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Photoluminescence Study of ZnO Nanostructures Grown by Hydrothermal Method

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The photoluminescence spectra of ZnO nanorods grown by the hydrothermal method were investigated. In the nanostructures the neutral donor bound excitons dominate in the ultraviolet (UV) region of the photoluminescence spectrum at liquid helium temperature. The presence of the band two electron satellite transitions (TES) of the donor bound excitons allow to determine the donor binding energies E_D of about 53 meV. On the basis of the measurements performed at different temperatures the thermal activation energy of the luminescence quenching ($E_a \approx 14$ meV) was obtained.

Keywords: Zinc oxide, Photoluminescence, Bound excitons, Hydrothermal method.

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1. INTRODUCTION

At this stage in the development of optoelectronics, gallium nitride is the main material for the commercial production of semiconductor light-emitting diodes and lasers, with radiation at short wavelengths of light. In 2014, the Nobel Prize in Physics was awarded for the development of GaN-based blue optic diodes that enabled the introduction of vivid and energy-efficient light sources. Approximately 20 years have been spent on solving of the problem of *p*-type conductivity in GaN. In order to further reduce the cost and increase the energy efficiency, it is necessary to design the devices emitting in the ultraviolet spectral region. It is advisable, according to many scientists, to use for this purpose zinc oxide. ZnO possesses a high exciton binding energy (60 meV, whereas in GaN – 28 meV), is widely spread and cheap semiconductor. The most challenging problem of ZnO based electrooptic devices is the lack of stable and reliable *p*-type doping; mainly due to the self-compensation property of ZnO [1]. For this reason ZnO-based LEDs were fabricated by combining *n*-type ZnO with a *p*-type semiconductor other than ZnO, for example, Cu_2O, ZnTe, $SrCu_2O_2$, AlGaN, GaN or *p*-type conduction polymers [2].

Known, reproducible methods of the synthesis of ZnO nanostructures are expensive metal-organic chemical vapor deposition and molecular-beam epitaxy. The problem of low-cost synthesis of ZnO nanostructures with good reproducibility still remains unresolved, but hopes rely on the improvement and development of «wet» chemistry methods [3].

The emission bands of the zinc oxide have not been completely interpreted. A precise understanding of the nature of these bands is necessary for creating of the light emitting diodes or lasers based on ZnO. A crucial factor is the fact that the luminescence of the ZnO is very sensitive to its surface state determined and modulated by a synthesis method [4, 5]. Till now, the low-temperature studies of photoluminescence (PL) spectra of single crystals, thin films and nanostructures of ZnO grown by non wet chemistry methods have been carried out [3, 9, 10].

This work is a continuation of our previous studies of the parameters and nature of ZnO nanostructures photoluminescence [4]. In this work, identification of the UV luminescence spectrum, measured at liquid-helium temperatures, of ZnO nanostructures, grown by the hydrothermal method, was performed.

2. EXPERIMENTAL

ZnO nanorods (Fig. 1) were grown by hydrothermal method [8]. For seed-supported growth of ZnO nanorods, the nanocrystalline ZnO seed particles were prepared in a solution of 0.005 mol/L zinc acetate [$Zn(CH_3CO_2)_2$] dissolved in ethanol at 90 °C for 15 min. The seed solution was then spin-coated onto Al_2O_3 substrate. Subsequently, the seed-coated substrates were thermally annealed at 300 °C for 5 min to remove the residual solvent. The procedures of spin coating and thermal annealing were repeated twice for ZnO seed growth. On the next stage the Al_2O_3 substrate with ZnO seeds were immersed in the same main growth solution consisting of 0.05 mol/L zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$), 0.025 mol/L hexamethylenetetramine ($C_6H_{12}N_4$) and distilled water. ZnO nanorods were grown at 90 °C for 90 min.

Morphology of the samples was examined using REMMA-102-02 Scanning Electron Microscope-Analyzer (JCS SELMI, Sumy, Ukraine).

