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Structure and substructure of zinc selenide films

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Received June 15, 2010

Structure and substructure characteristics of zinc selenide layers were investigated. The dependence of the orientation factor, lattice constant, coherent scattering domain size, microdeformation level from deposition temperature of films chalcogenide, are established.

Исследованы характеристики структуры и субструктуры слоев селенида цинка. Установлена зависимость структурного фактора, постоянной решетки, размера областей когерентного рассеивания и уровня микродеформаций от температуры осаждения пленок халькогенида.

1. Introduction

Nowadays II–VI films compounds are widely investigate because of their possibility of use in opto- and microelectronics, solar energy, etc [1]. At that for instrumental usage is necessary to have a layers with optimized structural parameters — monophase, with stable crystalline modification, low micro- and macrostress level, extensive and three-dimensional defects concentration, controlled stoichiometry.

Zinc selenide which owing to it's wide band gap (E_g = 2.7 eV) find an application as a "window" layer in solar cells, based material of of green-blue irradiation spectra light-diodes, filters, electrochemical cells, thin-film transistors, etc [1, 2].

For produce ZnSe thin films different authors used such methods of their obtain: cathode electrodeposition from water solution [3], vacuum evaporation of compound [4] or their components [5], close-spaced vacuum sublimation (CSVS) method [6–8], etc. Last method because of the construction features of evaporator allows to obtain the stoichiometric samples with well-controlled physical and technological process. Therefore the CSVS method was used for ZnSe films deposition. But structural and substructural characteristics of zinc selenide layers, obtained by this method, and the influence onto these layers of physical and technological condensation regimes are not well-studied. Thus in work [7] were studied by authors only ZnSe structural characteristics obtained at the room-temperature. More fundamental investigation was carried out in [6] where studied films obtained by a CSVS method at the substrate temperatures 473–623 K. But structural characteristics of ZnSe layers in works [6, 7] were determined by the archaic methods. So, the microstress level was discovered by authors [6] by the difference of the lattice spacing of the charge material and film, that is methodical irregular since parameter *a* in a great extent depends from the condensates stoichiometry. By the determine of the coherent scattering domain (CSD) size from X-ray graphs was used a Debye-Sherrer equation since was not took into info a presence in condensates microdeformations and stacking fault dislocation. Measuring of the lattice parameter and substructural characteristics of ZnSe films was carried out by authors [6, 7] by line (111) on less

angles that adduced to the considerable mistakes of the determine of these characteristics.

In this work was carried out a complex investigation of the structural and substructural properties of zinc selenide films, obtained in wide range of the substrate temperatures with using a modern methods of the X-ray graphs analysis.

2. Experimental details

Zinc selenide films were deposited by a CSVS method on well-cleaned glass substrates in vacuum equipment VUP-5M. Detail description of films deposition equipment is presented in [9]. The temperature of evaporator was T_e = 1073 K. Substrate temperature was varied in the range of: T_s = 373–973 K. Layer's time of deposition was t = 8–10 min. Film's thickness (d) was (6–8) μm.

Structural investigations of films were carried out by X-ray diffractometer DRON 4-07 in Ni-filtered K_α-irradiation of copper anode. The samples were measured in the continuous registration mode within the 2θ-angle range from 20° to 80°, where 2θ is the Bragg angle. A curves were normalized by the intensity of (111) peak of cubic phase. Phase analysis was estimated by a comparison of interplanar spacings and comparative intensities from investigated samples and standard by JCPDS data [10]. At measuring a focusing of X-ray irradiation by Bragg-Brentano was used.

Texture of the films chalcogenides was evaluated by the Harris method [11, 12]. Pole density was measured by equation:

$$P_i = \frac{(I_i/I_{0i})}{\frac{1}{N}\sum_{i=1}^{N}(I_i/I_{0i})}, \quad (1)$$

where I_i, I_{0i} are the integral intensities of i-diffraction peak for a film sample and standard; N is a number of lines on diffractogram. Orientation factor f was estimated by ratio: $f = \sqrt{\frac{1}{N}\sum_{i=1}^{N}(P_i - 1)^2}$. As a standard of non-textured samples a ZnSe powder was used.

