Electrodeposition of Cu–In–Se precursors for chalcopyrite solar cells

N.P.Klochko, G.S.Khrypunov, N.D.Volkova[*], V.R.Kopach, V.M.Lyubov, O.V.Momotenko, A.V.Kopach

National Technical University "Kharkiv Polytechnic of Institute", 21 Frunze Str., 61002 Kharkiv, Ukraine
[*]National Aerospace University "Kharkiv Aviation Institute", 17 Chkalov Str., 61070 Kharkiv, Ukraine

The work is devoted to an investigation of structure and physical properties of different electroplated compositions of copper, selenium and indium in order to obtain the optimized combinations for creating of precursors for CIS based solar cells. Analysis of the crystal structure and surface morphology of the electrodeposited films and film compositions has revealed that only possible sequence of CIS precursor components in terms of optimization of mentioned above characteristics is Cu–In–Se. Particularly, the formation of CuIn and Cu_2In intermetallic compounds during electrodeposition of In onto Cu promotes improvement of the interlayer adhesion, the In_2Se_3 phase formed during electrodeposition of Se onto In has comparatively perfect nanostructure, while immediate contact of Cu and Se is undesirable, for example, because of generation of Cu_2Se crystal phase with considerable strained microstructure.

Работа посвящена исследованию структуры и физических свойств различных электроосажденных композиций меди, селена и индия с целью создания оптимальных комбинаций для прекурсоров солнечных элементов на основе CIS. Анализ кристаллической структуры и морфологии поверхности электроосажденных пленок и пленочных композиций выявил, что единственной приемлемой последовательностью компонентов прекурсора CIS с точки зрения оптимизации его характеристик, является Cu–In–Se. В частности, формирование интерметаллических соединений CuIn и Cu_2In в процессе электроосаждения In на поверхность Cu способствует улучшению адгезии между этими слоями, фаза In_2Se_3, которая формируется при электроосаждении Se на поверхность In, имеет достаточно совершенную наноструктуру, в то время как непосредственный контакт Cu и Se является нежелательным, например, из-за образования кристаллической фазы Cu_2Se с очень напряженной микроструктурой.

1. Introduction

The main technical and economic performance of terrestrial solar cells (SC) along with the conversion efficiency is the cost of electric energy produced by these cells, since at present it is in 3–8 times above the market price of electricity from conventional sources [1]. It is considered [1–3] that thin film solar cells must ensure competitiveness in the energy market because of their lower material and energy production expenditure compared to silicon SC analogues. A highest conversion efficiency of thin film solar cells (20 %) was reached for the base layers of chalcopyrite compounds $CuInSe_2$ (CIS) and $Cu(In_xGa_{1-x})(S_ySe_{1-y})_2$ (CIGS), and some industrial companies in the US, Germany and Japan have already started serial production of such solar cells [1–5]. However, at the present time the most effective chalcopyrite solar cells are

Table. Electrochemical deposition parameters and calculated thickness of the obtained films

Sample No.	Electrodeposition stage	Cathode current density, j, mA/cm^2	Deposition time, t, min	Calculated film thickness, d, μm
1	Cu onto Mo/glass	25	10	5.5
2	Cu onto SnO$_2$:F/glass	25	10	5.5
3	Se onto SnO$_2$:F/glass	1	10	0.3
4	Cu onto Mo/glass	18	10	4.0
	In onto Cu/Mo/glass	29	1	0.9
5	Cu onto Mo/glass	28	10	6.2,
	In onto Cu/Mo/glass	24	10	7.8
	Se onto In/Cu/Mo/glass	3	40	3.1
6	Cu onto Mo/glass	14	10	3.1
	In onto Cu/Mo/glass	16	10	5.2
7	Se onto Mo/glass	3	10	0.8
8	Se onto Mo/glass	3	10	0.8
	Cu onto Se/Mo/glass	25	10	5.5

