EXCITON AND PERCOLATION PROCESSES IN TWO-PHASE CORE-SHELL SiO_2/ZnO STRUCTURES WITH A LARGE DENSITY OF SURFACE NANOCLUSTERS

N.V. BONDAR,[1] M.S. BRODYN,[1] YU.V. YERMOLAYEVA,[2] M.V. DOBROTVORSKAYA,[2] A.V. TOLMACHEV[2]

[1]**Institute of Physics, Nat. Acad. of Sci. of Ukraine**
(46, Nauky Ave., Kyiv 03028, Ukraine; e-mail: jbond@iop.kiev.ua)

[2]**Institute for Single Crystals, Nat. Acad. of Sci. of Ukraine**
(60, Lenin Ave., Kharkiv 61001, Ukraine)

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We report the results of studies of two-phase core-shell (SiO_2/ZnO) structures with a large density of ZnO nanoclusters on the surface of spherical SiO_2 nanoparticles. It is proved that, due to the large surface energy of the latter, nanoclusters grow in the form of quantum disks with diameter exceeding 10 nm and with height of the order of the Bohr radius of an exciton in ZnO. The height was estimated in the effective mass approximation and agrees well with experimental data. It is first shown that the photoluminescence spectra of these structures can be caused by the phase percolation transition of excitons on the spherical surface of nanoparticles which is realized due to a large density of ZnO nanoclusters. This results in the interaction of the latter, but the space effect of excitons does not vanish in this case, unlike the 3D one. The exciton wave function acquires macroscopic dimensions resulting in the appearance of an intense band from deep levels related to vacancies and complexes of oxygen and zinc.

1. Introduction

Low-dimensional multilayer spherical core structures (substrates) with the surface coated by semiconductor nanoclusters (NC) that provide a functional response are now actively investigated. Such heteroparticles possess a wonderful set of morphological parameters for the realization of their close-packed arrangement, allow one to specify the functional properties by choosing a shell material, and represent ideal structure-forming elements of new types of consolidated nanomaterials. Synthesized cores (hereinafter, nanoparticles (NPs)) such as SiO_2, carbon, polystyrene, and TiO_2, have a diameter of the order of 100–500 nm. Due to the chemical reaction running at the deposition of the corresponding constituents of a semiconductor onto the surface of NPs, an array of NCs is formed [3–6]. As the energy gap of an NP material is larger than that of an NC, this creates a potential barrier for charge carriers (excitons) impeding their penetration to cores and gives rise to the spatial effect of carriers in an NC. As for the II–VI semiconductors, the possibility to immobilize ZnO NCs onto spherical submicron templates such as SiO_2, polystyrene, bacteria, and micelles in order to obtain "core–shell" heteroparticles representing promising structural units of consolidated optical materials is most actively studied [7]. The growth of NCs on spherical substrates 40–500 nm in size has considerable advantages as compared with ordinary macrosubstrates, because nanoparticles on the surface of a nano- or submicrosphere must be absorbed much more actively due to the large surface energy and the curvature of a surface. In addition, a high mobility of such nanotemplates will allow one to expand the range of application of heterostructures produced on their basis. The highest interest is attracted by ordered 2D or 3D arrays of such objects with a periodic modulation of the refractive index on scales commensurable with the light wavelength in the visible or infrared ranges that can form photon crystals [8].

This work reports the results of studies of the semiconductor structures that represent SiO_2 NPs (cores) with ZnO NCs synthesized on their surface that were obtained by drying a deposit on quartz substrate films. In spite of the active researches of these structures [4, 6], there remain a lot of unclear questions. For example, it was experimentally shown that, in the case where the radii of ZnO NCs in these structures (or similar CdS NCs [3]) significantly exceed the Bohr radius of an exciton in crystalline ZnO, their optical spectra indicate the presence of a dimensional effect for excitons which conserves due to unclear reasons. Another problem that has not been studied till now is the formation of a percolation transition of excitons on a spherical surface. It is well known that, at the critical density of NCs in dielectric or polymeric 3D matrices, NCs start to interact with one another. Moreover, a percolation level of excitons, at which the quantum effect disappears due to a macroscopic in-