Precision determine of the ZnSe lattice constant was carried out by the location of $K_{\alpha 1}$ constituent of X-ray lines. Chalcogenide lattice constants were measured by Breadly-Jay and Nelson-Riley extrapolation methods [11, 12]. For dots approximation was used the least — squares method. The division of K_α doublet was carried by Rechinger method using the program package DIFWIN, which applies to DRON 4-07.

Results of diffractometrical investigations were also used for estimate of the average size of the CSD (L), microstress level (ε) in films by the halfwidth of lines.

For a division of the diffraction widening due to physical and instrumental effects were used the approximations of the X-ray line profile by the Gauss and Cauchi functions. Further contribution's division from CSD size and microdeformation dispersion was carried out by the Hall graphic method because of their different dependence of the diffraction angle. Were built graphs in position data: $\beta \cos\theta/\lambda - (4 \sin\theta/\lambda)$ and $(\beta \cos\theta/\lambda)^2 - (4 \sin\theta/\lambda)^2$, where β is a physical widening of X-ray line; λ is a wavelength of X-ray. Besides that the microdeformations and CSD sizes were estimated by approximation method with rendering the X-ray line of the functions threefold convolution [11–13].

3. Results and discussion

Obtained ZnSe films had a polycrystalline structure and consisted of crystallites, their size in the layer area (plane) was increased at increasing of the condensation temperature analogue to another condensates chalcogenides. More detailed growth mechanism of polycrystalline II–VI films compounds onto non-oriented substrates and an influence of condensation temperature on their surface morphology were described in works [9, 13, 14].

Diffractograms of zinc selenide films obtained at different substrate temperatures present on Fig. 1a. As a rule on the diffractograms were registered reflections from crystallography areas (111), (200), (220), (311), (400), (331), (420) of zinc blend phase (sphalerite). Dominant by intensity was reflection from area (111) that says about the presence in films texture [111]. With zinc blend phase in pattern in low number was presented a hexagonal phase (wurtzite). Except there took place a presence on diffractograms of weak reflections from area (101) of wurtzite on angles 29.08–29.33°. As a rule a relative intensity of according peak ($I_{(101)W}/I_{(111)Zb}$) on diffractograms was (0.7–3.3) % is bigger by increasing of condensation temperature and decreasing of film thickness. Thickness dependence of peak intensity says about gen-

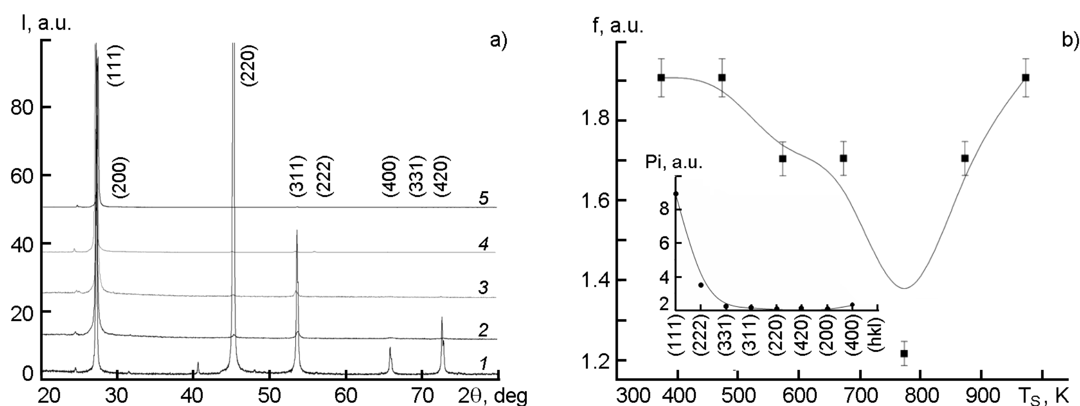

Fig. 1. Diffractograms of ZnSe films obtained at different substrate temperatures: *1* — charge; *2* — 373 K; *3* — 473 K; *4* — 673 K; *5* — 873 K (a) and dependence of orientation factor from substrate temperature (b). On insertion resulted measuring of the pole density for film obtained at T_s = 573 K.

