INFLUENCE OF THE ORDER OF ION IMPLANTATION
ON LUMINESCENT SPECTRUM OF ZnSe NANOCRYSTALS†

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The paper presents the results of mathematical treatment of the luminescent spectra of ZnSe nanocrystals. The samples were formed by the implantation of 150 keV Zn^+ and 170 keV Se^+ ions in silicon dioxide layer obtained by oxidation of a silicon substrate. We analyzed two sorts of the samples obtained with different implantation sequences: Zn^+ were implanted first, and Se^+ implanted next (sample A); reverse sequence with Se^+ implanted at the beginning (sample B). The spectra obtained for different implantation sequences A and B differed from each other. It was found that besides the intensive evident bands with maxima at 2.3 eV (540 nm) and 2.85 eV (430 nm), which were associated with ZnSe intrinsic luminescent centers, there were two bands with maxima at 1.9 eV (650 nm) and 2.6 eV (480 nm), which were related to intrinsic SiO_2 defects. Hereby the effect of the medium (silicon dioxide matrix) on luminescent spectra of SiO_2 films with ZnSe nanocrystals formed by ion implantation was demonstrated. Mathematical treatment of the band shape with a maximum of 2.85 eV showed that the parameters such as full width at half maximum, skewness and kurtosis indicated the dependence of size distribution of ZnSe nanoparticles on the implantation sequence of ions. The results are in a good agreement with the data of Transmission Electron Microscopy.
Keywords: zinc selenide, ion implantation, luminescence spectrum, fitting by Gaussian functions.
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Progress of science and technology requires the creation of new functional materials with special properties to solve various technical problems. In recent years, semiconductors and optical elements based on selenides have been widely studied and used [1–3]. Much attention is paid to the properties of nanosized crystals of zinc selenide (ZnSe) (see, for example, [1–2, 4]).

Zinc selenide has unique optical properties, due to which it is used in modern optical and electronic devices [5]. For example, an optical fiber with a ZnSe core has significantly improved signal transmission at infrared and visible range of the spectrum [6]. There are quite a few ways to get zinc selenide crystals production. The formation of the ZnSe agglomerate was carried out chemically by the deposition of the reaction products between dimethylzinc, dimethylselenide and hydrogen in the pores of the optical fibers under high pressure. It should be noted that zinc selenide crystals are usually grown in medium that are chemically neutral to them. For example, ZnSe was grown by organometallic chemical vapor deposition on a GaAs substrate at 280°C [4] or by precipitation on a neutral substrate (teflon) after a chemical reaction [7].

For some scientific and technical problems, zinc selenide crystals are grown in the form of certain geometric shapes, namely, nanowires and nanorods. The results of growing ZnSe in the form of a nanowire by the method of "vapor-liquid-crystal" are presented in [8]. There are also other methods of obtaining nanocrystals of zinc selenides. They can be formed from zinc and selenium atoms, which are injected into the surface layer of the sample or epitaxial film by bombarding the surface with a beam of high energy ions of these elements. In [2, 9], ZnSe nanocrystals were formed from implanted zinc and selenium atoms in the SiO_2 layer, which was created by oxidation on the surface of a silicon substrate.

Luminescent technique is widely used method of studying dielectrics and semiconductors [10]. Experimentally obtained spectra carry information about the energy structure of a sample being studied and the presence of different types of defects. In addition, the size of crystals also influences the parameters of these spectra [1]. It causes the appearance of characteristic bands in the structure of the spectrum. Some bands may overlap due to close arrangements of their maxima or certain correlation of intensities, which does not allow visualizing the shape of the bands in the experimental spectrum. In this case, a special mathematical processing of experimental data is used allowing identi-fying details and features of the spectrum structure. In this sense fitting of spectra by Gaussian functions is an effective method [11]. In general Gaussian approximation, namely single Gaussian and mixtures of Gaussians are most popular probability models, and they are used for many applications (see [12] and references herein). A progress of Gaussian representation was made by T. Kato and coauthors [12] by development a new probability model, 'asymmetric Gaussian', which is an extension of usual Gaussian

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and describes spatially asymmetric distributions. As applied to the processing of spectra, this method is often used for decomposing into different emission bands by fitting Gaussian func-tions. For example, recent study of silica glass luminescence during low energy H^+, He^+ and O^+ irradiation performed at the 200 kV Ion Implanter was based on spectrum decomposition into four different emission bands by fitting Gaussian functions [13].

This paper presents the results of mathematical processing of photoluminescent spectra of ZnSe nanocrystals formed in an amorphous SiO_2 film by ion implantation [2].

