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Preparation and Optical Properties of ZnSe Films

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Microwave method was applied for the synthesis and purification of the initial ZnSe salt. The obtained powder was used for the deposition of ZnSe thin films on the ultrasonically cleaned glass substrates by the method of thermal evaporation in quasi-closed volume under the following conditions: the constant evaporation temperature T_e = 800 °C, the substrate temperature T_s = 100-600 °C. Investigation of the optical characteristics allows to calculate the band gap of condensates and specify their phase composition.

Keywords: Zinc selenide, Microwave synthesis, Film, Structure, Optical characteristics.

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1. INTRODUCTION

Production of light-emitting diodes for the visible and, especially, ultraviolet spectral regions is an actual problem of semiconductor optoelectronics. Zinc selenide – wide band-gap semiconductor material – is one of the most promising materials for use in such devices [1]. Moreover, ZnSe is also applied in micro-, opto-, and acoustoelectronics as the base layers of detectors of different radiation types [2-5].

Recently, wide band-gap ZnSe (ZnS) compounds attract heightened attention of researchers as an alternative CdS material for windows of thin-film solar cells (SC) on the basis of absorbing layers CIS ($CuInSe_2$), CIGS ($CuGaSe_2$) [6], $Cu_2ZnSnSe_4$ (CZTSe), Cu_2ZnSnS_4 (CZTS) [7-8]. Zinc selenide (E_g = 2,67 eV) has larger band gap width than CdS (E_g = 2,42 eV) that allows to expand the range of photosensitivity of transducers and increase their short-circuit currents [9]. Moreover, it agrees rather well with the specified absorbing layers by the lattice constant that is the key condition of the production of heterojunctions close to the perfect ones by their electrical properties [10]. It is important from the ecological point of view that ZnSe is non-toxic ("Cd-free") material because of the absence of heavy metals in the composition.

Efforts of scientists led to the fact that, for example, coefficient of efficiency of SC based on heterojunction ZnSe/$Cu(In,Ga)Se_2$ is equal to 15,7% at present that is close to the efficiency of photo-transducers with CdS window (20,1%) [11]. However, further decrease in the production cost of both absorbing and buffer layers is necessary for a large-scale application of SC with ZnSe window.

As a rule, ZnSe films for instrument use are deposited by vacuum evaporation of charge obtained by the grinding of monocrystalline material [12-13]. This considerably increases the cost of layers, since in order to obtain monocrystals of semiconductor purity one needs high synthesis temperatures (> 1500 °C), pressure of inert gas in the growth chamber 10-100 atm., complex growth equipment, ultrapure initial components [14]. In connection with this, alternative methods of production of ZnSe films are developed fast: by evaporation of compound components [15], chemical synthesis of material from solution [16], electrochemical synthesis [17], etc.

The aim of the present work was the synthesis of the initial ZnSe charge by the microwave (MW) method that allows to realize it at normal atmospheric conditions; production of polycrystalline compound films of high purity from charge; investigation of the structural and optical properties of the obtained condensates.

2. INVESTIGATION TECHNIQUE

2.1 Synthesis of zinc selenide powder

To realize interaction of the initial components in the production of zinc selenide powder, the proper design of single-mode device of MW synthesis was developed; it allows to vary the radiation power within the range of 0,1-1,2 kW (generation frequency 2,45 GHz). Stoichiometric mixture of Zn and Se of the total mass of 10-15 g was put into quartz tube sealed from one end. Quartz tube with the mixture was placed into the MW device. Synthesis was performed in air. Power of the microwave radiation was equal to 0,5 kW and the exposure time – 5 minutes. After irradiation sample was cooled to room temperature and taken from ampule. The obtained precursor was annealed in vacuum ($P = 10^{-2}$ Torr) at the temperature of 800 °C during 1 hour and then cooled to room temperature. The annealed powder was used for the film deposition.

2.2 Production of ZnSe films

ZnSe films were produced on the cleaned glass substrates in the vacuum plant VUP-5M. The method of thermal evaporation in quasi-closed volume [18] was applied for their deposition. The evaporator temperature was equal to T_e = 800 °C. The substrate temperature varied in the range of T_s = 100-600 °C. The deposition time was 10 minutes.

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2.3 Equipment for the investigation

Investigation of the surface morphology of powders and films was carried out using the scanning microscope JSM-6390LV.

Diffractometer Siemens D500 was applied for the X-ray phase analysis of the synthesized powders. Investigations were performed in copper radiation with graphite monochromator in secondary beam. Full-profile X-ray diffraction patterns are measured in the angle range of $10° < 2\theta < 90°$, where 2θ is the Bragg angle, with the step of 0,02 and storage time of 10 sec in each point.