erally placing of present phase in junction of microcrystalline layer of film near the substrate.

For evaluation of the cubic phase texture quality were measured us a pole density and orientation factor of ZnSe films. It was confirmed about the presence of well-marked [111] axial texture (insertion on Fig. 1b). This texture is typical for ZnSe films obtained by vacuum methods [4–7]. It was determined that a dependence of orientation factor for area (111) f versus films condensation temperature T_s has a difficult view (Fig. 1b). As we can see on figure perfection of ZnSe films texture is some worsened at T_s ~ 780 K. It may to explain about change of the film's growth mechanism from layer-wise to columnar. It should be noted that such results were obtained us [9, 13, 15] and another authors [16] for CdTe, ZnTe and ZnS films obtained by the same condensation method.

A lattice constant of II–VI compounds is a characteristic which is extremely sensitive to stoichiometric change of the material, dash impurity, oxidation, etc. Therefore a precision determine of the lattice constant gives an opportunity to study these processes. Was carried out us X-ray diffractometrical determination of the charge lattice constant from which was estimated evaporation, and of ZnSe films obtained at different condensation regimes. It was estimated that a results obtained using the Breadly-Jay and Nelson-Riley methods were similar (Fig. 2). But since the last method is more precise, later on discussed a results obtained exactly by this method.

It was estimated that cubic phase of ZnSe charge has a lattice constant which is a = 0.56661 nm. At the change of condensa-

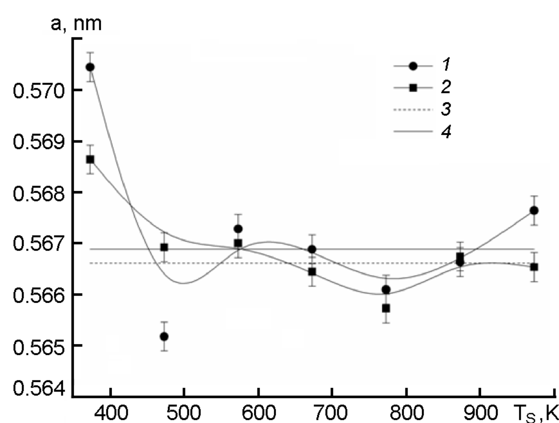

Fig. 2. Lattice constant versus condensation temperature dependence of ZnSe films. *1* – Method Breadly-Jay; *2* – Method Nelson-Riley; *3* – charge; *4* – JCDPS.

tion temperature the lattice constant of sphalerite phase of the films was changed in the range of $a = (0.56557 \div 0.56864)$ nm. These results are well-correled with data, presented in JCDPS for massive material a = 0.56688 nm [10] and the experimental data a = (0.566–0.571) nm obtained by the line (111) for films deposited by a CSVS method [6]. As we can see on Fig. 2 the dependence of the lattice constant from condensation temperature had a difficult view. At that a view of dependences obtained by Breadly-Jay and Nelson-Riley methods were similar. It's may be explain about a change of compound stoichiometry owing by their non-congruent evaporating.

