EFFECT OF Eu DOPING ON THE OPTICAL PROPERTIES OF ZnO NANORODS PREPARED BY CHEMICAL BATH DEPOSITION

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Abstract

We report on the properties of Eu-doped ZnO nanorods prepared by chemical bath deposition from aqueous solutions in an autoclave. The autoclave enables to grow the nanorods above the boiling point of water. The nanorods were characterized by scanning electron microscopy, secondary ion mass spectroscopy, and low temperature photoluminescence spectroscopy. Under the UV light excitation, the nanorods show a strong blue emission at 450 nm, which is associated with the $4f^6 5d$ - $4f^4$ transitions of Eu^{2+} ions. We discuss the mechanisms responsible for the blue luminescence. We further clarify how the growth parameters affect the morphology and the optical properties of the nanorods. Growth temperatures above the boiling point of water significantly influence the intensity ratio of the near band edge emission to the deep level emission and greatly enhance optical quality of the nanorods.

Keywords: ZnO nanorods, rare earth elements, europium, energy transfer, luminescence

1. INTRODUCTION

The low growth temperature of chemical bath deposition generally results in a high density of native point defects, which strongly affect electrical and optical properties of ZnO nanorods (NRs) [1]. Defect control in ZnO is one of the major issues to be solved for successful application in optoelectronic devices. While the growth temperature in conventional reactors is limited by the boiling point of the chemical bath (water solution), polypropiolactone (PPL) lined autoclaves enable to increase the temperature to 280 °C.

ZnO is also attractive as a host material for visible luminescence centers. This is because ZnO or its nanostructures have a potential to be used as highly efficient and environmentally friendly phosphors [2-6]. In recent years, doping of ZnO with Eu ions has attracted a great attention. Eu can be incorporated either as Eu^{3+} ions, which show red luminescence, or as Eu^{2+} ions, which show blue luminescence. The emission from the Eu state under UV excitation is associated with the energy transfer from the host ZnO to Eu ions. The direct energy transfer from the ZnO exciton level to Eu excited state is unlikely, because the radiative/nonradiative decay of ZnO excitons is much faster than the energy transfer to the rare earth [5]. However, deep defect levels have been shown to facilitate energy transfer, resulting in efficient luminescence from Eu ions [6]. In this work, we demonstrate how the growth in an autoclave can improve optical properties of ZnO NRs. We further report on blue luminescence from Eu doped ZnO NRs.

2. EXPERIMENTAL

The nanostructured ZnO seed layers were prepared by the sol-gel synthesis on n-type Si substrates. Detailed information on the preparation of c-axis oriented seed layers was given in our previous work [7], where the oriented seed layer was shown to be a prerequisite for the vertical alignment of ZnO NRs. The ZnO NRs were grown on the seed layers by chemical bath deposition from aqueous solutions consisting of zinc nitrate hexahydrate and hexamethylenetetramine (HMTA) in PPL lined autoclave placed in a muffle furnace at 95 - 280 °C for 1 - 6 h. Europium nitrate hydrate was used for the doping of ZnO NRs with Eu. The surface morphology of undoped and Eu-doped ZnO NRs was observed by scanning electron microscopy (SEM). The seed layer thickness was evaluated from the cross section SEM images. PL spectra were measured with a

set-up comprising a HeCd laser (325 nm) as an excitation source, a grating monochromator Jobin Yvon THR 1000, a closed cycle He optical cryostat, and a photomultiplier detection system (S1 operated at 77 K). The PL spectra for all samples were measured at identical condition (slits, power density, and set-up configuration). Secondary-ion mass spectrometry (SIMS) was used to analyze the composition of ZnO:Eu NRs and to determine the Eu dopant depth concentration using the time of flight SIMS spectrometer installed in a dual beam (FIB-SEM) chamber. All TOF-SIMS spectra were measured using the Ga$^+$ ion beam with the energy of 30 keV and current of 200 pA.

