Functional Materials 14, No.3 (2007) © 2007 — Institute for Single Crystals

Electrodeposition of copper indium diselenide films using pulse plating technique

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Received January 19, 2007

Parameters of rectangular potential pulse electrolysis which have provided the obtaining of nearly stoichiometric copper indium diselenide layers have been selected using the examination of those films by energy-dispersive X-ray spectroscopy, anodic stripping, scanning electron microscopy and the film resistivity measurements.

С помощью исследований электроосажденных пленок диселенида меди и индия методами рентгеновской дисперсионной спектроскопии, анодного стравливания, растровой электронной микроскопии, а также измерения электросопротивления этих пленок выбраны оптимальные параметры электролиза в режиме прямоугольных импульсов потенциала, позволившие получить слои примерно стехиометрического состава.

According to a recent publication [1], the thin-film ternary chalkopyrite semiconducting compounds and solid solutions based thereon are almost unique (except for cadmium telluride) semiconductor family of good prospects for optimized solar cell band structures. The homojunction copper indium diselenide ($CuInSe_2$, or CIS) cells with efficiency exceeding 16 % were described as early as in 1996 [2].

The one-step electrodeposition of copper indium diselenide films is among the most promising manufacturing techniques of that semiconductor material, taking into account a low cost and large-scale production possibility [3]. However, the reported efficiency of solar cells based on electrodeposited CIS films remains low as compared to those obtained with evaporated ones [1, 2]. Perhaps the low efficiency is due to the presence of binary compounds observed [3] in the electrodeposited films in addition to CIS phase.

As far as we know [4, 5], one of the most promising ways to improve properties of the electrodeposited films is to use the pulse plating techniques. Nevertheless, rare attempts to employ a pulsed potential technique for CIS electrodeposition were unsuccessful up to now. So, the purpose of this work is to investigate the influence of different pulse plating conditions on CIS film chemical composition and electrical properties in order to reveal the ways to improved CIS films quality.

The CIS films were electrodeposited at room temperature on cathodes in aqueous acidic chloride electrolyte containing 0.9 mM CuCl, 4.5 mM $InCl_3$, and 1.5 mM SeO_2 (pH 1) in three-electrode cell with platinum counter-electrode and saturated Ag/AgCl reference electrode (SAE). The electrodes were fixed but the electrolyte was agitated by a magnetic stirrer. Electropolished molybdenum plates or glass sheets covered with SnO_2:Sb conductive layers prepared by chemical vapor deposition method [6] were used as cathodes. The electrodeposition was carried out under pulse plating conditions at amplitudes of rectangular potentials U_a varying from 0.6 V to 1.0 V (i.e. when cathode potential U_c was switched on, it was varied from 0.2 V to −0.4–0.8 V vs. SAE). The potential pulse frequency was varied from 0.7 Hz up to 7 kHz. The relative pulse duration $Q = t/t_i$, where t is the pulse period and t_i, the pulse duration, was

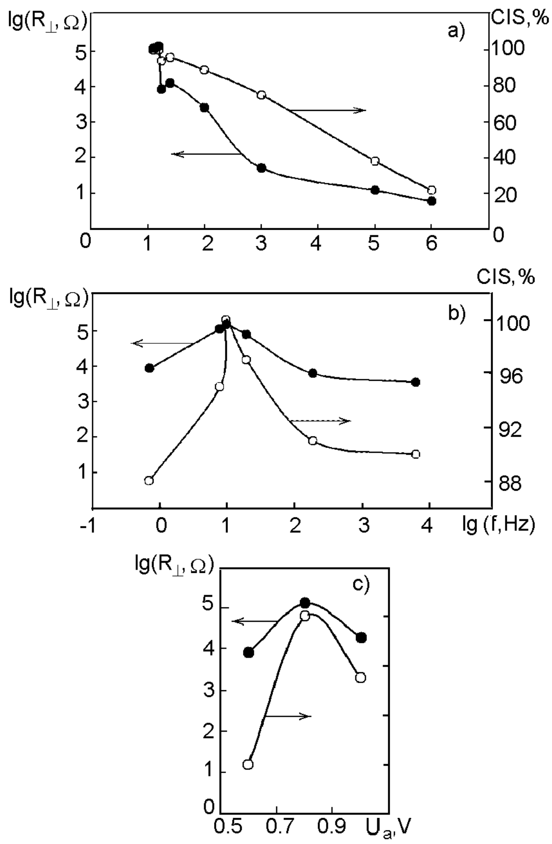

Fig. 1 Composition and cross resistances of CIS films electrodeposited using pulse plating technique: *a* – U_a=0 V, f =10 Hz; *b* – Q=1.2, U_a=0.8 V; c – Q=1.2, f = 10 Hz.

