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Structure of Cu–In–Se thin films of variable composition

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TEM investigation of Cu–In–Se thin films obtained by thermal evaporation of copper and indium selenide on KCl substrates using Vekshinsky method has been carried out. The method allows to obtain all phases of the Cu–In_2Se_3 film system in horizontal plane. It has been found that α, β-CIS crystallites with tetragonal lattice have preferred orientation (001) CIS ∥ (001) KCl and contain microtwins along (112) planes. β-CIS has been revealed due to (100) and (110) superstructure reflections. Along these reflections, the streaks have been observed aiming to the existence of antiphase boundaries in the β-CIS.

Проведено электронно-микроскопическое исследование плёнок Cu–In–Se, полученных путём термического испарения меди и селенида индия по методу Векшинского на подложки KCl. Метод позволил в горизонтальной плоскости получить весь набор фаз, принадлежащих системе Cu–In_2Se_3. Установлено, что кристаллики α- и β-CIS с тетрагональной решёткой имеют преимущественную ориентировку (001) CIS ∥ (001) KCl и содержат микродвойники по плоскостям (112); β-фаза CIS выявляется по сверхструктурным рефлексам типа (100) и (110). От этих рефлексов наблюдаются тяжи, которые могут указывать на наличие антифазных границ в β-фазе CIS.

$CuInSe_2$ (α-CIS) of chalkopyrite structure and its solid solutions is among semiconductor materials of good promise in development of thin film solar cell structures and can be used to make low-cost photovoltaic devices [1–4]. The α-CIS advantages include high light absorption coefficient, stability of characteristics, and high conversion efficiency attaining 18 %. 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 [5]. 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 paticular, there is no common opinion on the presence of stable phases and crystal structure thereof within the concentration range corresponding to $CuIn_3Se_5$ phase (β-CIS) [6], or either existence of separate non-stoichiometric phases having a broad solubility region or formation of stacks of ordered phases having a relatively narrow stability interval are supposed. Six compounds are reckoned in the specified concentration range, namely, $Cu_2In_4Se_7$, $Cu_8In_{18}Se_{32}$, $Cu_7In_9Se_{32}$, $Cu_{14}In_{16.7}Se_{32}$, $Cu_3In_5Se_9$, and $CuIn_3Se_5$. The recent studies [7] confirm that the $CuIn_3Se_5$ phase has a "distorted" tetragonal lattice containing a high vacancy density in the cationic sites. 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 [8,9], and the structure and phase composition have been studied.