By line (101) it is may to measure a lattice constant of the hexagonal phase which has a small number in patterns. These values lied in the range of $a = (0.3975 \div 0.3982)$ nm and

Table 1. ZnSe films substructure characteristics

T_s, K	L, nm			$\varepsilon \cdot 10^3$		
	approximation by		Threefold convolution	approximation by		From convolution
	Gauss	Cauchi		Gauss	Cauchi	
charge	55.53	65.83	70.09	1.26	0.45	1.27
373	48.67	54.84	40.92	3.61	1.53	0.55
473	42.30	65.93	39.68	3.35	2.85	1.12
573	39.73	85.25	63.80	2.34	1.92	2.04
673	50.91	122.55	76.02	2.45	2.03	1.88
773	96.57	193.79	88.84	2.49	1.96	2.32
873	37.12	44.66	76.53	1.19	1.02	1.39
973	59.20	89.61	64.37	2.29	1.52	1.94

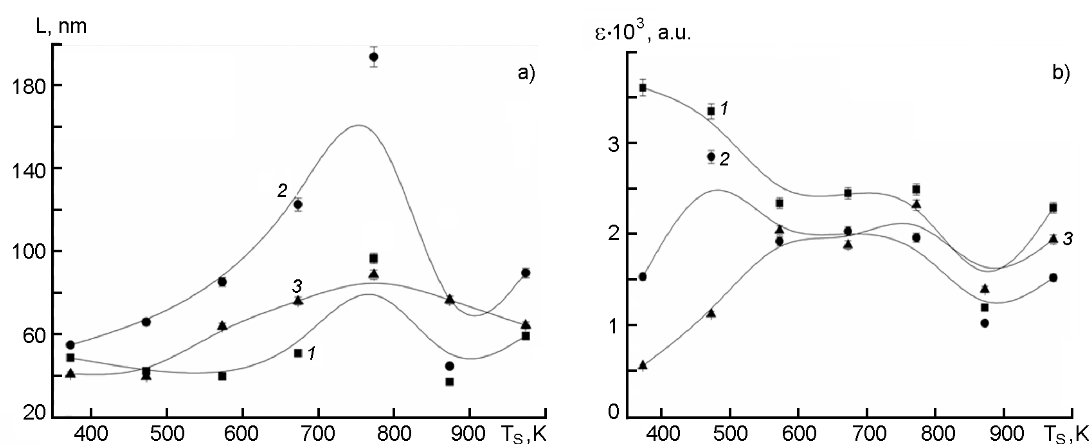

Fig. 3. Dependences of CSD size (a) and microdeformation level (b) from condensation temperature. *1* – Gauss; *2* – Cauchi; *3* – from convolution.

c = (0.6503÷0.3982) nm for films, obtained at different substrate temperatures. It should be noted that obtained values are some smaller than presented in JCPDS for massive samples: a = 0.4003 nm, c = 0.6540 nm [10].

In compliance with the method stated in [9, 13], X-ray diffractometrical values were also used for investigations of charge and ZnSe films substructure by a widening of the diffraction peaks (111)–(222) of cubic phase. It was accepted that a physical widening of lines is caused as a subgrains disperse also presence of microdeformations, then it has a possibility to measure the CSD size and microdeformation level. It should be noted that a precise of measuring of these values by three-fold convolution functions is no more less then 11–16 % in dependence of X-ray investigation conditions, at the same time that an experimental mistake at using the Hall method may to achieve 30–50 % [9].

Corresponding to the results of L and ε measuring with using the presented methods were systematized in Table 1. As we can see from the Table 1 the values of films substructure parameters obtained using the different approximations are well-correled each other as it's may be from the theoretical view. It shows about the reliable of obtained results.

CSD size versus T_s dependences in the direction which is perpendicular to the atomic planes (111) and the microdeformation level in this direction obtained using the three different approximations shown on Fig. 3.

