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Characteristics of the structure, composition and properties of electrodeposited zinc selenide films

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The actuality of new processes for zinc selenide (ZnSe) films manufacture is explained by good prospects of their potential applications in optoelectronics. However, the films obtained on cathode by means of electrolysis in aqueous solutions have some distinctive properties and hence require a detailed study of structure, composition and properties thereof. Transmission electron microscopy examination of electrodeposited zinc selenide films has revealed that those are inhomogeneous in composition and structure: the fine-grained film body is formed by ZnSe nanocrystallites of cubic zinc blende structure and clusters of larger $Zn(OH)_2$ microcrystals are included into the body. The film surfaces are coated by amorphous sublayer consisting of Se, SeO_2 and $OSe(OH)_2$. According to electrical studies, such electrodeposited films are n-type semiconductors.

Актуальность новых разработок в области изготовления пленок селенида цинка (ZnSe) объясняется перспективой их использования в оптоэлектронике. Вместе с тем, пленки, полученные на катоде в процессе электролиза водных растворов, имеют ряд отличительных особенностей и поэтому нуждаются в детальном анализе структуры, состава и свойств. Методом просвечивающей электронной микроскопии обнаружено, что электроосажденные пленки селенида цинка имеют неоднородные состав и структуру: в тело мелкодисперсных пленок из нанокристаллов ZnSe кубической модификации типа цинковой обманки вкраплены кластеры, представляющие собой скопление более крупных кристалликов $Zn(OH)_2$. Поверхность таких пленок покрыта тонким аморфным слоем из Se, SeO_2 и $OSe(OH)_2$. Согласно исследованиям электрических свойств, электроосажденные пленки являются полупроводниками n-типа.

Zinc selenide (ZnSe) films obtained by means of electrolysis from water solutions on cathode have some specific properties [1–4]. For example, the presence of equal amounts of zinc and selenium in the films does not exclude their complex chemical composition and the peculiarities of their crystal structure connected therewith, that causes characteristic properties of such films. Basing on the actuality of this material for optoelectronics and on the necessity to improve its preparation method, this work is devoted to detailed investigation of structure, composition and properties of electrodeposited zinc selenide films.

The electrodeposition of ZnSe films, the determination of their thickness and investigation methods of the morphology and composition have been reported in [5]. The structure of the electrodeposited ZnSe films

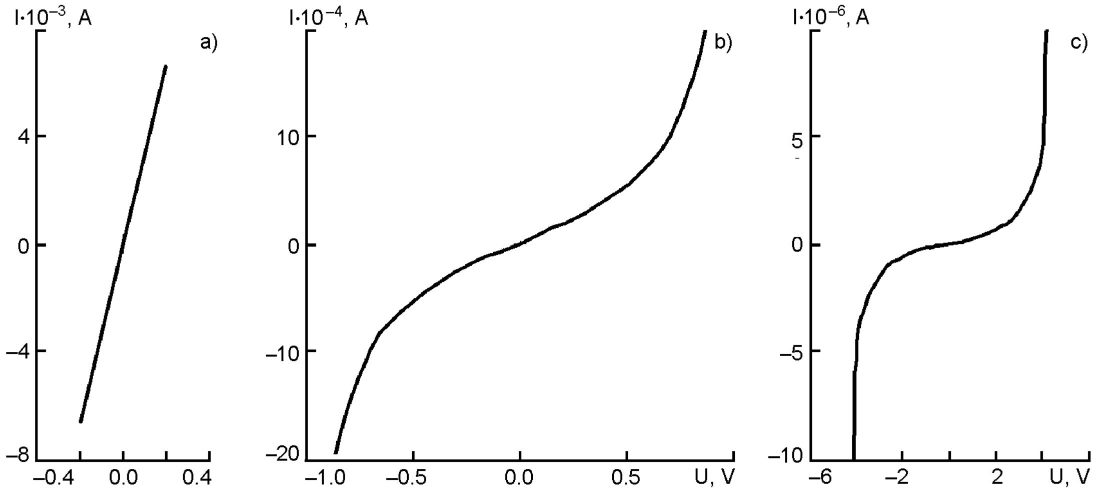

Fig. 1. Change of IVC shape for ZnSe films electrodeposited on TiN substrates as a function of the electrodeposition time τ and of film thickness Δ ($U > 0$ correspond to the substrate positive charge): (a) τ = 10 min, Δ = 80 nm; (b) τ = 15 min, Δ = 120 nm; (c) τ = 20 min, Δ = 160 nm.