3.   RESULT AND DISCUSSION

Figure 1 shows top-view and cross-sectional SEM images of ZnO NRs prepared in both a conventional open-system reactor (batch reactor) [8] and in the autoclave.
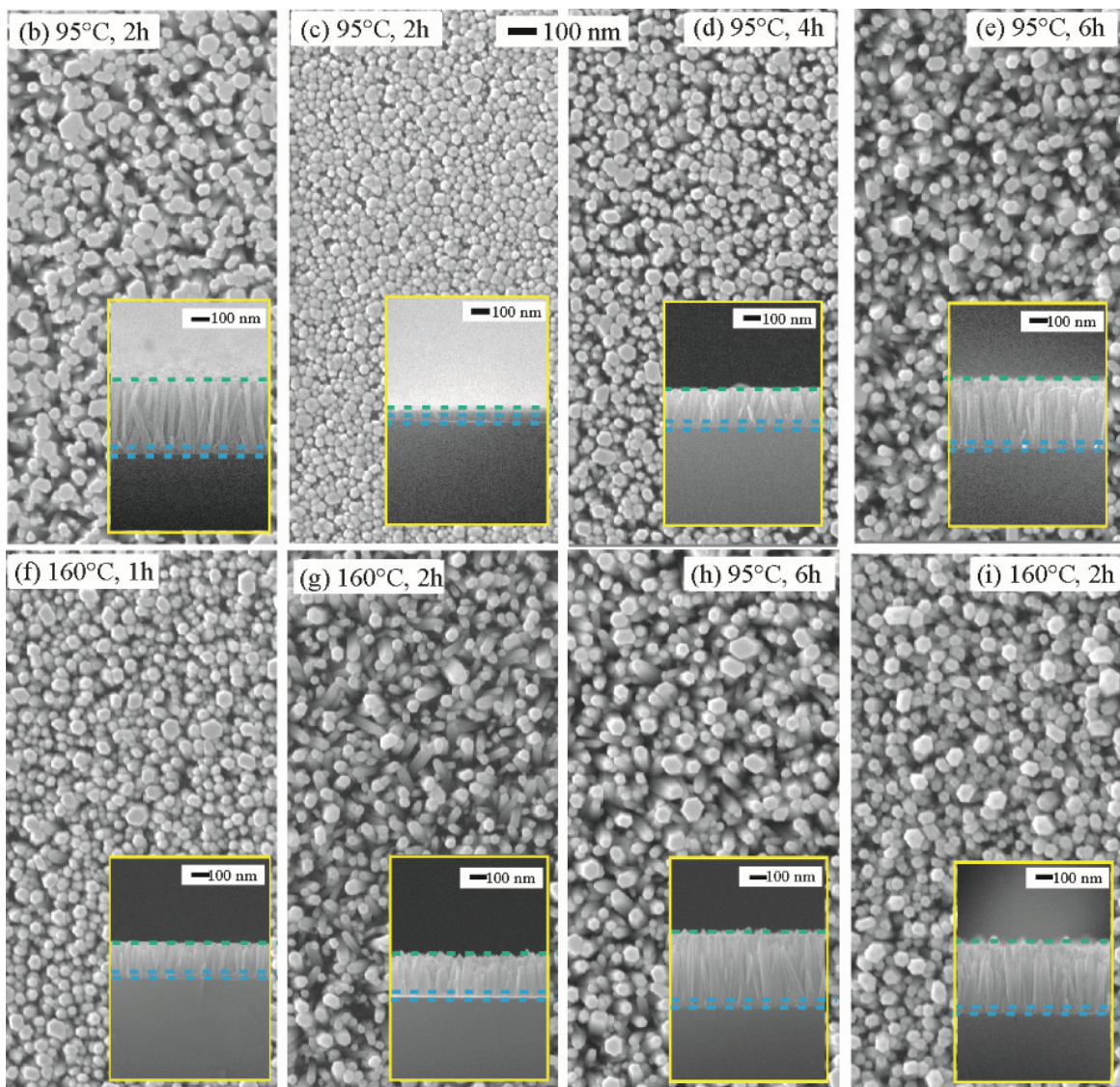

Figure 1 Top-view and cross-sectional SEM images of: (b) undoped ZnO NRs grown in the batch reactor and (c-g) in the autoclave; and (h,i) Eu doped ZnO NRs grown in the autoclave

Vertically oriented NRs with the diameters corresponding to the size of the nanocrystals of the seed layer were grown in both reactors when identical growth conditions (95 °C and 2 h) were employed (**Figure 1b,c**).

