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The dependence of emission spectra of rare earth ion on the band-gap energy of $Mg_xZn_{1-x}O$ alloy

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Abstract

Rare-earth (RE) Tb^{3+} ion doped ZnO and $Mg_{0.15}Zn_{0.85}O$ thin films were successfully fabricated by the sol-gel deposition method. The Tb^{3+} ion was substituted for the Zn^{2+} ion in the host material, as revealed by X-ray diffraction and optical absorption spectra. The cathodoluminescence properties of the doped samples were also studied. The RE $^{3+}$ luminescence mechanism is discussed.

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1. Introduction

Rare-earth (RE) ions doped semiconductors have been of considerable interest for possible applications in light-emitting devices and for their unique optical properties [1,2]. The RE luminescence has a very narrow emission band and a slight correlation with the nature of the host and the ambient temperature. The 4f orbits of RE ions incorporated into semiconductors are so deeply buried within the electronic shell that the energy levels of the 4fⁿ configuration are only slightly perturbed as compared to free-ion energy levels.

Recently, the photoluminescence (PL) and electroluminescence properties of GaN doped with RE ions have been studied [3,4].

Zinc oxide (ZnO), a wide-band-gap semiconductor, is widely used as a bright green luminescence phosphor in vacuum fluorescent devices [5]. There is some prior work in the literature concerning RE doped in ZnO [5–7]; however, the RE ion did not substitute for the Zn^{2+} ion position in the lattice. They were just located at the grain boundary. In this work, the Tb^{3+} ion doped ZnO and MgZnO alloy thin films were successfully fabricated by the sol-gel deposition method. The effect of RE doping on the band gap was also evaluated by cathodoluminescence.

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2. Experimental procedure

The sol was composed of $\text{Zn}(\text{CH}_3\text{COO})_2$, $\text{Mg}(\text{CH}_3\text{COO})_2$, $\text{Tb}(\text{sal})_3$ and polyvinyl butyral (PVB) in ethanol solution. The total concentration of metal ions was 0.1 mol/l, and the concentrations of Mg^{2+} and Tb^{3+} were adjusted to 0.02 and 1×10^{-3} mol/l, respectively. They were spin-coated on $\text{Si}(100)$ and quartz substrates at 2500 r/min. After the deposition, the substrates were initially heated at 100°C in air for 10 min to evaporate the solvent, and then at 350°C in O_2 for 30 min to eliminate the organic component in the film. The process of spin coating and doping was repeated until the desired thickness was achieved (about 500 nm). Finally, the samples were cut into several pieces for different experiments, and then thermal annealing performed for 1 h under an O_2 ambient at 1000°C to crystallize the doped zinc oxide films. The infrared spectrum, as measured by a BIO-RAD FTS-3000 spectrophotometer having a resolution of 4 cm^{-1} in the range 400 – 4000 cm^{-1} , indicated that there were no organic components in the film above 350°C.

X-ray diffraction (XRD) measurements were done using a D/max-rA X-ray diffractometer (Rigaku), and a UV-360 Spectrophotometer (Shimadzu) was used for optical characterization.

3. Result and discussion

The XRD spectra of samples are shown in Fig. 1. In the spectra, all the diffractive peaks originate from ZnO with a wurtzite structure and the (002) diffractive peak position is a little different for these samples. The (002) peaks are located at 34.56° , 34.72° and 34.63° for pure ZnO , $\text{Mg}_{0.85}\text{Zn}_{0.15}\text{O}$ and $\text{Mg}_{0.85}\text{Zn}_{0.15}\text{O}:\text{Tb}$ thin films, respectively. Since the ionic radii are different for Mg^{2+} (0.57 Å), Zn^{2+} (0.60 Å) and Tb^{3+} (0.92 Å), lattice deformation occurs in the alloy thin films. When the Tb^{3+} ion is situated at the ZnO grain boundary, the ZnO crystal lattice cannot be affected by Tb^{3+} ion and diffractive peaks related to the terbium oxide can be detected by the XRD measurement. But in our experiment, only the ZnO wurtzite structure is obtained and the lattice

