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**Current Versus Voltage Characteristics of
Electrodeposited CIS Films**

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The purpose of carried out researches consisted in the determination of the preparation conditions for creation of thin film p-n junction on the base of electrodeposited copper indium diselenide (CIS) that possesses I-V characteristic similar to I-V characteristic of Shockley diode.

The influences of electrodeposition and following annealing conditions on the film I-V characteristics and types of the film conductivity were investigated by means of both characteriscope technique and hot-probe method. CIS film structure and chemical composition were studied by means of SEM, XRD, EDX as well as by laser mass-spectrometry method.

The comparison of preparation conditions influence on electrical properties, structure and chemical composition of investigated CIS films has shown, that cathode electrodeposition under potentiodynamic regime from aqueous acidic chloride electrolyte contained 0.9 mM CuCl, 4.5 mM InCl₃ and 1.5 mM SeO₂ (pH 1) at cathode potential ramped from -0.50 V up to -0.85 V (vs. saturated Ag/AgCl reference electrode) at rate 0.5 mV/s allows to obtain approximately 1 μm thick CIS films, in which p-CuInSe₂ / n-CuIn₃Se₅ junctions with I-V characteristics similar to Shockley diode I-V characteristic were arisen after CIS films annealing in an argon at 400°C during 1 hour.

Keywords: CuInSe₂, electrodeposition, annealing, structure, I-V characteristic, p-n junction.

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I. Introduction

Now electrodeposited (ED) polycrystalline films of copper indium diselenide (CIS) as well as p-n junctions on their base are considered as investigated very promising precursors for development and production of really inexpensive and highly efficient thin film solar cells [1, 2]. It is conditioned by the fact that the electrochemical deposition ensures considerably less energy-consumptive, technically more simple, and also economically and ecologically more preferable method for large-scale thin-film solar sells manufacture. From the other side, efficiency of 14.2 % reached in case of solar cells based on ED p-CdTe films [3] shows an actual possibility to

increase the efficiency of thin-film solar cells with CIS active layers not less than twice as much in comparison with their efficiency of 6.5 % reached recently [4].

In accordance with [1,4], the main reasons of the indicated low efficiency of solar cells with architecture Mo/CIS/CdS/ZnO based on p-CIS films with the thickness less than 2 μm electrodeposited under one-step potentiostatic regime and then annealed in selenium atmosphere are the losses because of large recombination of minority carriers in a very thin dead layer in the CIS films near to CdS layer. From this point of view the p-n junction on the base of ED CIS film instead of ED p-

CIS film can be (after optimisation of such p-n junction manufacturing technology) more perspective photoelectrical active medium separated the non-equilibrium electron - hole pairs for creation of inexpensive thin film solar cells with efficiency much greater than 10 %.

The purpose of our researches was the determination of the electrodeposition conditions for the preparation of thin film p-n junctions on CIS base with I-V characteristics similar to I-V characteristic of Shockley diode [5], because such p-n junction is more preferable for solar cells in comparison with obtained and investigated earlier [2]. Alongside with the investigation of CIS film I-V characteristics we investigated structures, types of conductivity and chemical compositions of the electrodeposited films before and after their annealing in an air and in a flowing pure argon as well as influence of such annealing on I-V characteristics of prepared films.

II. Experimental

Both potentiostatic and potentiodynamic regimes of electrodeposition were realized by using of a three-electrode cell contained cathode (conducting substrate), platinum counter-electrode and saturated Ag/AgCl reference electrode (SAE) ($E_{SAE} = 0.22 \text{ V vs. standard hydrogen electrode}$). All values of cathode potential U_C provided by a programmable impulse potentiostat PI-0.5- 1.1. were measured vs. SAE.

As substrates we used electropolished and slightly chemically etched molybdenum plates, molybdenum coated glass sheets and glass sheets covered by high conductive $\text{SnO}_2\text{:Sb}$ films prepared (as well as earlier [9]) by means of chemical vapor deposition method. All CIS films were electrodeposited on cathodes at room temperature in aqueous acidic chloride electrolyte contained 0.9 mM CuCl , 4.5 mM InCl_3 , 1.5 mM SeO_2 (pH 1).

As was established earlier [10] this electrolyte composition provides at $U_C = -0.60 \text{ V}$ reproducible electrodeposition of CIS film with thickness equal to 1-2 μm characterized by averaged relative contents of copper, indium and selenium atoms proportional to 1:1:2. Therefore in the present

work some CIS film samples were electrodeposited under one-step potentiostatic regime at $U_C = -0.60 \text{ V}$. Besides we used different U_C value intervals from -0.50 V up to -0.90 V and ramping rates of 0.2 mV/s and 0.5 mV/s for realization of potentiodynamic regime with the purpose to determine interval of U_C value ramping that can permit the electrodeposition of about 1 μm thick CIS film having p-n junction with I-V characteristic similar to I-V characteristic of Shockley diode. Thickness of the CIS film electrodeposited under potentiostatic regime was determinate immediately by the electrodeposition duration. Thickness of the CIS films obtained under potentiodynamic regimes depended from the intervals of the ramped U_C values and from the ramping rate values.

