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PHASE TRANSFORMATIONS IN TWO-LAYERED In_2Se_3-Cu FILM SYSTEM

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In the article Cu-In-Se thin films obtained by dosed deposition of Cu onto indium selenide starting layer with the further annealing of the two-layered composition in Se atmosphere were investigated by transmission electron microscopy (TEM) and by energy-dispersive X-ray spectroscopy (EDS). The samples with various Cu content, Cu/In<1 and Cu/In>1, were prepared. It was revealed that all films after selenization had a modulated structure, which was formed due to Cu diffusion into the indium selenide film. Such modulated structures have been formed by both equilibrium phases of the Cu_2Se-In_2Se_3 pseudo-binary section of the Cu-In-Se ternary system and by metastable ones.

1. INTRODUCTION

At present, α-$CuInSe_2$ (α-CIS) semiconductor compound with a chalkopyrite-type structure and its solid solutions are the most promising materials for realizing a new generation of thin film solar cells [1-4]. One of the advantageous methods to produce $CuInSe_2$ base layers is sequential vacuum deposition of indium selenide and copper with the following annealing in selenium atmosphere (selenization) of the two-layered composition [5-9].

From the literature [10-11] it is reported that in attempting to synthesize a chalkopyrite phase, a number of additional phases were identified, namely: δ-$CuInSe_2$, $CuIn_3Se_5$ (β-phase CIS with a chalkopyrite structure with ordered vacancies in Cu sub-lattice), $CuIn_5Se_8$ (γ-CIS), $Cu_2In_4Se_7$, $Cu_3In_5Se_9$, Cu_5InSe_4, $Cu_7In_{19}Se_{32}$, $Cu_8In_{18}Se_{33}$. The main difficulty that arises during phase identification is the fact that the electron-diffraction patterns taken from these films contain only several intense lines and a great number of very weak ones. In so doing, the crystallographic parameters of different phases are so close to each other and to the parameters of the base Cu_2Se and In_2Se_3 phases that these intense lines cannot be identified by TEM.

In the article, Cu-In-Se thin films obtained by dosed deposition of Cu onto indium selenide starting layer with the further annealing of the two-layered composition in Se atmosphere were investigated by transmission electron microscopy (TEM) and by energy-dispersive X-ray spectroscopy (EDS). The samples with various Cu content, Cu/In<1 and Cu/In>1 were prepared. All films were annealed in a Se atmosphere at 550 °C. The elemental and phase compositions as well as the structure of the obtained films were determined. The CIS growth mechanism in the two-layered film system was examined.

2. METHOD AND PREPARATION

Copper (purity 99,999%) was deposited in a 10^{-3} Pa vacuum at 200 °C onto In(Se) layer, which was previously formed with a sequence: In_2Se_3 (T_{sub}=250 °C)+Se (T_{sub}=350 °C)+In_2Se_3 (T_{sub}=500 °C) + Se (T_{sub}=550 °C). Next, the two-layered In_2Se_3-Cu composition was annealed in a Se atmosphere at 550 °C. The elemental composition of the samples with different Cu content was analyzed by EDS, while the structure was investigated by TEM.

3. RESULTS AND DISCUSSION

The samples of three types were prepared. According to EDS data, the samples of the first type were Cu-poor. Cu/In ratio was 0,64 as compared to a stoichiometric CIS. On the β-In_2Se_3-Cu_2Se quasi-binary section of the Cu-In-Se equilibrium phase diagram, this chemical composition corresponds to the region of the β-CIS phase. The samples of the second type had the Cu/In ratio equal to 1,12, and the samples of the third type had a composition with Cu/In = 1,25. The samples of the second and third types were attributed to the two-phase (α-$CuInSe_2$ + Cu_2Se) region of the Cu-In-Se equilibrium phase diagram. All samples had an excess of Se as compared to stoichiometric $CuInSe_2$.

Fig. 1,a-c represents typical structure and microdiffraction patterns of the first type films. A complex contrast in the form of dark and bright triangles was revealed in Fig. 1,a. Such a contrast may be formed either by stacking faults lying parallel to the film surface or by thin lamellas of secondary phases with a lattice that correlates coherently with that of a base matrix.