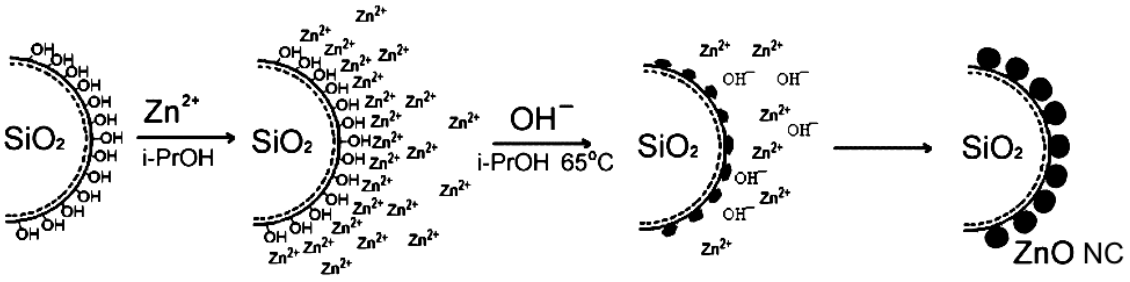

Fig. 1. Diagram of formation of ZnO NCs on a spherical SiO_2 nanotemplate

crease of the size of their wave function, is formed [9]. In this work, we first study this problem by the example of SiO_2/ZnO heteroparticles. It will be demonstrated that the formation of the percolation transition does not result in the vanishing of the quantum effect of charge carriers, which can be of applied importance.

2. Experimental Part

2.1. Fabrication technique of SiO_2ZnO structures

Spherical silica (SiO_2) NPs with the diameter $D = 2R = 200$ nm and with size dispersion $< 7\%$ were synthesized by the basic hydrolysis of tetraethyl orthosilicate in the medium of absolute ethanol employing the Stober technique [7] optimized by us. The diameter of obtained SiO_2 spheres was regulated by the ratio of the reagents, temperature, and process rate. ZnO nanocluster coatings on silica spheres (SiO_2/ZnO heteroparticles) were obtained by the template synthesis in the exchange reaction between zinc acetate ($ZnAc_2{\times}2H_2O$, reagent grade) and NaOH (reagent grade) in the propan-2-ol medium at a temperature of 65 °C in the presence of silica spheres. For characterization, we used films obtained by the drying of presynthesized heteroparticles on quartz substrates. The obtained samples were thermally heated during 2 h at various temperatures (150, 300, and 450 °C). Electron-microscope researches of heteroparticles were carried out using a PEM-125 transmission electron microscope with an accelerating voltage of 100 kV. The surface composition of the samples was studied by means of X-ray photoelectron microscopy using an XSAM-800 Kratos spectrometer with a resolution of 1 eV and the accuracy of determination of the binding energy equal to 0.2 eV. Photoelectrons were excited by MgK_α-radiation ($h\gamma = 1253.6$ eV). The consideration of the recharging effect and the calibration of spectra were performed with the use of the position of the C1s-shell line (E_b=285 eV) from hydrocarbon compounds absorbed by the sample surface. The composition of the sample surface was determined from the ratio of the areas of lines of the C1s, O1s, Zn3p, and Si2p core shells with regard for the sensitivity coefficients. The thickness of the analyzed layer was ∼5 nm. The chemical state of zinc atoms was revealed by analyzing the shape and the position of the ZnLMM Auger line which are sensitive to changes in the closest surroundings of zinc atoms. The technique used to obtain SiO_2/ZnO heteroparticles with the "core–shell" structure is based upon the template synthesis of ZnO NCs on the surface of a spherical nanosubstrate (nanotemplate) in an alcohol solution in water. It includes the following stages: 1) diffusion of precursor ions (Zn^{2+}, OH^-) to the template surface and their adsorption on the surface; 2) chemical transformations on the template surface; 3) formation of crystallization centers (critical nuclei), and 4) growth of the critical nuclei. The general scheme of the formation of a ZnO NC array on the surface of a SiO_2 sphere is presented in Fig. 1.