MATHEMATICAL TREATMENT AND DISCUSSION

The nanocrystals of ZnSe was formed by sequential implantation of Zn^+ and Se^+ ions with energies of 150 and 170 keV, respectively, in the silicon dioxide matrix [2]. The energies of ions were chosen for reasons of maximum overlap of the concentration profiles of the implanted atoms. Both implantations of Zn^+ and Se^+ ions were done at the same fluence of 4×10^{16} ions/cm^2. The study was performed for two sets of samples with different implantation sequences: the first set (sample A) were implanted at first with Zn^+ ions and after that with Se^+ ions, the second set (sample B) was obtained by reverse order of implantation: at first with Se^+ ions and after that with Zn^+ ions.

For both samples, the photoluminescence spectra consisted of two broad bands with maxima of about 2.3 and 2.85 eV. The intensities of corresponding bands for the sample A were greater than for the sample B. To identify the structure of the spectra, we used the Gaussian fitting analysis of optical spectra (see, for example, [14]). Since luminescence is an equilibrium stochastic process, the probability of different electronic transitions is described by the Gaussian distribution function. Thus, it is important to perform the fitting of luminescent spectra represented in energy units. According to the chosen technique, the spectra were represented as the sum of several peaks, each of which is described by a Gaussian function.

The smallest error was achieved by the use of four Gaussians to fit the experimental spectra. The results of the processing for both samples are shown on Fig. 1. This procedure revealed, that in addition to ZnSe typical bands with maxima at 2.3 eV (540 nm) and 2.85 eV (430 nm), two more ones with maxima at 1.9 eV (650 nm) and 2.6 eV (480 nm) were found. The last two bands are associated with intrinsic silica defects [13]. Locations of the maxima of corresponding peaks are the same for both samples.

Bands with maximum at 1.9 eV corresponded to intrinsic silica defect such as non-bridging oxygen hole centers. One of the valence bonds of oxygen of such a defect has an unpaired electron: ≡Si-O●, where "≡" denotes three bonds, "●" — an unpaired electron [15]. The band with a maximum at 2.6 eV was associated with another intrinsic silica defect — oxygen deficient centers: ≡Si-Si≡ [15].

Thus, the analysis of the luminescent spectra of ZnSe nanocrystals allows obtaining information also about the medium in which they are formed — a layer of SiO_2 matrix on a silicon substrate. The luminescence was excited at room temperature by He-Cd laser at a wavelength of 325 nm. Such radiation effectively excites the luminescent centers of ZnSe nanocrystals [16]. It should be noted that although the SiO_2 layer is almost transparent to light with a wavelength of 325 nm, but the excitation of defects can take place on the "tails" of the absorption bands of silicon dioxide [17]. This explains relatively low intensity of the maxima.

Bands with maxima at 2.3 and 2.85 eV were associated with electronic transitions in ZnSe nanocrystals [2, 4, 8]. Their origin is connected with the presence of intrinsic crystallographic defects in the formed crystals, donors, acceptors and donor-acceptor pairs [2].

The luminescence intensity in the bands is proportional to the total number of ZnSe crystals that were created in the sample during implantation. The measured profiles of the distribution of elements by depth of penetration showed that there were areas where the concentration of one of the elements is greater than the other [2]. In these areas, a smaller number of ZnSe nanocrystals can be formed in comparison with the areas with the same concentration of both elements and, thus, the contribution to the total luminescence is also relatively smaller. The analysis of the measured profiles of element concentrations in both samples showed that in term of percentage ratio the area where the concentrations of elements coincide was larger for sample A than for sample B. Thus, the luminescence intensity of the first sample should be higher, which was confirmed by the spectra (see Fig. 1).

In addition to the factor of a medium, the shape of the luminescent spectra is also affected by the size of the nanocrystals, as suggested in [2]. As it was demonstrated earlier [1], the full width at half maximum (FWHM) of the band with a maximum at 2.85 eV is determined by the relationship between the size of ZnSe nanocrystals and the position of the maximum of the blue band luminescence. According to this work, the position of the maximum of the blue band depends on the size of the nanocrystals and shifts to the range of lower energies with increasing particle size (redshift). Thus, the shape of the blue band of the experimental spectrum is a superposition of the radiations from individual nanocrystals of different sizes. FWHM can allow finding qualitatively distribution of nanocrystals sizes.

In the case of sample A (Zn^+/Se^+ sequence of implantation), the blue band FWHM was 48 nm, for sample B (Se^+/Zn^+ sequence) — 51 nm. This indicates a larger variation in the size of the nanocrystals in the second sample. Such results are well confirmed by the data on the particle sizes obtained by electron microscopy [2]. In the case of initial implantation of Se ions, the layer of the formed clusters is thinner (150 nm compared to 200 nm for the case of initial implantation of Zn ions), and their size in the area of maximum concentration is larger (10–20 nm instead of 8–15 nm).

