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Blue Cathodoluminescence from Highly Er-Doped ZnO Thin Films Induced by the Phonon Bottleneck Effect *

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The room-temperature blue cathodoluminescence (CL) from highly Er-doped ZnO thin films has been studied by using different electron beam currents (EBCs). The ZnO:Er thin films used in our experiment were prepared by simultaneous evaporation from two sources. The x-ray diffraction spectra show that the thin films have a strong preferential c-axis (0002) orientation with a hexagonal crystalline structure. The blue emission at 455 nm originating from the intra-4f shell transition (${}^4F_{5/2}\cdot{}^4I_{15/2}$) *in* Er^{3+} *ions was observed at room temperature. The nonlinear dependence of the CL intensity on the EBC shows a more intense blue emission above the threshold EBC of 0.6 µA, which is attributed to the phonon bottleneck effect.*

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In recent years, wide band-gap semiconductors (WBGs) ZnSe- and GaN-based materials have brought much attention because of their potential applications in optical and optoelectronic devices. They are coming into practical use.[1−5] A stimulated WBG material named ZnO, which has an energy gap of 3.24 eV at room temperature, has been paid much attention in relation to ultraviolet (UV) emissions. This is because ZnO has a large exciton binding energy of 60 meV at room temperature, which is about three times as large as those of ZnSe and GaN. Another notable property is the large Zn-O bond strength, which allows a high damage threshold for laser irradiation.[6] Up to date, many different techniques have been used to prepare ZnO thin films.[7] The photoluminescence (PL) spectra of the polycrystalline ZnO thin films usually show an emission band around 520 nm correlated to deep-level defects[8,9] and UV emission from the free-excitons.

In this Letter, the rare earth metal Er was introduced into the ZnO matrices in order to make use of the emission energy correlated to deep-level defects in the ZnO thin film. The near-infrared (IR) luminescence from ZnO:Er thin films is well recorded in the literature.[10−12] However, the visible luminescence has been lacking so far. A blue cathodoluminescence (CL) in our experiment was first observed at room temperature for the Er-doped ZnO thin films, which were prepared by simultaneous evaporation from two sources. It is a radiative transition from the excited state (${}^4F_{5/2}$) to the ground state (${}^4I_{15/2}$) of the Er^{3+} ions. The phonon bottleneck effect[13] is used to discuss the mechanism of blue luminescence.

In our experiment, a hydraulic press was used to prepare ZnO tablets using a high pressure of 28 ton/cm^2. Compressed-powder tablets were composed of ZnO (purity 99.99 %). The rare earth metal Er (solid, purity 99.99 %) was ground. Then, they were evaporated to prepare ZnO:Er thin films with an approximate thickness of 200 nm (Er density of $\sim 10^{20}\,\mathrm{cm}^{-3}$). The substrate temperature was about 400°C. The films were formed on a quartz substrate in an O_2 ambient of 10^{-4} Torr by simultaneous evaporation from two sources, i.e., the ZnO:Er thin films used in our experiment were made by electron beam evaporation, and simultaneously the rare earth (RE) metal Er was incorporated into the ZnO matrices by resistance heating of a molybdenum boat. After deposition, the ZnO:Er thin films were annealed at 650°C for 5 min in an O_2 ambient to activate the Er^{3+} ions. To characterize the structure of ZnO:Er films, x-ray diffraction (XRD) spectrum ($\theta-2\theta$) was measured by using a D/max-rA x-ray diffractometer (Rigaku) with the Cu K_α line of 1.54 Å. To study the optical properties, the sample was excited by an electron beam. The emitted light was collected using a quartz lens on the entrance slit of the UV-360 Spectrophotometer (Shimadzu). The optical signal was detected by a photomultiplier.

The XRD spectrum ($\theta-2\theta$) of the ZnO:Er thin films is measured as shown in Fig. 1. There is only

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one strong (0002) ZnO peak. The result indicates that the ZnO:Er thin films have a strong preferential c-axis (0002) orientation with a hexagonal crystalline structure. In order to evaluate the average grain size of the sample, Scherrer's[7] formula is adopted. The size is about 20 nm.

Fig. 1. x-ray diffraction spectrum of the ZnO:Er thin film with the (0002) orientation.

Fig. 2. Cathodoluminescence of the ZnO:Er thin film excited by the cathode-ray with the anode acceleration voltage of 10 kV and the electron beam current of 6 μA at room temperature.

Figure 2 shows a cathodoluminescence (CL) spectrum observed from the ZnO:Er thin film excited by the cathoderay (CR) with the anode acceleration voltage of 10 kV and an electron beam current of 6 μA at room temperature. The spot of the electron beam is about 7 mm^2. The emission spectrum consists of four peaks at 364 nm, 385 nm, 455 nm and 520 nm. The weak peak at 364 nm is attributed to the transition from the excited state ($^4G_{9/2}$) to the excited state ($^4I_{15/2}$) of the Er^{3+} ions.[14] The 385-nm UV peak is from the exciton emission of ZnO. The wide luminescence band around 520 nm, as shown in Fig. 2, is considered to be mainly due to the defect-related deep level emissions in the ZnO:Er thin films. Another radiative transition from the excited state ($^2H_{11/2}$) to the ground state ($^4I_{15/2}$) of the Er^{3+} ions is very weak with a narrow line width, and is submerged in the wide band around 520 nm.