During the electrodeposition all three electrodes were motionless, but electrolyte was stirred by a magnetic stirrer. After the electrodeposition all CIS film samples were carefully washed out by distilled water and then dried up in an air. The thicknesses of ED films were checked by mechanical surface profiler "Alpha-step 200".

Side by side with as-prepared CIS films we investigated CIS films annealed in an air at 200°C and at 400°C as well as CIS films annealed at 400°C in Ar-flow at Ar pressure 7.5 mbar (partial pressure of residual gases in the annealing vessel was less than 10^{-4} mbar). The durations of the annealings were 30 minutes in the air and 1 hour in the argon flow, respectively; the heating and the cooling rates were 7°C/min and 9°C/min, correspondingly.

I-V characteristics were measured in the air at room temperature by characterioscope EMG-1579-102 "Orion, EMG" and 370 Programmable curver tracer "Sony, Tektronix". The reversing of applied to the sample voltage polarity was carried out by means of mechanical switch. For these measurements we used samples in which molybdenum plates or molybdenum covered glass sheets were utilized as a bottom electrodes. As a top counter-electrode we used very softly pressed Mo or W probe with the polished hemispherical surface of approximately 50 μm radius. The use of such top counter-electrode allowed us: i) to avoid a penetration of counter-electrode material into

deepest pores in CIS films and thus to prevent the film partial shunting by counter-electrode; ii) to observe the influence of oxygen electrodiffused into CIS films on I-V characteristics. The type of conductivity of the CIS films was determined by hot probe method in the air.

Surface morphology of CIS films and their bulk chemical composition were investigated by means of "LEO 1530" in scanning electron microscopy (SEM) and energy dispersing X-ray spectroscopy (EDX) regimes. To increase the precision of determination of CIS film chemical composition we additionally used laser mass-spectrometry method realized by means of laser energy-mass-analyser "EMAL-2".

Investigation of CIS film phase composition and evaluation of microcrystallite dimensions in CIS films were carried out by XRD method by using of a "Philips PW 1820" goniometer with $\text{CuK}\alpha$ -radiation. Alongside with XRD for investigation of phase composition of CIS films we used inversion volt-amprometry (anodic stripping) method [11]. This method was used for investigation of CIS films electrodeposited onto $\text{SnO}_2\text{:Sb}$ sublayers for elimination of influence of oxidation of substrate conducting material on results of measurements.

III. Results and discussion

Typical I-V characteristics of $1.1\ \mu\text{m}$ thick CIS films electrodeposited under potentiostatic regime and characterized by averaged through the thickness chemical composition corresponded to stoichiometric compound CuInSe_2 ($\text{Cu:In:Se} = 1:1:2$) are shown on Fig.1. Curves 1-1' were obtained for as-deposited film and curves 2-2' were obtained for this film air annealed at 200°C . Note that such I-V characteristics were observed for above-mentioned films irrespective of the top counter-electrode material.

On curves 1 and 2 obtained in case of positive polarity of top counter-electrode and negative polarity of bottom electrode (such voltage polarity corresponds to $V < 0$ on this and on all consequent I-V characteristics) one can clearly see regions typical for forward branch of tunnel diode I-V characteristic [5]. From this point of view the N-shaped region on

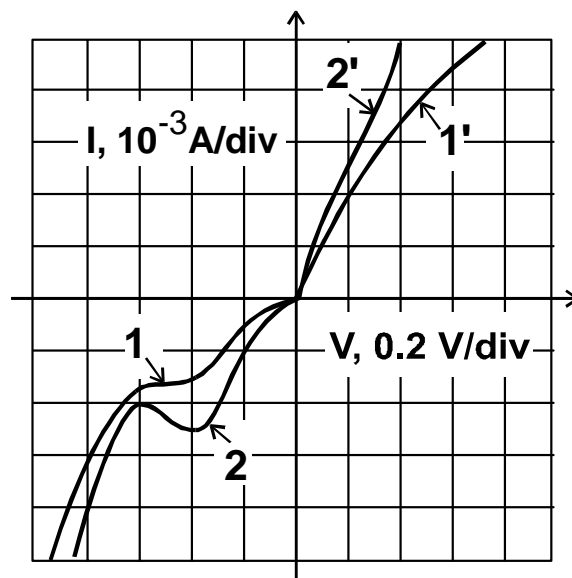


Fig. 1. Experimental I-V characteristics of $1.1\ \mu\text{m}$ thick CIS film electrodeposited onto Mo substrate under potentiostatic regime at $U_C = -0.60\ \text{V}$. Curves 1-1' are measured for as-electrodeposited film; curves 2-2' are measured after film annealing in an air at 200°C during 30 minutes. Values $V > 0$ (curves 1' and 2') correspond to positive polarity of the bottom electrode and negative polarity of the top counter-electrode.