Nevertheless, in the autoclave, the length of the ZnO NRs was significantly lower, while their density was larger, which is related to higher nucleation density of the NRs in the autoclave. This difference in the NR length is related to the fact that the growth is diffusion limited; the growth units are quickly incorporated into the c-planes of the NRs and the diffusion is the limiting factor. The larger is the integral area of c-planes, the lower is the vertical growth rate. The NR length can be easily tuned by increasing the growth time (**Figure 1c-e**). At elevated temperature of 160 °C, the top surface of the nanorods changes form flat to pyramid-like morphology (**Figure 1g**). This change in morphology can be ascribed to the etching of ZnO nanorods by the undersaturated growth solution. At higher temperatures, the growth solution becomes quickly depleted of the growth units by both homogeneous and heterogeneous nucleation and growth. Growth times increased above 2 h result in the etching of the seed layer. **Figures 1h** and **1i** show SEM images for Eu-doped ZnO NRs (5 % in the growth solution) prepared under optimum growth conditions.

Figure 2 shows positive ion mass spectra of undoped ZnO NRs (a) and Eu-doped ZnO NRs (b) grown under the same conditions (160 °C, 2 h) with well pronounced peaks of Ga, Zn, Si and Eu ion isotopes. Corresponding depth distribution of ^{151}Eu and ^{64}Zn ion isotopes is shown in **Figure 3**. Depth of the interface corresponds to the NR height distribution observed by SEM. The higher ion yield close to the ZnO/Si interface is related to the unique geometry enhancing the generation of secondary ions.
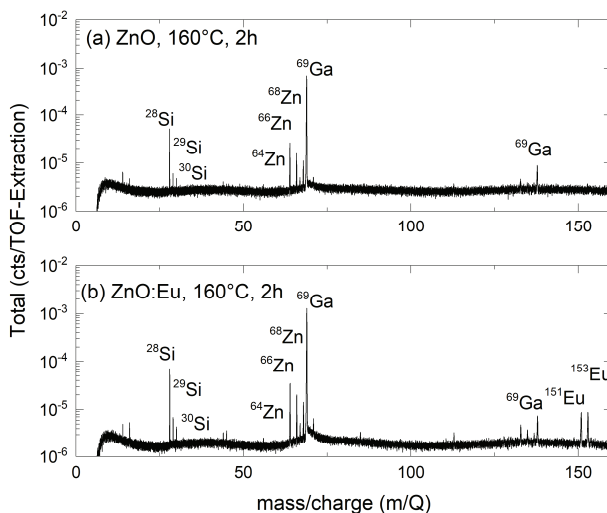

**Figure 2** Mass spectra for undoped ZnO NRs (a) and Eu-doped ZnO NRs (b)
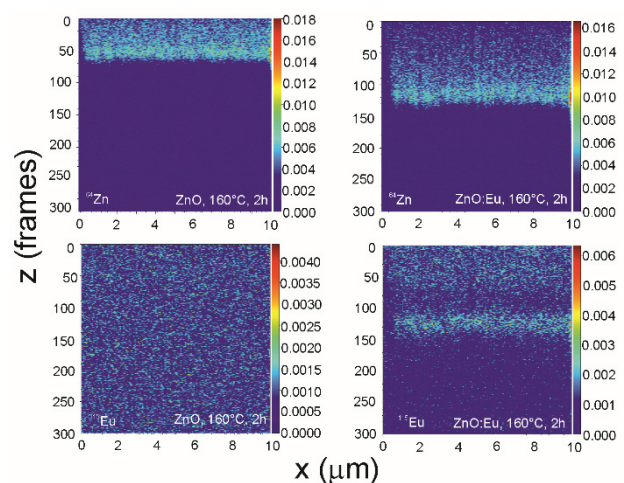
Figure 3 Depth distribution of the ^{64}Zn (top) and ^{151}Eu (bottom) ion isotopes for ZnO NRs and Eu-doped ZnO NRs

