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Effect of Chemical Treatment of the Surface on Optical Properties of ZnSe<Al> Substrates

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The influence of the surface morphology of single-crystal ZnSe<Al> substrates on the formation of their luminescence and absorption spectra was studied. It was established that the treatment of substrates in the chrome etchant Cr_2O_3:HCl = 2:3 leads to the formation of a mirror surface, and in a solution of the composition H_2SO_4:H_2O_2 = 3:1 – of matte. Analysis of the AFM-topograms of the mirror surface shows that the root-mean-square roughness does not exceed 0.6 nm, and such a surface can be considered an atomically smooth. AFM image of a matte surface is a set of smoothed pyramidal grains with lateral dimensions of 30-300 nm, and their maximum height reaches ~ 200 nm. Nanoclusters with an average lateral size of ~ 90 nm and a maximum height of ~ 27 nm are also observed on the surface of these substrates. In the luminescence spectra of samples with a surface nanostructure, in contrast to substrates with a mirror surface, the edge emission band and a wide U-band appear in the range of photon energies $\hbar\omega$ larger than the bandgap E_g of zinc selenide. In this case, the U-band is formed by the tops of small pyramidal grains, and its large half-width and lack of structure is due to the dispersion of the lateral sizes of these grains. It was found that the optical absorption edge of substrates with a mirror surface is described by the «crystalline» approximation of the Urbach rule, and the energy position of the focal point E_f is consistent with $E_g \approx 2.81$ eV of zinc selenide at 0 K. The behavior of the optical absorption edge of samples with a surface nanostructure obeys the «glassy» approximation of the Urbach rule, and its displacement with increasing temperature to the low-energy region occurs without a change in the slope. This is a consequence of static disordering, in contrast to samples with a mirror surface, for which dynamic disorder due to electron-phonon interaction dominates.

Keywords: Zinc selenide, Mirror and matte surfaces, Surface nanostructure, Luminescence, Absorption, Urbach rule.

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1. INTRODUCTION

Chemical processing of semiconductor substrates is, apparently, one of the most important and crucial operations when they are further used in research processes or the creation of electronic devices [1]. This is due to the fact that the composition of the solutions and the etching modes largely determine the condition of the treated surface – its morphology, degree of perfection, type and concentration of defects, the presence and composition of oxide layers, etc. For binary and more complex semiconductors, chemical treatment can also lead to a violation of the stoichiometry of the surface layers, which changes the nature of the electronic processes that determine the bulk physical properties of the material. The difficulties of predicting the dominant factors and their quantitative accounting require in each specific case experimental studies to identify the most characteristic links between the parameters of chemical treatment and the resulting surface.

The technologies leading to the formation of surface nanostructures (SNS) may be especially important and promising in this regard. The latter, practically without affecting the volume parameters of the material, can drastically change those characteristics of semiconductor substrates and devices based on them, which depend on the surface properties. First of all, this concerns optical processes, the nature of the flow of which is largely determined by the state of the surface of the samples used. In this paper, such questions are considered for zinc selenide, one of the most promising materials in modern optoelectronics [2].

2. SAMPLES AND RESEARCH METHODS

The base substrates were plates of $4 \times 4 \times 1$ mm^3, which were cut from a bulk ZnSe crystal grown from a melt of stoichiometric composition with the addition of 0.1 mole percent Al. After mechanical grinding and polishing, the plates were subjected to chemical etching in two different solutions. As a result of processing in the chrome etchant Cr_2O_3:HCl = 2:3, the surface of the substrates was visually perceived as a mirror (type 1), and in a solution of composition H_2SO_4:H_2O_2 = 3:1 – matte (type 2) [3]. Removal of etching products was carried out by prolonged (5-10 min) washing in boiling distilled water, and to remove a possible layer of ZnO by short-term (5-10 s) rinsing in concentrated acetic acid. As a result of the technologies used in both types of substrates, volumetric photoluminescence (PL) was observed, which was absent in samples that underwent only mechanical polishing.

The optical transmission T_ω and luminescence N_ω spectra were measured on a universal installation, containing an MDR-23 diffraction monochromator, an PEM-79 photomultiplier, and a halogen lamp and a N_2-laser $\lambda_m \approx 0.337$ µm. The optical absorption spectra α_ω

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were calculated using a simplified formula $\alpha_\omega \approx 1 - T_\omega$ and plotted in coordinates $\ln\alpha_\omega - \hbar\omega$, the choice of which was determined by the Urbach rule [4]. The transmission spectra were measured in the temperature range of 295-373 K. The surface morphology of the substrates was emitted using an NanoScope IIIa Dimension 3000™ atomic force microscope in the mode of periodic contact of a silicon probe with a nominal tip radius of ~ 10 nm.