I-V characteristic measured at $V < 0$ after the film air annealing at 200°C looks most obviously. The asymmetry of the curves shown on Fig.1 also are similar to I-V characteristics of tunnel diodes, however differ from the latter by poorly expressed sublinear dependence of current I upon voltage V in case of negative polarity of top counter-electrode and positive polarity of bottom electrode ($V > 0$) at $V < 0.8\ \text{V}$ before (curve 1') and at $V < 0.3\ \text{V}$ after (curve 2') films air annealing. After air annealing of such samples at 400°C their I-V characteristics became symmetrical and linear, and resistance of the samples calculated from such I-V characteristics had value in order of $1\ \Omega$. The last means that an appreciable amount of high conductive phase shunts the film sample. All investigated films before and after air annealing at 200°C had p-type of conductivity.

According to obtained both XRD and inversion volt-amprometry data (Fig. 2) as-electrodeposited films contained approximately 90 % of CuInSe_2 crystal phase. The crystallite average dimensions were about 6-8 nm. Additive high dispersed crystalline $\beta\text{-In}_2\text{Se}_3$ phase (JCPDS file № 20-494) was clearly

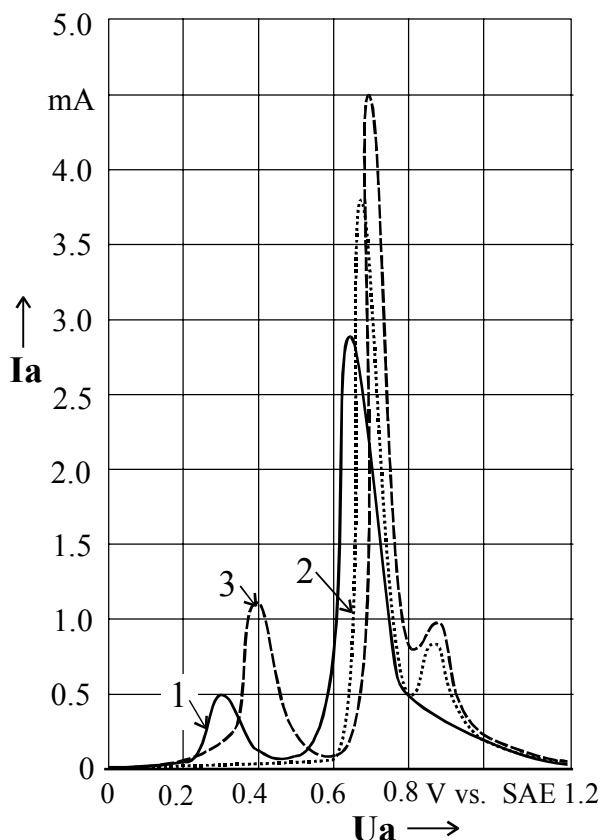


Fig. 2. Inversion voltammograms (anodic stripping curves) for 1.1 μm thick CIS film electrodeposited onto $\text{SnO}_2\text{:Sb}$ sublayers under potentiostatic regime at $U_C = -0.60$ V (1 – before an annealing; 2 – after air annealing at 200°C during 30 minutes; 3 – after air annealing at 400°C during 30 minutes).

identified. Note that this phase as well as phase Cu_2Se (or Cu_{2-x}Se) is responsible for additional maximum at voltage $U_a < 0.4$ V on the anodic stripping curve 1 on Fig.2 observed for those films which main maximum at $0.6 < U_a < 0.8$ V is characterized by dominate CuInSe_2 phase [10, 11]. At the same time the chemical composition of such films demonstrates that an apart from of $\beta\text{-In}_2\text{Se}_3$ phase (unambiguously discovered in these films by XRD method) the Cu_2Se (or Cu_{2-x}Se) phase should be presents too. However angular positions of main XRD peaks of CuInSe_2 and Cu_2Se (or Cu_{2-x}Se) phases are very close (JCPDS files: № 40-1487 and № 4-839 (or № 6-680)) On the same time high dispersed CuInSe_2 phase considerably predominates in the films. Therefore direct information concerned to the presence of Cu_2Se (or Cu_{2-x}Se) phase in such films is absent. However, according to [12], the presence of

copper selenide admixture phases alongside with In_2Se_3 admixture phase in CIS films electrodeposited under one-step potentiostatic regime from aqueous sulphate acidic electrolyte and containing Cu, In and Se atoms in quantities 25.1 at.%, 25.8 at.% and 49.1 at.%, correspondingly, was experimentally proved.