Microdiffraction pattern taken from this area exhibits the reflections with hexagonal symmetry corresponding to the (001) plane of the β-In_2Se_3 or $CuIn_5Se_8$ (γ-CIS) phases, which have hexagonal lattices with close parameters. But the most intense reflections (see Fig. 1,a), may be originated from both (300) β-In_2Se_3, (110)γ-CIS, and (220) α- or β-CIS phases. Weak reflections in a position of ½ (200) corresponding to α-CIS, which closely fitted to these of (100)-type β-CIS were also revealed. Basing on this data, one can conclude that in a plane normal to the electron beam, the platelets of at least twophases (γ-CIS and β-CIS) are matched in such a manner that their crystallographic relationships are as follows: (001)γ-CIS || (112) β-CIS. In these phases, the planes are occupied only by Se atoms and have an identical structure. The distance between Se atoms in the (001) plane of hexagonal γ-CIS is 0,404 nm [4], whereas along the (112) plane of the β-CIS it corresponds to 0,407 nm [4]. A mismatch between these two lattices is 0,7% and it can be compensated by elastic deformations of the lattices and by the formation of a triangular network of misfit dislocations. There is also a good correlation between crystalline lattices of β-In_2Se_3 and γ-phase CIS: $3a_{\gamma\text{-phase}} \cong \sqrt{3}\, a_{\beta\text{-In2Se3}}$. Along (001) plane they form a common boundary with a "discrepancy" of 1,5%. This mismatch is partly compensated by elastic deformations of the lattices or by triangular network of grain-boundary dislocations. With such a correlation the microdiffraction patterns of these two phases are almost identical. Strong diffuse coils, observed in Fig. 1,a, may originate from the γ-CIS phase with a lattice containing Cu-excess atoms – zones of β-CIS phase (like Guiner-Preston zones). Assuming the above mentioned, one can speculate that in a direction normal to the film surface and on the base of β-In_2Se_3 grains (001 plane || to the film surface), take place the formation of three-layered structure, containing β-In_2Se_3 - γ-CIS - β-CIS phases, which are in coherent position.

In a grain marked A (see Fig. 1), one can observe a very thin lamellas lying parallel to the electron beam. At microdiffraction pattern, such a grain revealed strong reflection of (112) type, which was attributed to both β- and α-CIS phases. A long bar extends from such a reflection and this also points to the existence of thin lamellas in this grain. In addition, there are some lamellas along (112) plane inclined to the electron beam. On these lamellas we revealed a striped contrast like from inclined staking faults. Obviously, in this case we deal with thin lamellas of the α-phase incorporated into β-matrix.

In Fig. 1,b, we observed a line of closely pitched reflections associated with γ-CIS with trigonal lattice [4]. Fig. 1,c shows electron-diffraction image and microdiffraction pattern taken from the film area, where in the direction of an electron beam the two layers of the γ-phase with trigonal and hexagonal lattices are formed.

