UDC 621

S.N. Grigorov[1], A.V. Taran[1], V.S. Taran[2], A.I. Timoshenko[2]

Preparation and structure of $CuInSe_2$ thin films for solar cells at low substrate temperatures

CIS epitaxial films were grown on (001) KCl surface with PbS sublayer and on glass-ceramic at 400°C. Annealing of the (α + β)-CIS films *on glass-ceramic*, in two-step vacuum-arc plasma discharge at 550°C provided the formation of a homogeneous large-crystalline α-CIS.

Эпитаксиальные плёнки CIS были выращены на (001) KCl с подслоем PbS при 400°C. Отжиг плёнок (α + β)-CIS на ситалле в несамостоятельном газовом разряде при 550 °C приводит к образованию фазы α-CIS.

Ключевые слова: *халькопирит меди, солнечный элемент, структура, фазовый состав, электронная микроскопия.*

Introduction

Ternary semiconductor compounds based on $CuInSe_2$ (α-CIS) are of great interest for the production of solar cells and other optoelectronic devices [1,2]. Their utilization in such areas places more stringent requirements upon the structure of the obtained ternary compounds. Traditionally, the synthesis of large-crystalline $CuInSe_2$ semiconductor films takes place at rather high substrate temperatures (600-650°C). In recent years, due to production of solar cells on flexible polyamide substrates, a demand arose for the development of preparation methods of α-CIS films having a perfect structure at relatively low substrate temperatures (< 450°C) [3]. There are only few works aimed at oriented growth of $CuInSe_2$ thin films. Those are grown mainly by molecular beam epitaxy on various substrates. Different crystal modifications of $CuInSe_2$ phase are revealed in the films so obtained, the film microstructure being characterized by presence of various defects (dislocations, nanotwins, stacking defects, antiphase boundaries). In this work, to study the $CuInSe_2$ film structure formation at low substrate temperature, three-component Cu-In-Se films of variable composition have been prepared using the Vekshinsky technique and the structure and phase composition have been studied.

1. Preparation of Cu-In-Se thin films

The Cu-In-Se films were prepared in a standard VUP-5 vacuum device in $5*10^{-3}$ Pa vacuum on (001) KCl crystals with a thin PbS sublayer and glass-ceramic at T_{sub} = 400°C. The KCl crystals were placed on a long substrate, one side of which was positioned right opposite to the evaporator of copper and the other one to the indium selenide crucible, both at 100 mm distance. The evaporation was done simultaneously. This provided films of variable composition changing from one spot to other, so a broad spectrum of compounds of the ternary Cu-In-Se system was formed along the substrate. To prepare the films, a 99,999 % purity In_2Se_3 powder and copper (99,9999 % purity) were used. Indium selenide and copper were evaporated from alundum crucible and molybdenum boat, respectively. The structure of the obtained samples was examined using a PEM-125K transmission electron microscope.

The additional annealing of the CIS films, obtained by the Vekshinsky technique on glass-ceramic, in two-step vacuum-arc plasma discharge at 550°C was carried out.

2. Phase composition and structure

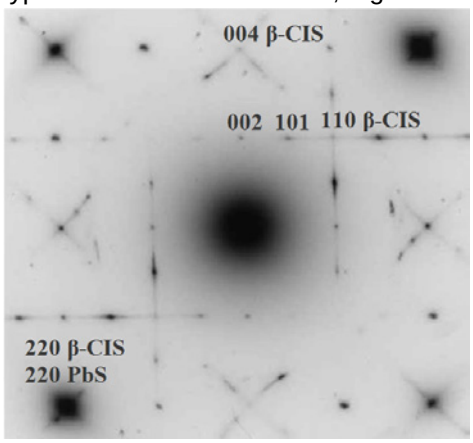
The films of variable composition have been investigated by transmission electron microscopy. Only two types of films that can be distinguished by their differing structures were revealed by TEM. The film with a tetragonal lattice was formed on KCl/PbS crystals located in front of copper evaporator Fig. 1a, whereas the two-phase film having a tetragonal and hexagonal crystallites formed in front of a crucible containing indium selenide Fig. 1b.

The α-CIS ($CuInSe_2$) and β-CIS ($CuIn_3Se_5$) phases have a tetragonal lattice, whereas the γ-CIS ($CuIn_5Se_8$) phase has a hexagonal one. The film having a tetragonal lattice is presented in Fig.1a. Besides the strong Bragg reflections of (220) and (400) types attributed to α-CIS, additional reflections at positions (002) and (110), revealed. For ideal α-CIS structure the (002) and (110) type reflections are not allowed. These reflections originate from the β-CIS phase with ordered vacancies in copper sub-lattice.