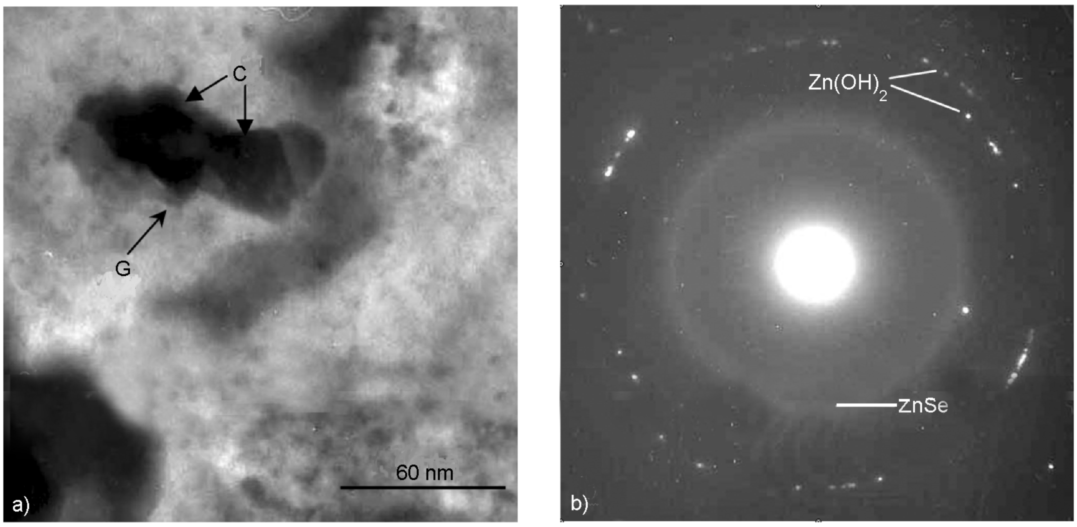

Fig. 2. The bright-field micrograph (a) and the electron diffraction pattern (b) for the same region of as-grown ZnSe film.

was studied by transmission electron microscopy (TEM) using a PEM-125K microscope at electron accelerating voltage 100 kV. The film samples were stripped from the substrates using gelatin according to standard method. The gelatin was dissolved in hot (80°C) distilled water; the samples were pulled out by electrolytic copper nets. The current-voltage characteristics (IVC) for the films were obtained using a EMG-1579-102 TR Orion Characteriograph including a source of amplitude-regulated alternating voltage, an AC resistor and an oscillograph. The molybdenum probe used for the measurements had polished semispherical surface of 100 μm radius and was pressed softly to the sample surface. The film conductivity type was determined by hot-probe method.

The study of electrical properties by considering the current-voltage characteristics of ZnSe films electrodeposited onto chemically inert substrates of titanium nitride (TiN) has revealed (Fig. 1) that the shape of zinc selenide film IVC varied depending on the film thickness increasing during the ZnSe electrodeposition. Table 1 presents the analysis of current-voltage curves which are shown in Fig. 1. It is seen that as the ZnSe film thickness (Δ) increases, the symmetrical IVC typical of the several tens nanometer thick films are replaced by IVC characteristic for spatial charge limited currents (CLSC) at single-energetic distribution of traps (for $\Delta = 0.12$ μm). As to thicker films ($\Delta = 0.16$ μm), IVC corresponded to CLSC at exponential distribution of traps. The increasing of ZnSe film thickness is accompanied by growing of sheet resistance (R_{Ω}), the resistance reduced to the unit contact area (R_{Ω}^{*}) and of the resistivity ρ. Such films had n-type of conductivity. For the thickest ZnSe film, we have calculated the effective concentration of the major charge carriers $n_{ef} = 1.3 \cdot 10^{15}$ cm^{-3}. Their small effective mobility ($\mu_{ef} = 0.03$ cm^2/V·s) and the junction height on grain boundaries $\Phi = 0.3$ eV, calculated in accordance with [6] basing on the relationship $\Phi = kT\ln(\mu_{cr}/\mu_{ef})$, where μ_{cr} is the major charge carrier mobility in zinc selenide single crystal (according to [6], $\mu_{cr} = 260$ cm^2/V·s), give evidence of nanocrystalline structure of electrodeposited ZnSe films.

The examination by transmittance electron microscopy and by scanning electron microscopy with electron probe microanalysis (EPMA) have revealed that the as-grown 0.08–0.16 μm thick films are inhomogeneous in composition and structure. Fig. 2a presents the bright-field micrograph of zinc selenide film. The electron diffraction pattern of the same region is presented in Fig. 2b. According to the electronic density contrast in the bright-field micrograph, the main volume of the film has nanocrystalline structure with grain dimensions of ≤2 nm. The clusters (arrow G in Fig. 2a) which are accumulations (conglomerations) of more coarse (of the 10 nm order) crystals (arrows C) are embedded into this fine-grained film. The broad ring from the plates with interplane distance $d = 0.326$ nm in the electron diffraction pattern (Fig. 2b) corresponds to the nanocrystalline structure. This electron diffraction ring can be associated with cubic ZnSe phase ($a = 0.5669$ nm).