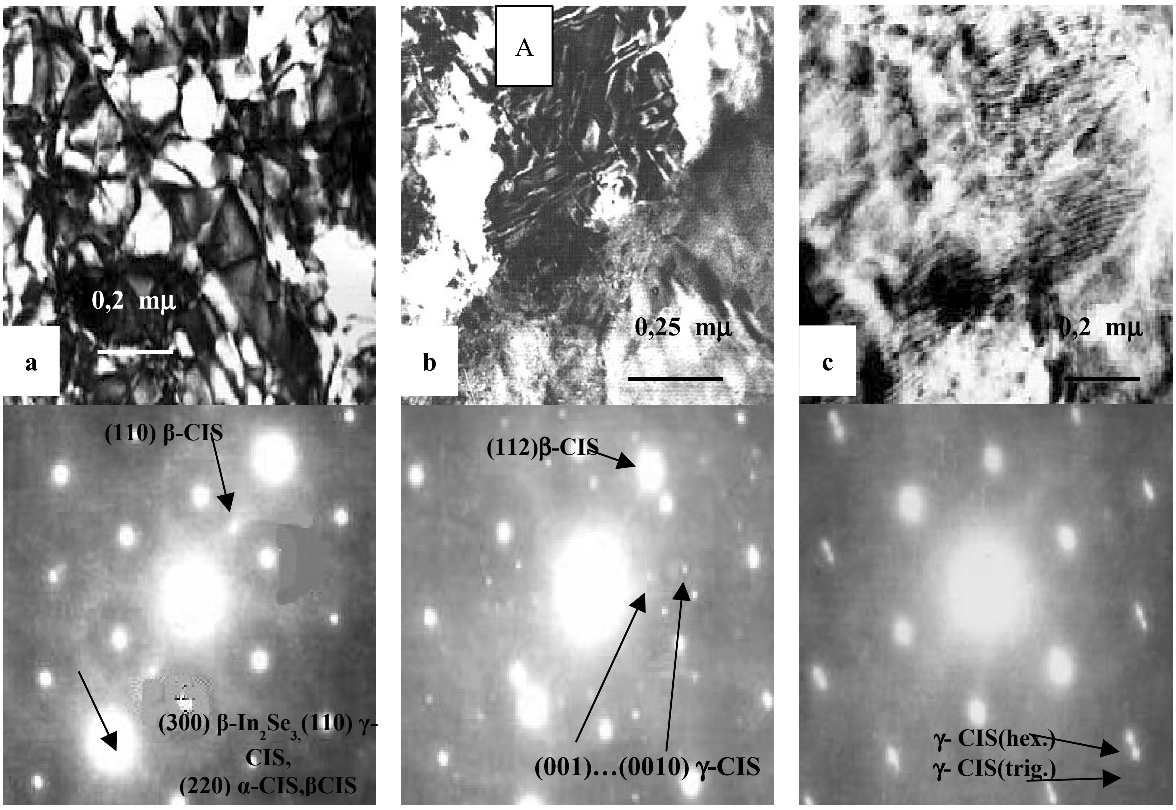

Fig. 1. TEM images and microdiffraction patterns from the film of the first type, Cu/In = 0,64

The microstructure and microdiffraction patterns of films of the second type with Cu/In = 1,12 are shown in Fig. 2. Such a structure is mainly characterized by a great number of thin twinned lamellas. Among the phases that are formed in a considered system, the twins can originate only in phases with a chalkopyrite structure i.e. α- or β-CIS. In a chalkopyrite structure the twinning take place along (112)-type planes which form tetrahedron. Microdiffraction pattern (see Fig. 2) has verified the fact that in lamella crystallite with the structure of β-phase with (112) plane parallel to the film surface take place the formation of thin twinned lamellas along three another tetrahedron planes. It is in this case that we had observed cross-like bars near the (112)-type reflections. The intensification at the ends of such cross-like bars has also drawn our attention. This phenomenon may take place, when the Evald's sphere is crossed by strained sites of (101) and (103)-types of the invert lattice of chalkopyrite structure with microtwins along all tetrahedron planes. As the films of the second type had a great amount of β-phase, which is In- rich, there remains an excess of Cu. Therefore, the excess of Cu interacts with Se and the film should contain Cu_2Se phases. However, in our investigations we could not find any traces of Cu-rich selenides.

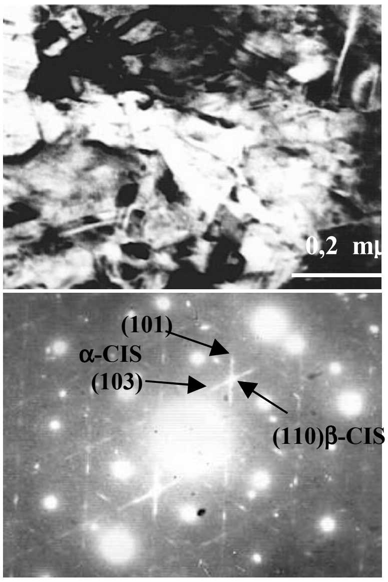

Fig. 2. TEM image and microdiffraction pattern from the film of the second type, Cu/In = 1,12

The microstructure of the films of the third type (Cu/In ratio 1,25) had almost the same features as compared to the structure of the second type films. Here, we have also revealed a number of packets with parallel microtwins of α- and β-CIS. But, in this case, such thin lamellas of the β-CIS were incorporated into grain matrix of α-phase. At microdiffraction pattern in Fig. 3,a, the hexagonal reflection network corresponds to a large crystallite of the α-phase lying in the (112) $CuInSe_2$ plane parallel to the film surface, whereas (110)-type reflections of the β-phase with bars were very weak.

