



Photoluminescence characterization of vertically aligned ZnO microrods

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ABSTRACT

A detailed optical characterization of vertically aligned ZnO microrods (μ Rs) grown using a Ni-based catalyst was carried out by excitation-power- and temperature-dependent photoluminescence (PL) measurements. Low-temperature PL spectra of ZnO μ Rs are dominated by near-band-edge (NBE) emission consisted of a series of sharp lines typical for the bulk ZnO. Starting from the higher energy free exciton (FX) emission feature, the majority of them can be explained by radiative recombination of excitons bound to neutral donors (D^0X), defect bound exciton (DBX), two-electron satellites emission, free-to-bound, i.e. free electrons to the neutral acceptors (eA^0) transition, as well as their longitudinal-optical phonon replicas. An additional excitonic line located in between the FX and D^0X lines, denoted as the surface excitons (SX) for ZnO μ Rs is observed. The intensity of the SX line is found to be smaller than that of the nanosized counterpart and has been attributed to the surface–volume ratio effects. The excitation-power-dependent results of FX line at low and high power regimes show quite close values corresponding to, respectively, $p=2$ and $p=1$ limits of the theoretical power law expression $I \sim I^p$ and larger deviations for the D^0X , SX and DBX lines. The temperature-dependent measurements confirmed the presence of eA^0 line showing $kT/2$ influence to the position of eA^0 emission line in comparison with FX. FX emissions persist up to 300 K and together with the dominant eA^0 emission govern the line shape of the NBE emission range, while D^0X and SX lines are quenched completely at 150 K.

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1. Introduction

A wide direct band gap ZnO semiconductor with a large exciton binding energy is recognized as a very promising material for short-wavelength optoelectronic devices [1,2]. One-dimensional (1D) ZnO nanostructures, such as nanowires and nanorods, have been extensively investigated due to their functional device applications as nanolasers [3], nanogenerators [4], light-emitting diodes [5], photodetectors [6,7], bistable memory devices [8], etc. Such 1D-structures have not yet attained the quantum confinement state but they are small enough to exhibit the enhanced surface effects.

In comparison with the photoluminescence (PL) results of bulk ZnO [9–11] and the cathodoluminescence (CL) data obtained from ZnO microwires [12], the low-temperature PL spectra of nanosized materials show quite different spectral features in the near-band-edge (NBE) range. For the nanosized materials [13,14], the appearance of an additional prominent NBE PL peak around 3.367 eV was shown. Moreover, its intensity increases with the

decreasing size; thus it was assigned to the recombination of surface excitons (SX) [15,16]. Also, the low-temperature emission band at 3.31 eV has been observed by PL and CL in a great variety of research works on ZnO materials. In the majority of the relevant works, the observed feature has been interpreted as the transitions of free electrons to neutral acceptor states (eA^0) [11,17,18], electron–hole recombination from donor–acceptor pairs (DAP) [19,20] and to longitudinal-optical (LO) replicas of free excitons (FX) recombination [21–23]. Schirra et al. [18] showed by detailed line shape analysis at different temperatures that the band originates from an eA^0 transition with the acceptor binding energy of 130 meV. Using CL measurements, it was concluded that the localized acceptor states are located in the basal plane stacking faults. Furthermore, Travlos et al. [17] attributed the acceptors to zinc vacancies. Zhang et al. [19] suggested that the emission peak is due to DAP at low temperature, and it is correlated to eA^0 appearing at 14 meV higher than DAP emission with the temperature increasing. Moreover, taking into account the intensity raise of DAP recombination with the increase of indium content for In-doped ZnO, Liu et al. [20] suggested that DAP emission is related to In doping. On the other hand, Chen et al. [23] have pointed out that whereas the no-phonon FX emission usually prevails in bulk ZnO, it is often weak in micro- and nanostructures where LO phonon-assisted

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FX transitions dominate. This phenomenon has been attributed by Voss et al. [24] to enhanced exciton–phonon coupling, but the exact mechanism remains still unclear.

In the present paper, the PL of vertically aligned ZnO microrods (μ Rs), grown using a Ni-based catalyst, with the diameter around $\sim 1 \mu\text{m}$ is investigated. Being a frontier object between bulk and nanosized materials, the arrays of ZnO μ Rs are used to identify the influence of the surface-to-volume ratio to PL properties. The PL recombination mechanisms are clarified by carrying out the excitation-power- and temperature-dependent measurements. The results are presented and discussed.

2. Experimental

Vertically aligned ZnO μ Rs were grown on the catalyst-coated sapphire substrates by thermal evaporation under a mixture flow of O_2 and N_2 with a mixture of Zn and ZnO [25]. The as-growth morphology and structure of ZnO μ Rs were investigated by a JEOL-JSM 6500 F field emission scanning electron microscopy (FESEM) with an accelerating voltage of 15 kV. The as-grown samples represent a slender, uniform and vertically aligned ZnO μ Rs (Fig. 1(a)) with the diameter of $\sim 1 \mu\text{m}$ (Fig. 1(b)) and a long length of $\sim 10 \mu\text{m}$ (Fig. 1(c)). For PL measurements, a 325 nm line of a He–Cd laser with a full power of $\sim 35 \text{ mW}$ and a spot diameter $\sim 1 \text{ mm}$ was used as the excitation source. PL emission was analyzed using a 2400-line/mm grating Jobin-Yvon “TRIAX 550” spectrometer equipped with a “SIMPHONY” charge coupled device camera. Wavelength calibration of the spectrometer was provided by scanning the 365.015 nm emission line of an Ocean Optics HG-1 mercury argon calibration light source. For low temperature measurements, a closed-cycle cryogenic refrigerator equipped with a digital thermometer controller was used to control the measurement temperature between 10 and 300 K with a temperature stability of 0.5 K or better.