In accordance with anodic stripping curves the air annealing of our CIS films at 200°C and at 400°C (curves 2 and 3 on Fig.2) results in disappearing of $\beta\text{-In}_2\text{Se}_3$ and Cu_2Se (or Cu_{2-x}Se) phases. However during the annealing at 200°C new impurity phase responsible for additional maximum on the anodic stripping curve (curve 2 on Fig. 2) at $U_a > 0.8$ V is appeared alongside with increasing of CuInSe_2 phase content approximately up to 95 % as a result of thermoactivated chemical reaction $\text{Cu}_2\text{Se} + \text{In}_2\text{Se}_3 \rightarrow 2\text{CuInSe}_2$ [12]. During the air annealing at 400°C one more new impurity phase responsible for the second additional maximum at $U_a \approx 0.4$ V on the anodic stripping curve (curve 3 on Fig.2) is appeared alongside with above mentioned impurity phases. As a result of the air annealing at 400°C the CuInSe_2 phase content in the films is considerably decreased up to 75 % and the admixture phases contents were increased up to 25%

To our opinion, the above-cited results give evidence that as-electrodeposited CIS films with thicknesses about 1 μm characterized by chemical composition corresponded to $\text{Cu}:\text{In}:\text{Se} = 1:1:2$ are indium-enriched in lower (adjacent to the substrate) layer and copper-enriched in the surface layer. The interaction of such films with atmospheric oxygen is accompanied not only by oxygen chemisorption on the film surface but also by oxygen penetration into intergrain boundaries. Oxygen can easy diffuse through intergrain boundaries into CuInSe_2 bulk [13, 14]. According to [14] the latter should result in additional enrichment of upper film layer by holes. Because of acceptor properties of atomic oxygen the lower indium-enriched film layer became poor by electrons, so this layer acquires a p-type of conductivity too.

As it is known [15, 16], the air annealing of CuInSe_2 compound at temperatures lower than 350°C results in formation of very thin oxide layer on CuInSe_2 surface. Depending on

oxidation conditions the oxide layer can contain In_2O_3 (with SeO_2 admixture) and Cu_xO oxide phases. Therefore it is reasonably to assume that the well observable additional maximum at $U_a > 0.8$ V on anodic stripping curve of the air annealed at 200°C CIS sample characterized by occurrence of copper-enriched layer near the surface (curve 2 on Fig. 2) is a cause of the second oxide Cu_xO phase in the external and internal surfaces of copper-enriched CIS layer occurrences. Moreover, the quantity of the latter phase is so large that it is sufficient for the registration. We also suppose that the thinnest oxide, on the whole consisted from In_2O_3 phase, can appear on internal surfaces of indium-enriched layer as a result of such annealing. However, apparently because of less intensive penetration of oxygen into indium-enriched CIS layer than into copper-enriched CIS layer during the annealing at 200°C the phase In_2O_3 is present in the bulk of the CIS film in considerably smaller quantity and therefore is not detected by anodic stripping method. Obviously, during the air annealing of CIS film at 400°C the quantity of In_2O_3 phase in both indium-enriched and copper-enriched layers should essentially increase and, apparently, it provides the presence of second additional maximum at $U_a \approx 0.4$ V on the anodic stripping curve (curve 3 on Fig. 2). Note, that as a result of such annealing the In_2O_3 phase can be essentially copper-enriched by means of copper inclusions embedded into In_2O_3 matrix [16]. From our point of view the latter circumstance is responsible for a qualitative modification of I-V characteristics of CIS films after their air annealing at 400°C leading to transition of such films to a shorting state.

Above mentioned analysis of oxygen influence on type of conductivity and on phase structure of considered CIS films allows to explain I-V characteristics at $V > 0$ of as-electrodeposited samples and air annealed at 200°C films as follows.

In the case of the bottom electrode positive polarity and of the top counter-electrode negative polarity (if all film has p-type of conductivity) the sublinear part of I-V characteristic is conditioned by influence of Schottky barriers existed at both sides of

neighbors semiconductive microcrystallites. The latter Schottky barriers can contact immediately one another or through a thinnest oxide interlayer and are connected in opposite directions towards one another [17]. Depletion of the microcrystallite boundary regions by copper and indium during the film annealing, i.e. appearing in the indicated regions of copper and indium vacancies served as acceptor centers in CIS [18,19] results in increasing of hall concentrations in CIS microcrystallites. The presence of admixture phase Cu_2Se (or Cu_{2-x}Se) in as-deposited films can cause the additional copper vacancies occurrence in this phase after film annealing that also should increase hall concentration in such initially degenerate semiconductor phase of p-type of conductivity. The indicated increasing of majority carriers concentration in microcrystallites is the reason of potential barrier height decreases at the inter-grain boundaries. This leads to the increasing of conductivity of polycrystalline semiconductive layers and to the decreasing of electrical breakdown voltage of Schottky barriers switched in reverse direction [17,20]. These evolution peculiarities are clearly illustrated by I-V characteristics comparison for as-electrodeposited film (curve 1' on Fig. 1, $V > 0$) and for the film air annealed at 200°C (curve 2' on Fig. 1, $V > 0$).

In case of reversed voltage polarity the oxygen atoms primarily chemisorbed in indium-enriched CIS layer on intergrain boundaries and turned because of their acceptor properties into anions are extracted by positively charged top counter-electrode. As a result the indium-enriched CIS layer that initially had p-type of conductivity induced by chemisorbed oxygen acquires n-type of conductivity. Thus, the intrinsic p-n junction inherent to the electrodeposited CIS film in absence of oxygen influence because of p-type of conductivity of copper-enriched layer and of n-type of conductivity of indium-enriched layer [2,7] is restored.