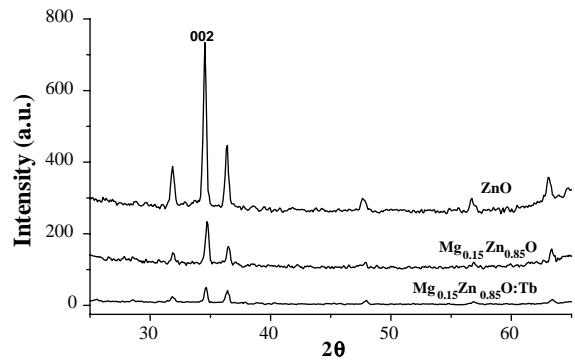


Fig. 1. The XRD patterns of pure ZnO , $\text{Mg}_{0.85}\text{Zn}_{0.15}\text{O}$ and $\text{Mg}_{0.85}\text{Zn}_{0.15}\text{O}:\text{Tb}$ thin films on Si substrate.

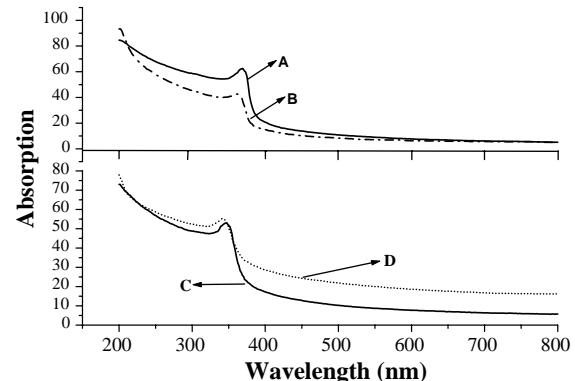


Fig. 2. The optical absorption spectra of (A) ZnO , (B) $\text{ZnO}:\text{Tb}$, (C) $\text{Mg}_{0.85}\text{Zn}_{0.15}\text{O}$ and (D) $\text{Mg}_{0.85}\text{Zn}_{0.15}\text{O}:\text{Tb}$ fabricated on quartz substrate.

deformation is observed, which indicates that the Tb^{3+} ion is inside the ZnO grains and substituted for the Zn^{2+} ion position in the host matrices successfully. Because all the ions mix well in the sol, the Tb^{3+} ion could be doped in the ZnO crystal lattice easily during the crystallization process. Also, the *c*-axis orientation becomes weak induced by doping Mg^{2+} and Tb^{3+} ions into the ZnO crystal lattice.

Fig. 2 shows the optical absorption spectra of ZnO (A), $\text{ZnO}:\text{Tb}$ (B), $\text{Mg}_{0.85}\text{Zn}_{0.15}\text{O}$ (C) and $\text{Mg}_{0.85}\text{Zn}_{0.15}\text{O}:\text{Tb}$ (D). All the samples were highly transparent in the visible region from 400 to 800 nm and have a narrow absorption band in the ultra-violet (UV) region. There is no absorption

peak related to the 4f electronic transition of the Tb^{3+} ion in the spectra for samples B and D. For the RE^{3+} ions scattered inside the ZnO grains, the strong absorbance of ZnO in the UV region would forbid their direct excitation whereas their location at the surface of the ZnO grains could allow such an excitation [7]. The excitonic nature of the films is clearly apparent in the spectra at room temperature, which indicates that the exciton binding energy is almost as large as ZnO for all. The excitonic absorption peak and the absorption edge are blue-shifted to the higher energy position with the Tb^{3+} ion doping into the host lattice. This is probably due to enhanced stress effect induced from the lattice distortion.

The cathodoluminescence (CL) (10 kV, 10 μA) spectra of these samples are shown in Fig. 3. For the undoped samples (A, C) there are only two emission bands in the spectra; one is a free exciton emission in the UV region, and the other is a broad green band which may be due to the radiative recombination of electrons from the conduction band with holes trapped at surface states. In the ZnO thin film doped with Tb^{3+} (sample B) there are some sharp emissions at 545 and 550 nm in the spectra, which is due to the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ electronic transition of Tb^{3+} ion. The transition from $^5\text{D}_3$ level is not present in the spectra. The emissions from the host material can also be seen. Also, the exciton emission in the UV region is broad compared with the undoped sample A. But for the sample D only some emission peaks