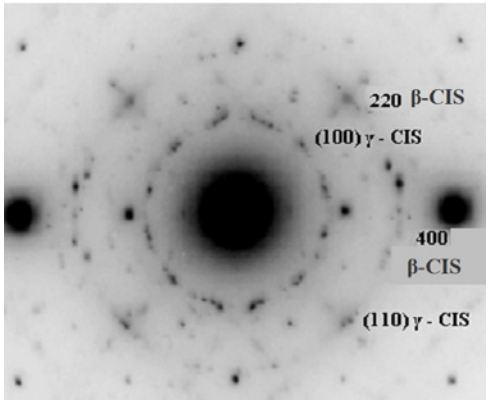
The set of main reflections (200), (220) and (400) β-CIS, PbS and their geometry confirms epitaxial growth of the β-CIS on the (001) PbS. The β-CIS crystallites grow on the (001) PbS surface in two equivalent epitaxial orientations: (001), [100] β-CIS || (001), [100] и [010] PbS.

This set contains (101) type reflection from the β-CIS phase that points to the existence of crystallites in the film with another two equivalent epitaxial orientations: (010), [001] β-CIS || (001), [100] и [010] PbS.

If we take into consideration only geometrical aspect of the β-CIS and PbS lattices matching, so all indicated orientations are equivalent, because the period of the tetragonal lattice of β-CIS along *c*-axis is two times greater as compared to *a*- axis. Because of this the (200) and (004), (400) and (008) type reflections are identical, Fig.1a.



a



b

Fig. 1. Micro-diffraction patters taken from the Cu-In-Se films grown on a KCl surface with PbS sublayer at 400°C (a) – on crystals, placed in front of cooper evaporator; (b) – on crystals, placed in front of In_2Se_3 evaporator

In Fig.1b in addition to reflections from the β-CIS crystallites in epitaxial orientations, a set of reflections of (112) β-CIS appears indicating worsening of preferred epitaxial growth. The (100) and (110) diffraction coils originate from the γ-CIS phase with a hexagonal lattice. The γ-CIS crystallites grow on the PbS surface in the following orientation: (001), [001] γ-CIS || (001), [001] PbS.

The presence of twins is one of the distinctive features of the micro-diffraction pattern in Fig.1a. The twins streaked along [110] and $[1\bar{1}0]$ directions were reveled near the (200) type reflections. Weak reflections at streaks ends are not attributed to the (001) section of the reciprocal lattice. Similar reflection sets connected with long streaks were also observed near (220) and (400) diffraction maxima. It is well known that the typical defects of the β-CIS tetragonal lattice are twins along (112) planes. The sites of reciprocal lattice from these twins are not getting into (001) section of the reciprocal lattice of the matrix. Thee reflections from the twins and double diffraction situated in planes neighboring to the (001) one can be observed in electron diffraction together with those from the matrix due to insignificant film bending. This situation is well known and has been discussed to explain some diffraction patterns taken from twinned crystals of Au.

If the crystallites in twinned position are very thin, a long diffuse streaks normal to the twinning and (001) planes appear in the electron diffraction pattern. It is just such streaks that are seen in Fig. 1a near (200), (220), and (400) reflections. Thus, the electron diffraction pattern taken from the β-CIS epitaxial crystallites in the (001) orientation indicates the existence of microtwins along (112) planes. Some microtwins have been also revealed in β-CIS films in crystallites of other orientations.

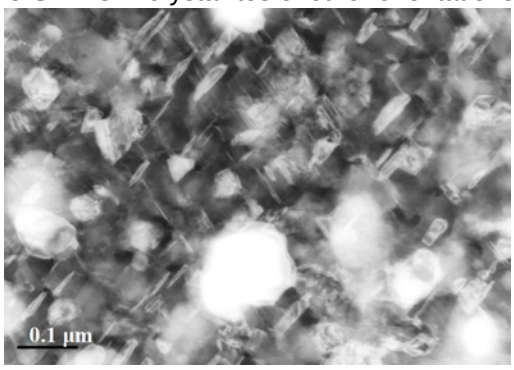


Fig. 2. TEM dark-field image using $(1\bar{1}2)$, $(1\bar{1}\bar{2})$ and (200) reflections from the β-CIS crystallites on (110) and (001) orientations with twinned lamellas

Fig. 2 shows a dark-field image using $(1\bar{1}2)$, $(1\bar{1}\bar{2})$ and (200) reflections from β-CIS crystallites in the (001) and (110) orientation rotated by 90° to one another. The micro twined lamellas in (001) oriented crystallites are trapezium-shape (they originate from the (112) planes inclined to the electron beam), whereas microtwin lamellas in (110) orientation are needle-like (they are parallel to the electron beam).

A great number of microtwins in the film structure is a result of the fact that a single-phase β-CIS films grown in In-rich conditions inherit the structure of the two-phase α-CIS + β-CIS film in which ultrathin α-CIS layers are coherently matched with the ultra thin β-CIS layers by twinned boundaries.