The reflections in a position of 1/3(424) and 2/3(424) of $CuInSe_2$ phase were also observed in the film. They can originate from the twin boundaries. There was revealed a number of large grains with microtwins attributed to α-CIS only (see Fig. 3,b). From these twinned crystallites we revealed the existence of (220)-type reflections but without the indication of (110) ones. Evidently, the transformation from the twinned lamella crystallites of the β-phase to these of the α-phase took place via formation of modulated structures, which consist of alternating twinned lamellas of α- and β-phases. As the films of the third type were Cu-rich, so they should contain Cu_2Se, however, at microdiffraction patterns cooper selenide was not found. But there was revealed a great number of similar lamella structures with phases, which we couldn't attribute to any of known In-Se, Cu-Se or Cu-In-Se compounds. This situation can be explained basing on the ideas described in [12]. All observed phases in the samples that correspond to β-In_2Se_3-Cu_2Se pseudo- binary section of the Cu-In-Se phase diagram have common crystallographic features. They are formed by alternating closed-packing Se layers and of these containing only cation of metals.

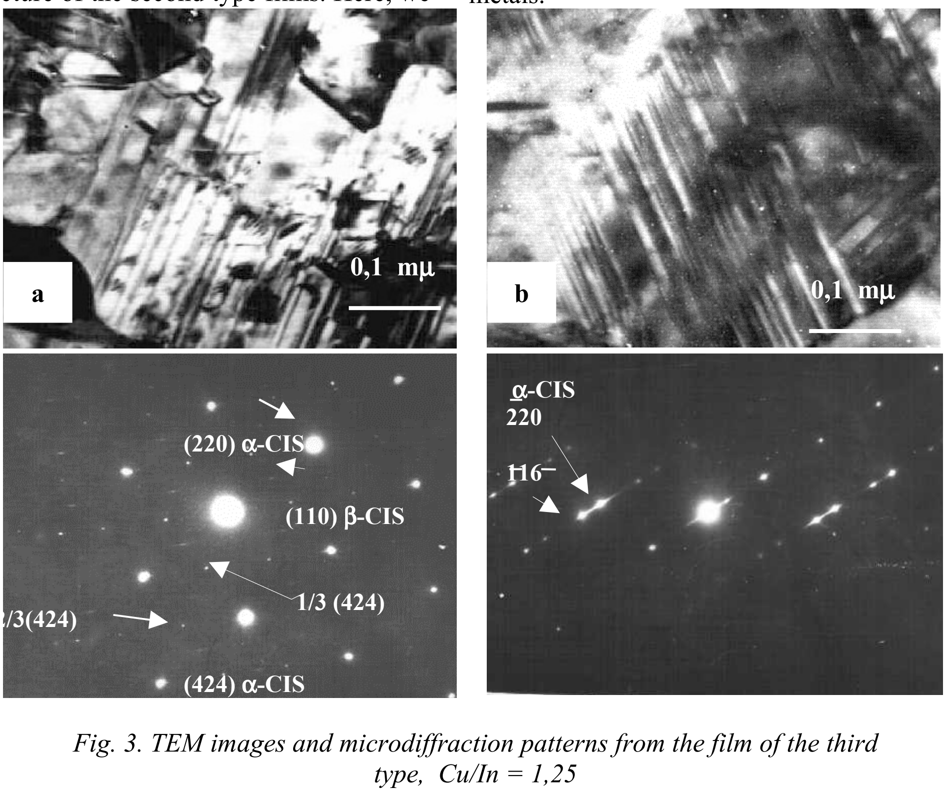

Fig. 3. TEM images and microdiffraction patterns from the film of the third type, Cu/In = 1,25

The crystalline lattices of these two phases may correlate by a common anion plane

In so doing, along with equilibrium phases the metastable homogeneous modifications can also be present in the film. On microdiffraction patterns these modifications reveal reflections which are different from those of equilibrium phases. Besides that, some additional reflections were revealed due to diffraction on the modulated structures.