Structural investigations of the grown films were performed on diffractometer DRON-4-07 in Ni-filtered K_a-radiation of copper anode. Survey was carried out in the angle range of 2θ from 20° to 80°. Focusing of the X-ray radiation by Bragg-Brentano was applied in the investigations. Diffraction patterns were normalized on the peak (111) intensity of the cubic phase.

Phase analysis of the structure of powders and films was realized by the comparison of the interplanar spacings and relative intensities of the X-ray peaks from the studied samples and etalon by the JCPDS data [19].

To obtain precision values of the lattice constant of material we have used the Nelson-Reilly extrapolation method [20]. Linear approximation of the found points was realized by the least square method.

Infrared spectra from the synthesized powders in the form of pressed tablets were obtained on the Fourier IR-spectrophotometer SPECTRUM ONE (Perkin Elmer).

Measurement of the optical characteristics of the produced condensates was realized by spectrophotometer SF-26 in the wavelength range of $\lambda = 360$-1200 nm. Spectral dependences of the reflection $R(\lambda)$ and transmission $T(\lambda)$ coefficients were taken. The add-on PZO-2, which provided double reflection of light from the surface of experimental samples during survey, was used in order to obtain the $R(\lambda)$ spectra.

3. RESULTS AND DISCUSSION

3.1 ZnSe synthesis

In Fig. 1 we show the results of the X-ray analysis of ZnSe precursor synthesized in the microwave field at the solid-phase interaction of zinc and selenium in air and of the same powder annealed in vacuum. According to the diffractometer investigations, obtained samples were the polycrystalline ZnSe with cubic lattice whose period was equal to $a = 0{,}56661 \pm 0{,}00002$ nm. Reflections, which belong to the hexagon phase of zinc oxide and pure zinc, were also fixed on the diffraction patterns from freshly synthesized samples along with the main reflections typical for zinc selenide. Lines of ZnSe cubic modification only were observed for the samples after thermal annealing in vacuum.

The absorption bands in the region of 3650-3100 cm^{-1} with the maximum at 3420 cm^{-1} and of 1550-1700 cm^{-1} with the maximum at 1620 cm^{-1}, which correspond, respectively, to the valence and deformation vibrations of water molecules are present in the IR-spectrum of ZnSe precursor (Fig. 2a). The weak absorption in the region of 1500-1300 cm^{-1} with the maximum at 1382 cm^{-1}, absorption in the region of 1200-1000 cm^{-1} with the maximum at 1100 cm^{-1} and weak peak at 490 cm^{-1} are also observed. The presence of the absorption band at 490 cm^{-1} is determined by the vibrations of Zn-O bonds [21, 22]; absorption in the region of 1200-1000 cm^{-1} is connected with the presence of SeO_3^{2+} ion [23].

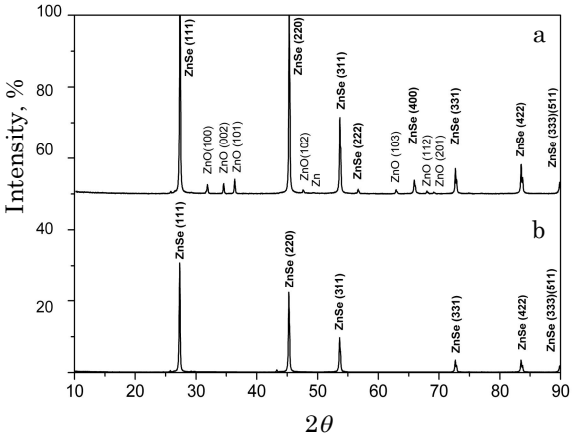

Fig. 1 – X-ray patterns of ZnSe precursor directly after MW synthesis of elements (a) and after annealing in vacuum (b)

Absorption in the region of 1500-1300 cm^{-1}, to our opinion, is connected with the presence of the oxygen-containing impurity; however, we could not identify it by the absorption bands.

Absorption bands connected with the presence of the oxygen-containing impurities were not fixed in the IR-spectra of the annealed samples (Fig. 2b). Thus, vacuum annealing allows to purify the synthesized ZnSe from impurities of zinc oxide, zinc, and selenium.