Since the values of substructure parameters of ZnSe films were measured from three-fold convolution are more less precise and similar to real, further discuss of the results were being by these methods. Therefore it needs to check that a regularity of change of L, ε versus T_s were typical using

Table 2. Microstress and dislocations density in ZnSe films

T_s, K	L, nm	$\varepsilon \cdot 10^3$	σ, 10^{-8} Pa	ρ_L, 10^{-14}, lin/m^2	ρ_ε, 10^{-14}, lin/m^2	$\rho_{L\varepsilon}$, 10^{-14}, lin/m^2
charge	70.09	1.27	1.05	6.1	0.63	1.5
373	40.92	0.55	0.46	18.0	0.12	1.1
473	39.68	1.12	0.93	19.0	0.05	0,71
573	63.80	2.04	1.69	7.4	1.6	2.6
673	76.02	1.88	1.56	5.2	1.4	2.0
773	88.84	2.32	1.93	3.8	2.1	2.1
873	76.53	1.39	1.15	5.1	0.76	1.5
973	64.37	1.94	1.61	7.2	1.5	2.4

three methods of determination the films substructure parameters.

As we can see on Fig. 3 at increasing of T_s CSD size in direction which is perpendicular to (111) planes in films chalcogenides at first increase from L ~ 40 nm to L ~ 89 nm, further decrease to L ~ 64 nm. It's present an optimal temperature range (T_s = 750–850 K) where this size is maximal. So the microdeformation level in this direction at first some increase from $\varepsilon \sim 0.55 \cdot 10^{-3}$ to $\sim 2.32 \cdot 10^{-3}$, then some decrease to $\sim 1.94 \cdot 10^{-3}$ by increasing of T_s.

At the well-known values of microdeformations (Table 1) was measured microstress level (σ) in ZnSe films. At that for all further investigations were used films substructure parameters determined by threefold convolution method as more precise. At the measuring of microstresses a value of Young module E = 83 GPa was used. Measuring of E was estimated us by the values of flexibility c_{ij} ($c_{11} = 8.10 \cdot 10^{10}$ Pa, $c_{12} = 4.88 \cdot 10^{10}$ Pa, $c_{14} = 4.41 \cdot 10^{10}$ Pa) presented in [1].

It was estimated that microstresses in patterns were varied in the range of σ = 46–193 MPa. Maximum values σ = 193 MPa was proved essential less by the value then estimated by X-ray method by difference of lattices in films and in massive material in [6] (σ = 870 MPa) in ZnSe condensates deposited by a CSVS method at T_s = 473–623 K. It should be noted that method of obtain σ by authors [6] is doubtful since it not takes into account change of the lattice in films by change of their stoichiometry, dash impurity, etc.

CSD size in investigated us films (L = 40–89 nm) was more than found in [7] by the widening of (111) X-ray line (L = 2.95–47.55 nm) in films with different thickness (d = 0.13–0.85 μm) deposited by a CSVS method at T_s = 573 K. It is also should be noted that obtained in [7] values of L are overpriced since authors considered that a widening of X-ray lines caused only by disperse of the films microstructure. The results of investigations of ZnSe films substructure shows about their more large structure perfection comparatively with condensates obtained by a CSVS method by another authors.

It is well-known that sub-boundaries of blocks formed by dislocations, situated on their boundaries simultaneously dislocations are arranged inside CSD volume, brang to arise in material microdeformations. It's may to estimate the average dislocation density in ZnSe films by the microdeformations value ε and CSD size L. Corresponding ratios for determine averaging-out by pattern dislocation density that formed boundaries and situated in subgrains presented in [6, 17]. Some another ratios for estimate the general dislocations concentration in material which simultaneously takes into account as value L as ε, presented in [18]. A results of the average dislocations density measurements in ZnSe films using the presented ratios presented on Table 2. These values in border by order are well-correled each other. As we can see films characterized by some low (see as example [5] where $\rho = (0.33–2.57) \cdot 10^{15}$ lin/m^2 and [6] where $\rho = (1–35) \cdot 10^{15}$ lin/m^2) dislocations concentration which in general concentrate on CSD boundaries. Since dislocation have a well recombination centres, polycrystalline films with depressed concentration of the defects may be used as basis layers of devices with improved characteristics.