1.1, 1.2, 1.25, 1.4, 2.0, 3.0, 5.0 or 6.0. The film thickness measured by interferometer was increased from 0.2 μm up to 1.9 μm as the *Q* value decreased. The deposition time was 15 min.

The bulk film chemical composition was investigated using two methods. In the first one, a LEO 1530 scanning electron microscope in energy-dispersive X-ray spectroscopy (EDX) mode was used. The second method was anodic stripping in accordance with [7, 8] consisting in recording of voltammograms registered in a non-stirred 0.5 M H_2SO_4 during scanning of SnO_2:Sb electrode potential towards the anodic region from 0.0 V up to 1.4 V (vs. SAE) at the scan rate of 1 mV/s. The surface morphology of the electrodeposited CIS films was studied by the LEO 1530 instrument in scanning electron microscopy (SEM) mode. Cross resistances of as-deposited CIS films $R_\perp$ were investigated by one probe method. Hot probe measurement technique was used to determine the conductivity type of the films.

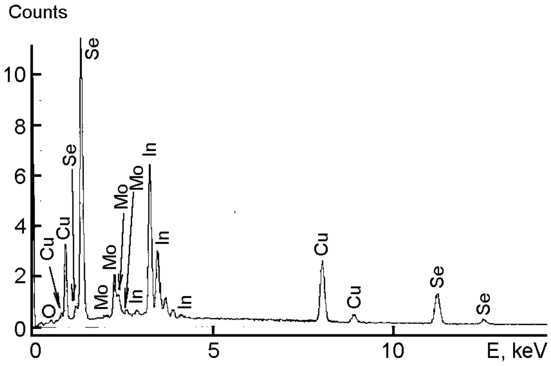

Fig. 2. EDX analysis spectra of CIS films electrodeposited at U_c = 0.8, Q = 1.2 and at frequencies 10 Hz.

Two peaks were revealed in the anodic stripping curves. The first peak is within the anodic potential region of $-0.2 \le U_c \le -0.4$ V vs. SAE and, according to [7, 8], it corresponds to oxidation of impurity binary compounds, for example, $Cu_{2-x}Se$, Cu_2Se and/or In_2Se_3. The second peak at $-0.6 \le U_c \le -0.8$ V vs. SAE, in accordance with [7, 8], is due to $CuInSe_2$ oxidation.

Comparison of anodic stripping curves obtained for CIS films electrodeposited under same potential pulse amplitude (0.8 V), pulse frequency (f = 10 Hz) but at different *Q* values demonstrated that the films deposited under high *Q* values contained significant proportion of binary impurities, while those deposited at *Q* values near one did not contain impurity phases essentially (Fig.1a). Note that such observation agrees well with energy-dispersive X-ray spectroscopy data.

Investigation of the potential pulse frequency influence on CIS film composition revealed an extreme dependence (Fig.1b). The anodic stripping curves for the films obtained at U_a = 0.8 V and Q = 1.2 at low ang high frequency values showed the significal content of impurity binary compounds. Especially great their concentrations were observed for the films obtained at $f \ge 200$ Hz. At the same time, the anodic stripping curves for the films deposited at $8 \le f \le 20$ Hz have shown nearly stoichiometric $CuInSe_2$ composition that was confirmed by EDX analysis. Fig. 2 shows a near-stoichiometric $CuInSe_2$ film (26 at.% Cu, 49 at.% Se, 25 at.% In) electrodeposited at the same values of amplitude potential and *Q*, but at a moderate frequency (f = 10 Hz). When comparing Fig. 3a and Fig. 3b, the stoichiometric film (Fig. 3b) is seen to have

