ULTRAVIOLET ELECTROLUMINESCENCE OF LED DEVICES BASED ON n -ZnO NANORODS GROWN BY VARIOUS METHODS AND p -GaN FILMS

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Light emitting diodes (LEDs) structures based on p -GaN film/ n -ZnO nanorods quasiarray heterojunction were fabricated. ZnO nanostructures were grown on the p -type GaN templates using two different methods. The turn-on voltages of ZnO/GaN heterojunctions based on ZnO nanorods grown using the gas-transport reaction and hydrothermal methods were equal to 3.2 V and 6.5 V, respectively. The diode-ideality factors were estimated to be of around 45 and 36 for the samples with ZnO nanorods grown using the method of the gas-transport reaction and the hydrothermal method, respectively. The large values of the ideality factors can be explained by a high density of trap states and quality of the contacts with the $p-n$ junctions. The electroluminescence (EL) spectra of LEDs with ZnO nanorods grown by the gas-transport reaction and hydrothermal methods were approximated by four and three Gaussians, respectively. On the basis of the X-ray diffraction (XRD), electrical and optical studies data, one can conclude that the emission peaks at 389–391, 410–412, 436–438 and 502 nm correspond to the near-band-edge (NBE) recombination in ZnO, interface carriers recombination in ZnO/GaN junction, the electrons transition from GaN conduction band to Mg²⁺ doping level, and to the emission from the defect levels in ZnO, respectively. The LED based on ZnO nanorods synthesized using the hydrothermal method emitted a more pure ultraviolet (UV) light.

Key words: zinc oxide, gallium nitride, nanorods, heterojunction, electroluminescence.

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I. INTRODUCTION

Ga-containing materials still remain the main materials for the production of light emitting diodes and lasers with radiation at short wavelengths. The condition of further cheapening and increasing the energy efficiency of the optoelectronic devices demands application of cheaper wide band gap materials such as ZnO and “non-epitaxial” manufacturing technologies.

The most challenging problem of the electrooptic devices based on ZnO homojunction is the lack of stable and reliable p -type doping [1]. In this situation, ZnO-based LEDs usually are fabricated by combining n -type ZnO with a p -type semiconductor other than ZnO, for example, Cu₂O, ZnTe, SrCu₂O₂, AlGaN, GaN or p -type conduction polymers [2, 3].

The combination of n -type ZnO nanostructures and p -type GaN layers in a single heterostructure allows one to create the LED structure without using the expensive GaN material with n -type electrical conductivity, and at the same time to avoid the problems associated with a stable hole conductivity in ZnO and heterointerfaces quality [4].

In this paper, we compare the electroluminescent properties of the LEDs devices based on n -ZnO nanorods grown using various methods on the p -type GaN templates.

II. EXPERIMENT

For the creation of the investigated heterojunction we used commercially available p -type GaN templates purchased from UNIPRESS (Poland) such as magnesium-doped GaN (0001)-oriented 2 μ m thick layer grown using the MOVPE method on a 430 μ m thick sapphire substrate with GaN non-conductive 1.5 μ m thick buffer layer. According to the passport data, p -GaN film is characterized by a relatively low dislocation density — $(3-5) \times 10^8$ cm⁻²; the concentration of the embedded magnesium impurity is 2×10^{19} cm⁻³; the concentration of the electrically active holes is $(2-3) \times 10^{17}$ cm⁻³.

ZnO nanostructures were grown on the p -type GaN templates using two different methods. Figure 1 shows the ZnO nanorods produced using the method of gas-transport reactions [3]. For seed-supported growth of ZnO nanorods, nanocrystalline ZnO seed particles were prepared in a solution of 0.005 mol/L zinc acetate [Zn(CH₃CO₂)₂] dissolved in ethanol at 90°C for 15 min. The seed solution was then spin-coated onto p -type GaN templates. Then, the seed-coated p -type GaN substrates were thermally annealed at 300°C for 5 min to remove the residual solvent [5]. The mixture of the powdered high purity zinc oxide, metallic zinc and graphite in the proportion of 1:1:1 was taken as an initial material for vaporization. This material and p -GaN templates were placed into a quartz tube. The mixture of the

powders was placed in a sealed end of the tube whereas the substrates — near the open end. The quartz tube was placed into a horizontal oven. The powder mixture was heated to the temperature of about 1050°C and the substrates were located in the zone with the temperatures of 700–750°C. These temperature distributions were maintained for 1 h. Afterwards the oven was shut off and cooled spontaneously to room temperature. This yielded a deposited white layer of zinc oxide on the substrates. Since the *p*-GaN substrates were placed with a partial overlap, the ZnO nanostructure did not grow on the entire substrate surface.

