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Influence of vacuum annealing on the composition of electrochemically deposited zinc selenide layers

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The paper is devoted to the analysis of electrodeposited zinc selenide films compositions and to the research of their homogenization and purification probabilities by vacuum annealing. In order to investigate the surface morphology and the composition of electrodeposited films electron-probe microanalysis and X-ray photoelectron spectroscopy (XPS) methods were used. It was revealed that as-electrodeposited films were enriched with selenium and consisted of $ZnSe$ and $Zn(OH)_2$, covered with Se, SeO_2 and $OSe(OH)_2$ layers. The film compositions before annealing were not homogenous. There were friable conglomerates, consisting mostly of $Zn(OH)_2$, on their surfaces. Vacuum annealing at 100–350°C provided for $Zn(OH)_2$ transformation into ZnO, for water removing from the films and partially for the desorption of oxygen and selenium. The second part of surplus selenium in the chemical state of Se, SeO_2 and $OSe(OH)_2$ during the vacuum annealing at 350°C interacted with $Zn(OH)_2$ or ZnO and hydrogen occluded in the films due to supplementary cathode process of water reduction. As a result of such interaction, $ZnSe$ was obtained. The friable conglomerates after the annealing were enriched by selenium that also led to the generation of $ZnSe$.

Работа посвящена анализу состава пленок и изучению возможности их гомогенизации и очистки от примесей посредством вакуумных отжигов. Для анализа морфологии поверхности и состава электроосажденных пленок использованы методы рентгеновского микроанализа и рентгеновской фотоэлектронной спектроскопии. Обнаружено, что свежеосажденные пленки были обогащены селеном и состояли из $ZnSe$ и $Zn(OH)_2$, покрытых слоями Se, SeO_2 и $OSe(OH)_2$. На поверхности пленок до отжига имелись рыхлые скопления, состоящие преимущественно из $Zn(OH)_2$. Отжиги в вакууме при 100–350°C обеспечивали превращение $Zn(OH)_2$ в ZnO, удаление из пленок воды и частичную десорбцию кислорода и элементарного селена. Другая часть избыточного селена в форме Se, SeO_2 и $OSe(OH)_2$ в процессе отжига при 350^0C взаимодействовала с $Zn(OH)_2$ и ZnO и окклюдированным в пленках водородом, образующимся в результате побочной катодной реакции восстановления воды, с образованием $ZnSe$. Рыхлые скопления в результате отжига обогащались селеном и также превращались в $ZnSe$.

The development of new manufacturing processes for zinc selenide (ZnSe) films is of importance because ZnSe can be used in various optoelectronic devices, for example, as buffer layers in solar cells (SC) with base layers of $CuInSe_2$ or other chalcopyrite semiconductors, or for the SC base layers formation from $CuInSe_2$–2ZnSe solid solutions [1, 2].

Studies of ZnSe film electrodeposition kinetics allowed us [3] to determine the potential of substrate cathode at which the films containing selenium and zinc could be grown. Mass-spectrometric and spectrographic analyses [4] supported the conclusions of these investigations by showing that at the cathode potential $U_c = -1.15$ V versus Ag/AgCl reference electrode (SCE) in aqueous electrolyte containing Na_2SO_4 (0.1 M), $ZnSO_4$ (0.02 M) and SeO_2 ($5{\cdot}10^{-4}$ M) at pH 5.5, cathodically electrodeposited layers containing equal amounts of selenium and zinc were formed. So, one can expect that these layers consisted of zinc selenide. However, as the films were deposited from aqueous solutions, they apparently contained not only zinc and selenium but also different impurities which, in our opinion, could be removed at least partially by vacuum annealing. According to [5–7], the annealing conditions are the factors which, along with the electrolyte composition and the deposition potential, define the composition and structure of the obtained films. So, this paper is devoted to the study of as-electrodeposited and vacuum annealed zinc selenide films composition.