The photoluminescence spectra (PL) were measured using automated monochromator/spectrograph M266 (SolarLS JSC, Minsk, Belarus) connected with CCD camera, based on Hamamatsu S7030-1006S sensor. The samples were excited by FQSS266-Q2 Nd:YAG laser (266 nm). The sample was placed in a closed loop helium cryostat, equipped with a cryocooler DE-202A (Advanced Research Systems, Macungie, USA) and a temperature regulator Cryocon 32 (Cryogenic Control Systems Inc., Rancho Santa Fe, USA).

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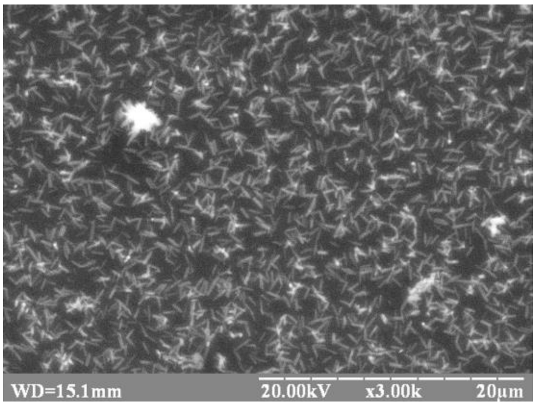

Fig. 1 – Microphotographs of ZnO nanorods

3. RESULTS AND DISCUSSION

The morphology of ZnO nanorods is shown in Fig. 1. ZnO nanorods are characterized by the length of about 1.5 µm with an average diameter of about 200 nm.

As can be seen from Fig. 2, the room temperature PL spectra of the ZnO nanorods exhibit two bands in the UV (around 380 nm) and visible (around 600 nm) regions.

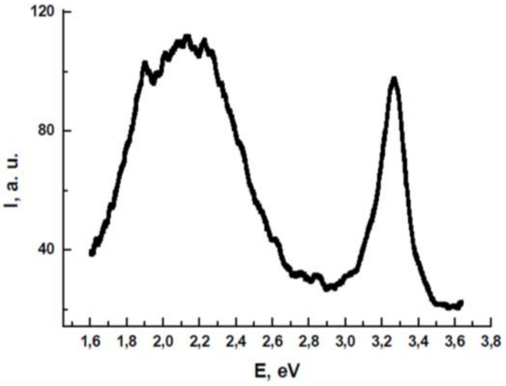

Fig. 2 – Room temperature PL spectra of ZnO nanorods

The UV band is typical for ZnO and arises due to recombination of the free excitons, bound excitons and transitions in the donor-acceptor pairs. The wide band in the range from approximately 450 nm to 750 nm is caused by defects, first of all, by uncontrolled impurities and stoichiometry defects. According to [9] the emission of ZnO nanorods peaking near 600 nm is originating from the hydroxyl groups attached to the ZnO nanorods.

Fig. 3 presents the data of the typical color coordinates measurements of the room temperature PL spectra of the ZnO nanorods. Fig. 3 reveals that the emitted light manifests a cold white impression with the color coordinates $C_x \approx 0.41$ and $C_y \approx 0.43$ (equivalent to $T = 3700$ K).

Fig. 4 presents the temperature evolution of the photoluminescence spectra of the investigated sample in UV region.

In the spectra presented in Fig. 4, the two peaks are clearly distinguished at low temperatures: more intense with a maximum at 3.36 eV and a weaker at 3.32 eV. In our case the intensive band with the maximum at 3.36 eV has to be related to the recombination of

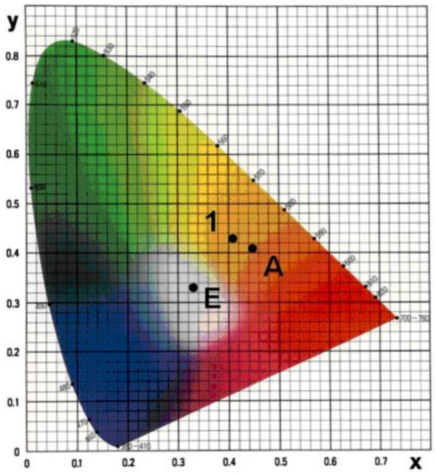

Fig. 3 – Room temperature PL spectra of the ZnO nanorods in color coordinates: 1 – experimental sample. *A*, *E* – the standard illuminants