Figure 4i shows photoluminescence (PL) spectra of ZnO nanorods from **Figure 1**. The measured spectra are typical for the nanorods grown from solutions with the near band edge emission (NBE) in the UV region and the broad deep level emission (DLE) in the visible region. At room temperature the DLE is composed of the red luminescence at 1.82 eV (RL), orange luminescence at 2.05 eV (OL), and yellow luminescence at 2.2 eV (YL) [7,8]. The quantitative picture of the PL spectra for different growth temperatures and different growth times does not change (**Figure 4i-b,c,d,e**); however, when the growth temperature increases, the NBE/DLE intensity ratio also increases. This indicates substantial improvement of the optical and structural properties of the ZnO NRs (inset **Figure 2i**). The low temperature PL spectra in **Figure 4ii-c,d,e**, show that when the length of the ZnO NRs is higher than 500 nm, the near band edge emission is dominated by the donor bound exciton at 3.36 eV (DBE) and donor-acceptor transition 3.22 eV (DAP) [9]. The lines at 3.31 eV labeled as A are associated with the bound exciton to structural defect transition and were observed only for the seed layers or for the NRs with the length lower than 500 nm [8,10]. The presence of the luminescence at 3.31 eV for the ZnO NRs (I < 500nm) is due to superimposed defect luminescence from the seed layer.
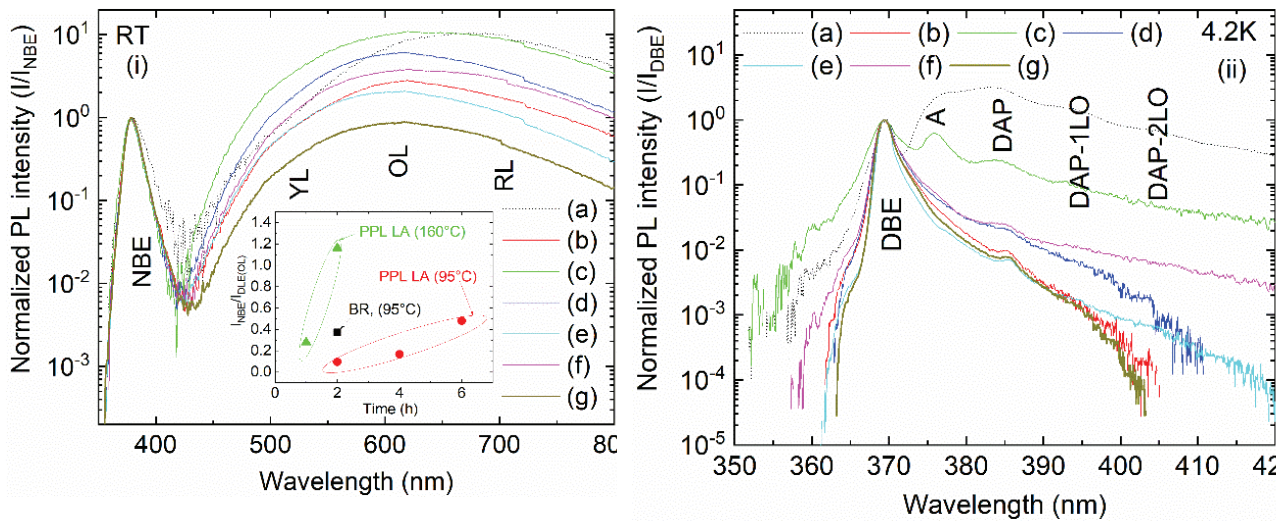
Figure 4 PL spectra measured at (i) room temperature and (ii) at 4.2 K. The samples (b) - (g) correspond to nomenclature from Figure 1. (a) PL spectra for the seed layer prepared by the sol-gel method. The inset shows the I_{NBE}/I_{DLE} ratio as a function of the growth time. BR - batch reactor, PPL LA - autoclave.