Alongside with extraction of O^- ions from indium-enriched CIS layer the high electrical field can result in bulk electrodiffusion of interstitial copper cations Cu_i^+ from copper-enriched layer to indium-enriched layer.

Recently [21] redistribution of copper conditioned by its electrodiffusion influenced by external electrical field was used for creation of a transistor structure in p-CuInSe₂ single crystal. The mechanism of interstitial ions Cu_i⁺ origin in CIS influenced by oxygen is well known [14, 22]. Besides as it is known [18, 19], the Cu_i particles in CIS are shallow donors. Therefore the discussed here electrodiffusion processes should increase hall concentration in p-CIS layer as well as electron concentration in n-CIS layer. Obviously, the above mentioned in turn should lead to formation of p⁺-n⁺ junction, i.e. to transformation of an initial CIS film into object with the tunnel diode properties. Manifestation of these properties more clearly expressed by I-V characteristics of the film after their air annealing at 200°C (curve 2 on Fig. 1) we connect with increasing quantity of interstitial copper atoms in CIS, and consequently with higher possibilities to increase the concentration of majority carriers in neighbor layers of n- and p-types of conductivity if electrodiffusion of these Cu_i particles take place.

The diffusion nature of p⁺-n⁺ junction formation influenced by the external voltage is exhibited by means of comparatively long delay-time of steady-state I-V characteristic shaping at V < 0. The marked peculiarity consists in similarity of I-V characteristics immediately after reversing of voltage polarity applied to the sample from V > 0 up to V < 0 at |V| ≤ 0.2 V. However during the increasing of |V| up to higher values the gradual transition to I-V characteristic shown on Fig. 1 at V < 0 is observed. The transition is continued from several seconds up to one minute. The steady-state transition time for the I-V characteristic at V < 0 depends on peak value of measuring voltage applied to the sample by means of characterioscope, and is reduced with increasing of this voltage peak value. I-V characteristics represented on Fig. 1 are enough well reproduced under repeated reversing of voltage polarity if take into account above mentioned delay-time of steady-state I-V characteristics at V < 0.

To our opinion, foregoing experimental results and their analytical consideration confirm the fact of presence of indium-enriched

CIS layer under copper-enriched CIS layer in electrodeposited at U_C = -0.60 V films with averaged through film thickness chemical composition corresponded to Cu:In:Se = 1:1:2. However such films cannot be suitable for use as precursors with p-n junctions for device diode structures even in case of back-wall superstrate thin film solar cells [23], as the indium-enriched CIS layer of such films can easy change a type of conductivity influenced by oxygen-contained environment..

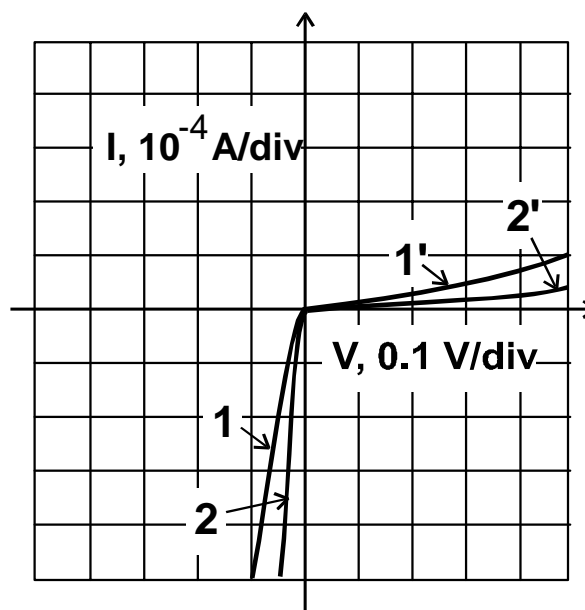


Fig. 3. Experimental I-V characteristics of 1.4 μm thick CIS film electrodeposited onto Mo substrate under potentiodynamic regime at U_C ramped from – 0.60 V to – 0.75 V at rate 0.2 mV/s. Curves 1-1' are measured for as-electrodeposited film; curves 2-2' are measured after argon annealing at 400°C during 1 hour. Values V > 0 (curves 1' and 2') correspond to positive polarity of the bottom electrode and negative polarity of the top counter-electrode.

Experimental I-V characteristics typical for CIS films electrodeposited under potentiodynamic regime at U_C ramped from – 0.60 V to – 0.75 V at rate 0.2 mV/s are showed on Fig. 3 for as-deposited (curves 1-1') and for argon annealed (curves 2-2') 1.4 μm thick CIS films. The films before and after annealing in an argon had chemical composition (averaged through the thickness) 22 at. % Cu, 28 at. % In, 50 at. % Se corresponded to Cu/In ≈ 0.79 and were characterized by n-type of conductivity. It is obviously from the XRD data that as a result of the film annealing the In₂Se₃ phase (not

completely reacted in as-electrodeposited film) disappears after the film annealing and the microcrystallite average dimensions increase approximately from 6 nm up to 40 nm.