produced by co-evaporation of precursor elements from several separate sources. Such production method increases of device cost because of high temperature of deposition and evaporation, a necessity of mass-spectrometry using to monitor and control element flows on purpose to obtain required base layers. Also it leads to large losses of evaporating material and needs for disposal of selenium toxic emissions. Among other alternative methods for production of CIS and solid solutions on its basis cathode electrodeposition from aqueous solutions is used by a number of companies and firms including "Solopower", "CIS Solartechnic GmbH" and "Odersun" [5]. In so-called one-step electrochemical deposition of CuInSe$_2$ layers electrolytes contain selenium, copper and indium compounds simultaneously. The main problem of one-step process is a big difference between the electrochemical potentials of copper, indium and selenium, leading to necessity of use low electrolytes concentrations (units of mM/l) and complexons [4−7]. It causes instability in electrodeposition processes and requires complex equipment for the control and regulation, that therefore eliminated all advantages of this technology as cheap and suitable one for large-scale production. Two-stage method is consisted in electrodeposition of copper, indium and selenium layers from separate electrolytes, that is a much simpler task. Since electrochemical metallization has been widely used in electronics for a long time, these electrodeposition processes are well studied and mastered

in industrial conditions. Electrolytes are stable, contain high ions concentrations and therefore do not require frequent adjustments during layers electrodeposition. It should be noted that in both electrochemical methods precursors are subsequently transformed into CIS by laser or heat treatments, often it is fulfilled in selenium or in hydrogen selenide vapors. Unfortunately, CIS base layers prepared in such ways have efficiencies lower than 11 % [5] that is almost twice less than efficiency of photovoltaic cells with analogous base layers deposited in vacuum. Probably, it is associated with specific structures and phase compositions of the electrodeposited Cu–In–Se precursors. Therefore, identification of undesirable combinations and sequences of layer depositions and development of optimal conditions for plating of precursors for chalcopyrite photovoltaic cells are the urgent technical problems and their solving has become the objective of this work.

2. Experimental

Electrochemical deposition of copper, indium and selenium was carried out at room temperature in two electrode cells in simple aqueous electrolytes without organic additives. Copper electrolyte was consisted of 90 g/l CuSO$_4$·5H$_2$O and 120 g/l H$_2$SO$_4$. A solution of 230 g/l InCl$_3$ and 100 g/l NH$_4$Cl was used for indium electrodeposition. Electrochemical selenium deposition was carried out with a solution containing 55 g/l SeO$_2$. During the deposition of copper films the copper plate was used as anode, while

graphite anodes were utilized for indium and selenium plating. Table presents parameters of electrodeposition process and film thicknesses calculated by Faraday's law with assuming of absolute current yield.

X-ray diffraction studies of the film structures were carried out using diffractometer DRON-4. Shooting of diffraction spectrum was taken at constant 2θ-scan with a Bragg-Brentano focus in cobalt anode radiation ($\lambda_{CoK\alpha} = 1.78897$ Å). A program New_Profile3.4(375) was used for determination of the individual peak parameters, namely half-width and asymmetry factor, due to approximations by Cauchy and Gauss functions. Lattice parameters for corresponding crystal system were calculated according to [8]. Precision determinations of lattice spacings of the electrodeposited layers were carried out by Nelson-Riley method [9]. Considering that systematic error was primary induced by X-ray absorption in a pattern, a straight extrapolation of calculated lattice spacing values was used for cubic lattice as a function of lattice spacing vs $\cos^2\theta(1/\sin^2\theta + 1/\theta)$. Lattice parameters for other crystal systems were calculated on the base of two last indexed lines in X-ray diffraction patterns in accordance with [9]. Investigation of the film preferable orientation was performed by analysis of the diffraction maxima and by calculating of the texture ratio P_i (otherwise, a pole density, i.e. the probability with which the normal to the pattern surface coincides with the normal to a plane, in other words, the part of grains in which this plane is parallel to the sample surface) [10]:

$$P_i = \frac{(I_i/I_{0i}) \cdot N}{\sum\limits_i I_i/I_{0i}}, \qquad (1)$$

where I_i is an intensity of the experimentally obtained i peak; I_{0i} is an intensity of i peak according to the JCPDS card; N is number of the experimentally detected diffraction peaks. In the absence of texture $P_i = 1$, therefore texture coefficient is calculated in relative units against to the probability of this orientation for non-textured pattern. An angle φ between the texture axis and normals to reflective planes for all reflection planes $(hkl)_i$ was determined according to [10] for certain crystal systems. It was concluded from the curve shape of the diagram $P_i = f(\varphi)$ about the degree of texture perfection. The texture is founded to be more perfect if P_i decreases faster with increasing of φ.