According to JCPDS data (card 37-1463), the most strong (100 %) line for cubic ZnSe reveals from (111) plane with $d = 0.3273$ nm. Note that electrodeposited ZnSe films reported in literature [1, 3] also had the zinc blende structure. The diffraction rings consisting of individual (separate) reflexes arise from more coarse crystals included in clusters. Basing on processing of the electron diffraction patterns from the different regions of the film, we have determined the set of interplane distances for the reflecting planes in such crystals.

Table 2. Interplane distances (d) for crystallites included in clusters in electrodeposited ZnSe films and in $Zn(OH)_2$

$d^{\pm 0.005}$, nm (experiment)	d,nm $Zn(OH)_2$ JCPDS, 41-1359	Int., %	(hkl)
	1.2210	<1	
	0.6600	<1	101
	0.5787	2	103
	0.4772	4	105
	0.4176	<1	008
0.392	0.3912	5	107
0.359			
	0.3332	11	202
	0.3250	<1	109
	0.3154	<1	204
0.308	0.3031	13	211
0.300	0.2990	1	
0.287	0.2902	100	206
	0.2777	<1	215
	0.2777	<1	1011
	0.2380	7	2010
	0.2315	9	224
	0.2271	<1	301
0.211	0.2150	2	305
	0.2150	2	2111
0.208	0.2086	3	228
	0.2086	3	0016
0.203	0.2046	<1	307
	0.1959	<1	2113
	0.1959	<1	2014
0.193	0.1928	<1	309
	0.1886	<1	321
	0.1886	<1	1017
0.184	0.1854	<1	323
0.181	0.1819	33	325
	0.1819	33	3011
0.173	0.1702	21	3013
	1702	21	1019

These interplane distances are collected in Table 2, where the interplane distances for $Zn(OH)_2$ (card 41-1359 JCPDS) are also presented for comparison. It could be noted a good agreement of experimental data and JCPDS ones. The above agrees well with the EPMA data [5]. According to [5], the friable

Table 1. Electrophysical parameters of ZnSe films electrodeposited on TiN

Sample No	Deposition time τ, min	Δ, μm	IVC type	R_Ω, Ω	R^*_Ω, Ω·cm^2	ρ, Ω·cm	Conductivity type
79	2	0.02	$I \sim U$	$1.5\cdot10^{-6}$	2	0.75	–
81	5	0.04	$I \sim U$	$7.5\cdot10^{-6}$	10	1.9	–
82	10	0.08	$I \sim U$	$2.2\cdot10^{-5}$	30	2.8	–
83	15	0.12	$I \sim U^2$	$2.2\cdot10^{-3}$	$3\cdot10^3$	$1.1\cdot10^2$	*n*
84	20	0.16	$I \sim U^3$	3	$4\cdot10^6$	$1.5\cdot10^5$	*n*

conglomerations consist mainly of from zinc, oxygen, and only small amounts of selenium (the zinc-to-selenium atomic ratio in these conglomerations is 9:1).

At the same time, according to X-ray photoelectron spectroscopy data [5], the electrodeposited film surface is coated by thin layer consisting of Se, SeO_2 and $OSe(OH)_2$, therefore, the 10 nm thick subsurface layer is characterized by excessive selenium and oxygen content (the Zn/O ratio is 3/5 while the Zn/Se one, 2/5), and the electrodeposited zinc selenide films are enriched as a whole in selenium. So, the structural research of electrodeposited zinc selenide films presented here and the earlier composition studies of these films [5] allow to conclude that the thin sublayer on the film surface consisting of Se and its compounds is amorphous, the conglomerates of $Zn(OH)_2$ are included into main volume of the nanocrystalline film consisting of polycrystalline fine-dispersed ZnSe grains of cubic crystal modification.

Thus, as the electrolysis duration increases (and thus the film thickness rises), the electrodeposited zinc selenide films acquire the electrical properties of semiconductors of *n*-type of conductivity. These films have nanocrystalline structure consisting mainly of the cubic ZnSe nanocrystals of ≤2 nm grain size and included conglomerates of larger (about 10 nm) $Zn(OH)_2$ crystallites.

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Особливості структури, складу та властивостей електроосаджених плівок селеніду цинку

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Актуальність нових розробок у галузі виготовлення плівок селеніду цинку (ZnSe) пояснюється перспективою їх використання в оптоелектроніці. Разом з тим, одержані на катоді в процесі електролізу водних розчинів плівки мають ряд особливостей і тому потребують детального аналізу структури, складу та властивостей. Методом просвічуючої електронної мікроскопії виявлено, що електроосаджені плівки селеніду цинку мають неоднорідні склад і структуру: у тіло дрібнодисперсних плівок з нанокристалів ZnSe кубічної модифікації типу цинкової обманки вкраплено кластери, що являли собою скупчення більш великих кристаликів $Zn(OH)_2$. Поверхню таких плівок було вкрито тонким аморфним шаром з Se, SeO_2 і $OSe(OH)_2$. Згідно досліджень електричних властивостей, електроосаджені плівки є напівпровідниками *n*-типу.