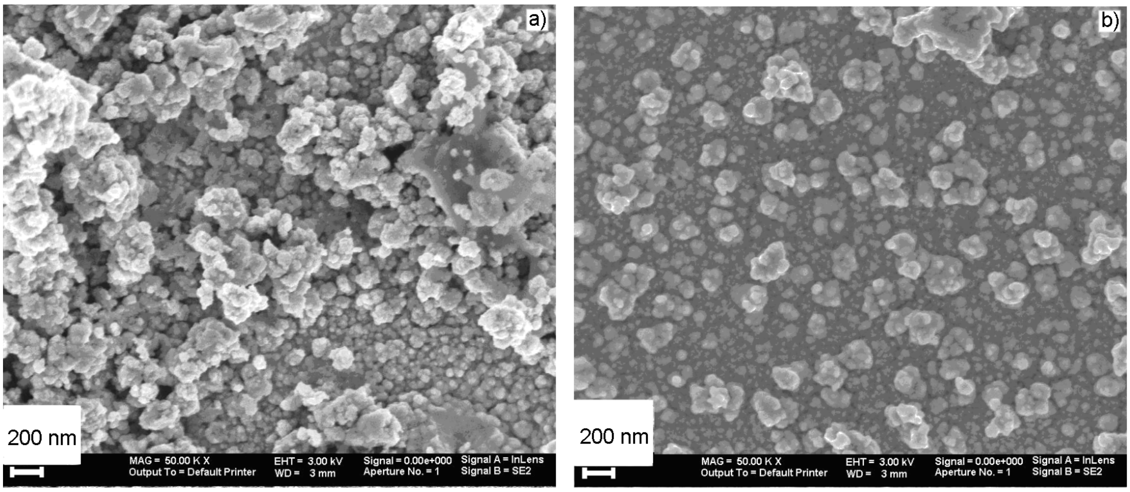

Fig. 3. SEM images of CIS films electrodeposited at U_c = 0.8 V, Q = 1.2 and at frequencies 1 kHz (a); 10 Hz (b).

a more smooth surface than the indium-enriched one (Fig. 3a).

Moreover, to determine the optimal pulse amplitudes more accurately, the measurements of film cross resistances $R_{\perp}$ were used, since, as is well known [9], the preferred segregation of binary phases on the grain boundaries results in short-circuited photovoltaic cells or in cells with low shunt resistance. The electrical measurements confirmed EDX and anodic stripping data for the films shown in Fig. 2 and Fig. 3: the near-stoichiometric CIS films showed the highest $R_{\perp}$ values (Fig.1). On the other hand, these measurements made it possible to select the optimal pulse amplitude value and to compare the films obtained under pulse mode with those electrodeposited in potentiostatic mode in accordance with [8]. It turned out that within the range from 0.6 V to 1.0 V, the best pulse amplitude U_a amounted 0.8 V at U_c value dropping from 0.2 to −0.6 V vs. SAE. Comparison with potentiostatic mode [8] has revealed that the pulse electrodeposition provides the most single-phased $CuInSe_2$ films characterized by highest $R_{\perp}$ values of the order of 10^5 Ohm and resistivity values of the order of 10 Ohm·cm. All the above-mentioned electrodeposited CIS films have shown the p-type conductivity.

Thus, the pulse plating technique provides an improvement of the electrodeposited CIS film quality. Optimization of rectangular potential pulse electrodeposition parameters using the EDX, anodic stripping, SEM and electrical measurements data have provided near-stoichiometric $CuInSe_2$ films with resistivity of the order of 10 Ohm·cm at Q = 1.1 to 1.2, the cathode potential amplitude 0.8 V and at frequencies $8 \le f \le 20$ Hz.

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Електроосадження плівок диселеніду міді та індію в імпульсному режимі

Н.П.Клочко

Шляхом дослідження електроосаджених плівок диселеніду міді та індію методами рентгенівської дисперсійної спектроскопії, анодного травлення, растрової електронної мікроскопії, а також вимірювання електроопору цих плівок вибрано оптимальні параметри електролізу у режимі прямокутних імпульсів потенціалу, які дозволили одержати плівки близького до стехіометричного складу.