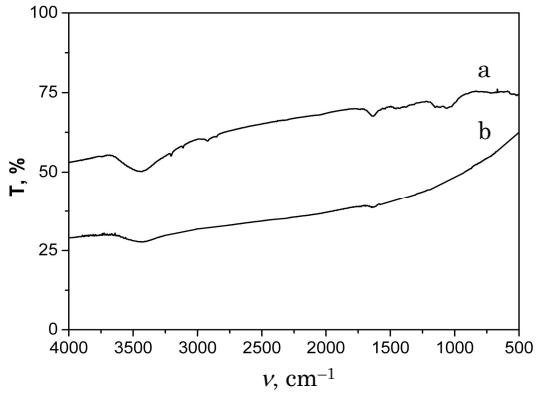

Fig. 2 – IR-spectra of ZnSe precursor after MW synthesis of elements (a) and after annealing in vacuum (b)

3.2 Deposition of ZnSe films

In Fig. 3 we show the micrographs of ZnSe films obtained at different physical and technological deposition conditions. At the substrate temperature of 100 °C film has a highly dispersed structure. With the increase in the substrate temperature T_s up to 350 °C, increase in the crystallite size to 0,2-0,5 μm is observed. Films obtained at $T_s = 450$ °C are mainly formed by spherical particles of the diameter of 0,2-0,5 μm. At further increase in T_s crystallites in the films are grinded that is connected with the decrease in the condensate thickness due to the secondary re-evaporation of material

from the substrate. As we have shown earlier [24], in this range of the condensation temperatures, grain size in the films of A_2B_6 compounds significantly depends on the substrate temperature.

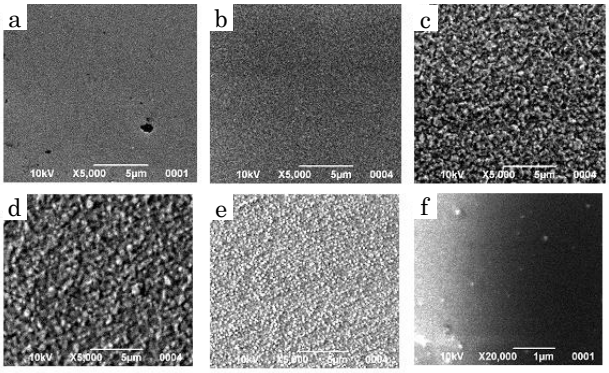

Fig. 3 – Micrographs of ZnSe films obtained on glass substrates at the evaporator T_e = 800 °C and substrate temperature T_s, °C: 100 (a), 200 (b), 300 (c), 250 (d), 350 (e), 500 (f)

Diffraction patterns from the ZnSe films obtained at different substrate temperatures T_s are illustrated in Fig. 4.

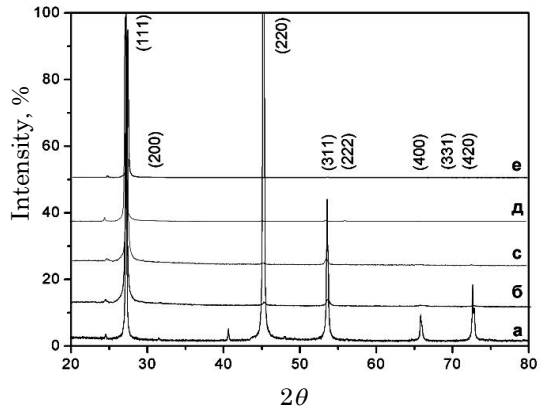

Fig. 4 – X-ray diffraction patterns of ZnSe films obtained at different substrate temperatures T_s, °C: 100 (a), 200 (b), 300 (c), 250 (d), 350 (e), 500 (f)

According to the analysis of the experimental data, all obtained ZnSe films had the cubic structure of the sphalerite-type with the lattice constant of a = 0,56572-0,56700 nm. Oxide and other foreign impurities are not fixed at the specified accuracy of the method.

3.3 Optical characteristics of ZnSe films

Spectral dependences of the reflection $R(\lambda)$ and transmission $T(\lambda)$ coefficients for the Investigated ZnSe films are represented in Fig. 5.

Study of the optical characteristics of the films has shown that layers had a sufficiently high transmission (~ 60-80%) in the visible spectral region up to λ > 490-500 nm, which then decreased to the ultraviolet region corresponding to the band-to-band transitions in the compound. The coefficient of reflection of light from the condensates was changed in the range of 5-35% in the same spectral range.

Sufficiently high coefficients of specular reflection of the all investigated films are conditioned by their weakly expressed relief. Interference peaks presented on the reflection spectra of the films indicate the uniformity of layers by area.