Calculation of crystallite size for studied films was carried out by Williamson-Hall formula [11]. A profile of an actual diffraction distribution β was calculated depending on the type of approximation function by means of program New_Profile3.4(375). By using approximation by Cauchy's function we obtained β_C:

$$\beta_C = B - b, \qquad (2)$$

where B is an integral width of the investigated diffraction pattern, b is an integral width for the standard specimen. By using of Gauss's approximation we obtained β_G:

$$\beta_G = \sqrt{B^2 - b^2}. \qquad (3)$$

The β value we calculated as arithmetic average:

$$\beta = \frac{\beta_G + \beta_C}{2}. \qquad (4)$$

Since such characteristics of crystal grains as coherent-scattering region size (grain size in this case) t and microstrain $\Delta d/d$ influence on the diffraction profile expansion, therefore β can be explained as follows:

$$\beta = \frac{0.94\lambda}{t\cos\theta} + 4\tan\theta\Delta d/d. \qquad (5)$$

So, t and $\Delta d/d$ were obtained by graphical solving of equation (5).

Surface morphology of the electrodeposited layers was studied using scanning electron microscope REM-100V by registration of secondary and reflected electrons at accelerating voltage 30 kV.

For the electrochemical deposition of CIS precursor we used substrates with Mo layers and fluorine doped tin oxide FTO films deposited on glass plates, because by reason of molybdenum chemical activity the leading Europe laboratories [5] search for ways to manufacture base layers precursors using alternative back contacts made of titanium and zirconium nitride or electrically conductive oxides such as indium tin oxide ITO or FTO.

3. Results and discussion

At the beginning the task was to determine the possibilities for precursor's production by successive electrochemical deposition from simple electrolytes which did not contain complexons or surfactants, which could decrease the quality of CIS base layers.
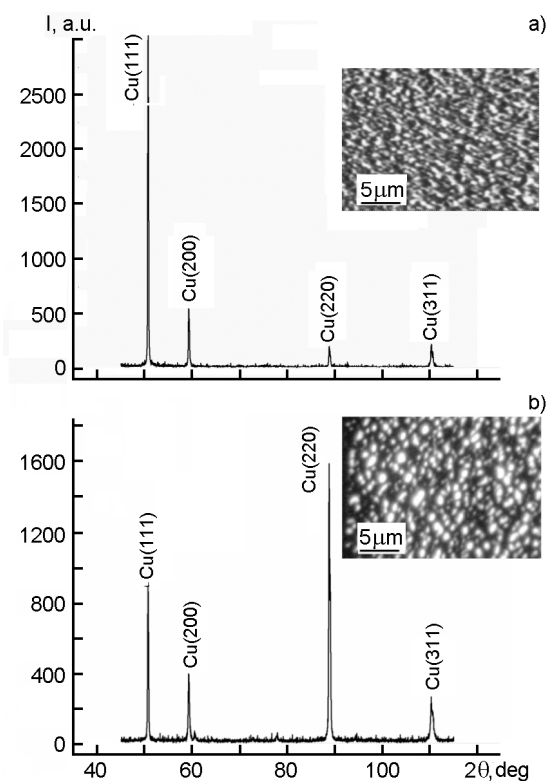
Fig. 1. X-ray diffraction patterns of copper films electrodeposited onto Mo/glass (*a* −No.1) and onto FTO/glass (*b* − No.2) and corresponding scanning electron microscopy images of the surface (inserts).

Fig. 2. Precision determination of lattice parameters for the electrodeposited copper films.