3. RESULTS AND DISCUSSION

A fragment (1 × 1 μm) of the AFM-topogram of the surface of one of the type 1 samples is shown in Fig. 1a, and its profilograms – in Fig. 1b. Since the mean square surface roughness of this sample does not exceed 0.6 nm, it can be considered atomically smooth. After treatment in the etchant H_2SO_4:H_2O_2 = 3:1, the surface morphology of the substrates is significantly different from the type 1 samples discussed above.

This is illustrated in Fig. 2a, from which it can be seen that the AFM-image of a fragment (5 × 5 μm) of the surface of a matte substrate is a set of smoothed pyramidal grains, on which nanoclusters are distinguished. A detailed analysis of the profilogram shows that the lateral grain sizes for this sample vary within 30-300 nm, and their maximum height reaches ~ 200 nm. It should be noted that nanoclusters (see light points in Fig. 2a) are distributed over the surface of type 2 samples more or less evenly. In this case, the average lateral size of nanoclusters is ~ 90 nm, and the maximum height reaches ~ 27 nm, which is illustrated by a histogram of their distribution in height, Fig. 2b. Thus, we can assume that the surface of type 2 substrates, in contrast to type 1, is nanostructured, which should cause certain changes in their physical properties, including optical ones. In this connection, let us consider in more detail the effect of the morphological differences of the surfaces of the ZnSe<Al> substrates on the transformation of their luminescence spectra and optical absorption.

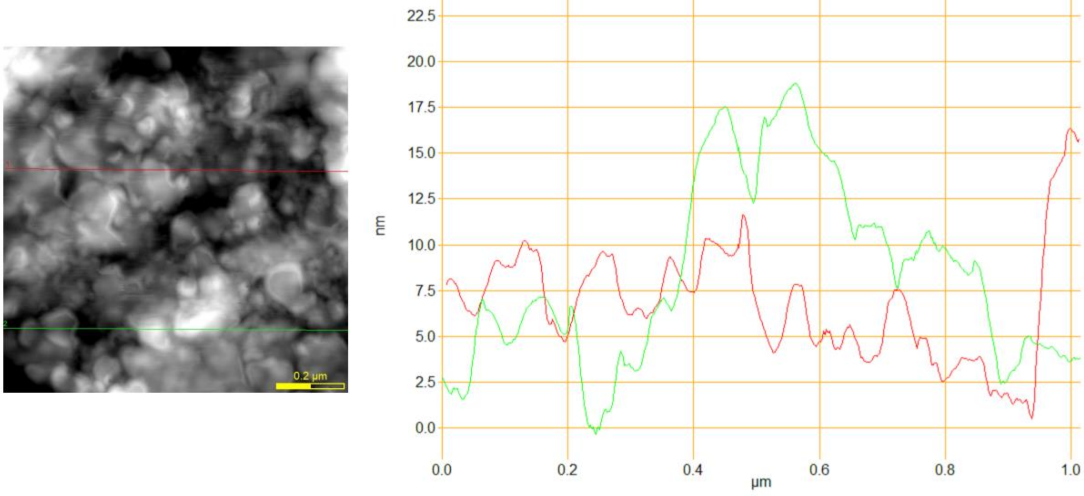
The discussion will begin with an analysis of the PL spectra, which are shown in Fig. 3 for both types of samples. It can be seen that the emission spectra of type 1 substrates are represented by a single U-band with a maximum near 2.1 eV. According to [5], it is caused by associates $\left(V''_{Zn}V^{\bullet}_{Se}\right)$ and $\left(V''_{Zn}Al^{\bullet}_{Zn}\right)$, the contribution of each is determined by many factors, like crystal growth and cooling modes, Al distribution along the ingot, level of excitation, etc. Here, the symbols denote: V''_{Zn} is a negative doubly charged zinc vacancy, $V^{\bullet}_{Se}$ is a positive single charge selenium vacancy, $Al^{\bullet}_{Zn}$ is a positive aluminum ion in the cation sublattice of ZnSe. At the same time, V''_{Zn} form deep acceptor, $V^{\bullet}_{Se}$ and $Al^{\bullet}_{Zn}$ are the shallow donor centers with energies $E_\alpha \approx 1.2$ eV and $E_d \approx 0.03$ eV, respectively [5]. We note two more features of the PL spectra of the ZnSe<Al> type 1 substrates. The first consists in the complete absence of edge radiation, which is not observed at 300 K even at the maximum level of excitation ($L \approx 10^{18}$ quantum/s). The second feature is the identity of the contours of the PL spectra of samples with specular, etched, and cleaved surfaces, which indicates a high surface recombination rate, which suppresses the edge luminescence of these samples.

