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Synthesis and photoluminescence of Eu-doped ZnO microrods prepared by hydrothermal method

Meili Wang [a], Changgang Huang [a,b], Zhi Huang [a], Wang Guo [a], Jiquan Huang [a], Hong He [a], Hai Wang [a], Yongge Cao [a,c,*], Quanlin Liu [b], Jingkui Liang [a]

[a] *Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China*
[b] *School of Materials Science and Engineering and State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing, Beijing 100083, PR China*
[c] *School of Materials Science and Engineering, Northwestern Polytechnical University, XiAn 710072, Shanxi Province, PR China*

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ABSTRACT

Eu-doped ZnO microrods, with wurtzite structure and [0001] growth direction have been successfully synthesized on Si (100) substrates by a simple hydrothermal method. The samples were characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), lifetime decay curves, photoluminescence (PL) and photoluminescence excitation (PLE) spectra, respectively. These results indicate that Eu^{3+} ions are located in the distorted lattice sites near the surface of the ZnO microrods. Additionally, it is also suggested that the surface defects may act as a step in the process of energy transfer from ZnO to Eu^{3+} ions.

1. Introduction

II–VI semiconductor micro- and nano-structures doped with luminescence centers have been extensively studied because of their excellent luminescence properties [1–3]. In particular, rare earth (RE)-doped semiconductors are expected to be important materials in optoelectric devices and have received considerable interest for their applications in phosphors, display monitor, X-ray imaging, scintillators, optical communication and fluorescence imaging [4–6]. Zinc oxide (ZnO) with a wide bandgap of 3.37 eV and a bound exciton energy of 60 eV has a potential as a attractive host lattice for doping luminescence centers. Among the RE-doped ZnO activators, the red emission of Eu^{3+} is intensively studied and widely used in light-emitting devices [7–10]. However, the strong quenching effect of the broad green and yellow emissions due to self-activated defect centers largely reduced the intensity of red emission of Eu^{3+} [11,12]. For advanced display and lighting applications, an efficient energy transfer between the ZnO matrix and Eu^{3+} light emission center is highly desired, and the incorporation of RE^{3+} ions into ZnO lattice is crucial for efficient energy transfer. However, due to the large differences in ionic size and valence state between RE^{3+} ions ($r \sim 95$ pm) and Zn^{2+} ions ($r = 74$ pm), it is still hard work to incorporate RE^{3+} ions into ZnO lattice [3]. Simultaneously, it is unfortunate that the direct energy transfer from ZnO to Eu^{3+} is theoretically impossible because the lifetime of exciton in ZnO is much shorter than the energy transfer rate [13]. Thus, novel ideas are urgently required to realize the energy transfer.

In recent years, much efforts have been made to prepare Eu-doped ZnO materials, and various methods such as sol–gel, micro-emulsion, hydrothermal, spray pyrolysis, solid-reaction, radio frequency reactive magnetron sputtering, and electrodeposition have been employed [3,7–10,14–16]. Various morphologies, including nano-particle [17], nano-urchin [9], and nano-flower [18] have been obtained by hydrothermal method, films were always achieved by spray pyrolysis [14] and radio frequency reactive magnetron sputtering [16], and rods have been synthesized by micro-emulsion [8], solid-reaction [19], and electrodeposition [10] route. Fortunately, the characteristic red emissions of Eu^{3+} ions and the energy transfer have been observed, which suggests that Eu^{3+} ions can be incorporated into ZnO lattice with nanostructure successfully if the synthesis condition is well designed. Additionally, it is reported that the surface defects, serving as energy traps, may play a key role in the process of energy transfer [7,9,10,17]. Compared with other approaches, hydrothermal method is regards as an attractive candidate for synthesis of Eu-doped ZnO due to the

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[*] Corresponding author. Address: Key Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, PR China. Tel./fax: +86 591 83721039.

E-mail addresses: caoyongge@fjirsm.ac.cn, caoyongge@gmail.com (Y. Cao).

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advantages of simple, easy-control, low-cost, and especially the large amount of surface defects. Surprisingly, few reports have incorporate Eu^{3+} into ZnO nanorods by hydrothermal method, which is the most common product shape via this route. In this paper, in order to clarify whether Eu^{3+} ions can be incorporated into ZnO microrods via hydrothermal route, we introduced Si substrate for epitaxially growing ZnO rods, and Eu-doped ZnO microrods were successfully fabricated. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques were used to establish the morphology and structure of as-prepared samples. Lifetime decay curves, photoluminescence (PL) and photoluminescence excitation (PLE) spectra were employed to investigate emission and excitation processes in Eu-doped ZnO samples.

2. Experimental

The ZnO:Eu microrods were fabricated by a hydrothermal method, as described by Vayssieres et al. [20]. Firstly, a 50 ml Teflon-lined stainless steel autoclave was filled with an equimolar (0.1 M) aqueous solution of zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and methenamine ($(CH_2)_6N_4$). After stirring for several minutes, $Eu(NO_3)_3 \cdot 6H_2O$ was added to the mixture solution, and then the mixture solution was stirred for half an hour vigorously. The molar ratio of Eu^{3+} ions to Zn^{2+} ions was 0.05. A Si (1 0 0) substrate was ultrasonically cleaned in acetone and ethanol, and then dried under N_2 gas flow. After the substrate was immerged into the autoclave vertically, the autoclave was sealed tightly and placed in the ultrasonic bath for 30 min. Subsequently, the sealed autoclave was heated to 95 °C for 24 h in a conventional laboratory oven. Finally, the autoclave was cooled down and a white coating was obtained on the Si (1 0 0) substrate. The residual salts in the coating were removed through deionized water washing and the products were then dried in air for characterization. To achieve better crystalline, the as-prepared samples were annealed in air for half an hour at 400 °C.