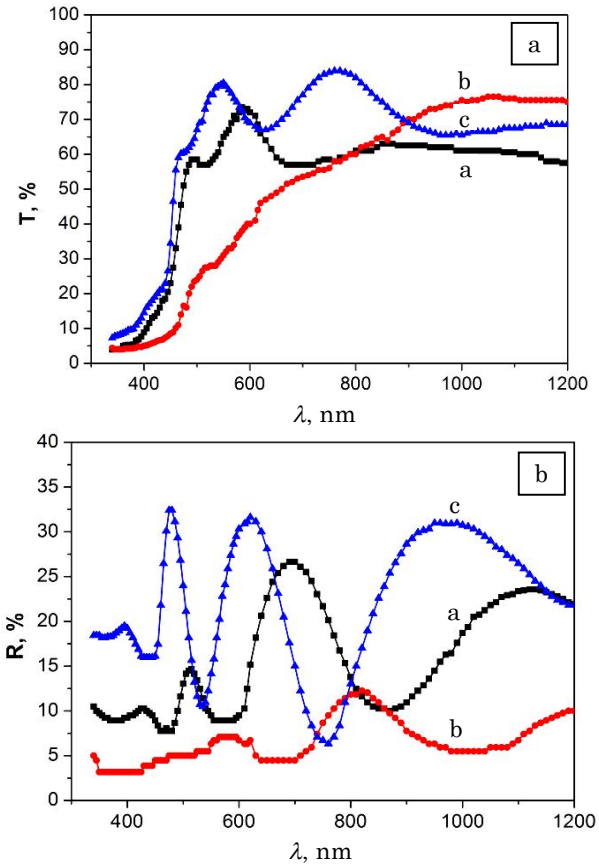

Fig. 5 – Transmission (a) and reflection (b) spectra of ZnSe films obtained at different T_s, °C: 100 (a), 250 (b), 500 (c)

To determine the band gap optical width E_g of film ZnSe, the following correlation was used [24]:

$$\alpha h\upsilon = A(h\upsilon - E_g)^{\frac{1}{2}}, \qquad (1)$$

where A is a some constant depending on the effective mass of charge carriers in material; $h\upsilon$ is the energy of optical quanta; α is the absorption coefficient of material.

As follows from (1), extrapolation of the linear part of the graph on the energy axis allows to define the band gap width of the investigated material. Absorption coefficients of the films with the thickness d at different wavelengths of the incident radiation were found by the transmission and reflection spectra using the folllowing relation [25, 26]:

$$\alpha = -\frac{1}{d}\ln\left(\frac{1}{R^2}\left(-\frac{(1-R)^2}{2T} + \sqrt{\frac{(1-R)^4}{4T^2} + R^2}\right)\right). \qquad (2)$$

Spectral dependences of the absorption coefficient of ZnSe films in the coordinates $(\alpha h\upsilon)^2 - h\upsilon$, which will be used in the sequel in order to determine the band gap width of material, are shown in Fig. 6.

Results of the measurement of the film thickness and band gap width of two-component compound are represented in Table 1.

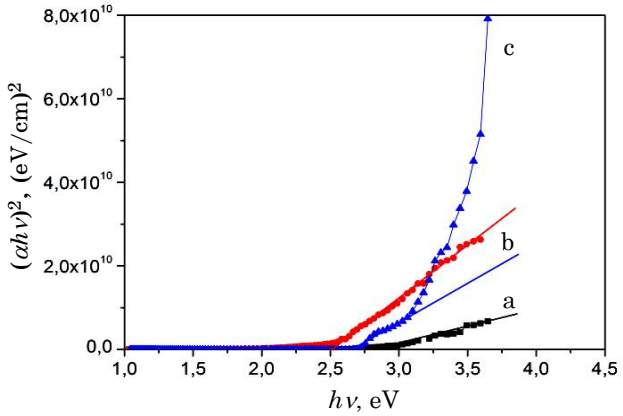

Fig. 6 – Determination of the band gap optical width of ZnSe films obtained at different T_s, °C: 100 (a), 250 (b), 500 (c)

Table 1 – Band gap width of ZnSe films obtained at different T_s

T_s, °C	d, μm	E_g, eV
100	2,0	2,61
200	5,0	2,62
250	1,0	2,60
350	1,0	2,61
450	0,7	2,60
500	0,7	2,63

We should note that the transitions typical for zinc oxide (E_g ~ 3,4 eV) were registered in the condensates obtained at high substrate temperature besides the transitions corresponding to the band-to-band transitions in ZnSe; this implies the presence of zinc oxide of small concentrations in the condensates [26].

4. CONCLUSIONS

The synthesis technique of ZnSe powder is developed and the possibility of the high-purity thin film formation from this powder by the method of thermal evaporation in quasi-closed volume is studied as well. The surface morphology, structure, and phase composition of the films synthesized at different substrate temperatures are investigated in the work. The absorption spectra and the values of the band gap width of ZnSe in the film state depending on the deposition temperature are calculated using the obtained spectral distributions of the transmission coefficients. It is established that ZnSe films of the cubic modification with a sufficiently high transmission coefficient (~ 60-80%) in the visible spectral region are formed during evaporation of synthesized charge and its condensation on glass substrates. Inclusions of oxide phase ZnO with small concentration (up to 3-5%) are registered by the optical method in high-temperature condensates.

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