The comparison of Fig. 3 and Fig. 1 shows qualitative difference of I-V characteristics of CIS films electrodeposited under potentiodynamic and under potentiostatic regimes. As it is visible from Fig. 3, the film electrodeposited under potentiodynamic regime has the asymmetry of I-V characteristic opposite to asymmetry observed for the film electrodeposited under potentiostatic regime. Besides I-V characteristics shown on Fig. 3 do not contain N-shape regions.

At first sight these I-V characteristics are very similar to I-V characteristics of true reversed diodes [23]. However, to our opinion, in this case the nature of experimentally observed I-V characteristic asymmetry is different. Such steady-state I-V characteristic at $V > 0$ is realized during 1 - 2 seconds after applying of the voltage to the sample, while the initial I-V characteristic at $V > 0$ is almost identical to I-V characteristic at $V < 0$, which is observed also in 1-2 seconds after the reversed voltage polarity was returned. Note, that if the measurements begin at $V < 0$, the appropriate branch of I-V characteristic is observed practically at once without detectable delay-time. The indicated properties of such I-V characteristics are reproduced at repeated reversing of voltage polarity.

Therefore we consider, that the observed asymmetry of steady-state I-V characteristics is provided by oxygen electrodiffusion into CIS film influenced by applied voltage. For example, the movement of oxygen anions at $V > 0$ along the intergrain boundaries from the film surface into film bulk results in majority carriers depletion or even in sign of majority carriers inversion first of all in surface CIS layer and then in the layers more removed from film surface. Obviously, that in this case either the trivial increasing of film electroresistance between electrodes or formation of p-n junction switched in reverse direction induced by the oxygen electrodiffusion take place.

At $V < 0$ the oxygen anions are extracted by top counter-electrode from film bulk that restores original higher majority carriers

concentration in film bulk. If at $V > 0$ the p-n junction was induced into the film, then at $V < 0$ the initial homogeneous concentration of majority carriers (electrons) in the film is restored.

Apparently, the increasing of I-V characteristic asymmetry for such film after argon annealing is conditioned by partial selenium losses on intergrain boundaries. The average value of these losses through the film thickness is less than 1 at.% so it is not registries by the equipment that we used for investigation of the chemical composition. As it is known [18,19], the selenium vacancies in CuInSe_2 are donors. So such vacancies enrich the n-CIS film by majority carriers and consequently increase the film conductivity, that is observed experimentally at $V < 0$, when oxygen is extracted by high electrical field from intergrain boundaries of the film.

Apparently, the increasing of penetrability of the intergrain boundaries for oxygen is one more consequence of selenium losses from the intergrain boundaries during argon annealing of such films. To our opinion, it explains the lower film conductivity after argon annealing by comparison with as-electrodeposited film conductivity at $V > 0$.

Thus the experimental results and their analyses allow as to conclude, that the potentiodynamic electrodeposition of CIS films at U_C ramped from -0.60 V to -0.75 V at rate 0.2 mV/s followed by argon annealing of the films at 400°C during 1 hour allowed to obtain approximately $1\ \mu\text{m}$ thick n-CIS films characterized by asymmetric steady-state I-V characteristics similar to I-V characteristics of reversed diodes. However the nature of I-V characteristics asymmetry for such films drastically differs from the nature of I-V characteristic asymmetry for the reversed diode. In the first from above-cited cases the I-V characteristic asymmetry is conditioned by peculiarities of CIS film interaction with oxygen depending on polarity of voltage applied to the film.

The U_C ramping range from initial value $U_C = -0.60$ V up to -0.90 V we use with the purpose to determine the upper U_C value at which admixture In_2Se_3 phase is saved in argon annealed approximately $1\ \mu\text{m}$ thick n-CIS

films. The U_C ramping rate was increased up to 0.5 mV/s.

The I-V characteristics of such films after their argon annealing are shown on Fig.4. The average chemical composition of the film was 18 at. % Cu, 32 at. % In and 50 at. % Se that corresponded to $Cu/In \approx 0.56$. It is obvious from XRD pattern, that the CIS film alongside with the main $CuInSe_2$ phase contains traces of admixture In_2Se_3 phase. The average dimensions of $CuInSe_2$ microcrystallites estimated from XRD patterns are