In order to form a uniform ZnO NC coating with low size dispersion, it is necessary to ensure a controlled ratio of the rates of generation and growth of crystal nuclei that, in our case, is regulated by the concentration and the type of used precursor compounds. We have found and optimized the solution parameters ($c[Zn^{2+}] = 3{\times}10^{-4}$ mole/l, c(NaOH) = 0.01 mole/l, and $T = 65$ °C) that support the formation of a large number of nuclei on the SiO_2 spherical surface and the suppression of their growth, which results in the uniform distribution of ZnO NCs over the template surface. As a result, it was established that, at such a low concentration of Zn^{2+} ions, the considered process provides a selective growth of nanoclusters at crystallization nuclei and almost completely suppresses the generation and the growth of new nuclei in the solution. The transmission electron microscopy images of SiO_2/ZnO heteroparticles obtained under the optimal conditions are presented in Fig. 2,*a,b*.

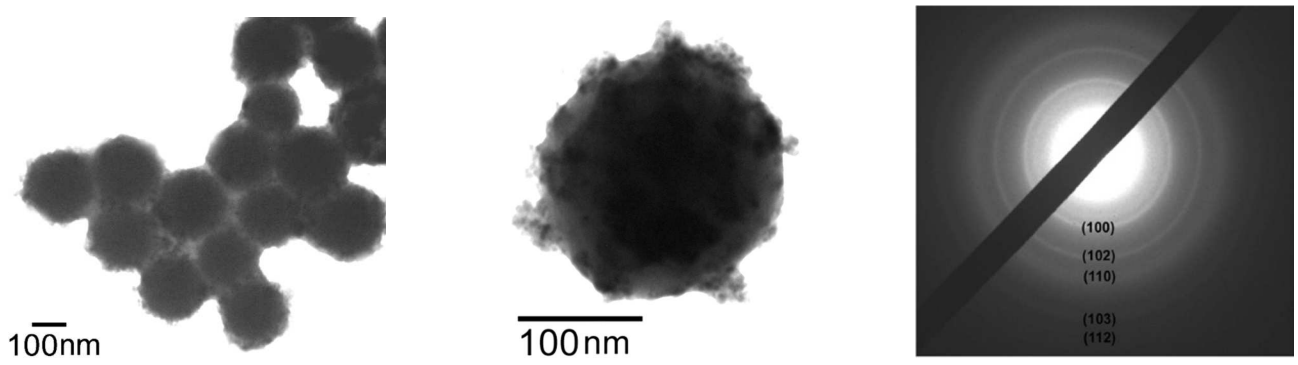

Fig. 2. Electron-microscopic images of SiO_2/ZnO heteroparticles (a), single SiO_2/ZnO heteroparticle (b), and microdiffraction from the periphery region of a heteroparticle (c)

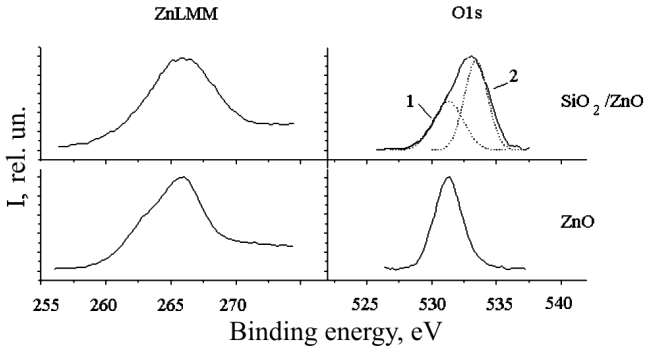

Fig. 3. Normalized ZnLMM Auger spectra and spectra of the O1s-shell from the surface of ZnO samples (reference) and SiO_2/ZnO heteroparticles (annealing at 450 °C)

The microimages testify to the formation of a uniform coating consisting of ZnO nanoparticles with the island structure. The electron microdiffraction picture obtained from the periphery of a particle (Fig. 2,c) gives evidences of the crystalline ZnO coating with a hexagonal crystal lattice on silica spheres, which was also confirmed by X-ray structural analysis [7]. According to the electron microscopy data, the size of ZnO NCs amounts to ∼10 nm. The surface composition of SiO_2/ZnO heteroparticles and the filling density of the nanotemplate surface by ZnO particles were determined using the technique of X-ray photoelectron spectroscopy. The normalized spectra of the O1s-shell and the ZnLMM Auger spectra for synthesized heteroparticles and the reference ZnO sample are presented in Fig. 3.

