

Green luminescence of ZnO microrods

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Investigations of the photoluminescence spectra of zinc oxide microrods grown from a vapor phase were performed. It was concluded that the green photoluminescence of ZnO can be related to the electronic transitions from Zn_i^+ donor levels on the V_{Zn} neutral acceptor levels and emission from the singly ionized oxygen vacancy V_O^+ levels, respectively.

Key words: Zinc oxide, Microrods, Photoluminescence, Luminescence kinetic characteristics, Intrinsic defects

1 Introduction

Zinc oxide is a wide-bandgap semiconductor whose unique properties make it the most realistic alternative to the more expensive gallium nitride in electronics [1]. In recent years, the extraordinary multifunctional properties of ZnO nanostructures were demonstrated. In particular on the basis of these materials field-effect transistors, nanogenerators, solar cells, light-emitting diodes, optically pumped lasers, chemical and biological sensors, detectors of ultraviolet and optical switches were realised [2]. Zinc oxide is non-hygroscopic, stable over a wide range of temperatures, mechanically robust, and sufficiently dense, 5,61 g/cm³. Currently, some compounds based on ZnO are considered as promising fast scintillators [3]. Efficient ultrafast (<1 ns) scintillations have been observed in ZnO:Ga and ZnO:In phosphors [3]. The ZnO:Zn scintillators containing ⁶Li, have been developed for high-counting rate neutron imaging [3]. The scintillators based on ZnO show a high radiation hardness and appropriate stopping power. Such scintillating materials could hold a central position among the fast scintillators, however, for many purposes the large-volume scintillators are required. Despite the long history of industrial

applications of ZnO, there is no clear understanding of some of the fundamental properties of this material [4, 5]. In particular, the emission bands of zinc oxide have not been completely interpreted. A precise understanding of the nature of these bands is necessary for creating of light emitting devices based on ZnO, such as light emitting diodes, lasers and scintillators. Thus, the nature of the green luminescence band of the undoped ZnO has been controversial for decades. In early papers the defects responsible for the green luminescence was uniquely considered to Cu^{2+} , ions replacing the zinc ions at the crystal lattice sites [2]. But now, the relevant defects are considered to be either oxygen (V_{O}), or zinc (V_{Zn}) vacancies, or interstitial zinc atoms (Zn_i) [2].

In this work the visible luminescence spectrum of ZnO microrods, grown from a vapor phase, was measured at liquid-helium temperatures and identified.

2 Experiment

ZnO hexagonal microrods were produced from a vapor phase on the single crystal (100) silicon substrates [6]. The mixture of the powdered high purity zinc oxide and graphite in the proportion of 1:2 was taken as an initial material for vaporization. This material and Si 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 850°C and the substrates were located in the zone with the temperatures of $600\text{--}650^\circ\text{C}$. These temperature distributions were maintained for 1.5 h. Afterwards the oven was shut off and naturally cooled to room temperature. This yielded a deposited white layer of zinc oxide on the substrates.

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 monochromator MDR-6 (LOMO, Saint Petersburg, Russia), connected with photosensor modules HAMAMATSU H9305-04. The sample was excited by GaN laser (405 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).

3 Result and discussion

The morphology of ZnO microrods is shown in Fig. 1. ZnO microrods are characterized by the length of about $25\ \mu\text{m}$ with diameter of about $0.5\text{--}3\ \mu\text{m}$.

The photoluminescence spectrum of the obtained sample, measured at $T = 13\ \text{K}$, is characterized by two intensive overlapping bands with the maxima at 500 nm and 560 nm in the visible region (Fig. 2). It was found that the decay kinetics of these two overlapping bands of photoluminescence at $T = 13\ \text{K}$ consists of two components – fast and slow (Fig. 3, Table 1).

