Spatially-resolved Study of the Luminescence from ZnO/MgO Core-shell Nanocrystal Structures

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The luminescent properties of core-shell nanocrystal structures were investigated with high spatial resolution. The composites consisting of ZnO/MgO core/shell nanoheteroparticles showed an increase in the relative intensity of the green luminescence after annealing while a suppression of green luminescence from samples of ZnO tetrapods in a MgO nanoparticle matrix was observed. Combined spatially-resolved combined through-the-lens-detector (TLD) and cathodoluminescence (CL) measurements revealed that the depletion of electrons in the ZnO nanocrystals could lead to a suppression of the luminescence.

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I. INTRODUCTION

Nanostructures made from ZnO ($E_g = 3.37 \text{ eV}$) and MgO ($E_g = 7.5 \text{ eV}$) nanocrystals have considerable potential for the manufacture of ultraviolet lightemitting diodes (LEDs) and lasers operating at room temperature. ZnO nanoparticles without a capping agent usually show green luminescence [1] while those with capping agents show strong ultraviolet (UV) emission [2,3]. Mahamuni *et al.* [2] reported an emission peak at 378 nm from tetraoctylammomium-bromide (TOAB)-capped ZnO, and Guo et al. [3] reported that polyvinylpyrrolidone (PVP) passivation of ZnO particles enhanced the UV and diminished the green emission. ZnO nanocrystals capped with the organic dye Rhodamine 6G (Rh6G) showed a remarkable decrease in visible emission intensity [4]. It is known that the surface properties of particles can be dramatically altered by surface segregation of elements or by the creation of a surface shell layer (e.g., MgO) over a core of a different composition (e.g., ZnO). Enhanced and more stable green emission of ZnO: MgO nanoparticles, resulting from the effective surface passivation of the ZnO core by an MgO shell, has been also reported [5]. The electrical and the optical properties of nanoscale materials exhibiting very large surface area-to-volume ratios have been effectively controlled by surface and interface states. Moreover, the space charge region (SCR), which can be significantly extended from the surface or interface, can have a strong effect on the optical properties of nanocrystals. An electric-field-induced color switching of the luminescence from ZnO:Mg nanoparticle/polymer structures [6], as well as optical modulation of the exciton luminescence from ZnO nanoparticles [7], was recently reported.

In this paper, we report on the luminescent properties of two different ZnO/MgO composites prepared from ZnO core/MgO shell nanoparticles and ZnO tetrapods capped by MgO particles. ZnO core/MgO shell nanoparticles annealed at 500 °C demonstrate an enhanced green emission. However, the annealed nanocomposites of the extended ZnO tetrapods/MgO nanoparticles show a rel-

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Fig. 1. (a) TEM micrograph and (b) electron diffraction pattern of ZnO/MgO core-shell particles annealed at 500 $^\circ\mathrm{C}.$

ative reduction of the green luminescence and an enhancement of the UV emission. The mechanism of the quenching of the green luminescence from the extended nanocrystal composites is discussed.

II. EXPERIMENT

The nanocomposites were prepared from ZnO core/MgO shell nanoparticles with sizes in the range of 8 – 100 nm and extended nanocrystals such as ZnO tetrapods (300 - 5000 nm in length and 20 - 500 nmin diameter) capped by MgO nanoparticles (3 - 50 nm). The first nanocomposite was synthesized by using the chemical solution deposition (CSD) technique with a colloidal zinc oxide solution and alcoholic solution of magnesium acetate, as previously described [8,9]. The extended nanocrystal-based composite was prepared from tetrapods grown by using the chemical vapor deposition (CVD) method [10] and MgO particles, which were obtained by thermolysis of a jelly-like product containing a mixture of magnesium acetate and sodium hydroxide alcohol solution [8]. Both nanocomposites were annealed at 400 and 500 °C in air. The low temperature annealing was used to prevent the diffusion of Zn^{2+} cations to the MgO lattice and Mg²⁺ cations to the ZnO lattice and to keep the cubic MgO and the hexagonal ZnO structures [8,11].