One of the methods of experimental luminescent spectrum analysis can be an analysis of curve shape deviation from Gaussian distribution function. Typically, such an analysis is performed by calculating such parameters of the

spectrum shape as skewness (A_s) and kurtosis (E_k) of the band [18]. Skewness and kurtosis as higher-order moments are widely used in modern data processing to analyze Gaussian distributions (see, for example [19]). Skewness characterizes the difference of the distribution shoulders (asymmetry) relative to its average value (Fig. 2). A positive skewness ($A_s > 0$) indicates a deviation of the distribution toward positive values (Fig. 2a). In our case, the positive skewness of the peak represented in energy units indicates a larger number of small particles. Negative skewness ($A_s < 0$) indicates a deviation of the distribution towards negative values (Fig. 2b), i.e. a larger number of nanocrystals of larger size compared to the average value for this distribution function [18].

Kurtosis characterizes the relative sharpness or planeness of the distribution peak (Fig. 2c). A sharp peak ($E_k > 3$) will indicate a strong nonuniform distribution of particle size relative to its average value; if maximum is flatter ($E_k < 3$), then size distribution is more uniform. Note that according to the definition, the Gaussian function has the following values of the parameters: $A_s = 0$, $E_k = 3$.
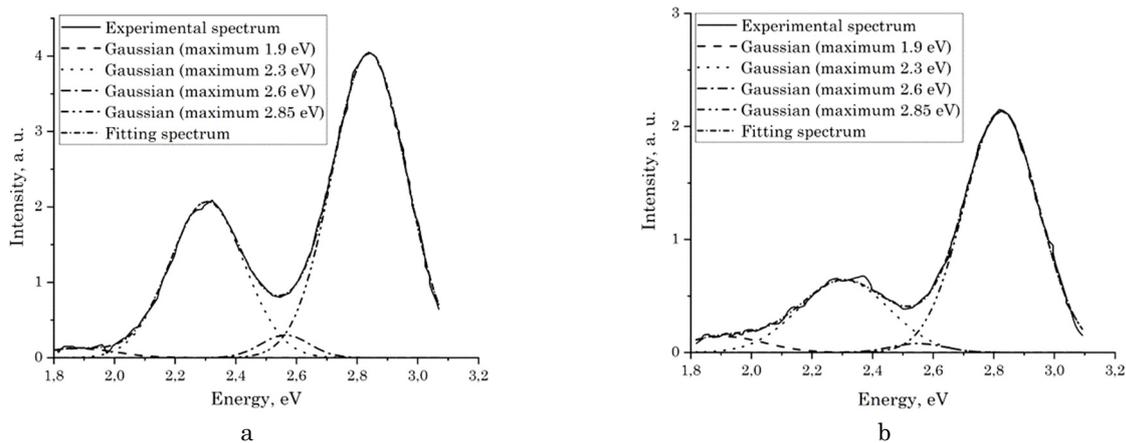

Figure 1. Luminescent spectra for samples A (a) and B (b):
experimental data [2] and calculated curves obtained by fitting with four Gaussian functions.

For samples A and B, the values of skewness in energy units are −0.40 and −0.48, respectively. The kurtosis is 2.33 for sample A and 1.84 for sample B. Fitting calculations were performed for the peak area where there was no effect of adjacent peaks.

Since the bands with a maximum at 2.85 eV were asymmetric and different in shape for samples A and B, the kurtosis and skewness being calculated allowed us to draw conclusions about the size distribution of nanocrystals.

For both spectra, the skewness was negative. It's larger modulo value in the case of sample B indicated the displacement of the spectrum wings toward red-wave direction (lower photon energies). It means a shift in the distribution of particles toward larger sizes. The flatter distribution, according to the calculated kurtosis, indicated that sample A had a narrower range of nanocrystal sizes than sample B. Such conclusions regarding the particle size distributions correlated well with the data obtained by electron microscopy, namely, 8–15 nm for sample A and 10-20 nm for sample B [2].
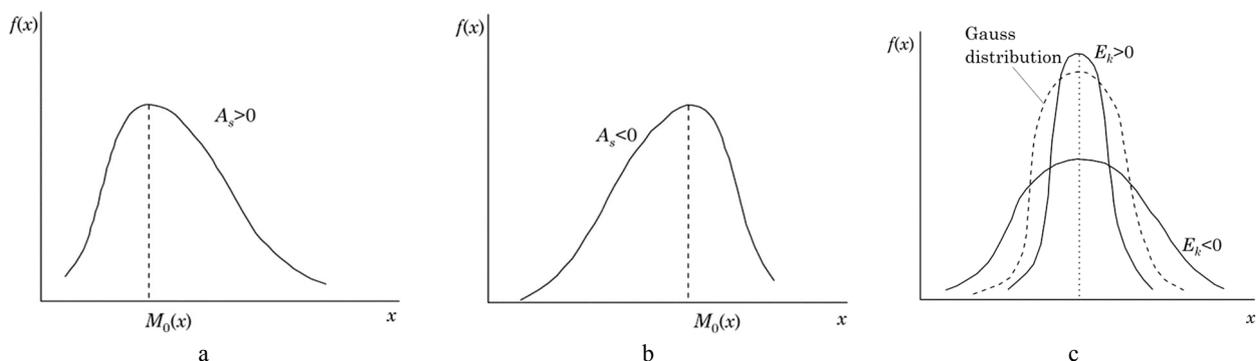

