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Eu-doped ZnO nanowire arrays grown by electrodeposition

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ABSTRACT

The preparation of efficient light emitting diodes requires active optical layers working at low voltage for light emission. Trivalent lanthanide doped wide-bandgap semiconducting oxide nanostructures are promising active materials in opto-electronic devices. In this work we report on the electrochemical deposition (ECD) of Eu-doped ZnO (ZnO:Eu) nanowire arrays on glass substrates coated with F-doped polycrystalline SnO_2. The structural, chemical and optical properties of ZnO:Eu nanowires have been systematically characterized by X-ray diffraction, transmission electron microscopy, Raman spectroscopy, X-ray photoelectron spectroscopy, secondary ion mass spectrometry, and photoluminescence. XRD results suggest the substitution of Zn^{2+} by Eu ions in the crystalline lattice. High-resolution TEM and associated electron diffraction studies indicate an interplanar spacing of 0.52 nm which corresponds to the (0 0 0 1) crystal plane of the hexagonal ZnO, and a growth along the *c*-direction. The ZnO:Eu nanowires have a single crystal structure, without noticeable defects. According to EDX, SIMS and XPS studies, cationic Eu species are detected in these samples showing the incorporation of Eu into the ZnO matrix. The oxidation states of europium ions in the nanowires are determined as +3 (74%) and +2 (26%). Photoluminescence studies demonstrated red emission from the Eu-doped ZnO nanowire arrays. When Eu was incorporated during the nanowire growth, the sharp $^5D_0$–$^7F_2$ transition of the Eu^{3+} ion at around 612 nm was observed. These results suggest that Eu doped ZnO nanowires could pave the way for efficient, multispectral LEDs and optical devices.

1. Introduction

For high-performance light emitting devices, efficient emissions are required by applying low voltages to an optically active layer [1–4]. Trivalent lanthanides doped semiconducting oxide nanostructures are one of the most promising nanomaterials for an active layer due to their stable intra-4f shell transitions in their ions [5]. In this context, zinc oxide (ZnO) possesses a great potential as a host material for europium-doped semiconductor [6–11] because it has a wide band gap of about 3.36 eV, a large exciton binding energy of 60 meV [7] and native defects [8,9]. The preparation and characterizations of the optical properties of ZnO doped with Eu^{3+} ions have been studied previously [10–21]. Pauporté et al. have developed an electrochemical precipitation technique for the preparation of the ZnO/Eu mixed layers [11,12]. In the Eu^{3+}-doped ZnO rod-shaped columns surrounded by a Eu/ZnO mixed basal layer, the energy transfer from ZnO to Eu^{3+} under UV light excitation was demonstrated [11]. The electrochemical preparation was explained in the light of a thermochemical study of the Eu–Cl–H_2O system [12]. Other growth routes from solution include spray pyrolysis [22,23], sol–gel [24] and coprecipitation [25]. Wang et al. [18] reported on defect-mediated energy transfer in red-light-emitting Eu-doped ZnO nanowire arrays prepared by a vapor transport method. Pan et al. [19] studied the growth by chemical vapor deposition of single crystal ZnO nanowires diffused with europium (Eu) from a solid source at 900 °C for 1 h. Chen et al. [17] reported on Eu-treated ZnO nanowires and found that the Eu^{3+} ions were in the Eu_2O_3-like state located at the surface of ZnO nanowire and red emission was detected. Yang et al. [15] showed Eu-doped ZnO nanowires prepared by high-temperature and high-pressure pulsed-laser deposition and emission near 611 nm and 755 nm.

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