The crystal structure of the products was characterized on a Rigaku-Dmax2500 X-ray diffractometer with high intensity Cu Kα ($\lambda = 1.5418$ Å) incident radiation at room temperature. The morphologies of the samples were characterized by field emission scanning electron microscopy (FE-SEM JEOL JSM 6700F). Energy dispersive spectrometry (EDS) attached to SEM and Ultima2 ICP optical emission spectrometer (ICP-AES) were employed to perform the elemental analyses of the products. Room temperature (RT) photoluminescence spectra (PL) measurements were carried out on an Edinburgh Instruments FLS920 spectrophotometer using a xenon lamp as excitation source.

3. Results and discussion

Fig. 1a and b shows the FE-SEM images of the undoped and Eu-doped ZnO materials fabricated by hydrothermal method. It can be seen clearly that a large amount of ZnO microrods, with average length of 10 μm and diameter in the range of 2–3 μm, were grown on the substrates. The microrods appear as disordered on the surface, but quite a part of microrods are perpendicular to the substrate. Before and after Eu doping, the products were kept rod shape. The as-prepared microrods are different from the ones which have been reported elsewhere [8,10,19]. All of the microrods are straight in shape and have hexagonal facets at both ends. Something strange, the microrods have an interface at the half length. The formation mechanism of the interface is still unclear.

The XRD patterns of the undoped and Eu-doped ZnO microrods are presented in Fig. 2a. All the peaks of the XRD patterns can be indexed to pure hexagonal wurtzite-phase ZnO (JCPDS Card, No. 36-1451). No diffraction peaks from europium oxides or other impurities were detected, indicating that the Eu^{3+} ions have incorporated into ZnO lattice. The strongest diffraction peaks at 34.5° for (0 0 2) plane imply that the most of the products are preferentially oriented in the *c*-axis direction. Comparing the XRD patterns of undoped and Eu-doped ZnO microrods, clear shift in peak positions are observed, further confirming the successful incorporation of Eu^{3+} ions into ZnO lattice. EDS and ICP-AES analysis were performed to investigate the Eu distribution. As shown in Fig. 2b, Zn and O peaks as well as Eu peak are evident in the spectrum. Similar amounts of Eu concentration are observed at different detecting points of the microrods, and the nominal Eu^{3+} content in the products is estimated to be 1.5 at.%.

Fig. 3A displays the room temperature photoluminescence (PL) and photoluminescence excitation (PLE) spectra of the undoped ZnO microrods. The near-band-dge (NBE) excitation peak at 368 nm was observed at the monitored wavelength of 600 nm. In addition, under the NBE excitation of 376 nm, a broad yellow emission centered at 576 nm was observed, indicating a large number of surface defects were existed. The yellow emission may be assigned to the transition between the single charged oxygen vacancy and the photoexcited holes in the valence band of the ZnO microrods [21].

Fig. 3B shows the PL spectra of Eu-doped ZnO microrods under the excitation of 466 nm. In order to exclude the possibility of Eu^{3+} in organic complexes, the photoluminescence properties of Eu-doped samples before and after annealing were investigated. Series of characteristic Eu^{3+} ions emissions and a broad green emission at around 520 nm were observed for the two samples. The yellow emission of undoped ZnO microrods (Fig. 3A) and green emission of Eu-doped ZnO microrods may be caused from different type of defects in ZnO microrods. After annealing, the crystalline quality has been improved and thus the defect-related green emission became weaker. Peaks centered at 579, 593, 615, 659 and 706 nm are attributed to the intra-4f transitions of ${}^5D_0 \rightarrow {}^7F_0$, ${}^5D_0 \rightarrow {}^7F_1$, ${}^5D_0 \rightarrow {}^7F_2$, ${}^5D_0 \rightarrow {}^7F_3$ and ${}^5D_0 \rightarrow {}^7F_4$ ($J = 0, 1, 2, 3, 4$) of Eu^{3+} ions, respectively. In addition, a splitting shoulder of ${}^5D_0 \rightarrow {}^7F_2$ at 623 nm was also observed. It is well known that the transitions

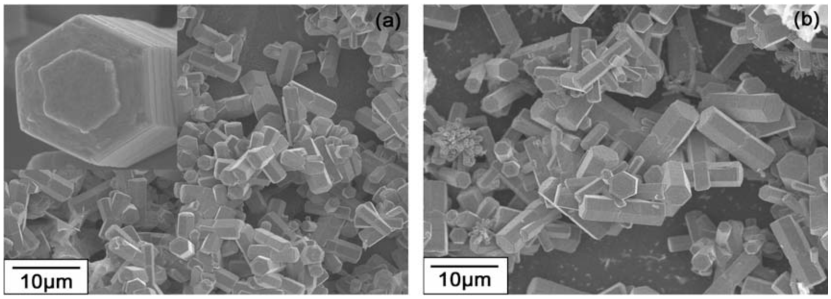

Fig. 1. (a) FE-SEM images of the Eu-doped and (b) undoped ZnO microrods; the inset shows the amplified image of the hexagonal facet.