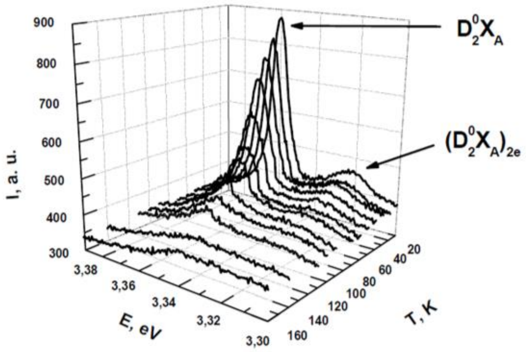

Fig. 4 – The temperature evolution of the photoluminescence spectra of ZnO nanorods in UV region. Temperature in the top-down succession, K: 10, 20, 30, 40, 50, 60, 70, 90, 100, 110, 140, 160

A excitons bound to the neutral donors ($D_2^0X_A$) [10]. One of the characteristic of the neutral-donor-bound exciton transition is the two-electron satellite (TES) transition in the spectral region of 3.32-3.34 eV for ZnO. These transitions involve radiative recombination of an exciton bound to a neutral donor, leaving the donor in the excited state, thereby leading to a transition energy which is less than the donor bound exciton energy by an amount equal to the energy difference between the first excited and ground states of the donor. In the effective-mass approximation, the energy difference between the ground-state neutral-donor-bound excitons and their excited states (TES) can be used to determine the donor binding energies (the donor excitation energy from the ground state to the first excited state is equal to 3/4 of the donor binding energy E_D) and catalog the different species present in the material [6]. In our case, according to [6], the peak at 3.32 eV $(D_2^0X_A)_{2e}$ corresponds to the excited state associated with the neutral-donor-bound exciton at 3.36 eV ($D_2^0X_A$). According to the hydrogenic effective-mass approach (EMA), the energy level ($E_{(\mathrm{TES})}$) of TES is given by [14]:

$$E_{(\mathrm{TES})} = E_{(D^0X)} - E_D(1 - 1/n^2), \qquad (1)$$

where $E_{(\mathrm{TES})}$ – the energy level of TES, $E_{(D^0X)}$ – binding energy of exciton bound to neutral donor, E_D – donor binding energy, n – principal quantum number.

Therefore, for $n = 2$ knowing the energy positions $E_{(D^0X)}$ and $E_{(\mathrm{TES})}$ of the D^0X and its corresponding TES transition, one can determine the related donor binding energy E_D. Separating the ground state and the corresponding excited states one can calculate the donor binding energies: 53 meV for the donor at 3.36 eV.

The temperature dependences of the energy positions of $D_2^0X_A$ and $(D_2^0X_A)_{2e}$ peaks are presented in Fig. 5.

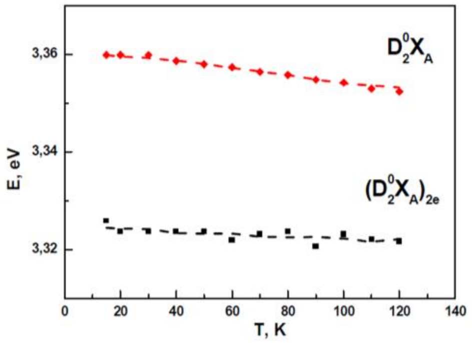

Fig. 5 – The temperature evolution of energy position of the maxima in the UV photoluminescence spectra

The temperature dependences of the corresponding peaks intensities in the photoluminescence spectra of ZnO nanorods are presented in Fig. 6. The temperature dependence of the integrated intensity I of the $D_2^0X_A$ peak could be expressed by the equation [15]:

$$I(T) = I_0/(1 + A\exp[-E_a / kT]), \qquad (2)$$

where $I(T)$ – integrated intensity, E_a – is the activation energy of the thermal quenching process, k – is the Boltzmann constant, I_0 – is the emission intensity at $T = 0$ K, T – is a thermodynamic temperature and A – is a constant.

For bound exciton transition the activation energy corresponds to the energy of the exciton localization [13].