Meanwhile, this radiation appears in type 2 substrates with a matte surface, and even at moderate L values, the B-band in Fig. 3. The position of its maximum $\hbar\omega_m$ correlates with the band gap of zinc selenide ($E_g \approx 2.7$ eV at 300 K [5]), and its large width indicates the complex structure of this band. Its identification and analysis require additional studies using modulation techniques and (or) low temperatures, which is beyond the scope of this work. At the same time, the presence of type 2 B-bands in the PL spectra indicates a significant decrease in the surface recombination rate, which, in our opinion, is a consequence of the SNS. This can be confirmed by the results of work [5], in which it was shown that such a SNS causes not only an enhancement of the edge radiation of CdTe substrates, but also a significant improvement in the physical and technical parameters of surface barrier diodes based on them.

The most interesting feature of the PL spectrum of type 2 substrates is the presence of photons in it with energies $\hbar\omega$ significantly higher than zinc selenide, the band in Fig. 3. Note that it cannot be caused by the formation of another chemical compound as a result of etching. This is confirmed by the similarity of the differential reflection spectra of not only the substrates of types 1 and 2, but also of samples with a cleaved surface. In this connection, it can be considered that the most likely reason for the appearance of the U-band in the PL spectra is the SNS, which was formed as a result of chemical etching in the H_2SO_4:H_2O_2 = 3:1 solution. Note that the picture of the surface of type 2 substrates is qualitatively consistent with the AFM-topograms of the surface of $Cd_{1-x}Mn_xTe$ substrates, in which SNS is formed due to self-organization processes [7]. A detailed study of the AFM-topograms of ZnSe<Al> type 2 substrates shows that their surface also consists of small (30-300 nm) pyramids, which are combined into large pyramids with lateral dimensions of 1-2 μm. In this case, the U-band is formed by the tops of small pyramids, and the absence of a structure in it is due to the dispersion of the sizes of these pyramids.

It should be noted that the large pyramids almost without taking part in the formation of the U-band significantly change the transmission spectrum due to the increasing role of scattering processes and multiple reflection of radiation. This leads not only to a decrease in absolute values of T_ω, but also to a shift of the short-wavelength edge of the transmission spectrum to the low-energy side [6, 8]. Since these effects are associated with structural changes in the surface, they must also be accompanied by a deformation of the so-called Urbach "tail," whose behavior in the objects of research will be considered in more detail.

Note that the empirical Urbach rule [4] is usually used to explain the exponential portions in the absorption spectra of various materials near the low-energy edge E_g. Meanwhile, in practice, two limiting cases of general exponential dependence are most often used, α_ω is the so-called «crystalline» and «glassy»



a b

Fig. 1 – Fragment of the AFM-topogram (a) and profilogram (b) of ZnSe<Al> type 1 substrates

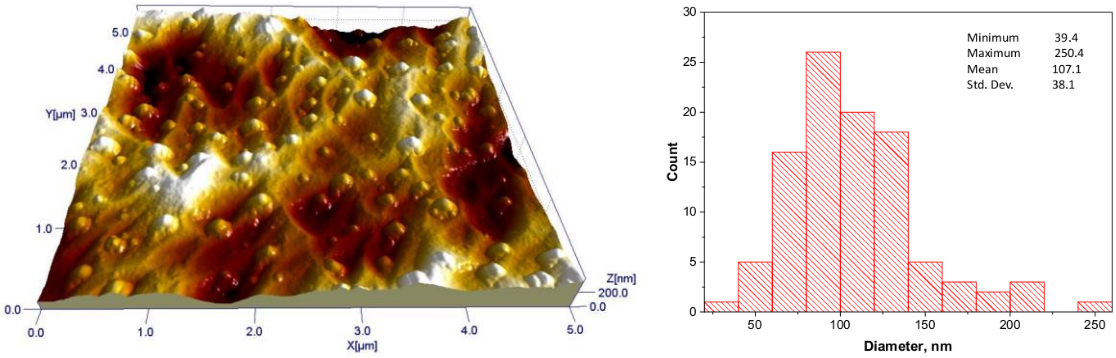


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Fig. 2 – Fragment of the AFM-topogram (a) and histogram (b) of ZnSe<Al> type 2 substrates