The ZnSe films were deposited from the above-mentioned electrolyte and at above-mentioned cathodic potential. To prevent chemical interaction during the electrodeposition and vacuum annealing, we used glass sheets coated with reactive-sputtered 500 nm thick titanium nitride (TiN) layers as the substrates. The electrodeposition was carried out in controlled potential regime by means of potentiostat provided with a programmer and three-electrode electrochemical cell containing a saturated Ag/AgCl reference electrode (SCE) ($U_{SCE} = 0.22$ V against the normal hydrogen electrode) and platinum counter-electrode of 100 cm^2 surface area. The electrolyte was agitated with a magnetic stirrer. During the electrolysis the temperature (t) was within limits of 30–40°C. The deposition time τ was 5–20 minutes, the current density J was 0.5–2.0 mA/cm^2. The thickness of the zinc selenide layers obtained was measured with a Fizo interferometer according to [8]. It increased with deposition time and current density from 0.02 μm to 0.16 μm. The electrodeposited ZnSe layers were annealed in vacuum 10^{-3} Pa at temperatures 100°C, 250°C, and 350°C, each time for 0.5 hour. The sample surface morphology and composition were studied by electron-probe microanalysis method (EPMA) using a JSM-820 electron microscope with Link AN1O/85S microanalysis system. The energy dispersion was analyzed using a Si(Li) detector with the X-ray output angle $\psi = 40°$ and the following characteristics of X-ray emission lines: ZnLα, ZnKα, SeLα, OKα. The electron accelerating voltage was 10–20 kV. The microscope resolution in this mode was about 10 nm. The analyzed depth was approximately 1 μm. The sample surface composition was examined by X-ray photoelectron spectroscopy (XPS) with XPS-800 Kratos spectrometer. The vacuum in the chamber was $5{\cdot}10^{-7}$ Torr. The photoelectrons were excited with MgK_α radiation ($h\gamma = 1253.6$ eV). X-ray gun power was 15 kV·20 mA. The photoelectron kinetic energy was analyzed with a hemispherical electrostatic analyzer. The instrument resolution was 1 eV, the accuracy of binding energy determination, 0.3 eV. The spectra were processed by computer: smoothing, the subtraction of constant and variable background (Shirley method), removing expanding effect of the X-ray line (iterative deconvolution) and decomposition of complex line into components were made. The sample surface composition was determined using the ratio of areas of photoelectron lines in the spectra of C1s, O1s, Zn3p, Se3d, Ti2p, N1s core levels with regard to their sensitivity factors [9]. Binding energy calibration and the consideration of charging potential were made using C1s ($E_b = 285$ eV) line as a reference. A layer of approximately 10 nm thickness was analyzed.

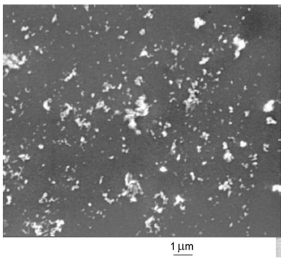

Fig. 1. Electron microscopic image of sample No.1.

To determine the compounds existing in the surface layer of the samples before and

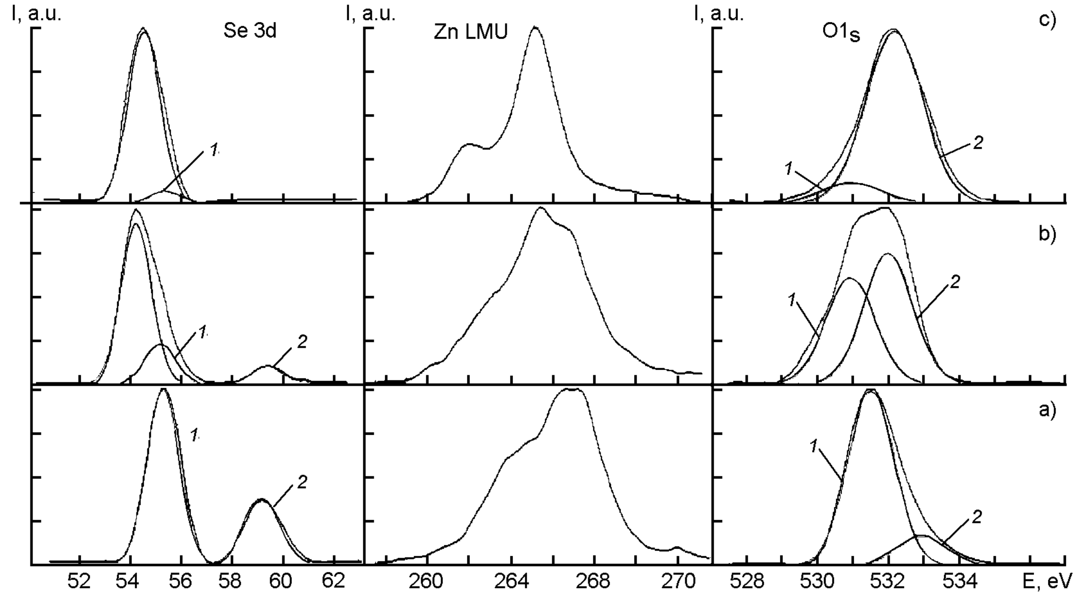

Fig. 2. Photoelectron spectra of sample No.1 before (a) and after annealing (b) and sample No.3 after annealing (c).

after the annealing, we analyzed the shapes of selenium and oxygen core level spectra. As for zinc, we analyzed the shape of Auger electron line Zn_{LMM}, because it is known that for some metals (Zn, Cu) the shape and the binding energy of Auger lines depend more on their chemical environment than photoelectron lines. This is connected with the fact that superatomic relaxation energy of the final state with two holes on *3d*-core level influences considerably the chemical shift value [10].