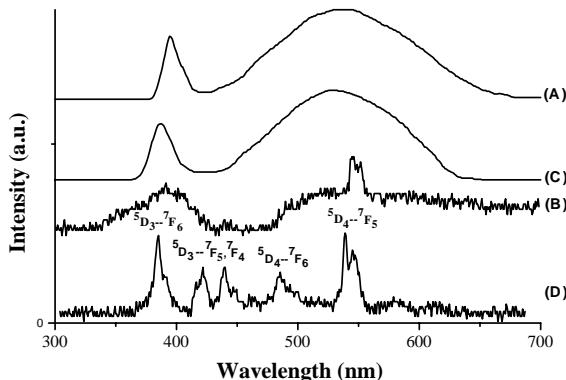


Fig. 3. The CL of (A) ZnO , (B) $\text{ZnO}:\text{Tb}$, (C) $\text{Mg}_{0.85}\text{Zn}_{0.15}\text{O}$ and (D) $\text{Mg}_{0.85}\text{Zn}_{0.15}\text{O}:\text{Tb}$.

origin from the Tb^{3+} ion appear in the spectra. No emission peak from the host could be observed.

The excitation processes of RE ions can be generally divided into two categories: direct and indirect excitation processes. The direct excitation process is the selective excitation of $4f^n$ electrons by photons (in PL selective excitation) or by collision with hot electrons (in CL). The indirect excitation process occurs via transfer of energy to the $4f^n$ electron system from electron–hole pairs generated by photons in PL or and hot carriers in CL.

In CL, since the hot electron has a high energy, the Tb^{3+} ion can be directly excited. There is also an indirect process, in which the Tb^{3+} ions could react with the host by the resonance effect. The possible energy transfer process is shown in Fig. 4. Because the doped Tb^{3+} is a trivalent ion, it could form a shallow donor level just below the conducting band (assigned as D_1 and D_2 in Fig. 4). For ZnO doped with Tb^{3+} , because the donor level in ZnO is a little lower than the $^5\text{D}_3$ energy level, the energy could not transfer from the electrons occupied on the donor level to the $^5\text{D}_3$ level of Tb^{3+} ion. On the contrary, the reversed energy transfer from the emission center to the host could be seen. The $^5\text{D}_4$ level of Tb^{3+} is excited via $(^5\text{D}_3 \rightarrow ^5\text{D}_4) \rightarrow (^7\text{F}_6 \rightarrow ^7\text{F}_0)$ cross

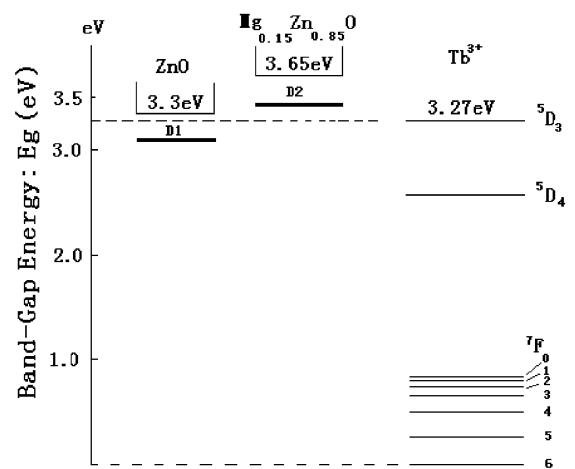


Fig. 4. The energy transfer process sketch map of doped samples.

relaxation process efficiently. Due to this reason, the transition from the 5D_3 level could not be present and the luminescence from the host and the 5D_4 level are dominant in the spectra. For sample D ($Mg_{0.85}Zn_{0.15}O:Tb$) the energy level of 5D_3 is just below the donor level (D_1, D_2), the emission center is excited via resonant energy transfer by the recombination channel in the host efficiently. This process leads to the maximum energy transfer from the host to the emission center Tb^{3+} ion. The recombination channel of electrons from the conduction band with holes trapped at surface states is also cut off. So the transitions from the 5D_3 , 5D_4 to the 7F_6 , 7F_0 of Tb^{3+} ion are dominated in the spectra, and the emissions from the host are not invisible.

In conclusion, RE Tb^{3+} ion doped ZnO and $Mg_{0.15}Zn_{0.85}O$ thin films were successfully fabricated by the sol–gel deposition method. The Tb^{3+} -ion-substituted Zn^{2+} ion position in the host material was characterized by X-ray diffraction and optical absorption spectra. By studying the CL properties of doped samples, an energy transfer should exist in the excitation process,

which leads to the $4f^n$ electronic transition of Tb^{3+} ion dominating the CL spectra.

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