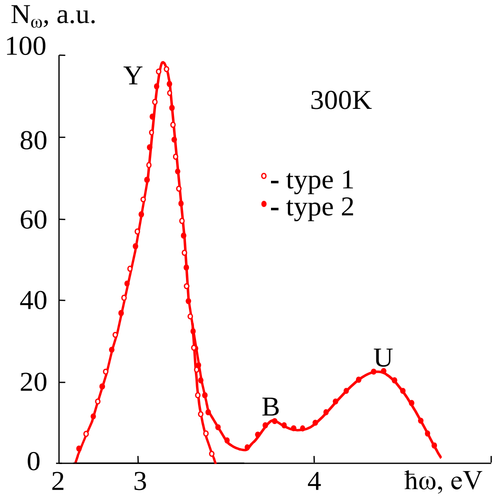

Fig. 3 – Photoluminescence spectra of ZnSe<Al> substrates with mirror and matte surfaces

approximations [10]. For the first one, the dependence $\alpha_{\omega,T}$ is described by the expression

$$\alpha_{\omega,T} = \alpha_{кр} \exp\left[\sigma\left(\hbar\omega - E_f\right)/kT\right], \qquad (1)$$

where

$$\sigma = \sigma_0\left(2kT/\hbar\omega_p\right) th\left(\hbar\omega_p/2kT\right), \qquad (2)$$

σ characterizes the temperature-dependent slope of the spectral characteristics, built in the $\ln\alpha_\omega - \hbar\omega$ coordinates; the meaning of the constant σ_0 is determined by the physical model used; $\hbar\omega_p$ is the effective phonon energy. The values α_{cr} and E_f are the coordinates of the focal point f, at which the spectral dependences of the absorption coefficient obtained at different temperatures are «converged».

As can be seen from Fig. 4, the behavior of the optical absorption edge of ZnSe<Al> type 1 substrates is well described by expression (1). At the same time, the experimental value of the parameter E_f was found to be 2.8 eV, which is consistent with the value of $E_g \approx 2.81$ eV of zinc selenide at 0 K [5]. The temperature dependence of the parameter σ is shown in the inset in Fig. 4, where the points correspond to the experimental values and the solid line is calculated by the formula (2). In the calculations, $\hbar\omega_p$ was assumed to be equal to the value of the highest-energy longitudinal optical phonon, which is ~30 meV for ZnSe [5]. The presence of the temperature dependence of the slope of the Urbach plots in the absorption spectra of type 1 substrates, as well as the agreement of the experimental and calculated values of the parameter σ,

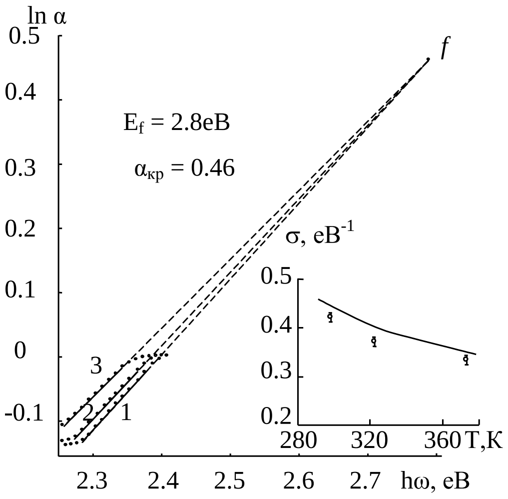

Fig. 4 – Absorption spectra of ZnSe<Al> type 1 substrates at different temperatures: 1 – 298, 2 – 323, 3 – 373 K. The inset shows the temperature dependence of the parameter σ. The points are the experiment, the solid line is calculated by the formula (2) at $\hbar\omega_p = 30$ meV and $\sigma_0 = 0.42$

indicate the predominant role of the dynamic disorder caused by the electron-phonon interaction.

In contrast to the above behavior of the absorption edge of type 2 samples, it is described by the «glassy» approximation of the Urbach rule [4]

$$\alpha_{\omega,T} = \alpha_{cm}\left[\hbar\omega / E_0 + T / T_0\right], \qquad (3)$$

where α_{cm} is a constant, T_0 is a certain characteristic temperature, and $E_0^{-1} = d(\ln\alpha)/d(\hbar\omega)$ is a temperature-independent slope of the spectral characteristic constructed in semi-logarithmic coordinates.