The photoluminescence (PL) spectra of the samples were obtained using a monochromatized 300W Xe lamp for excitation. Spatially-resolved cathodoluminescence and electric-field profile measurements were carried out using an XL 30S FEG high-resolution scanning electron microscope (HRSEM) with MonoCl imaging and spectroscopy systems and an electron through-the-lens detector (TLD) [12].

III. RESULTS AND DISCUSSION

The core/shell particles obtained by using the CSD technique have near-spherical shapes (Fig. 1(a)) and con-



Fig. 2. CL spectra of ZnO/MgO core-shell particles annealed at (a) 400 $^\circ \rm C$ and (b) 500 $^\circ \rm C.$

sist of MgO and ZnO phases. The electron diffraction pattern of the annealed nanocomposite contains both cubic MgO structure indices ([220], [200]) and wurtzite ZnO indices ([100], [002], [101], and [110]) (Fig. 1(b)).

Cathodoluminescence (CL) spectra of the core-shell nanoparticles are shown in Fig. 2. The composites annealed at 400 and 500 °C show two peaks, 376 and 512 nm, which are attributed to the free exciton luminescence and the oxygen-vacancy-related emission from ZnO. The blue shift of the excitonic luminescence indicates the quantum confinement effect in the ZnO particles. The relationship between the nanocrystal size and the band gap can be obtained using a number of models [13–15]. One such model is the effective mass model for spherical particles with a Coulomb interaction term [16,17], where the band gap E* [eV] can be approximated by [18]

$$E* = E_g^{\text{bulk}} + [(\hbar^2 \pi^2)/2er^2][(1/m_e m_0) + (1/m_h m_0)] - 1.8e/4\pi\varepsilon\varepsilon_0 r,$$
(1)

where $E_q^{\text{bulk}} = 3.2 \text{ eV}$ is the ZnO bulk band gap, r is the particle radius, $m_e = 0.26$ is the effective mass of the electrons, $m_h = 0.59$ is the effective mass of the holes, m_0 is the free electron mass, $\varepsilon = 8.5$ is the relative permittivity of ZnO, ε_0 is the permittivity of free space, \hbar is Plank's constant divided by 2π , and e is the charge of the electron. The size of the ZnO particles, estimated from Eq. (1) at 8 nm, is in good agreement with the TEM measurements. We noted that the relative intensity of the green luminescence increases with increasing annealing temperature (Fig. 2, curve b). This behavior of luminescence could arise from an increase in the density of radiative singly-ionized oxygen vacancies after the annealing as a result of an increase in the electron concentration in the ZnO particles and a decrease in the concentration of nonradiative centers.

Figure 3 shows PL spectra of ZnO tetrapods and tetrapods capped by MgO particles. The annealed tetrapods demonstrate a high intensity of green luminescence attributed to oxygen-vacancy-related defects. The tetrapods annealed with capping MgO nanoparti-



Fig. 3. Normalized PL spectra of (a) ZnO nanotetrapods (solid line) and (b) ZnO nanotetrapods covered by MgO (dotted line).



Fig. 4. (a) SEM image of the nanotetrapod structure and (b) profiles of the CL intensity and the TLD signal from the structure obtained by electron beam scanning (A-B line in Fig. 4(a)).

cles show, however, suppressed green emission and a relatively-enhanced excitonic luminescence (Fig. 3, curve b).

To study the electronic and the optical properties of the samples on a nanoscale, we carried out TLD and CL measurements. Figure 4(a) shows an SEM image of the tetrapod, and Fig. 4(b) shows profiles of the CL intensity and the TLD signal obtained from the structure by scanning an electron beam along the A-B line. The enhanced TLD signal indicates a depletion of the ZnO surface by electrons and SCR formation. The intensity of the CL from the depletion zone was significantly (about 25%) suppressed.