The position and the shape of the ZnLMM Auger-line of the SiO_2/ZnO sample practically coincide with those for the reference ZnO sample with an inessential broadening related to recharging effects. In the spectrum of the O1s-shell of the SiO_2/ZnO sample, one can mark out two lines: the first one with a lower binding energy (E_{b1} = 531.4 eV) corresponds to ZnO, and the second one (E_{b2} = 533.4 eV) is related to SiO_2. The ratio of the atomic concentrations $n = c_{Zn}/c_{Si}$= 1.4 in the surface layer of heteroparticles (∼5 nm) determined from the ratio of the intensities of the corresponding lines enabled us to estimate the continuity of the shell (or a degree of the filling of the SiO_2 spherical surface with ZnO NCs): Q ∼0.45 [7].

2.2. Optical spectra of the studied structures

Figure 4 shows the optical absorption and photoluminescence (PL) spectra of the studied SiO_2/ZnO structures. The spectra were recorded with the help of a spectrometer with a resolution not worse than 5Å/mm. The PL spectra were excited by a He–Cd laser with λ = 325 nm (3.84 eV).

In order to prevent the processes of photodarkening of the samples, the laser power was regulated with the help of neutral filters. All the obtained spectra are reproducible and were registered according to the common photon-counting technique. The absorption spectrum (curve *1*) of these structures contains a peak close to E_1 ∼3.5 eV that is absent in the samples without ZnO NCs. Taking into account that the energy gap width at T = 77 K, the radius, and the binding energy of an exciton in bulky ZnO are equal to E_{g0} ∼ 3.37 eV (marked by the arrow in the figure), a_x ∼ 2 nm, and ε_x ∼ 60 meV, respectively, one can assume that the peak in the absorption spectrum shifted to the short-wavelength side with respect to E_{g0} is related to excitons in the medium energy quantization mode. The absorption observed in the region $E > E_1$ is caused by the absorption in SiO_2. Figure 4 also presents the PL spec-

tra registered at $T = 77$ K (curve *2*) and 300 K (curve *3*) and excited by the He–Cd laser ($E_{\rm ex}$ is shown by the arrow). In the PL spectrum of the studied samples, we observed two bands with maxima at ∼3.5 eV, which coincides with E_1 of the absorption spectrum, and ∼2.5 eV. The correlation in the positions of the first band of the PL spectrum and the absorption peak testifies to the fact that it is caused by the recombination of excitons in ZnO NCs, while its blue shift with respect to E_{g0} amounts to ∼130 meV. The NC size dispersion equal to 17% according to our estimates results in the broadening of this band, due to which its short-wave wing overlaps with the laser excitation line. The PL band in the region of ∼2.5 eV actually consists of two bands, which is seen from the PL spectrum obtained at room temperature (curve *3*). The increase of the temperature results in the appearance of another band in the region ∼(2.1–1.9) eV, rather than in the shift of the band maximum. The origin of these two bands, "green" and "red" ones, is well known. They are related to oxygen ($V_{\rm O}$) and zinc ($V_{\rm Zn}$) vacancies and their complexes [10–12]. In our case, the radiation intensity in this spectral region allows one to make conclusion about the degree of localization of the exciton wave function in NCs. Of interest is also the absence of radiation in the spectral region 3.2–3.3 eV that is almost always observed in spectra of bulky samples and ZnO NCs of the spherical form and is caused by the recombination of excitons in the surface states of nanoclusters, as the "surface/volume" ratio in NCs considerably grows with decrease in the radius [10]. According to the transmission electron microscope (TEM) data, the diameters of the studied NCs exceed 10 nm. Therefore, in this case, this ratio is not determinative, and the main role is played by the internal rather than surface exciton states. The long-term thermal treatment of glass or polymer matrices with NCs results in an increase of their radii due to the Ostwald ripening and a decrease of their density in the matrix, which is seen from the red shift of the absorption and PL spectra. The inset in Fig. 4 shows the PL spectra of our samples treated at $T = 150$, 300, and 400 °C. In our case, ZnO nanoclusters are located on the SiO_2 sphere, so the thermal treatment does not result in an increase of their radii (surface diffusion is absent). That is why the spectral position of the absorption spectrum, the PL band (∼3.5 eV), and its intensity remain invariable (not shown in the inset). However, the intensity of the PL band related to deep levels significantly decreases, which is qualitatively explained in the following section.