At diffraction pattern taken from epitaxial crystals a long cross-like streaks near the (110) type reflections, appear (Fig.1a). The streaks are oriented along the [100] and [010] directions of the β-CIS lattice. It is worth noting that these streaks oriented along the [100] and [010] directions were only observed near reflections allowed for β-CIS phase (containing or-

dered Cu vacancies) and not allowed for the vacancy-free α-CIS phase. Considering the above mentioned, the streaks can be concluded to be due to two-dimensional defects belonging to cation sublattice of Cu and In atoms but leaving Se sublattice unchanged. The nature of such two-dimensional defects can be explained as a shift in the (001) β-CIS plane by a vector R = 1/2[110], which preserves Se sublattice undisturbed but causes the transition of Cu atoms into In sites. As a result, an antiphase boundary appears along the (100) and (010) planes seen as long streaks along [100] and [010] directions. A plurality of domains divided by antiphase boundaries causes a stripped contrast along the [100] and [010] directions in TEM image. An example of this type of contrast is presented in Fig. 3. A dark-field image in Fig.3. was made using the (110) reflection from crystallites on (001) orientations and the (101) reflection from the crystallites on the (010) orientations rotated by 90˚ to one another.

The streaks along the [001] direction near the (101) type reflections pointed to the existence of flat defects lying normal to *c* axis. We speculate that these defects are staking faults with R=½[110]. In Fig. 3 the flat defects normal to the [001] axis were revealed in (010) oriented extended areas rotated by 90˚ to one another.

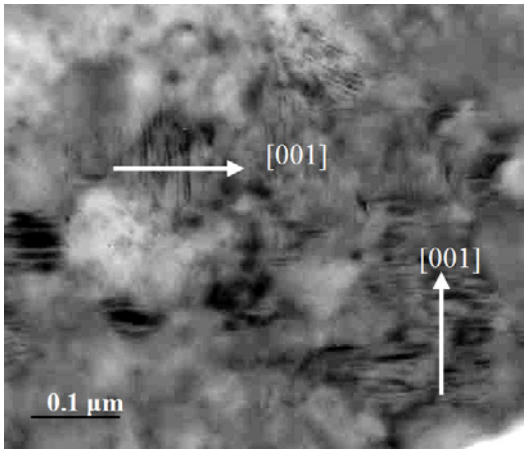


Fig. 3. TEM dark-field image using (110) reflection from the crystallites on (001) orientations and using the (101) reflection from the crystallites on the (010) orientations rotated by 90˚ to one another

The additional annealing of the (α + β)-CIS films, obtained by the Vekshinsky technique on glass-ceramic, in two-step vacuum-arc plasma discharge at 550°C provided β-CIS→α-CIS phase transition with the formation of homogeneous large-crystalline α-CIS phase. But the modulated structure of α-CIS grains is still preserved (Fig.4.)

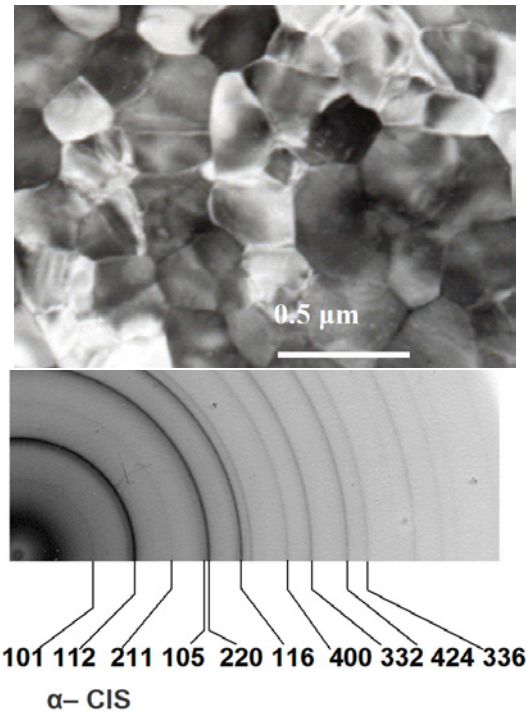


Fig.4 TEM image and electron-diffraction pattern of the α-CIS phase after annealing at 550°C

Conclusion

Investigations carried out showed that during CIS films synthesis by simultaneous deposition at low temperatures the structurization phenomenon associated with the formation of grains with modulated structure comprising of microtwins, antiphase boundaries and stacking faults take place instead of perfect α-CIS grains formation system. The additional annealing of the (α + β)-CIS films, obtained by the Vekshinsky technique on glass-ceramic in two-step vacuum-arc plasma discharge at 550°C provided β-CIS→α-CIS phase transition with the formation of homogeneous large-crystalline α-CIS phase.

References

1. *Rockett A.* Thin film photovoltaics / A. Rockett, H. Birkmire // J. Appl.Phys.Rev.- 1991.- V.70.- P.336.
2. *Ramanathan K*. Properties of 19.2% efficiency ZnO/CdS/Cu(In,Ga)Se_2 thin-film solar cells / K. Ramanathan, M.A. Contreras, C.L. Perkins // Progress in Photovoltaics: Research and Applications.- 1999.- V.11.- P.225-230.
3. *Tiwari A.N.* 12.8% Efficiency Cu(In,Ga)Se_2 solar cell on a flexible polymer sheet / A.N. Tiwari, M. Krejci, F-J. Haug, H. Zogg // Progress in Photovoltaics: Research and Applications.- 1999.- V.7.- P.393-397.

[1] *National Technical University (KPI), Kharkov, Ukraine*
[2] *Institute of Plasma Physics, KIPT, Kharkov, Ukraine*