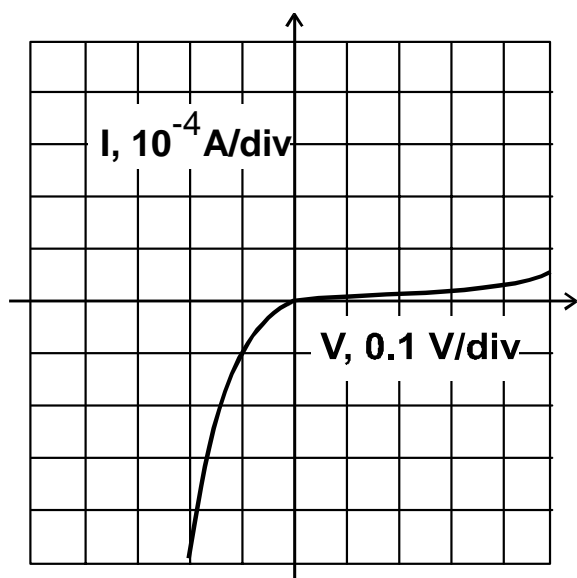


Fig. 4. Experimental I-V characteristics of 1.1 μm thick CIS film electrodeposited onto Mo substrate under potentiodynamic regime at U_C ramped from -0.60 V to -0.90 V at rate 0.5 mV/s and argon annealed at 400°C during 1 hour. Values $V > 0$ (curves 1' and 2') correspond to positive polarity of the bottom electrode and negative polarity of the top counter-electrode.

approximately 37 nm.

The comparison of Figure 4 and Figure 3 shows that I-V characteristics of the argon annealed films are qualitatively similar both in case of $Cu/In \approx 0.56$ and in case of $Cu/In \approx 0.79$. However in accordance with XRD data at $Cu/In \approx 0.56$ admixture n- In_2Se_3 or i- In_2Se_3 phases [24] are presented in the annealed films and therefore these films are less conducting at $V < 0$ than the films with $Cu/In \approx 0.79$ in which

impurity In_2Se_3 phase is absent.

It served as a signal of possibility of n- $CuIn_3Se_5$ layer with 1.3 eV band gap [13] formation between underlying n- $CuInSe_2$ layer and surface In_2Se_3 layer as it was observed [25] in $In_2Se_3/CuInSe_2$ film system obtained by a sequential vacuum deposition onto hot substrates of both atomic In-Se and Cu-Se vapors. Note, that the angular positions of most intensive XRD peaks of $CuIn_3Se_5$ phase practically coincide with angular positions of XRD peaks of $CuInSe_2$ phases [26] and consequently to detect $CuIn_3Se_5$ phase by XRD method is very difficult task, especially in the case of small microcrystallite dimensions.

At $V > 0$ I-V characteristics of above mentioned two compared films are quantitatively similar, that can be explained by similar nature of physical processes responsible for the steady-state I-V characteristics of the films.

The investigations of argon annealed CIS films contained admixture In_2Se_3 phase served as a basis for precise adjustment of potentiodynamic electrodeposition regime to prepare bilayer p- $CuInSe_2/n-CuIn_3Se_5$ structure. From this point of view we selected initial U_C value equal to -0.50 V because it should ensure the electrodeposition of lower CIS layer with $Cu/In > 1$. The final U_C value was reduced up to -0.85 V for complete expense of impurity In_2Se_3 phase during formation of $CuIn_3Se_5$ surface layer under argon annealing. The ramping rate in the above mentioned range of U_C values was 0.5 mV/s that provided approximately 1.3 μm thickness of the prepared films.

Average chemical compositions of such films both before and after film argon annealing were 23 at. % Cu, 26 at. % In and 51 at. % Se that corresponded to $Cu/In \approx 0.88$. As it is visible from XRD investigations the In_2Se_3 phase presented in the film before annealing is not registered after film annealing. The average dimensions of annealed CIS microcrystals estimated from XRD patterns were approximately 45 nm.

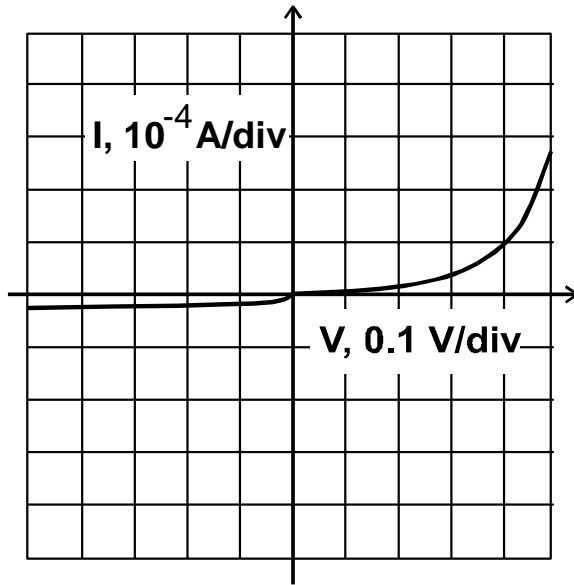


Fig. 5. Experimental I-V characteristics of 1.3 μm thick CIS film electrodeposited onto Mo substrate under potentiodynamic regime at U_C ramped from -0.50 V to -0.85 V at rate 0.5 mV/s and argon annealed at 400°C during 1 hour. Values $V > 0$ (curves 1' and 2') correspond to positive polarity of the bottom electrode and negative polarity of the top counter-electrode.