The visual consideration evidences that the electrodeposition process produces films which are sufficiently smooth to give the interference pattern, thin, hard, and adherent to TiN. A weak intensity of Ti2p line in the XPS spectra shows that the films obtained are solid (continuous) and are more than 10 nm thick throughout all the substrate surface. On the other hand, before as well as after vacuum annealing, no considerable amounts of titanium were registered in the electrodeposited films. So, we can claim that there was no interaction of these films with TiN. However, the films were not mirroring because they exhibit a fairly high light scattering, typical of electrodeposited ZnSe layers [5, 7].

The composition and the surface morphology analysis of electrodeposited film by EPMA showed (Fig. 1) that the composition

Table. Atomic concentration ratios for the elements found in the surface layers of the samples according to XPS data

Sample	Electrodeposition regime	O/Zn	Se/Zn	Ti/Zn
No.1 before annealing	$U_c = -1.15$ V, $J = 0.9-1.7$ mA/cm^2, $t = 37°$C, $\tau = 10$ min	2.5	3.2	0
No.1 after annealing at 350°C	–	1.3	0.3	~ 0.01
No.2 before annealing	$U_c = -1.15$ V, $J = 0.9-1.5$ mA/cm^2, $t = 33°$C, $\tau = 15$ min	1.5	1.8	~ 0.01
No.2 after annealing at 250°C	–	0.7	0.4	~ 0.01
No.3 before annealing	$U_c = -1.15$ V, $J = 1.4-2.3$ mA/cm^2, $t = 37°$C, $\tau = 10$ min	3.5	10.0	0
No.3 after annealing at 350°C	–	0.8	1.0	0

of freshly-deposited films of 0.08 μm and larger thickness was not homogenous. Loose conglomerations on their surfaces consisted mainly of zinc, oxygen and only small amounts of selenium. Zinc to selenium ratio in these conglomerations was 9:1. At the same time, according to XPS, 10 nm thick surface layer was characterized by excess selenium and oxygen (see Table).

Fig. 2 shows the photoelectron spectra of Se3d, O1s core levels and Auger electron line Zn_{LMM} for electrodeposited sample No.1 before and after vacuum annealing. The spectra of O1s core level before annealing (Fig. 2a) consists of two lines with binding energies 531.5 eV (line 1) and 533.0 eV (line 2). The consideration of literature [9, 11] shows that line 1 could be associated with oxygen in OH-groups (i.e. with $Zn(OH)_2$ and $OSe(OH)_2$), but line 2 could be connected with water adsorbed on the sample surface. After annealing, two lines appear in O1s core level spectrum: one with binding energy 531.0 eV (line 1 in Fig. 2b,c) that corresponds to oxygen in metal compounds (i.e. ZnO), and line 2 with binding energy 532.0 eV, that could be attributed to the adsorbed oxygen. The same changes were observed in [11] for Zn(Se,OH) buffer layers deposited by chemical bath deposition (CBD) process on $Cu(In,Ga)(S,Se)_2$ and annealed at 100°C.

The shape of Se3d core level peak also was considerably transformed during vacuum annealing. Prior to the annealing, two peaks are observed at 55.3 eV (line 1 in Fig. 2a) and at 59.2 eV (line 2 in Fig. 2a), that could be attributed to selenium in chemical states Se^0 and Se^{4+} (namely, in $OSe(OH)_2$ and SeO_2 compounds), respectively. After vacuum annealing, the line with binding energy 54.2 eV (line 3 on Fig. 2b,c) in the Se3d photoelectron spectrum becomes the main one, that is, characteristic for ZnSe compound. At the same time, the intensities of the peaks corresponding to Se^0 and Se^{4+} are reduced dramatically.

Apparently, $Zn(OH)_2$ impurity formation is a side process of ZnSe films electrodeposition due to water reduction and hydrogen formation reaction in aqueous electrolytes, especially at negative cathode potentials, according to the equation:

$$2H_2O + 2e^- = H_2 + 2OH^-. \quad (1)$$

According to [7], the hydrogen formation is thermodynamically possible throughout all the ZnSe electrodeposition range. The process (1) results in alkalization of the near-cathode space and, consequently, promotes the formation of $Zn(OH)_2$ impurity in the zinc selenide films due to reaction:

$$Zn^{2+} + 2H_2O + 2e^- = H_2 + Zn(OH)_2. \quad (2)$$

This is supported by the fact that when the cathode potential during zinc selenide deposition U_c is shifted towards more negative values, for example from −1.15 V to −1.25 V, a decrease of selenium content and increase of zinc and oxygen content in the films were observed.