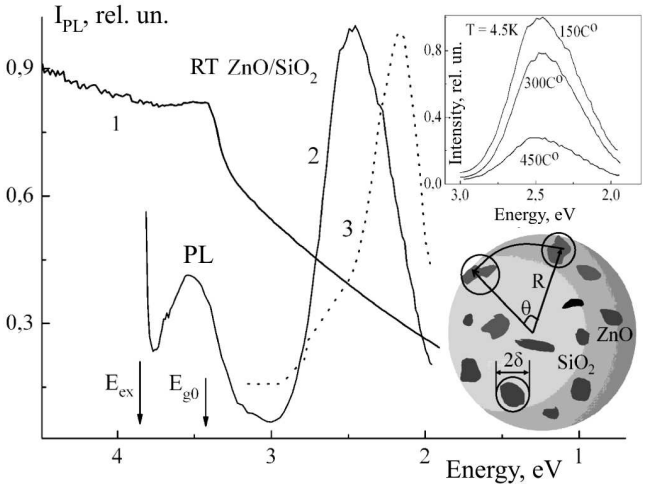

Fig. 4. Absorption (*1*) and photoluminescence (*2* – 77 K, *3* – 300 K) spectra of the studied SiO_2/ZnO samples. Inset: the intensity of the band from deep states as a function of the annealing temperature; the diagram of the SiO_2/ZnO structure: a sphere with a random surface distribution of ZnO nanoclusters (see text)

3. Discussion of the Results

Based upon the obtained data, we shall find out the reason why the quantum effect is conserved at the sizes of ZnO NCs considerably exceeding those of excitons in bulky ZnO, which follows from a shift of the short-wavelength PL with respect to E_{g0} (Fig. 4). It is obvious that, due to the specific character of growth of NCs at the spherical surface and the surface energy of SiO_2 nanoparticles, ZnO NCs grow in the form of quantum disks (QD), rather than spheres, whose radius [(δ), see the diagram] is several-fold larger than a_x, but their height (h) is commensurable with the latter, which results in the conservation of the quantum effect of excitons in spite of the considerable dimensions of NCs. In other words, the surface energy of a SiO_2 sphere induces the "expansion" of ZnO NCs over the surface, by forming QDs. As is known, the surface energy of a sphere depends on its radius, that is why the heights of generated ZnO NCs will also depend on it. As far as we know, this problem has not been considered till now. Let us estimate the value of h based upon the obtained experimental results. For this purpose, it is necessary to find the solution of the Schrödinger equation with the effective Hamiltonian

$$H = -\frac{\hbar^2}{2m_e^*}\nabla_e^2 - \frac{\hbar^2}{2m_h^*}\nabla_h^2 - \frac{e^2}{\varepsilon\,|r_e - r_h|} + V_e(r_e) + V_h(r_h), \quad (1)$$