The Influence of Eu-doping on the emission spectra of the ZnO NRs is presented in **Figure 5**. Under 325 nm excitation, a new blue emission band (BL) peaked at 450 nm was observed for the samples with the growth temperature higher than 160 °C. The BL emission can be associated with the $4f^65d$ - $4f^4$ transitions of Eu^{2+} [11]. The diagram of the energy transfer process from ZnO to Eu^{2+} is shown in **Figure 6**. Two mechanisms can be responsible for the BL; the Eu^{2+} 5d state is either excited directly by the 325 nm laser wavelength or the energy transfer is mediated by the deep levels.
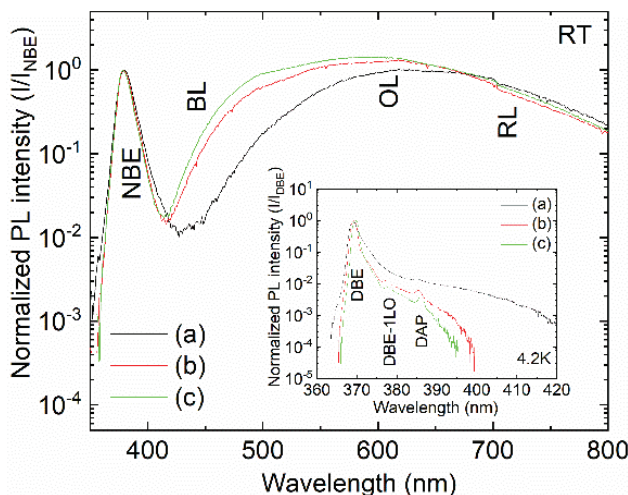
Figure 5 PL spectra measured at room temperature from ZnO NRs grown in the autoclave at 160 °C for 2 h. (a) undoped, (b,c) ZnO:Eu (5 %). The inset shows the PL spectra measured at 4.2 K.
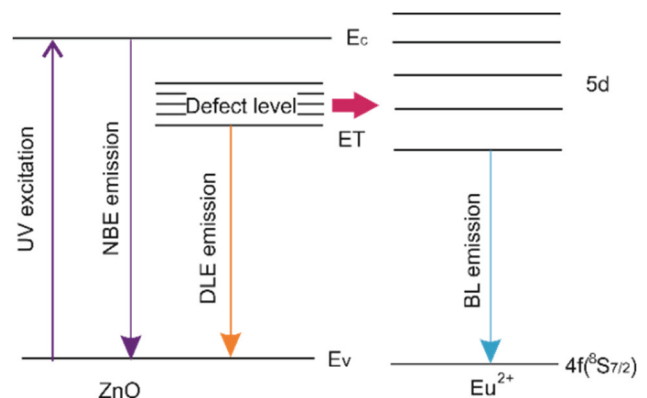
Figure 6 Energy level scheme: excitation and emission mechanisms of Eu^{2+} ions in ZnO

4.   CONCLUSION

We demonstrated that the ZnO NRs grown in the autoclave above the boiling point of water possess improved optical properties in comparison with conventionally grown NRs. Moreover, these elevated temperatures are

essential for the incorporation of Eu ions into ZnO crystal lattice. Under the 325 nm laser excitation, we did not observe the typically reported red emission associated with intra - 4d transition of Eu^{3+} ions. However, we did observe a blue emission peaked at 450 nm associated with the $4f^6 5d$ - $4f^4$ transitions of Eu^{2+}. We ascribed the origin of the blue luminescence to the energy transfer between the deep level defects in ZnO NRs and the Eu^{2+} ions.

ACKNOWLEDGEMENTS

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