Since the indium standard electrode potential is negative enough ($E^0_{In3/In}$ = −0.34 V versus normal hydrogen electrode), the release of gaseous hydrogen is reaction associated with metal electrodepositing from an aqueous electrolyte that may reduce the In adhesion to substrates. That is why to our opinion, it is better to use as the first layer of CIS three-layered precursor copper ($E^0_{Cu2+/Cu}$ = 0.34 V) or selenium ($E^0_{Se4+/Se}$ = 0.74 V). 3−6 μm thick copper films obtained by electrodeposition from a simple copper solution were smooth and well adhered to the Mo and FTO substrates. Fig. 1 shows scanning electron microscopy images of copper film surfaces on Mo and FTO substrates (samples No.1 and No.2, respectively), that indicate fine-crystalline and homogeneous surfaces. In both cases X-ray diffraction diagrams of these films detected single-phase structure of Cu (JCPDS 04-0836). Analysis of structural parameters and texture has showed that copper film obtained on FTO substrate is characterized by small preferred orientation (220), while Cu layers electrodeposited on Mo did not
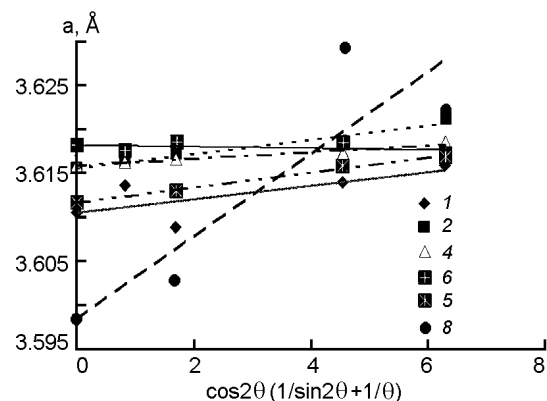
have pronounced preferred orientation. Precision detections of the crystal lattice parameters (Fig. 2) gave magnitudes closed to the JCPDS card data. It also coincided with the Williamson-Hall calculations, which showed very little microstrains in copper films electrodeposited on Mo (samples No.1, 4, 5, 6) and FTO (sample No 2) substrates. As a whole, the grain size of the electrodeposited copper films has increased with thickness from 36 nm to 187 nm, so the films were nanocrystalline. Thus, the electrodeposition of copper films from simple acidic sulfate solution using both types of substrates was found to be successful.

Selenium electrodeposition on copper surface from simple selenium solution, namely an aqueous solution of selenious acid H_2SeO_3 (pH = 1.5) formed due to interaction SeO_2 with water, was found impossible owing to chemical reaction on the Cu surface:

$$5Cu + 2H_2SeO_3 = \qquad (6)$$
$$= Se\downarrow + 4CuO\downarrow + CuSe\downarrow + 2H_2O.$$
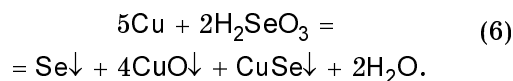
Therefore, at immersion copper film into this solution it was covered immediately by black layer, and eventually the volume of electrolyte was filled by black flakes Se, CuO and CuSe, coming off the surface.

At the same time, indium electrodeposition onto copper surface was not accompanied by difficulties and provided for well adhered smooth white film. The morphology images of these films (samples No.4 and No.6) are shown in Fig. 3. X-ray diffractometry study of thin (~ 0.9 μm) indium layer on copper surface has revealed only intermetallic compound of copper and indium CuIn (JCPDS
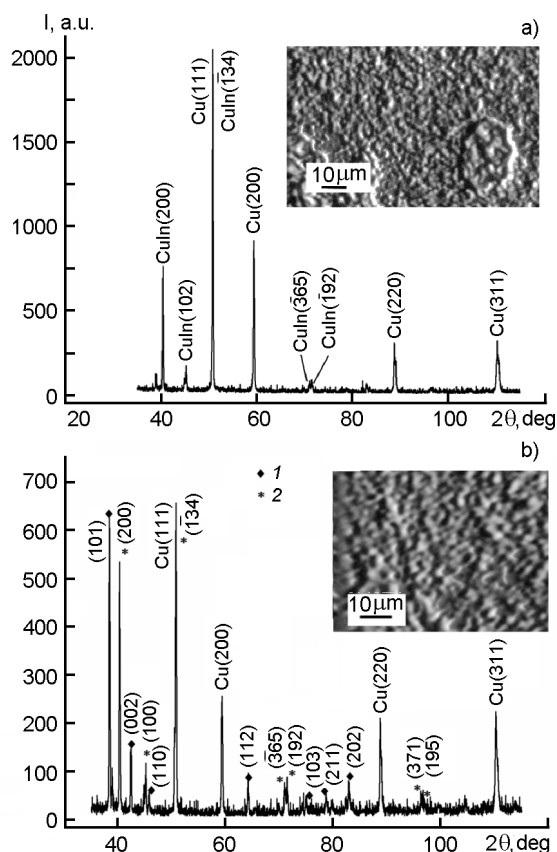
Fig. 3. X-ray diffraction patterns of 0.9 μm thick (*a* – No.4*)* and 5.2 μm thick (*b* – No.6) indium films electrodeposited onto Cu/Mo/glass substrates and corresponding scanning electron microscopy images of the surface (inserts).
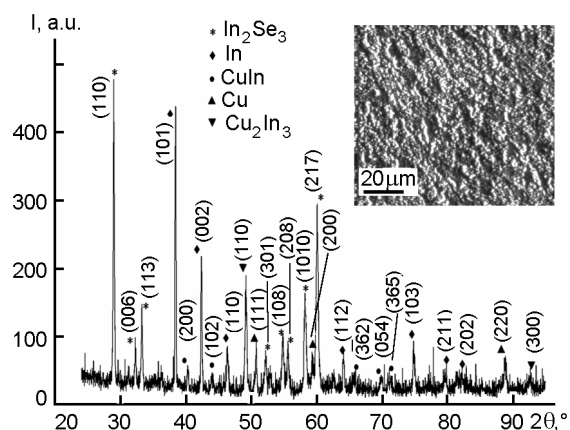