where $m_e^* = 0.24m_0$ and $m_h^* = 1.8 - 2.2m_0$ are the effective electron and hole masses, respectively, while the last two terms stand for the depths of their potential wells formed due to discontinuities of the conduction and valence bands, respectively. The exciton wave function can be chosen in the form $\Psi_0 = f_e(\rho_e)g_e(z_e)f_h(\rho_h)g_h(z_h)$, where ρ and z are the coordinates of carriers in the directions of the nanocluster radius and height, respectively: $f_i(\rho) = J_0(\chi\rho/\delta)$, $g_i(z) = \cos(\pi z/h)$, $(i = e, h)$, $J_0(x)$ is the zero-order Bessel function, and $\chi = 2.4048$ is its first root. The magnitudes of discontinuities of the conduction and valence bands at the interface of the ZnO NC and the matrix are unknown, so we consider that the potential wells for carriers are infinitely deep. Hence, the position of the first peak in the absorption spectrum can be determined from the solution of the Schrödinger equation in the following way [13]:

$$E(\delta, h) = E_{g0} + \left[\frac{\hbar^2}{2m_e^*} + \frac{\hbar^2}{2m_h^*}\right]\left[\left(\frac{\chi}{\delta}\right)^2 + \left(\frac{\pi}{h}\right)^2\right] - \varepsilon_x. \tag{2}$$

Taking into account that $E_{g0} \sim 3.37$ eV (at $T = 77$ K) and the NC radius $\delta \sim 5$ nm, we obtain $h \sim 3.4$ nm, which is less than the exciton diameter in crystalline ZnO and indicates that the space effect of excitons in such structures does not vanish even at a significant increase of the QD radius.

The presence of a "bulky" deep-state band in the PL spectrum can be caused by the formation of the exciton percolation level due to the considerable surface concentration of ZnO NCs. Their generation and distribution over the SiO_2 spherical surface represent a random process, so the position of each NC on the surface does not depend on the other ones. Such two-phase systems with the Poisson 3D distribution of one phase (for example, semiconductor NCs in matrices and composite and porous materials) have been recently actively investigated both theoretically and experimentally [9]. An increase of the density (ρ) of NCs and a decrease of the average distance between them in such systems result in the formation of finite-size clusters of NCs similar to the closest sites of the crystal lattice. At the critical density ρ_c, there appears the percolation (infinite) cluster as a result of the interaction between NCs and the delocalization of excitons, whose wave function acquires macroscopic sizes. Unlike the geometric percolation, where finite-size clusters are formed due to the direct contact of NC surfaces, they interact, in this case, with one another through the tunneling of carriers (excitons), which occurs due to the overlapping of their wave functions at separate NCs [9].

It is well known that the exciton percolation level is formed between the nearest neighboring NCs. That is why, it is most important to determine the average distance between them (ξ) at fixed ρ [14, 15]. The problem to determine ξ for a system of noninteracting points with the Poisson distribution and the density ρ was first solved by Hertz more than 100 years ago [14]. For the case of real NCs with a solid core, this problem was considered in [16]. Based upon the calculation results obtained there, we substantiated the appearance of a phase percolation transition of excitons in samples of borosilicate matrices with ZnSe and CdS NCs at $\rho = \rho_c$ [9]. At varying a space topology (transition from a volume surface to a spherical one), the determination of ξ becomes more complicated, as unlike 3D, there are no calculations of ξ for this case, which will evidently represent a geodesic line. The latter can be determined through the angle (θ) between two radii R drawn from the center of the SiO_2 sphere to the NC (see inset in Fig. 4). In [17], it was shown that the average angle $\langle\theta\rangle$ can be found using the Poisson distribution of this quantity: $P_1(\theta)d\theta{=}2\pi\rho\theta\exp(-\pi\rho\theta^2)d\theta$ for a plane or $P_1(\theta)d\theta = (N/2)\theta\exp[-(N/4)\theta^2]d\theta$ for a sphere:

$$\langle\theta\rangle = \int_0^\infty \theta P_1(\theta)d\theta = \frac{1}{2\sqrt{\rho}} = \sqrt{\frac{\pi}{N}}. \tag{3}$$