Figure 2. Illustration of definition of the terms that were calculated during the analysis of the deviation of the curve shape from the Gaussian distribution function: positive skewness (a), negative skewness (b), two different values of kurtosis (c).

CONCLUSION

The structure of the luminescent spectra of ZnSe nanocrystals in SiO_2 layer formed by oxidation on a silicon substrate was mathematically analyzed. Two cases of nanocrystal formation by sequential implantation of Zn and Se ions (two

different sequence of implantation: first Zn^+, then Se^+ and reverse one) were considered. Corresponding luminescent spectra, which differed slightly from each other, were treated by Gaussian fitting procedure. It was found that in addition to the intense bands with maxima at 2.3 eV (540 nm) and 2.85 eV (430 nm), associated with intrinsic ZnSe luminescent centers, there were two more bands with maxima of 1.9 eV (650 nm) and 2.6 eV (480 nm), corresponding to SiO_2 intrinsic defects, namely, non-bridging oxygen hole centre and oxygen deficiency center. Thus, an influence of the silicon dioxide matrix where zinc selenium nanocrystals were formed on luminescent spectra was shown.

The analysis of the measured profiles of element concentrations for both implantation sequences revealed that the luminescence intensity correlated with the number of ZnSe nanocrystals created in the samples.

Mathematical processing of the band with a maximum at 2.85 eV found that parameters such as full width at half maximum, skewness and kurtosis indicated narrower distribution in the size of ZnSe nanocrystals in the sample obtained by implanting first Zn^+ and then Se^+ ions, as compared with the case of the reverse order implantation. Such results are in a good agreement with the data from electron microscope.

Mathematical processing of the luminescent spectra of ZnSe nanocrystals allows one to obtain data on the size distribution of nanocrystals. It may also allow answering a question about a substance (matrix), in which the nanocrystals structures are formed. The results obtained can become the basis for an additional channel of information on nanocrystals for verifying finding measured by other methods.

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ВПЛИВ ПОРЯДКУ ЙОННОЇ ШМПЛАНТАЦІЇ НА ЛЮМІНЕСЦЕНТНИЙ СПЕКТР НАНОКРИСТАЛІВ ZnSe
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У статті представлені результати математичної обробки люмінесцентних спектрів нанокристалів ZnSe. Зразки були підготовлено шляхом імплантації йонів Zn^+ з енергією 150 кеВ та йонів Se^+ з енергією 170 кеВ в шарі діоксиду кремнію, отриманого окисленням кремнієвої підкладки. Ми проаналізували два типи зразків, отриманих за різною послідовністю імплантації: спочатку імплантували Zn^+, а потім Se^+ (зразок А); зворотна послідовність — з імплантованими на початку йонами Se^+ (зразок В). Спектри, отримані для різних послідовностей імплантації А і В, відрізнялися один від одного. Було встановлено, що крім інтенсивних смуг з максимумами 2,3 еВ (540 нм) і 2,85 еВ (430 нм), які були пов'язані з власними люмінесцентними центрами ZnSe, існували дві смуги з максимумами 1,9 еВ (650 нм) і 2,6 еВ (480 нм), які були пов'язані із власними дефектами SiO_2. Цим було продемонстровано вплив середовища (матриці діоксиду кремнію), де утворювались нанокристали ZnSe, на його люмінесцентні спектри. Математична обробка форми смуги з максимумом 2,85 еВ показала, що такі параметри, як повна ширина при половині висоти максимуму, асиметрія та ексцес вказують на залежність розкиду розмірів нанокристалів ZnSe від порядку імплантації йонів. Результати добре узгоджуються з даними трансмісійної електронної мікроскопії.
Ключові слова: селенід цинку, йонна імплантація, люмінесцентний спектр, фітування функціями Гауса.