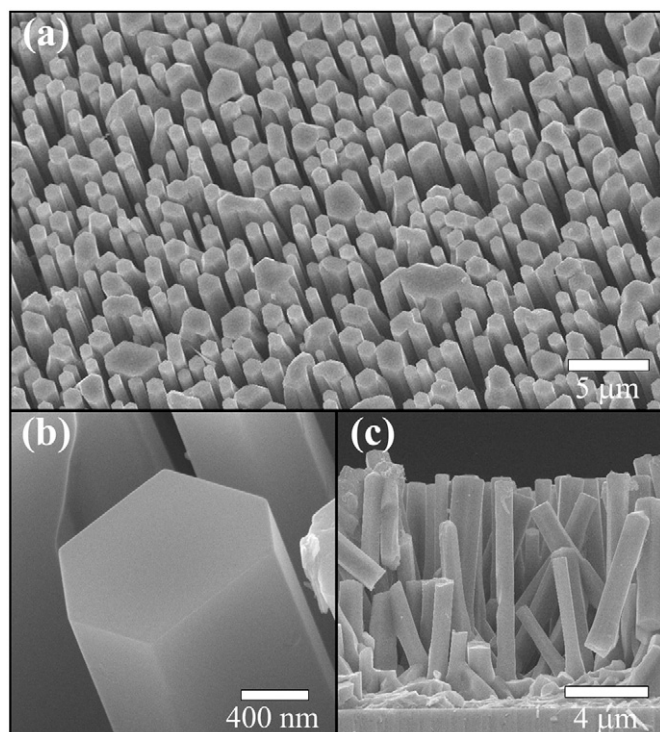
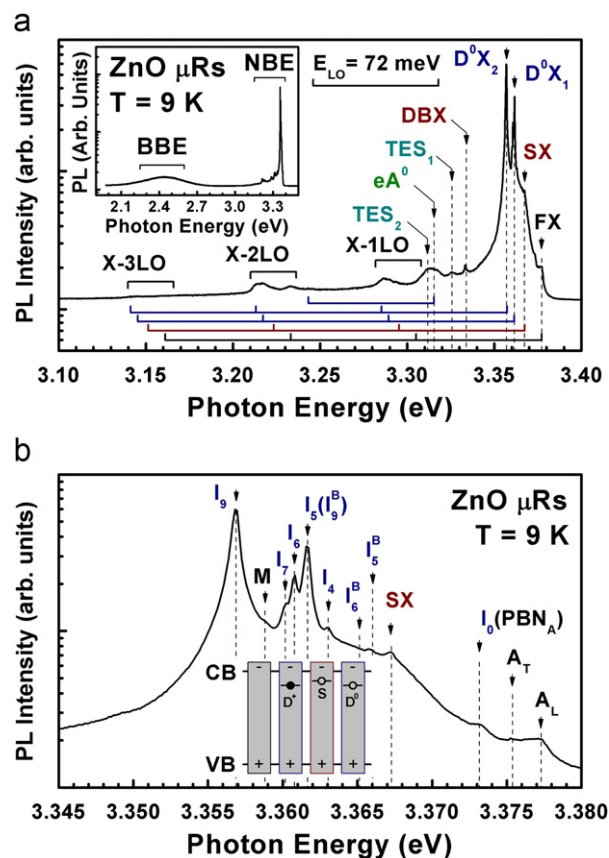


Fig. 1. FESEM images of ZnO μ Rs of (a) the array at a tilted angle, (b) a single MR and (c) the array from the cross-section.

3. Results and discussion

Being an intrinsic property of the material, free exciton emissions are common to all samples and therefore in PL spectra they should always be identified first since it can provide a reference for bound exciton identification. Free exciton emissions are usually the highest energy peaks which are the last NBE peaks to disappear with increasing temperature since bound excitons become thermally delocalized from their binding centers. The PL spectra of ZnO μ Rs measured at 9 K are shown in Fig. 2. Fig. 2(a) presents the NBE emission spectrum in the energy range between 3.1 and 3.4 eV. Starting from high to low energy, the emission lines are assigned to the free excitons (FX) recombination, surface excitons (SX), excitons bound to the neutral donors (D^0X), two-electron satellites (TES) emission, and free electrons to the neutral acceptors (eA^0) transition, as well as LO phonon replicas of the designated above emission lines. The inset of Fig. 2(a) shows in the visible range the rather weak broad-band-emission (BBE) which is related to the deep level defect at $\sim 2.45 \text{ eV}$, and NBE emissions in the UV region. The green BBE is generally regarded to be related to surface defects such as oxygen vacancy and/or Zn vacancy [26]. The origin and detailed analysis of the emission features observed in PL spectrum of NBE region are discussed as follows.

For a more detailed study of the NBE excitonic lines, PL spectrum in the energy range from 3.345 eV to 3.380 eV is presented in Fig. 2(b). In the FX emission region, two emission lines A_L (3.3773 eV) and A_T (3.3754 eV) are related to the position of the longitudinal and transverse free A-exciton energies, respectively. Such luminescence lines have been observed previously for



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