Fig. 1. Microphotographs of ZnO nanostructures grown using the method of gas-transport reactions and coated with a photoresist

Fig. 2. Microphotographs of ZnO nanorods grown using the hydrothermal method and coated with a photoresist

Figure 2 shows the ZnO nanorods grown using the hydrothermal method [6, 7]. For a seed-supported growth of ZnO nanorods, the nanocrystalline ZnO seed particles were also prepared on the *p*-GaN templates [5]. At the next stage, the *p*-GaN substrate with ZnO seeds were immersed in the same main growth solution consisting of 0.05 mol/L zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), 0.025 mol/L hexamethylenetetramine ($\text{C}_6\text{H}_{12}\text{N}_4$) and distilled water. ZnO nanorods were grown at 90°C for 90 min.

The contact with the *p*-GaN was formed using thermally evaporated Ni (30 nm) followed by Au (35 nm) [3]. The quartz-crystal microbalance was used as a thin-film deposition monitor [8]. The Ni/Au contacts were evaporated through the shadow masks in a circular area ~ 2 mm in diameter. To produce LEDs, the array of ZnO nanorods were partially covered with spin coating with an insulator layer of photoresist. This was followed by deposition of Au/Ti thin films as the top electrode using the magnetron sputtering method [4]. The Ti/Au contacts were evaporated through the shadow masks in a circular area ~ 2 mm in diameter. A liquid photo-positive resist based on o-naphto-chinon-diazide and novolack (a type of phenol-formaldehyde resin) “Positive 20” KONTAKT CHEMIE was used as the photoresist-insulator [2]. The schematic image of the LEDs is shown in Fig. 3.

Fig. 3. Schematic image of the LED devices based on *n*-ZnO nanorods grown using various methods on *p*-GaN films

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

The X-ray diffraction (XRD) measurements were carried out at room temperature using STOE STADI P diffractometer (STOE & Cie GmbH, Darmstadt, Germany) with a linear position sensitive detector in the transmission Bragg–Brentano geometry ($\text{Cu } K_{\alpha 1}$ radiation at $\lambda = 1.540598 \text{ \AA}$, Ge (111) monochromator, detector scanning step is 0.480° (2θ), accumulation time is 320 s, 2θ angle resolution is 0.015°).

The measurements of the current-voltage ($I - V$) characteristics were carried out using Keithley Model 2401 Low Voltage Source Meter (Keithley Instruments Inc., Ohio, USA) multimeter.

The room-temperature photoluminescence (PL) and EL spectra were measured using a portable fiber optic spectrometer AvaSpec-ULS2048L-USB2-UA-RS (AvantesBV, Apeldoorn, Netherlands) with an input slit of $200 \mu\text{m}$, a diffraction grating of 300 lines/mm and a resolution of 9 nm. The accumulation time was 100 msec. The detection of light in a spectrometer is carried out by a 2048 pixel CCD detector. Special software for automated computer control of the spectrometer and spectra processing was used. The samples were excited by FQSS266-Q2 Nd:YAG laser (266 nm) for PL.

III. RESULT AND DISCUSSION

The morphology of the ZnO nanorods grown using two different methods is shown in Figs. 1 and 2. ZnO nanorods obtained using the method of gas-transport reactions were found to possess the diameter ranging from 0.2 μm up to 0.5 μm . They can also form agglomerates of rods with a cross section of not more than 1.5–2 μm . ZnO nanorods grown using the hydrothermal method are characterized by the length of about 3–4 μm and an average diameter of about 200–500 nm.

The XRD pattern of the ZnO nanorods is illustrated in Fig. 4. The obtained peaks correspond to the hexagonal wurtzite pure phase of the ZnO with the lattice parameters $a = b = 3.2476 \pm 0.0014$ Å, $c = 5.2037 \pm 0.0029$ Å for ZnO nanorods obtained using the method of gas-transport reactions and $a = b = 3.2451 \pm 0.0015$ Å, $c = 5.1963 \pm 0.0035$ Å for the ZnO nanorods grown using the hydrothermal method. This result indicates that no other phases of ZnO or impurities are observed [9].

Fig. 4. XRD spectra of ZnO nanorods grown using: 1 — the hydrothermal method; 2 — the method of gas-transport reactions

Fig. 5. The room temperature PL spectra: 1 — ZnO nanorods grown using the hydrothermal method; 2 — ZnO nanorods grown using the method of gas-transport reactions

The room-temperature PL spectra of the ZnO nanorods (Fig. 5) grown using different methods consist of the two bands in the UV and visible regions. The band at 388 nm is typical of ZnO and arises due to the recombi-

nation of the free excitons, bound excitons and transitions in the donor–acceptor pairs [6]. 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 [6].