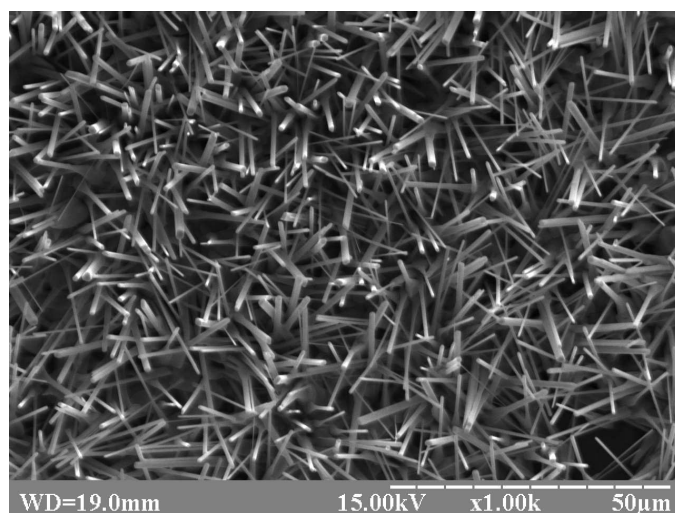


Fig. 1: Microphotographs of ZnO hexagonal microrods

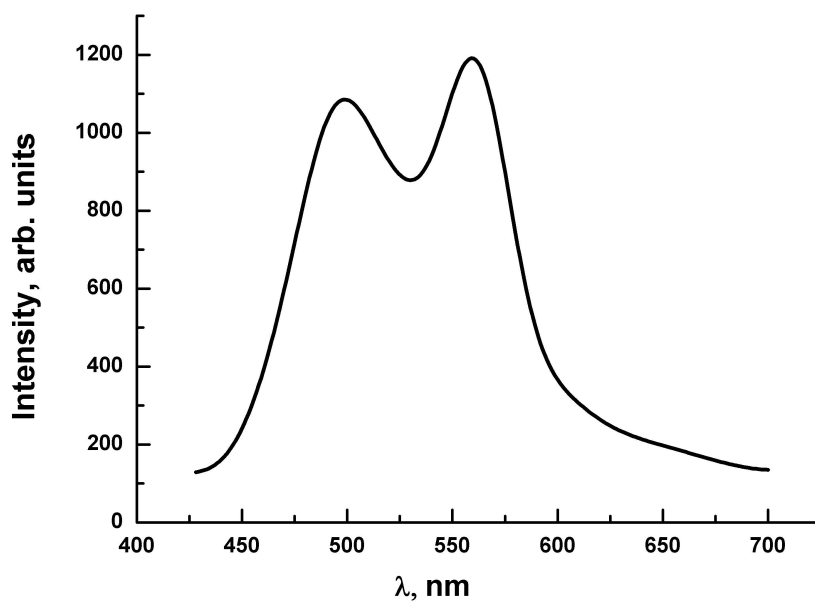


Fig. 2: The photoluminescence spectra of ZnO microrods measured at $T = 13$ K

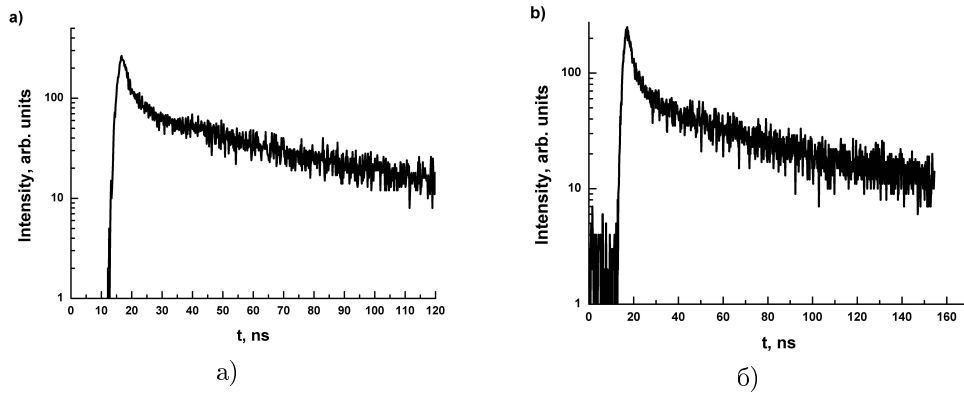


Fig. 3: The decay time curves of the ZnO microrods photoluminescence bands under GaN laser (405 nm) excitation, measured at $T = 13$ K: a) bands with a maximum at 500 nm; b) bands with a maximum at 560 nm