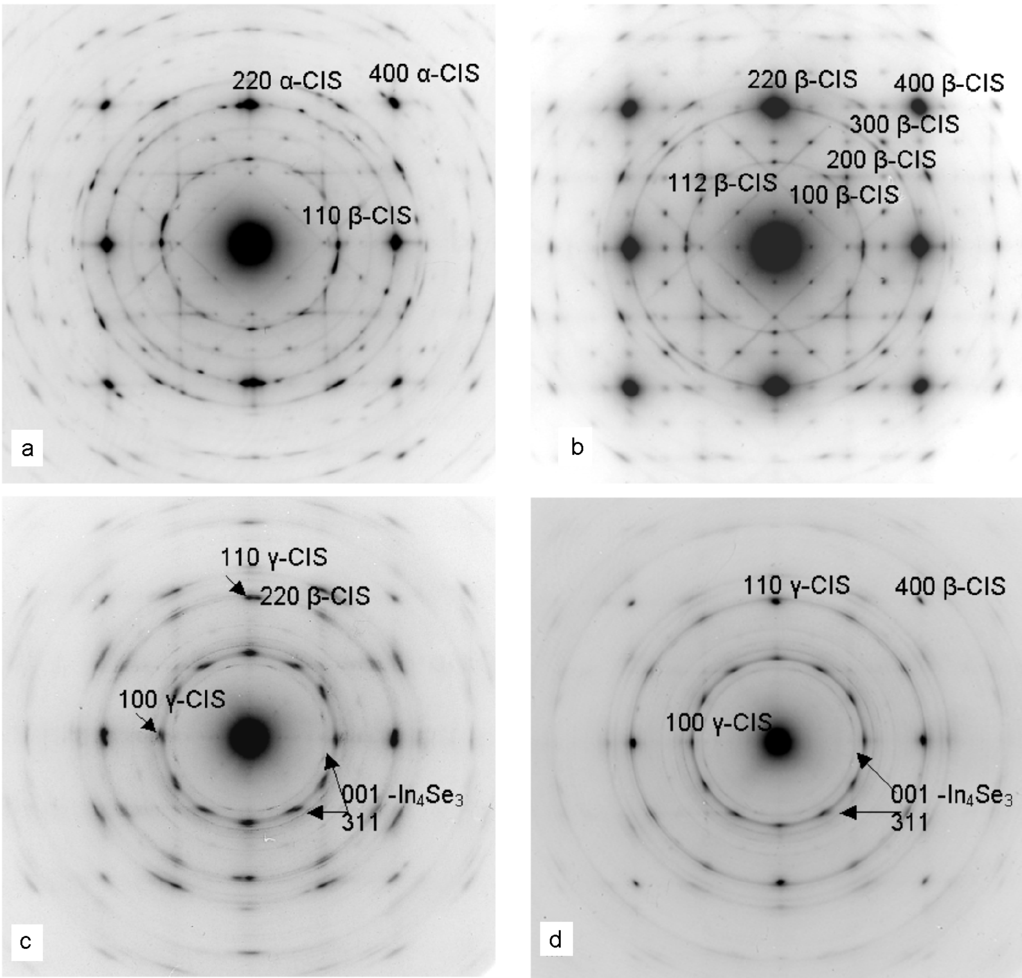

Fig. 1a–d. Electron diffraction patterns from four regions of a Cu–In–Se film of variable composition.

The Cu–In–Se films were prepared in a standard VUP-5 vacuum device in $5{\cdot}10^{-3}$ Pa vacuum on (001) KCl crystals 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.

Fig. 1a–d show electron diffraction patterns taken from four regions of the Cu–In–Se thin film of variable composition. The electron diffraction pattern in Fig. 1a was taken from the sample located straight in front of copper evaporator, whereas Fig. 1d illustrates the pattern from the film grown in front of a crucible containing indium selenide. Fig. 1b, c illustrate the patterns from intermediate regions. According to these patterns, it is possible to trace the variation of the Cu–In–Se thin film phase composition and to compare these data with the Cu_2Se–In_2Se_3 pseudo-binary section of the ternary Cu–In–Se phase diagram. The main lines (112), (200), (220) and (312) of the electron diffraction pattern in Fig. 1a correspond to two phases: $CuInSe_2$ (α-CIS) and $CuIn_3Se_5$ (β-CIS). The crystal lattice of the β-CIS phase is almost identical with the α-CIS one but contains ordered vacancies in the copper sublattice. This phase is revealed by weak (100) and (110) reflections which are not allowed for ideal α-CIS structure. In Fig. 1b, those reflections of the β-CIS phase

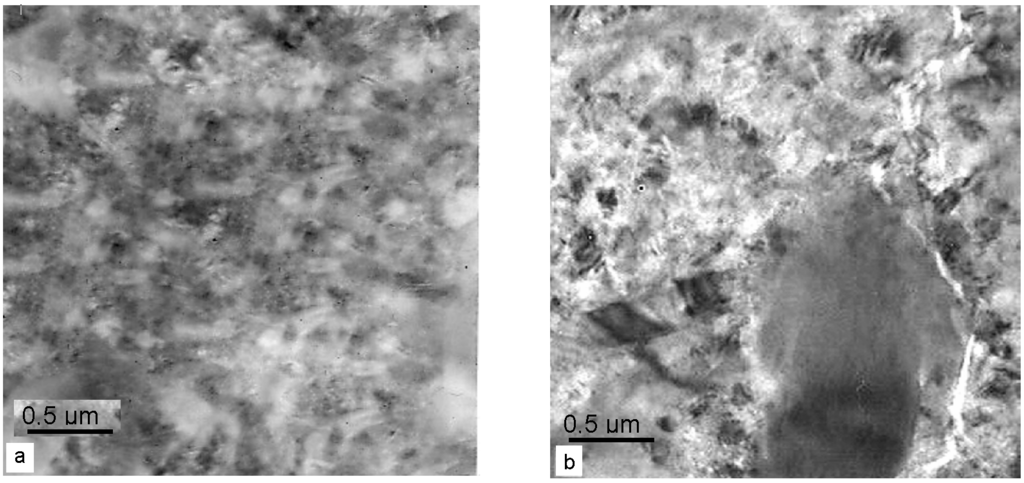

Fig. 2a, b. Structures of two neighboring regions of the Cu–In–Se film.

become more intense. Thus, the first region can be supposed to correspond to a mixture of α-CIS + β-CIS phases, whereas the second one, to the β-CIS phase.