I-V characteristic of such film measured after argon annealing is shown on Fig. 5. As it is visible from Fig. 5, this I-V characteristic qualitatively differs from I-V characteristics represented earlier on Fig.1, Fig.3 and Fig.4. Besides these I-V branches both at $V > 0$ and at $V < 0$ are observed at once after applying of the voltage to the film without noticeable transient processes.

I-V characteristic showed on Fig. 5 has shape similar to shape of I-V characteristic of Shockley diode, that alongside with their above-cited behaviour allows to establish the existence of p-n junction in the film with $\text{Cu/In} \approx 0.88$. We consider, that the p-n junction arises because of conjugation of the underlying layer p-CuInSe₂ with surface layer n-CuIn₃Se₅.

As it follows from this I-V characteristic slope to the voltage axis at $V < 0$ the rather high currents observed in the case of reverse switch of p-n junction are caused by their considerable shunting. The shape of I-V direct branch testifies quite a large value of diode saturation current in the p-CuInSe₂/n-CuIn₃Se₅ two-layer structure. We connect these circumstances with the influence of microcrystal film structure on

electrical properties of p-n junction. The latter contains developed network of intergrain surfaces responsible for the shunting of polycrystalline p-n junction and for additional recombination processes [27].

The enrichment of the electrodeposited CIS films by copper and selenium is considered [1] as the factor that promotes the film recrystallization during the annealing. Therefore it seems that small additional copper and selenium enrichment of p-CIS layer by means of more positive initial U_C value alongside with more optimum law of U_C monotonous increasing during potentiodynamic electrodeposition as well as more favourable annealing conditions will allow to prepare CIS films with average microcrystallite dimensions that will exceed the width of depletion region of p-n junction formed on the base of p-CuInSe₂ and n-CuIn₃Se₅ layers inside of such films. Now we begin these investigations.

In addition we want to pay attention to curious fact concerning to I-V characteristics of CIS films with $\text{Cu/In} \approx 0.88$. We observed that the latter I-V characteristics were not influenced by oxygen diffusion in contradistinction to CIS films characterized by other Cu/In values. From our point of view it is conditioned either by oxygen insensitivity of an electron subsystem of CuIn₃Se₅ phase or by barrier properties of CuIn₃Se₅ to electrodiffusion of oxygen into the film bulk at negative polarity of top counter-electrode. The nature of this interesting phenomenon should become a subject of special researches.

IV. Conclusions

The comparison of preparation conditions influence on I-V characteristics of CIS films electrodeposited under potentiostatic and under potentiodynamic regimes has shown, that cathode electrodeposition under potentiodynamic regime from aqueous acidic chloride electrolyte contained 0.9 mM CuCl , 4.5 mM InCl_3 and 1.5 mM SeO_2 (pH 1) at cathode potential ramped from $U_C = -0.50\text{ V}$ up to $U_C = -0.85\text{ V}$ at rate 0.5 mV/s allows to obtain $1.3\text{ }\mu\text{m}$ thick CIS films, in which p-CuInSe₂ / n-CuIn₃Se₅ junctions with I-V characteristics similar to I-V characteristic of

Shockley diode were arisen after argon annealing at 400°C during 1 hour.

The p-n junction obtained by above mentioned method is characterized by reduced shunting resistance as well as by high saturation diode current because of a developed network of intergrain surfaces in the depletion region.

It is supposed, that small copper and selenium enrichment of p-CuInSe₂ layer by means of optimum reduction of initial U_C value and by choice of the more optimum law of monotonous increasing of U_C value up to U_C = - 0.85 V during the film electrodeposition as well as the choice of more favourable CIS film annealing conditions are necessary for improvement of p-n junction quality. Now

these problems are under our investigations.

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Вольт-амперні характеристики електроосаджених плівок CIS

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Метою проведених досліджень було визначення умов виготовлення на основі електроосадженого діселеніду міді та індію (CIS) тонкоплівкового р-п-переходу, який має вольт-амперні (I-V) характеристики, подібні до I-V характеристик діода Шоклі.

Вплив умов електроосадження та наступного відпалу на I-V характеристики плівок та на їх тип електропровідності досліджували за допомогою методів характеріографа та термо-е.д.с. Структуру і хімічний склад вивчали шляхом використання SEM, XRD, EDX, а також методом лазерної мас-спектрометрії.

Співставлення впливу умов виготовлення на електричні властивості, структуру та хімічний склад досліджуваних плівок CIS показує, що катодне електроосадження в потенціодінамічному режимі з кислого водного хлоридного електроліту, який містить 0.9 mM CuCl, 4,5 mM InCl₃ та 1.5 mM SeO₂ (pH 1) при зміні катодного потенціалу від -0.50 В до -0.85 В (відносно насиченого Ag/AgCl електроду порівняння) зі швидкістю 0.5 мВ/с дозволяє одержувати плівки CIS з приблизною товщиною 1 мкм, в яких р-CuInSe₂/n-CuIn₃Se₅ переходить з I-V характеристиками подібними до I-V характеристик діода Шоклі утворюються після відпалу в аргоні при 400 °С протягом 1 години.