Vacuum annealing at 250°C and especially at 350°C, according to XPS studies, caused a decrease of selenium and oxygen contents and an increase of zinc content in the films (see Table). The surface composition of the sample No.3 containing a small amount of conglomerates before annealing corresponded after the annealing to stoichiometric ZnSe. In O1s spectrum of this sample, the peak corresponding to ZnO was practically absent. Se3d peak of the sample No.3 after the annealing corresponded to Se^{2-} (Fig. 2c).

The authors [11] explained similar transformations at such a moderate temperature for CBD deposited films as a consequence of impurity $Zn(OH)_2$ conversion into ZnO, especially during vacuum annealing, according to the equation:

$$Zn(OH)_2 = ZnO + H_2O. \quad (3)$$

The decrease of selenium concentration during the annealing took place in part due to elemental selenium evaporation [12]. Besides, Se^0 could interact with hydrogen occluded in the films as well as with ZnO and $Zn(OH)_2$:

$$Se + H_2 + ZnO = ZnSe + H_2O, \quad (4)$$

$$Se + H_2 + Zn(OH)_2 = ZnSe + 2H_2O. \quad (5)$$

The cause of Se^{4+} peak intensity decrease in XPS spectrum could be explained by the interaction of $Zn(OH)_2$ and ZnO with occluded hydrogen and Se^{4+} and ZnSe formation in the following reactions:

$$SeO_2 + 3H_2 + ZnO = ZnSe + 3H_2O, \quad (6)$$

$$SeO_2 + 3H_2 + Zn(OH)_2 = ZnSe + 4H_2O, \quad (7)$$

$$OSe(OH)_2 + 3H_2 + ZnO = ZnSe + 4H_2O, \quad (8)$$

$$OSe(OH)_2 + 3H_2 + Zn(OH)_2 = ZnSe + 5H_2O. \quad (9)$$

The supporting evidence for the running reactions (4)–(9) is the fact that Zn_{LMM} Auger peak is also transformed during the vacuum annealing and demonstrated the change of zinc chemical state (Fig. 2). Unfortunately, it was impossible to resolve this peak into its components because of complex structure of the peak and a large number of probable zinc compounds, but the shape and the binding energy of Zn_{LMM} spectrum for sample No.3 in Fig. 2c are characteristic for ZnSe [9].

In loose conglomerates, according to EPMA data, Zn to Se ratio remained almost unchanged after vacuum annealing at 250°C, but considerably (from 9.0 to 0.9) decreased at vacuum annealing at 350°. In other words, the loose conglomerates, consisting in the as-electrodeposited films mainly of $Zn(OH)_2$ and ZnO, were enriched in selenium during vacuum annealing due to the above-mentioned reactions (4)–(9) and to selenium diffusion into the conglomerates. So, the vacuum annealing resulted in homogenization of the film composition.

Thus, the consideration of X-ray photoelectron spectroscopy and electron-probe microanalysis data allows to conclude that the films consisting of ZnSe and $Zn(OH)_2$, coated with Se^0, SeO_2 and $OSe(OH)_2$ are formed on the TiN substrate surfaces in the course of electrodeposition. In the course of vacuum annealing, zinc hydroxide is transformed into zinc oxide, while the excess elemental selenium is partially desorbed and partially, as well as Se^{4+}, interacts with hydrogen occluded in the films and $Zn(OH)_2$ or ZnO forming ZnSe. So, vacuum annealing at 350°C allows obtaining zinc selenide films with minimum content of impurities.

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Вплив вакуумних відпалів на склад електрохімічно осаджених плівок селеніду цинку

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Робота присвячена аналізу складу електроосаджених плівок селеніду цинку та вивченню можливості їх гомогенізації й очищення від домішок за допомогою вакуумних відпалів. Для аналізу морфології поверхні та складу електроосаджених плівок використано методи рентгенівського мікроаналізу та рентгенівської фотоелектронної спектроскопії. Виявлено, що безпосередньо після електроосадження плівки були збагачені селеном і складалися з ZnSe і $Zn(OH)_2$, вкритих шарами Se, SeO_2 і $OSe(OH)_2$. Перед відпалами склад плівок не був однорідним. На їх поверхні існували розріджені скупчення, які переважно складалися з $Zn(OH)_2$. Відпалювання у вакуумі при 100–350 °C забезпечувало перетворення $Zn(OH)_2$ на ZnO, видалення з плівок води та часткову десорбцію кисню й елементарного селену. Інша частина надлишкового селену у вигляді Se, SeO_2 і $OSe(OH)_2$ у процесі відпалювання при 350 °C реагувала з $Zn(OH)_2$ і ZnO та оклюдованим у плівках воднем, отриманим під час супутньої катодної реакції відновлення води з утворенням ZnSe. Розріджені скупчення у результаті відпалу збагачувалися селеном, що також спричиняло виникнення ZnSe.