In Fig. 1c, additional reflection lines of (100) and (110) types attributed to γ-CIS and (011) and (311) for In_4Se_3 were found. Those become more intense and additional reflections from those phases are also revealed (Fig. 1d). The β-CIS phase preserves only strongest (220) and (400) reflections. γ-CIS has a hexagonal lattice and grows on the KCl surface in the following orientation: (001), [100] γ-CIS ∥ (001), [110] and [110] KCl.

Perhaps In_4Se_3 is formed due to deficiency of Se for the of In_2Se_3 formation.

Fig. 2a,b illustrates electron microscopic images of two neighboring (second and third) regions of the Cu–In–Se thin film. The β-phase microstructure is shown in Fig. 2a. It is seen that the fine-crystalline film with about 0.1 μm size grains is formed on KCl surface at 400°C. Many grains of β-phase exhibit a stripped contrast and its origination is discussed below. It has been revealed that the film contains at least three phases: β-CIS, γ-CIS, and In_4Se_3, which give strong Bragg reflections (Fig. 2b). However, the β- and γ-CIS phases cannot be resolved in the electron diffraction image. They have a similar fine crystalline structure and the phases are hardly identified even in TEM dark field mode due to close positions of diffraction lines. In_4Se_3 crystallites are well defined (grain size ~1 μm) and their diffraction lines contain a number of discrete reflections. In β-CIS films prepared in our experiment, we could identify only one phase with a tetragonal lattice and only the stripped contrast on grains evidences a possible complex structure of that phase. The electron diffraction pattern of the β-CIS phase and its interpretation are given in Fig. 3a, b. The set of reflections and their symmetry have shown a preferred epitaxial orientation

(001), $[1\bar{1}0]$ β-CIS ∥ (001), [110] and $[1\bar{1}0]$ KCl.

Moreover, some crystallites have the following orientations:

(110), $[1\bar{1}0]$ β-CIS ∥ (001), [110] and $[1\bar{1}0]$ KCl,
(114), $[1\bar{1}0]$ β-CIS ∥ (001), [110] and $[1\bar{1}0]$ KCl, (112), $[1\bar{1}0]$ β-CIS ∥ (001), [110], $[1\bar{1}0]$, [100] and [010] KCl.

All the orientations include a common [110] direction parallel to the [110] and $[1\bar{1}0]$ KCl substrate. Each (200) type reflection of the (001) epitaxial orientation shows crosslike streaks parallel to the [110] and $[1\bar{1}0]$ directions. Weak reflections (1, 2 and 3, 4) 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. The 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 in [10]

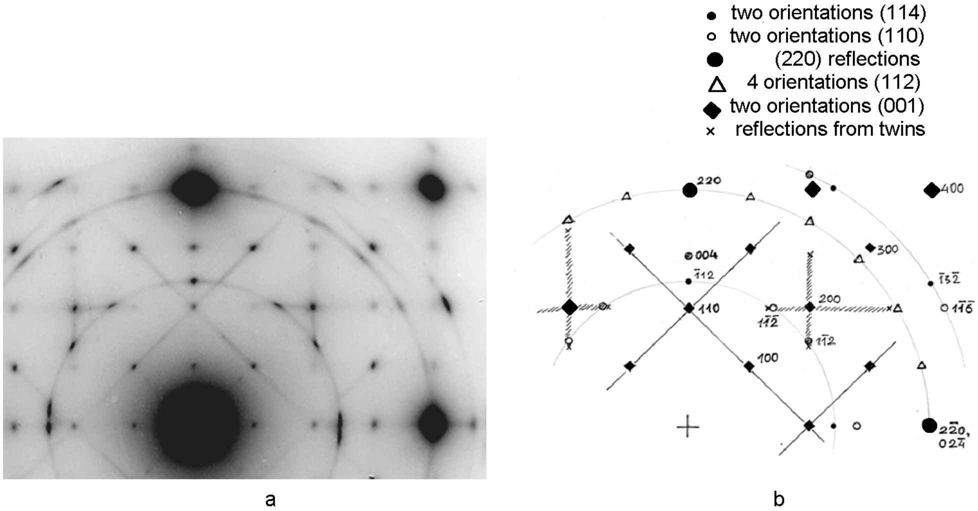

Fig. 3. Electron diffraction pattern from β-CIS phase (a) and its schematic interpretation (b).