For the ZnO nanorods grown using the hydrothermal method, the broad luminescence peak near 600 nm according to [6, 7] originates from the hydroxyl groups attached to the ZnO nanorods.

In our previous paper, the results of PL studies of *p*-type GaN templates purchased from UNIPRESS were presented [3]. The PL spectrum for Mg-doped GaN consisted of the narrow neutral acceptor bound exciton (ABE) band at 3.43 eV and the broad donor–acceptor pair (DAP) band at 3.27 eV.

a)

b)

Fig. 6. $I - V$ characteristics of the LEDs created on the basis of ZnO nanorods grown using the method of gas-transport reactions (a) and ZnO nanorods grown using hydrothermal method (b)

The $I - V$ characteristics of the LEDs created on the basis of ZnO nanorods grown using the two different methods are depicted in Fig. 6. The $I - V$ curves clearly show a nonlinear increase in the current under the forward bias, which indicates reasonable *p-n* junction characteristics and possibility of light emission. The diode turn-on voltage is defined as the inflection voltage that is determined by extrapolating the fitting line corresponding to the linear region of the forward $I - V$

characteristics to the abscissa axis. The turn-on voltages of the heterojunctions of ZnO/GaN in the cases of the ZnO nanorods grown using the gas-transport reaction and the hydrothermal methods were equal to 3.2 V and 6.5 V, respectively. The diode-ideality factors (η) were estimated from the slopes of the $\ln(I)$ versus V plots in the range from 2 to 7 V, using the equation:

$$\eta = e/k_B T [\delta(\ln I)/\delta V]^{-1} \quad (1)$$

where k_B is the Boltzmann constant and T is the operating temperature.

Fig. 7. Room temperature EL spectra of the LEDs under different injected currents at forward bias: LED on the basis of ZnO nanorods grown by the method of gas-transport reactions (a) and LED on the basis of ZnO nanorods grown by the hydrothermal method (b)

In our case the diode-ideality factors were found to be around 45 and 36 for the samples with ZnO nanorods grown using the gas-transport reaction and hydro-thermal methods, respectively. These results are in agreement with the data of the current-voltage behavior of n -ZnO/ p -GaN heterostructures presented in [10, 11]. Indeed, as it was reported by Le et al. [10], the value of the ideality factor was $\eta = 15$, whereas in [11] — $\eta \sim 48$. The large values of the ideality factor indicate a high density of trap states [12]. The considerable deviation of η from the ideal case ($\eta = 1$ for the thermionic emission model) may be also linked to the quality of the contacts to the p - n junction [10, 13].

Fig. 8. Integrated EL intensity of the investigated n -ZnO nanorods/ p -GaN diode structures as a function of the injection current (the solid lines represent the fitting results based on the power law $L = CI^n$): LED obtained on the basis of ZnO nanorods grown using the method of gas-transport reactions (insert — photograph of light emission at the forward current of 6.7 mA) (a), LED obtained on the basis of ZnO nanorods grown using the hydrothermal method (insert — photograph of light emission at the forward current of 3.3 mA) (b)

EL spectra of n -ZnO/ p -GaN LEDs created on the basis of ZnO nanorods grown using the two different methods are shown in Fig. 7. The EL spectra of both LEDs contain a single band in the UV region with a maximum at 390 nm. With the increase in injected currents the emission peak was significantly enhanced.

It should be noted that there is some difference between the PL and EL processes. The PL process depends on the recombination of nonequilibrium carriers in the surface layer, whereas the EL process is determined via the carrier recombination within the space charge region of the heterojunction. On the other hand, the junction heating effect under a constant injection current will cause band bending consequently leading to the red shift in the EL peak.

In order to clarify the mechanism of the variation in the EL intensity of n -ZnO/ p -GaN LEDs, the integrated

intensity of the EL peak as a function of the injection current in a log-log scale is plotted in Fig. 8. The results can be fitted with the power law $L = cI^n$, where n accounts for the influence of non-radiative defects in the characteristics of light emission [4, 14]. A linear increase in L with I , i.e., $n = 1$ can be expected when radiative recombination dominates, while non-radiative recombination becomes dominant when L shows a superlinear dependence on I , i.e., when $n > 1$.

Fig. 9. Gaussian fits of the EL spectra of LEDs created on the basis of: ZnO nanorods grown by the method of gas-transport reactions (a), ZnO nanorods grown by hydrothermal method (b)

Our result shows dependence with $n \simeq 0.99$ for both *n*-ZnO/*p*-GaN LEDs. This value indicates a low impact of non-radiative recombination centers in the space-charge region.