Fig. 4. X-ray diffraction pattern of selenium film electrodeposited onto In/Cu/Mo/glass substrate (No.5) and corresponding scanning electron microscopy image of the surface (insert).

35-1150) (Fig. 3, sample No.4) formed, probably, directly during indium electrodeposition onto copper surface. Increasing of the electrodeposited indium film thickness up to 3–8 μm causes to the appearance on X-ray diffraction patterns alongside with Cu and CuIn also In phase (JCPDS 05-0642) (Fig. 3, sample No.6) and Cu_2In phase (JCPDS 42-1475) (Fig. 4, sample No.5). In, Cu_2In and CuIn grains are nanocrystalline and characterized by small preferred orientations changed with layer combinations. The most significant microstresses were revealed in CuIn nanocrystals, but only in the case of comparatively thick In layer electrodeposition. As such as thickness of CIS base layer in the thin film SC equals 2–4 μm [2–3], each film thickness will be at most 1.4 μm, so, great strains in CuIn will be absent. From the other side, the creation of CuIn intermetallic compound will ensure perfect adhesion between the electrodeposited films. Thus, electrodeposition of in-

dium layer onto copper surface can be considered as an acceptable precursor's combination for CIS production. The following electrodeposition of selenium onto surface of such In/Cu/Mo/glass combination allowed producing well adhered dense CIS precursor layer. It turned out that the top layer contained crystalline In_2Se_3 phase (JCPDS 23-0294) (Fig. 4, sample No.5) with average grain size 99 nm and slight microstrains $(\Delta d/d = 2 \cdot 10^{-3})$. The creation of In_2Se_3 compound apparently will promote improved adhesion between indium and selenium films in the precursor.

Selenium films on Mo/glass and $SnO_2{:}F$/glass substrates were produced and analyzed for determination the possibility of Se electrodeposition on such substrates. Electrodeposition of selenium on fluoride doped tin oxide was not accompanied by complications: selenium film was adhevent, smooth and amorphous (Fig. 5, sample No.3). At the same time, owing to the large difference in standard potentials of molybdenum and selenium (−0.2 V and 0.74 V, respectively) Se electrodeposition onto Mo substrate surface required its immersion into selenium solution "on current", i.e. with switched dc supply. Without using of this procedure selenium film adhesion to the substrate was decreased by internal electrolysis. Selenium electrodeposition onto molybdenum surface was accompanied by intense releasing of hydrogen, however, we managed to get a dense layer of amorphous selenium, as such as its X-ray diffraction pattern (Fig. 5 (sample No.7)) showed only single weak peak of the molybdenum substrate. But it turned out that producing CIS
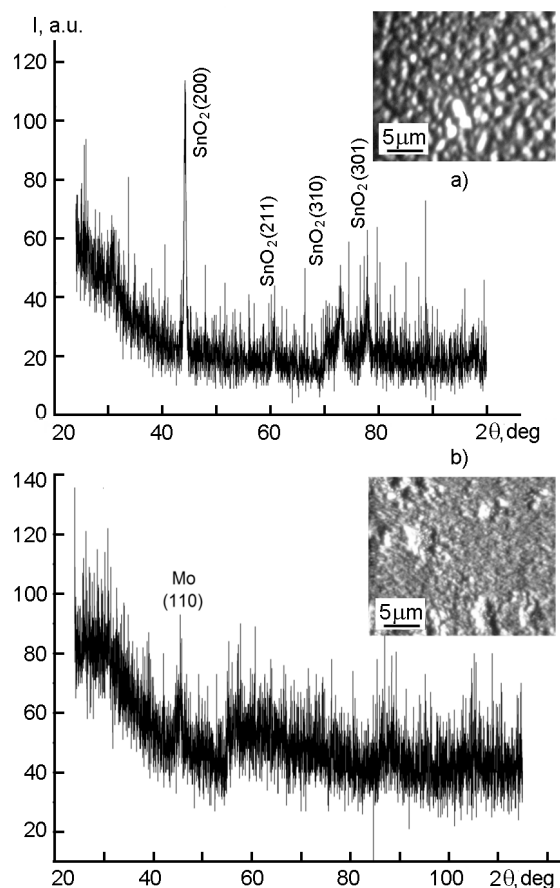
Fig. 5. X-ray diffraction patterns of selenium films electrodeposited onto FTO/glass (a –No.3) and onto Mo/glass (b – No.7) and corresponding scanning electron microscopy images of the surface (inserts).
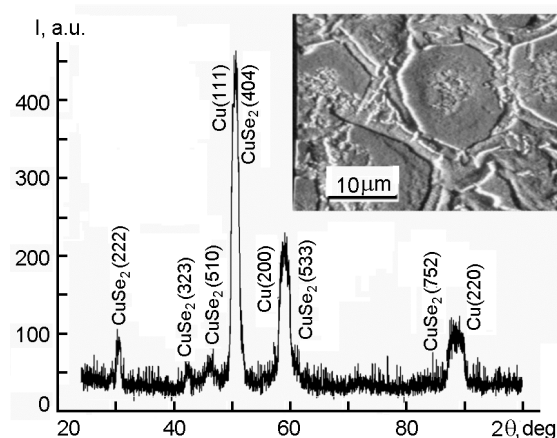