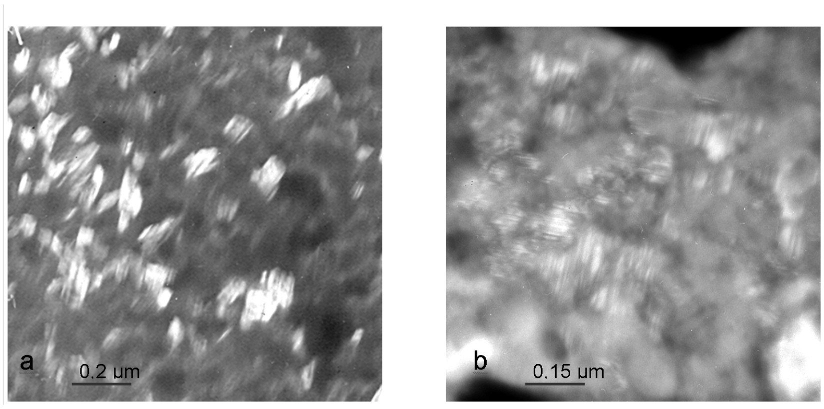

Fig. 4. TEM dark-field image using (1$\bar{1}$2) and (1$\bar{1}$ $\bar{2}$) reflections from the β-CIS crystallites in (110) orientations with twinned lamellas (a); TEM dark-field image of domains divided by antiphase boundaries with a stripped contrast along the [100] and [010] directions (b).

to explain some diffraction patterns taken from twinned crystals of Au.

If the crystallites and twinned lamellas contain irregularly arranged stacking faults, 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. 3a 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. The stacking faults along the (112) planes can also be considered as twins of monoatomic thickness. Some microtwins have been also revealed in β-CIS films in crystallites of other orientations. Fig. 4a shows a dark-field image using (1$\bar{1}$2) and (1$\bar{1}$ $\bar{2}$) reflections from β-CIS crystallites in the (110) orientation rotated by 90° to one another around the [001] KCl axis. In such crystallites, the microtwin lamellas are clearly seen. The angle between the lamellas in rotated crystallites is 25°. It is these microtwins grown normal to the film surface that exhibit a stripped contrast on the electron-diffraction image from β-CIS grains.

Another distinctive feature revealed at diffraction pattern taken from epitaxial crystals is the appearance of long crosslike streaks near the (110) type reflections. The streaks are oriented along the [100] and [010] directions of the β-CIS lattice. These streaks were only observed near reflections allowed for β-CIS phase (containing ordered 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 (010) plane seen as long streaks along [100] direction. 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. 4b.

Thus, the ternary Cu–In–Se thin films of variable composition have been prepared by simultaneous evaporation from In_2Se_3 and Cu sources onto (001) KCl crystals placed on a lengthy substrate at 400°C. There were revealed (α + β) CIS, β-CIS and (β + γ) CIS + In_4Se_3 phase areas corresponding to the Cu_2Se–In_2Se_3 pseudobinary section of the ternary Cu–In–Se phase diagram. The β-CIS crystallites of the (001) epitaxial orientation contain lamellas with microtwins along the (112) planes of the tetragonal lattice as well as antiphase boundaries along (100) planes.

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Структура плівок Cu–In–Se змінного складу

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Проведено електронно-мікроскопічне дослідження плівок Cu–In–Se, отриманих шляхом термічного випарювання міді й селеніду індію методом Векшинського на підкладки KCl. Метод дозволив у горизонтальній площині одержати усю сукупність фаз, що належать системі Cu–In_2Se_3. Встановлено, що кристалики α- і β-CIS з тетрагональною граткою мають переважне орієнтування (001) CIS ∥ (001) KCl і містять мікродвійники по площинах (112); β-фаза CIS виявляється за сверхструктурними рефлексами типу (100) й (110). Від цих рефлексів спостерігаються тяжі, які можуть вказувати на наявність антифазових меж у β-фазі CIS.