The quantity ξ is determined as $\xi \approx 0.02R\langle\theta\rangle$. This relation is used in Eq. (3) with regard for the NC densities for a plane and a sphere: $4\pi\rho = N$. Knowing the area of the SiO_2 surface, the degree of its coating ($Q \sim 0.45$), and the average NC area ($\pi\delta^2$), we obtain: $N \sim 7 \times 10^3$, and therefore $\xi \sim 7.7$ nm, i.e. the average distance between the neighboring NCs on the spherical surface is of the order of magnitude of their diameter, that is why they form conglomerates. However, it is only an estimate, because a more accurate analysis requires to take the real dimensions of disks into account, which, as far as we know, has not been done till now. In turn, this indicates that the exciton wave functions on a SiO_2 spherical surface are overlapped. The system's state appears much higher than the percolation level due to a large NC density, and the percolation cluster is, to a large extent, continuous rather than filamentary, as it is in 3D structures [9]. The delocalization of excitons on the SiO_2 spherical surface results in the formation of the bulk "green" and "red" PL bands almost never observed in single low-size ZnO NCs [10]. In addition to the radiation from the quantum states with $E > E_{g0}$,

one observes bands in the region 3.4–3.2 eV in such NCs related to surface NC states and donor-acceptor pairs absent in our case. With increase in NC sizes, the radiation from these states becomes ineffective. Instead, one observes the growth of the double PL band from the region 2.1–1.9 eV that is characteristic of bulky ZnO and is caused by the recombination of carriers at oxygen ($V_{\rm O}$) and zinc ($V_{\rm Zn}$) vacancies and their complexes [10]. Its intensity significantly increases in the case where the exciton wave function is delocalized and starts expanding not only over the surface of SiO_2 spheres, but also covers a considerable part of the latter that get to the laser excitation spot. The thermal treatment of the samples at various temperatures results in a considerable improvement of the NC stoichiometry reducing the number of defects, and the intensity of this band falls (see the inset in Fig. 4). However, the thermal treatment does not influence the PL band from quantum states, as its spectral position depends only on the NC height determined by the size of SiO_2 spheres, i.e. by their surface energy.

In conclusion, we note that the work qualitatively describes the process of generation of ZnO NCs in the form of quantum disks on the surface of SiO_2 spheres, where the quantization of the exciton energy is conserved along the height of the disks not vanishing even at large NC radii. From the obtained results, it also follows that the formation of a photon crystal can be of threshold character, because the formation of bulky periodic ZnO layers requires the appearance of a percolation transition of excitons in the array of ZnO NCs on the surface of SiO_2 spheres. The conservation of the quantum effect of excitons under the simultaneous formation of their percolation transition can be effectively used for the transport of carriers in films in the lateral direction.

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ЕКСИТОННІ ТА ПЕРКОЛЯЦІЙНІ ПРОЦЕСИ У ДВОФАЗНИХ СТРУКТУРАХ SiO_2/ZnO ТИПУ ЯДРО–ОБОЛОНКА З ВЕЛИКОЮ ЩІЛЬНІСТЮ ПОВЕРХНЕВИХ НАНОКЛАСТЕРІВ

М.В. Бондар, М.С. Бродин, Ю.В. Єрмолаєва, М.В. Добротворська, О.В. Толмачов

Р е з ю м е

У роботі наведено результати досліджень двофазних структур типу ядро–оболонка (SiO_2/ZnO) з великою щільністю нанокластерів ZnO на поверхні сферичних наночасток SiO_2. Обґрунтовано припущення, що в результаті значної поверхневої енергії останніх нанокластери ростуть у вигляді квантових дисків з діаметром >10 нм і висотою порядку борівського радіуса екситону в ZnO, яку оцінено в наближенні ефективної маси, і вона добре узгоджується з експериментальними даними. Вперше показано, що спектри фотолюмінесценції цих структур можуть бути зумовлені фазовим перколяційним переходом екситонів на сферичній поверхні наночастинок, який утворився внаслідок значної щільності нанокластерів ZnO. Це приводить до взаємодії останніх, але, на відміну від 3D, у даному випадку просторовий ефект екситонів не зникає. Хвильова функція екситонів набуває макроскопічних розмірів, приводячи до виникнення інтенсивної смуги глибоких станів, пов'язаних з вакансіями та комплексами кисню і цинку.