In all considered cases of phase formations in the two-layered In_2Se_3/Cu film composition we have determined two situations. In the film area in which indium selenide film contains grains with (001) plane parallel to the film surface, in initial two-layer composition take place the formation of multi-layered on thickness grains.

The copper content is increased layer by layer from some minimal value dependent on Cu/In ratio in this system to a maximal, which is also determined by this ratio.

Thus, in films with Cu/In = 0,64 we observed the transition from In_2Se_3 to β-phase $CuIn_3Se_5$, whereas in films with Cu/In = 1,25 take place the transition from β-phase $CuIn_3Se_5$ to $CuInSe_2$ or possibly to Cu_2Se. In some areas of the film in which indium selenide film is lying normal or inclined to the film surface, Cu diffuses through the bulk of indium selenide layer. In this case, alternating plates of two phases, lying normal or inclined to the film surface split indium selenide grains. So, the modulated structures were formed due to transformation of indium selenide cation sub-lattice. In a set of crystallographic modifications, which form modulated structure can exist both stable and metastable modifications.

CONCLUSIONS

It was revealed that all films after selenization had modulated structure, which was formed due to Cu diffusion into the In(Se) film. The modulated structures were formed by both equilibrium phases of the In_2Se_3-Cu_2Se pseudo-binary section of the Cu-In-Se ternary system and by metastable phases. In Cu-poor films, (Cu/In<1) such modulated structures were formed basing on the In_2Se_3, $CuIn_5Se_8$ and $CuIn_3Se_5$ phases. In Cu-rich films, the formation of modulated structures is based on $CuIn_3Se_5$ and α-$CuInSe_2$ phases. The correlation of phases in modulated structures is accomplished either by coherent phase boundaries, which contain misfit dislocations or by means of twinned boundaries. The most perfect structure had the films with Cu/In = 1,2. They contain large grains (~0,5 μm) of α-CIS with a great number of thin twinned lamellas of α- and β-CIS.

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ИССЛЕДОВАНИЕ ФАЗОВЫХ ПРЕВРАЩЕНИЙ В ДВУХСЛОЙНОЙ ПЛЁНОЧНОЙ СИСТЕМЕ In_2Se_3-Cu

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Проведены электронно-микроскопическое и рентгеноспектральное исследования плёнок Cu-In-Se, полученных путём дозированного осаждения меди на слой селенида индия и отжига двухслойной композиции в атмосфере селена. Были приготовлены образцы с различной концентрацией меди (Cu/In<1 и Cu/In>1). Установлено, что все пленки после селенизации имеют модулированную структуру, которая формируется в результате диффузии меди в пленку селенида индия. Наблюдались модулированные структуры, образованные как равновесными фазами, принадлежащими псевдобинарному сечению Cu_2Se-In_2Se_3 трехкомпонентной системы Cu-In-Se, так и метастабильными фазами.

ДОСЛІДЖЕННЯ ФАЗОВИХ ПЕРЕТВОРЕНЬ У ДВОШАРОВІЙ ПЛІВКОВІЙ СИСТЕМІ In_2Se_3-Cu

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Проведені електронно-мікроскопічне та рентгеноспектральне дослідження плівок Cu-In-Se, отриманих шляхом дозованого осадження міді на шар селеніду індію та відпалу двошарової композиції в атмосфері селену. Були виготовлені зразки із різною концентрацією міді (Cu/In<1 і Cu/In>1). Установлено, що всі плівки після селенізації мають модульовану структуру, що формується в результаті дифузії міді в плівку селеніду індію. Спостерігалися модульовані структури, утворені як рівноважними фазами, що належать псевдобінарному перетину Cu_2Se-In_2Se_3 трикомпонентної системи Cu-In-Se, так і метастабільними фазами.