Table 1: Parameters of photoluminescence decay curves of the ZnO microrods under GaN laser (405 nm) excitation, measured at $T = 13$ K

Emission band, nm	Decay time of the fast component t_1 , ns	Amplitude of the fast component, A1	Decay time of the slow component t_2 , ns	Amplitude of the slow component, A2
500	18	625	300	28285
560	23	1005	450	27455

In our previous works [7, 8], devoted to the thermally stimulated luminescence studies of ZnO nanostructures, grown from the vapor phase, in the temperature range of 110–480 K, we have established that the emission band with a maximum at about 490–500 nm can arise due to the electronic transitions from Zn_i^+ donor levels on V_{Zn} neutral acceptor levels. This conclusion correlates with the results of [9].

The authors of the papers [10–15] also observed the peak at about 560 nm in the photoluminescence spectrum of the ZnO nanostructures. It was related to the oxygen vacancies. The recombination occurs between a hole in the valence band and an electron deeply trapped in a singly ionized oxygen vacancy V_O^+ . Single ionized oxygen vacancy V_O^+ is thermodynamically unstable and immediately is transformed into V_O neutral oxygen vacancy after termination of excitation [12, 16].

On the basis of the literature data and our experimental results we relate the luminescence bands with the maxima at 500 and 560 nm to the electronic transitions from Zn_i^+ donor levels on V_{Zn} neutral acceptor levels and to the emission from the single ionized V_O^+

Conclusions

In summary, ZnO hexagonal microrods were produced from a vapor phase and their morphology was investigated. The photoluminescence spectrum of ZnO microrods in a visible range, measured at $T = 13$ K, was interpreted. The photoluminescence bands with the maxima at 500 and 560 nm were related to the electronic transitions from Zn_i^+ donor levels on the V_{Zn} neutral acceptor levels and to the emission from the singly ionized V_O^+ oxygen vacancy levels, respectively.

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Зелена люмінесценція мікрострижнів ZnO

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Мікрострижні ZnO, довжиною приблизно 25 мкм та з діаметром у діапазоні від 0,5 до 3 мкм, вирощено з парової фази на кремнієвій підкладці. Морфологію поверхні експериментального зразка досліджено за допомогою растрового електронного мікроскопа. За температури 13 К при збудженні напівпровідниковим GaN лазером з довжиною хвилі генерації світла 405 нм виміряно спектр фотолюмінесценції мікрострижнів оксиду цинку у діапазоні довжин хвиль від 425 до 700 нм. Цей спектр містив дві смуги, що перекривалися, з максимумами при 500 та 560 нм. Досліджено кінетику загасання даних смуг. Для обох смуг свічення виділено швидку та повільну компоненти загасання. На основі отриманих експериментальних результатів та опрацювання наукових даних, зроблено припущення, що смуги випромінювання в спектрах фотолюмінесценції мікроструктур ZnO з максимумами в околі 500 та 560 нм виникають внаслідок електронних переходів з донорного рівня одноразово іонізованого міжвузлового цинку Zn_1^+ на акцепторний рівень нейтральних вакансій цинку V_{Zn} та рекомбінації дірок з валентної зони з електронами, захопленими на рівні одноразово іонізованих вакансій кисню V_O^+ , відповідно. Оскільки одноразово іонізовані вакансії кисню V_O^+ є термодинамічно нестабільними і відразу ж після припинення збудження перетворюються на нейтральні вакансії кисню V_O , висловлено гіпотезу про те, що за швидку компоненту загасання смуг фотолюмінесценції в мікроструктурах відповідальними є саме такі власні дефекти в ZnO, як одноразово іонізовані вакансії кисню V_O^+ . ZnO – матеріал більш щільний, ніж пластмасовий сцинтилятор, негігроскопічний, стабільний в широкій області температур, механічно і радіаційно стійкий, недорогий. Тому кристали ZnO можна розглядати як перспективні сцинтилятори для прецизійних часових вимірів в широкому температурному діапазоні.

Ключові слова: оксид цинку, мікрострижні, фотолюмінесценція, кінетичні характеристики люмінесценції, внутрішні дефекти

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