In order to understand the origin of the light emission, the EL bands in the spectra of LEDs based on ZnO nanorods grown using the method of the gas-transport reaction and the hydrothermal method, were decomposed into four and three Gaussian parts, respectively, as is shown in Fig. 9. The emission peaks at 389–391, 410–412 and 436–438 nm correspond to the near-band-edge (NBE) recombination of ZnO [15–17], interface carriers recombination of ZnO/GaN [1, 18] and to the electrons' transition from the GaN conduction band to Mg^{2+} doping level, respectively [1, 18]. On the basis of the literature data [2, 19, 20] and our experimental results, the luminescence band with a maximum at 502 nm would be related to the emission from the defect levels in ZnO.

IV. CONCLUSION

In summary, one can conclude that *n*-ZnO nanorods/*p*-GaN film heterojunction LEDs structures have been created on the basis of ZnO nanorods prepared using the gas-transport reactions and hydrothermal methods. LEDs of the both types showed UV emission at different values of the forward injection currents.

The bands in EL spectra of the LEDs with ZnO nanorods grown using the method of the gas-transport reaction and the hydrothermal method were decomposed into four and three Gaussian parts, respectively. On the basis of the data of XRD, electrical and optical studies, one can conclude that the emission peaks at 389–391, 410–412, 436–438 and 502 nm correspond to the NBE recombination of ZnO, interface carriers' recombination of ZnO/GaN, the electrons' transition from the GaN conduction band to Mg^{2+} doping level, and to the emission from the defect levels in ZnO, respectively. However, a LED based on ZnO nanorods synthesized using the hydrothermal method emitted more pure UV light.

The obtained results would be fruitful for designing highly-efficient, low cost nanoscale heterojunction UV LEDs with optimized parameters.

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УЛЬТРАФІОЛЕТОВА ЕЛЕКТРОЛЮМІНЕСЦЕНЦІЯ СВІТЛОДІОДНИХ ПРИСТРОЇВ НА ОСНОВІ НАНОСТРИЖНІВ *n*-ZnO, ВИРОЩЕНИХ ЗА РІЗНИМИ МЕТОДАМИ, ТА ПЛІВОК *p*-GaN

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Створено світловипромінювальні діодні структури (світлодіоди) на основі гетеропереходу плівка *p*-GaN/*n*-ZnO квазішар із нанострижнів. ZnO наноструктури вирощено двома різними методами на поверхні підкладок GaN з *p*-типом провідності. Морфологію поверхні експериментальних зразків досліджено за допомогою растрового електронного мікроскопа. Нанострижні ZnO, отримані методом газотранспортних реакцій, мали діаметр від 0.2 мкм до 0.5 мкм, і деякі з них утворювали агломерати стрижнів із поперечним діаметром не більшим за 1.5–2 мкм. Нанострижні ZnO, вирощені гідротермічним методом, мали довжину приблизно 3–4 мкм і середній діаметр – приблизно 200–500 нм. Спектри фотолюмінесценції виміряні за кімнатної температури нанострижнів ZnO, вирощених двома різними методами, містили дві смуги в ультрафіолетовому та видимому діапазонах хвиль світла. Смуга з максимумом за 388 нм є типовою для ZnO і може виникати внаслідок рекомбінації вільних екситонів, зв'язаних екситонів та переходів у донорно-акцепторних парах. Широка смуга в межах приблизно від 450 нм до 750 нм пов'язана з дефектами, насамперед із неконтрольованими домішками та дефектами стехіометрії. Напруги ввімкнення гетеропереходів ZnO/GaN у світлодіодах із нанострижнів ZnO, вирощених, дорівнювали 6.5 В і 3.2 В відповідно. Отримані значення факторів ідеальності діода приблизно мали 36 і 45 для зразків з нанострижнями ZnO, вирощеними гідротермічним та газотранспортних реакцій методами відповідно. Великі значення факторів ідеальності вказують на високу щільність станів пасток і також можуть бути пов'язаними з якістю контактів до *p*–*n* переходів. Спектри електролюмінесценції світлодіодів із нанострижнів ZnO, вирощених методом газотранспортних реакцій та гідротермічним методом, апроксимовано, відповідно, чотирма та трьома гаусіанами. На основі даних дифракції Х-променів, електричних та оптичних досліджень піки електролюмінесценції за 389–391, 410–412, 436–438 та 502 нм пов'язано з прикорайовою емісією в ZnO, інтерфейсною рекомбінацією носіїв у ZnO/GaN-переході, електронними переходами зі зони провідності GaN на рівень легуючої домішки Mg²⁺ та з емісією з дефектного рівня в ZnO відповідно. Світлодіод на основі нанострижнів ZnO, вирощених гідротермічним методом, випромінював чистіше ультрафіолетове світло.

Ключові слова: оксид цинку, нітрид галію, нанострижні, гетероперехід, електролюмінесценція.