4. Conclusions

Was carried out a complex investigation of structural and substructural properties of the zinc selenide semiconductor films obtained by a CSVS method at the different substrate temperatures. It was estimated than the films were monophase, have a stable zinc blend modification. Besides that in all cases well expressed texture [111] was observed. Was revealed a dependence of orientation factor, lattice constant, CSD size and microdeformation level from deposition temperature.

It was estimated that dependence of CSD size from condensation temperature has a view of curve with maximum, and the microdeformation level in most cases was decreased at the increasing of T_s. By the value of microdeformation ε and CSD size L was carried out an evaluation of the medium dislocation density in ZnSe films crystallines, which generate a boundaries and situated inside subgraines. It was established that films are characterized by the low concentration of dislocation density, which in general amass on the CSD size boundaries. Polycrystalline ZnSe films with low dislocations concentration obtained by a CSVS method may be used as basis layers of devices with improved characteristics.

References

1. S.Kasap, P.Capper, The Springer Handbook of Electronic and Photonic Materials, Springer, Berlin (2007).
2. M.Ohring, The Materials Science of Thin Films, Academic Press, New York (1992).
3. A.Moses Ezhil Raja, S.Mary Delphineb, C.Sanjeevirajac, M.Jayachandrand, *Physica B: Phys. Condens. Matter*, **405**, 2485 (2010).
4. S.Venkatachalam, Y.L.Jeychandran, P.Sureskumar et al., *Mater.Charact.*, **58**, 794 (2007).
5. S.Venkatachalam, D.Mangalaraj, Sa K.Narayandass et al., *Vacuum*, **81**, 928 (2007).
6. Y.P.Vencata Subbaiah, P.Pratap, M.Device, *Phys.B*, **365**, 240 (2005).
7. G.I.Rusu, M.Diciu, C.Pirghie, *Appl.Surf.Sci.*, **253**, 9500 (2007).
8. G.I.Rusu, M.E.Popa, G.G.Rusu, *Appl.Surf. Sci.*, **218**, 222 (2003).
9. V.Kosyak, A.S.Opanasyuk, P.M.Bukivskij et al., *J.Cryst.Growth*, **312**, 1726 (2010).
10. Selected Powder Diffraction Dats for Education and Training (Search Manual and Data Cards), USA (1988).
11. B.E.Warren, X-Ray Diffraction, Dover, New-York (1990).
12. D.K.Bowen, K.Brian-Tenner, X-Ray Metrology in Semiconductor Manufacturing, Taylor&Francis Group, Oxford (2006).
13. D.Kurbatov, H.Khlyap, A.Opanasyuk, *Phys. Stat.Sol(a)*, **206**, 1549 (2009).
14. D.Kurbatov, V.Kosyak, M.Kolesnyk et al., *Integrated Ferroelectrics*, **103**, 32 (2009).
15. S.M.Danylchenko, T.G.Kalinichenko, M.M.Kolesnyk, A.S.Opanasyuk, *Visnyk Sums'kogo Dergavnogo Universytetu*, **1**, 115 (2007).
16. Luschitz, B.Siepchen, J.Schaffner et al., *Thin Solid Films*, **517**, 2125 (2009).
17. L.S.Palatnik, M.Ja.Fuks, V.M.Kosevych, Formation Mechanism and Substructure of Condensed Films, Nauka, Moscow (1972) [in Russian].
18. T.Mahalingam, V.S.John, G.Ravi, P.J.Sebastian, *Cryst Res.Technol.*, **37**, 329 (2002).

Структура та субструктура плівок селеніду цинку

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Досліджено характеристики структури та субструктури шарів селеніду цинку. Встановлено залежність структурного фактору, сталої гратки, розміру областей когерентного розсіювання та рівня мікродеформацій від температури осадження плівок халькогеніду.