The experimentally observed shift of the absorption edge with increasing temperature to the low-energy region occurs without a change in the slope, i.e. parameter E_0^{-1} Fig. 5. This is a consequence of static disordering caused by the presence of SNS. Note that in this case, according to [4], the temperature dependence of the absorption edge should correspond to the temperature dependence E_g, i.e.

$$\hbar\omega(0) - \hbar\omega(T) = E_g(0) - E_g(T) = \beta T, \qquad (4)$$

$E_g(0)$ and $E_g(T)$ are the widths of the band gap at 0 and T K, respectively, $\beta = dE_g/dT$ is the temperature coefficient of its change in the linear region. The value of β is easily determined from the slope of the temperature dependence of the cut-offs $\hbar\omega_c$ on the energy axis at $\ln\alpha = 0$, which in this case is depicted as a straight line, inset in Fig. 5. Its slope was found to be $7.1\cdot10^{-4}$ eV/K and it is in good agreement with the known value for zinc selenide $\beta \approx 7.2\cdot10^{-4}$ eV/K [5].

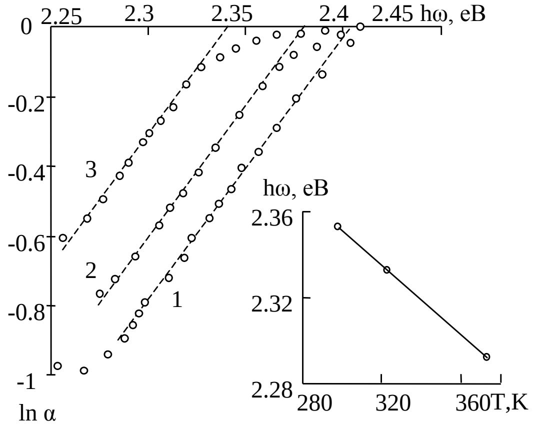

Fig. 5 – Absorption spectra of ZnSe<Al> type 2 substrates at different temperatures: 1 – 298, 2 – 323, 3 – 373K. Inset, the temperature dependence of the cut-off $\hbar\omega_c$ on the energy axis

4. CONCLUSIONS

Thus, the results presented in the paper indicate that it is possible to control the surface parameters of ZnSe<Al> substrates by chemical etching. It was found that treatment in a H_2SO_4:H_2O_2 = 3:1 solution causes the formation of a surface nanostructure, which is confirmed by AFM-topograms. The surface nanostructure leads to the appearance of an edge band and radiation in the energy region larger than the band gap of ZnSe, as well as to an increase in the contribution of static disordering to the formation of Urbach segments in the absorption spectra.

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Вплив хімічної обробки поверхні підкладинок ZnSe<Al> на їх оптичні властивості

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Досліджено вплив морфології поверхні монокристалічних підкладинок ZnSe<Al>на формування їх спектрів люмінесценції та поглинання. Встановлено, що обробка підкладинок у хромовому травнику Cr_2O_3:HCl = 2:3 приводить до утворення дзеркальної поверхні, а в розчині складу H_2SO_4:H_2O_2 = 3:1 – до матової. Аналіз АСМ-топограм дзеркальної поверхні показує, що середньоквадратична шорсткість не перевищує 0.6 нм і її можна вважати атомарно-гладкою. АСМ-зображення матової поверхні являє собою набір згладжених пірамідальних зерен з латеральним розміром 30-300 нм, а їх максимальна висота досягає ~ 200 нм. На поверхні цих підкладинок також спостерігаються нанокластери з середнім латеральним розміром ~ 90 нм і максимальною висотою ~ 27 нм. У спектрах люмінесценції зразків з поверхневою наноструктурою, на відміну від підкладинок із дзеркальною поверхнею, з'являється смуга крайового випромінювання і широка U-смуга в діапазоні енергій фотонів $\hbar\omega$ більших за ширину забороненої зони E_g селеніду цинку. При цьому U-смуга формується вершинами мілких пірамідальних зерен, а її велика півширина та відсутність структури обумовлені дисперсією латеральних розмірів цих зерен. Встановлено, що край оптичного поглинання підкладинок із дзеркальною поверхнею описується «кристалічним» наближенням правила Урбаха, а енергетичне положення фокальної точки E_f узгоджується з $E_g \approx 2.81$ еВ селеніду цинку при 0 К. Поведінка краю оптичного поглинання зразків з поверхневою наноструктурою підпорядковується «склоподібному» наближенню правила Урбаха, а його зміщення з ростом температури у низькоенергетичну область відбувається без зміни нахилу. Це є наслідком статичного розупорядкування, на відміну від зразків із дзеркальною поверхнею, для яких домінуючим є динамічний безпорядок, обумовлений електрон-фононною взаємодією.

Ключові слова: Селенід цинку, Дзеркальна і матова поверхні, Поверхнева наноструктура, Люмінесценція, Поглинання, Правило Урбаха.