The corresponding activation energy obtained from the inverse temperature dependence of the photoluminescence intensity (Fig. 7) was found to be $E_a \sim 14$ meV. The E_a value corresponding to D^0X is in a good agreement with the exciton-to-defect binding localization energy since it has been reported that the binding energy of the exciton to the defect-pair complexes ranges from 10 to 20 meV [14]. The values of activation energy of thermal quenching obtained in our study were found to be quite close to the results of Meyer et al. ($E_a = 16$ meV) [15]. According to [15], the impurity of Ga would be considered as the donor responsible for the presence of a $D_2^0X_A$ band in the UV photoluminescence spectrum of ZnO.

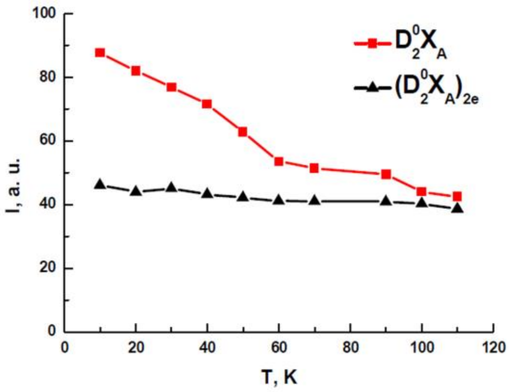

Fig. 6 – The temperature dependences of $D_2^0X_A$ and $(D_2^0X_A)_{2e}$ peaks intensities

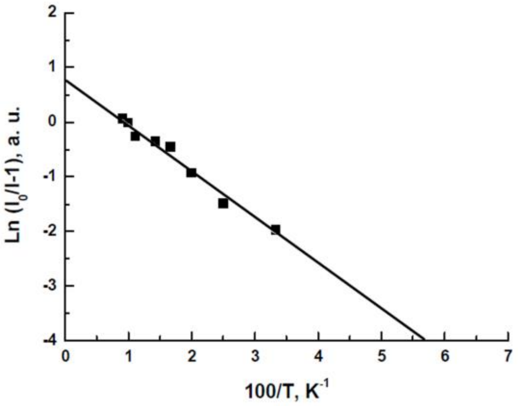

Fig. 7 – Inverse temperature dependences of the luminescence intensity for the donor-bound exciton band for ZnO nanorods

4. CONCLUSION

The investigation of low temperature photoluminescence spectra of ZnO nanostructures grown by hydrothermal method was carried out. The UV luminescence spectra of ZnO nanostructures at different temperatures were interpreted. The intensive band with the maximum at 3.36 eV has been related to the neutral donor-bound exciton transition ($D_2^0X_A$).The binding energy of donor giving rise to neutral donor bound exciton recombination at 3.36 eV have been determined from the observations of its two electron satellite transition.

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Исследование фотолюминесценции ZnO наноструктур, выращенных гидротермальным методом

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Исследованы спектры фотолюминесценции наностержней ZnO, выращенных гидротермальным методом. Связанные на нейтральном доноре экситоны доминируют в ультрафиолетовой (УФ) области спектра фотолюминесценции наноструктур при температуре жидкого гелия. Наличие полосы двухэлектронных переходов с участием связанных экситонов (TES) позволило определить энергию связи донора E_D (примерно 53 мэВ). На основе измерений, проведенных при различных температурах, было получено значение энергии активации процесса термического тушения ($E_a \approx 14$ мэВ).

Ключевые слова: Оксид Цинка, Фотолюминесценция, Связанные Экситоны, Гидротермальный Метод.

Дослідження фотолюмінесценції ZnO наноструктур, вирощених гідротермічним методом

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Досліджено спектри фотолюмінесценції нанострижнів ZnO, вирощених гідротермічним методом. Зв’язані на нейтральному донорі екситони домінують в ультрафіолетовій (УФ) області спектру фотолюмінесценції наноструктур при температурі рідкого гелію. Наявність смуги двоелектронних переходів за участю зв’язаних екситонів (TES) дозволила визначити енергію зв’язку донора E_D (приблизно 53 меВ). На основі вимірювань, проведених за різних температур, було отримано значення енергії активації процесу термічного гасіння ($E_a \approx 14$ меВ).

Ключові слова: Оксид Цинку, Фотолюмінесценція, Зв’язані Екситони, Гідротермічний Метод.

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