The green luminescence from ZnO nanocrystals is generally explained by singly-ionized oxygen vacancies V_o^+ [19]. The mechanism for the observed suppression of the green luminescence from the nanocomposite structure can be explained by an electron depletion of the ZnO nanocrystals due to the band bending on the interface between the ZnO and the MgO capping agent (Fig. 5). In the part of this depletion region where the Fermi level E_F passes below the V_O^+/V_O^{2+} energy level, all oxygen vacancies are in the nonradiative V_O^{2+} state (Fig. 5(b)), and the green luminescence from the nanocrystals is sup-



Fig. 5. (Color online) Energy band diagrams of heterojunctions: (a) a ZnO/MgO core-shell particle and (b) a ZnO nanotetrapod covered by MgO particles. E_f is the Fermi energy (dashed line - as grown, dash-dotted line – after annealing). The oxygen vacancy level marked as V_o^+/V_o^{2+} can have one (solid circles) or two holes (open circles).

pressed [20]. In the case of uncapped tetrapods, the electron density (the oxygen vacancies' concentration) is relatively high, and the green emission from such samples is good.

In the case of ZnO/MgO core-shell nanoparticles, the green luminescence's intensity is increased with increasing annealing temperature (Fig. 2). Such behavior can be explained by an increase in the oxygen-vacancy-related defect density and an increase in the electron Fermi energy with increasing temperature of annealing (Fig. 5(a)). Both processes may lead to the observed enhancement of the green luminescence intensity. We should note that the impact of an electron depletion region on the luminescence from nanocomposite structures depends on the size of the crystals, their conductivity (the position of the Fermi level) and the density of electron traps. The depletion region width (W) of ZnO crystals nearby the interface depends on the density of

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states induced by the surface (interface) and the density of donors in the nanocrystals:

$$W = (2\epsilon_{\rm ZnO}V_{bi}/eN_d)^{1/2}, \qquad (2)$$

where ϵ_{ZnO} is the dielectric constant of ZnO, V_{bi} is the potential barrier, e is the electron charge, and N_d is the donor density. The electron density in the as-grown ZnO core/MgO shell particles is usually very low due to low density of surface defects (the low growth temperature), which leads to a considerable electron depletion of asgrown particles (Fig. 5(a), E_F -dashed line). The annealing of such particles at higher temperature increases the donor defect density and shifts the Fermi level to the conduction band (Fig. 5(a), E_F -dash-dotted line). As a result, the green luminescence from the annealed core/shell particles increases. In the case of extended nanocrystals such as tetrapods, the electron density of the as-grown crystals grown at high temperatures is usually relatively high (Fig. 5(b), E_F -dashed line), and the green emission from such samples is good. The extended crystals capped with MgO particles show an electron depletion of the ZnO surface due to a high density of electron traps on the ZnO/MgO interface and the band bending. The density of these states is much higher than in the MgO shell/ ZnO core particle interface. Moreover, annealing the capped tetrapods leads to annihilation of oxygen vacancies and shifts the Fermi energy (Fig. 5(b), dash-dotted line). Furthermore, the height of the potential barrier on the interface depends on the density of surface (interface) states and can be tailored by using an electric field. This makes possible an adjustment of the luminescence from the ZnO/MgO nanocomposites by using a bias voltage. The results obtained from the spatially-resolved CL and TLD measurements indicate that the luminescence from the surface space-charge region of the tetrapods is suppressed. The effect is more pronounced for the more conductive nanocrystals, the size of which is comparable to the width of the surface depletion region, and for a high density of surface/interface states.

IV. CONCLUSION

The luminescent properties of ZnO/MgO nanocomposite structures consisting of ZnO nanocrystals (particles, tetrapods) and MgO shells were investigated. The obtained results show that the hexagonal ZnO and the cubic MgO phases in ZnO/MgO nanocomposites are thermally stable up to 500 °C. The nanocomposites based on ZnO core/MgO shell nanoparticles demonstrate an increased relative intensity of the green luminescence after annealing while a suppressed PL green emission is observed from the annealed nanocomposites consisting of extended ZnO nanocrystals such as tetrapods capped by MgO nanoparticles. Spatially-resolved CL and TLD measurements showed that the luminescence from the extended ZnO crystals was suppressed in the SCR due to a built-in electric field and an enhanced density of nonradiative centers. The covering of the extended nanocrystals by MgO particles led to an electron depletion of ZnO and to the formation of surface band bending, which increased the portion of nonradiative states (doubleionized oxygen vacancies).

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