Fig. 6. X-ray diffraction pattern of copper film electrodeposited onto Se/Mo/glass (No.8) and corresponding scanning electron microscopy image of the surface (insert).

precursor by layerwise electrodeposition in the Se–Cu–In sequence was impossible. Attempts to copper electrodeposition onto selenium surface led to the formation of cracked loose precipitation, containing copper Cu and copper(I)selenide Cu_2Se (Fig. 6 (sample No.8)). Distortions in the crystal lattice of copper film deposited on selenium layer were supported by its strongly reduced parameters (Fig. 2) and especially by the small grain sizes ($t = 7$ nm) and high values of tensile microstrains ($\Delta d/d = 1.14 \cdot 10^{-2}$), which probably caused the cracking of the copper film on selenium surface. The Cu_2Se phase obtained during copper electrodeposition onto selenium surface has more smaller and strained grains, therefore the preparation of CIS precursor by the layer electrodeposition in sequence Se–Cu–In was found to be impossible.

4. Conclusions

So, we created comparatively perfect nanocrystalline copper layers by means of electrochemical deposition in simple aqueous solution onto molybdenum and fluorine doped tin oxide surfaces. Intermetallic Cu_2In and CuIn compounds were formed during indium electrodeposition onto copper surface that caused perfect adhesion of the adjacent layers. Selenium electrodeposition onto indium surface results in the formation of In_2Se_3 compound, which apparently will promote improved adhesion between electrodeposited indium and selenium films in CIS precursor. Only possible sequence of components of CIS precursor on the base of electrodeposited films is copper-indium-selenium, because all other layer combinations and orders of the film electrodeposition either impossible or not ensure properties required for the following transformation of the precursor into base layer of the solar cell.

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Електроосадження прекурсорів Cu–In–Se для халькопіритних фотоелектричних перетворювачів

Н.П.Клочко, Г.С.Хрипунов, Н.Д.Волкова, В.Р.Копач, В.М.Любов, О.В.Момотенко, А.В.Копач

Робота присвячена дослідженню структури і фізичних властивостей різних електроосаджених композицій міді, селену та індію з метою створення оптимальних комбінацій для прекурсорів сонячних елементів на базі CIS. Аналіз кристалічної структури і морфології поверхні електроосаджених плівок і плівкових композицій виявив, що єдиною прийнятною послідовністю компонентів прекурсора CIS з погляду оптимізації його характеристик є Cu–In–Se. Зокрема, формування інтерметалічних сполук CuIn та Cu_2In у процесі електроосадження In на поверхню Cu сприяє поліпшенню адгезії між цими шарами, фаза In_2Se_3, яка формується при електроосадженні Se на поверхню In, має порівняно досконалу наноструктуру, в той час як безпосередній контакт Cu та Se є небажаним, наприклад, через утворення кристалічної фази Cu_2Se з дуже напруженою мікроструктурою.