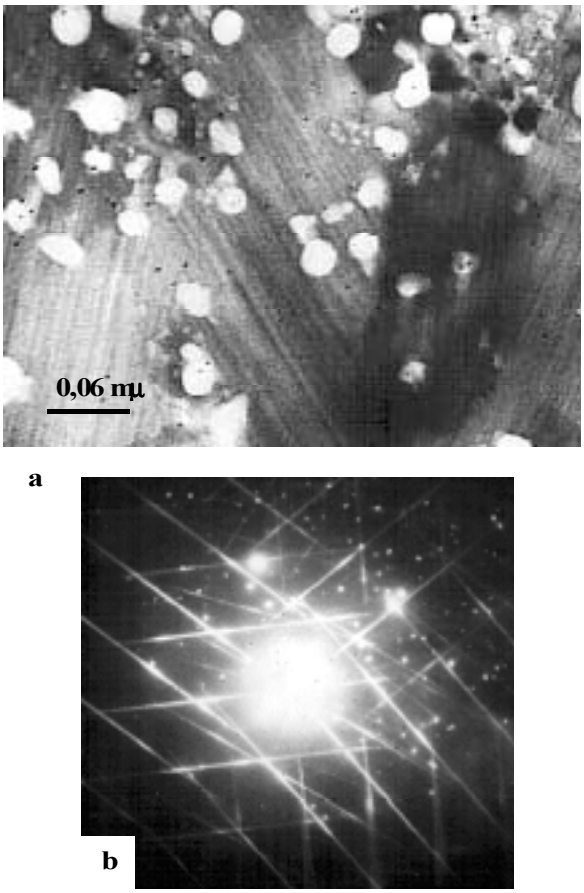

Fig. 3. TEM image and microdiffraction pattern from In(Se) film after in-situ annealing.

The films grown on KCl substrates become polycrystalline after annealing at 300°C, whereas the films on a glass substrate crystallize after annealing at 400°C. The films annealed at 300, 400 and 500°C had almost identical structure. A typical TEM image and electron diffraction pattern of the re-crystallized indium selenide film are shown in Fig. 2 a,b. All diffraction

reflections correspond to the β-In_2Se_3 phase described in [9] but with parameters for β-In_2Se_3 phase, which were different with those reported in [7]. A complex stripped contrast is revealed at TEM micrograph exhibited in Fig. 2a. In one case, it is a moiré fringe contrast, and in the other it is formed by laminar crystallites. The Fig. 3c depicts the long bars originated from the packets of laminated crystals lying parallel to the electron beam, whereas the diffraction maximums, from the packets inclined to the beam, were situated on ellipsis. On the microdiffraction pattern, the calculated period of thin lamellas in packets was about 10 nm. This corresponds to the period revealed at TEM image. The microdiffraction patterns can't be longer interpreted within the framework of a single-phase system. Some additional lines with ($d = 0{,}324^{\pm 0{,}002}$ nm and $d = 0{,}303^{\pm 0{,}002}$ nm) may associate either with the β-In_2Se_3 phase [7] or the γ-In_2Se_3 [10]. Evidently, we deal, at least with a two-phase system. The films are not monoblock on thickness. They consist of overlapping packets, in which thin lamellas lie both in parallel and inclined positions to the film surface. The moiré contrast is observed from the packets lying parallel to the film plane.

After 2-month exposure in air, there were revealed some grains in the film from which at microdiffraction patterns we observed the presence of point reflections with long period instead of thin bars (Fig. 2d). However, none of these reflections were attributed to the indium selenide phases given in JCPDS.

In-situ annealing of the amorphous indium selenide films was carried out. In this case, the annealing conditions were even more non-equilibrium and the temperature was higher then during the prolonged heating in a vacuum chamber. Fig. 3a,b shows transmission-electron images and microdiffraction patterns. As is seen from Fig. 3a, the structure represents the laminated (plate-like) packets with very thin layers.

IV. Conclusions

It was revealed that crystallization of amorphous indium selenide films started below 100°C. During this stage the In(Se) crystalline modification characterized by a high vapor pressure is formed. This phase reevaporated during the further heating. As a result, the In and Se ratio in the film could be changed. The second crystallization stage in films grown on KCL and glass substrate started at 300°C and 400°C respectively. The laminated crystals with modulated structure were revealed in the film in which the layers were formed by metastable indiume selenide phases of various compositions. The electron-diffraction patterns of such films can be interpreted on the base of a single-phase system.

[1] A. Rockett, F. Abou-Elfotouh. // *J. Thin Solid films*, 237, pp. 1-11 (1994).
[2] H.W. Schock et. al. // *J. Appl. Surf. Sc.,* 92, pp. 606-616 (1996).
[3] S. Zweigart et. al. // *J. Sol. Energy Mat. and Solar Cells*, 42, pp. 219-229 (1996).
[4] S.N. Grigorov et. al. // *Functional Materials*, **5**(3), pp. 335-342 (1998).
[5] J. Kessler et. al. // *Proc. Of 12th European Photovoltaic Sol. Energy Conf.* Amsterdam. (1994).
[6] S.N. Grigorov et. al. // *Jpn. J. Appl. Phys.*, **39**(1), pp. 179-180 (2000).
[7] С.А. Семилетов. // *ФТТ.,* **3**(3), сс. 746-753 (1961).
[8] J. Rigoult et. al. // *Acta Crystallogr.*, Sec. B., 36, p. 916 (1980).
[9] Powder Diffraction File. Alphabetical Index Inorganic Compounds, (JCPDS International Center for Diffraction Date, 1601 Park Lane, Swarthmore, Pennsylvania 19081 USA, 1977) 20-494.
[10] Powder Diffraction File. Alphabetical Index Inorganic Compounds, (JCPDS International Center for Diffraction Date, 1601 Park Lane, Swarthmore, Pennsylvania 19081 USA, 1977) 20-492.

С.Н. Григоров, В.М. Косевич, С.М. Космачев, А.В. Таран

Кристалізація аморфних плівок селеніду індію при відпалі

Національний технічний університет „Харківський політехнічний інститут",
вул. Фрунзе 21, Харків, 61002, (0572) 400-092, sngrigorov@kpi.kharkov.ua

Проведено електронно-мікроскопічне дослідження кристалізації аморфних плівок селеніду індію, осаджених на поверхню скла та на поверхню відколу кристалів KCl при кімнатній температурі. Спостерігалися фазові і структурні перетворення в плівках, що відбуваються в процесі їхнього відпалу у вакуумній камері при різних температурах, при відпалі електронним пучком безпосередньо в колоні електронного мікроскопа, а також після тривалої витримки відпалених плівок при кімнатній температурі.