The sharp peak at 455 nm originates from the intra-4f shell transition in the Er^{3+} ions of ZnO matrices, which is from the excited state ($^4F_{5/2}$) to the ground state ($^4I_{15/2}$).[14] In general, it is difficult to observe the blue emission from ZnO:Er thin film for the general density exciting. In order to explain this experimental result, Fig. 3 shows the energy diagram of highly Er-doped ZnO thin film.[15] From Fig. 3, we reasonably think that if the energy from the emission correlated to deep-level defects can transfer to the Er^{3+} ions in the ground state ($^4I_{15/2}$), a resonant excitation will occur and the Er^{3+} ions in the ground state will be directly excited by CR, resulting in a direct transition from the ground state ($^4I_{15/2}$) to the excited state ($^2H_{11/2}$). Consequently, the excited Er^{3+} ions will fill the excited state ($^2H_{11/2}$). According to the phonon bottleneck effect, the non-radiative relaxation rate for these ions is reduced,[16] accompanying by a saturation of multiphonons. In other words, the multiphonon relaxation processes from the excited state ($^4F_{5/2}$) to the excited state ($^2H_{11/2}$) in the Er^{3+} ions will be effectively suppressed when the ZnO:Er sample was excited by the high-energy light with a high excited state density. Thus, we should observe a luminescence with wavelengths shorter than green emission related to the deep-level defects from the ZnO:Er thin films under the condition of a high excited state density due to the bottleneck effect. In fact, we obtained a blue CL from the Er-doped ZnO thin films on the quartz substrate at room temperature.

Fig. 3. Energy band diagram of Er-doped ZnO. The wavelengths shown for transition between the Er^{3+} ion levels are experimentally measured in the ZnO:Er thin film. The electron energy of the electron beam current is also quantitatively shown.

As expected, the Er^{3+} ions in the ground state

($^4I_{15/2}$) resonantly absorb the energy from the green emission correlated to deep-level defects of the ZnO matrices. As seen from Fig. 3, the Er^{3+} ions have to reach the excited state ($^2H_{11/2}$) directly from the ground state ($^4I_{15/2}$), then many excited Er^{3+} ions will fill the excited state ($^2H_{11/2}$). This leads to a decrease of the non-radiative relaxation rate of these ions.[16] Thus, transitions from the excited state ($^4F_{5/2}$) to the ground state ($^4I_{15/2}$) of the Er^{3+} ions in the ZnO matrices will be significantly enhanced due to the phonon bottleneck effect. In other words, the non-radiative relaxation processes are effectively suppressed from the excited state ($^4F_{5/2}$) to the excited state ($^2H_{11/2}$) of the Er^{3+} ions in the ZnO matrices. Hence, the blue light emission was observed in our experiment.

Fig. 4. Cathodoluminescence intensity of the blue emission for the ZnO:Er thin film as a function of the electron beam current with the anode acceleration voltage of 10 kV at room temperature.

To understand the blue emission at 455 nm, the CL spectra were measured for the highly Er-doped ZnO samples excited by different EBC densities at room temperature. Figure 4 shows the intensity of the blue emission as a function of the EBC. From Fig. 4, the threshold EBC (I_{th}) of 0.6 μA can be seen to cause an intense blue emission. As an EBC is above the threshold EBC and less than 1 μA, the intensity of the blue emission increases super-linearly. Afterwards, it increases slowly for the EBC in the range of 1–7 μA. Finally, the saturated CL intensity is observed for the EBC over 7 μA. These results can be explained by considering the phonon bottleneck effect, which occurs at high-density excitations. When the EBC density is low, the emission related to deep-level defects is weak. Very little energy from the emission correlated to deep-level defects can transfer to the Er^{3+} ions in the ground state ($^4I_{15/2}$). Also, there are few Er^{3+} ions in the excited state ($^2H_{11/2}$). Thus, the non-radiative transitions from the excited state ($^4F_{5/2}$) to the excited state ($^2H_{11/2}$) of the Er^{3+} ions in the ZnO matrices are not effectively suppressed, which leads to a weak blue emission. When the EBC density is over the threshold EBC, the blue emission intensity increases rapidly, which is due to the fact that many Er^{3+} ions in the ground state ($^4I_{15/2}$) resonantly absorb the energy from the green emission correlated to deep-level defects of the ZnO matrices to fill the excited state ($^2H_{11/2}$). Thus, the non-radiative transitions from the excited state ($^4F_{5/2}$) to the excited state ($^2H_{11/2}$) of the Er^{3+} ions, accompanied by releasing phonons, are effectively suppressed. The intensity of the blue emission, as shown in Fig. 4, is determined by the number of optically active Er^{3+} ions in the film, i.e., almost all optically active Er^{3+} ions are excited by the energy transfer and CR. Therefore, the saturated intensity of the blue emission was observed. An analogous phenomenon has been reported in the literature.[17]

In conclusion, highly Er-doped ZnO thin films have been prepared by simultaneous evaporation technique. The XRD spectra exhibit that the ZnO:Er thin films have a strong preferential c-axis (0002) orientation with a hexagonal crystalline structure. An room-temperature blue emission, which originates from the transition from the excited state ($^4F_{5/2}$) to the ground state ($^4I_{15/2}$) within intra-$4f$ shell of Er^{3+} ions doped into ZnO matrices, was observed, and depends strongly on the pump light intensity. The nonlinear dependence of the CL intensity on the EBC shows that the threshold EBC (I_{th}) is 0.6 μA. The blue emission is attributed to the phonon bottleneck effect. The experimental result indicates that this is an efficient way to obtain a blue emission from the Er^{3+} ions doped into ZnO WBGs by utilizing the phonon bottleneck effect.

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References

[1] Haase M et al 1991 *Appl. Phys. Lett.* **59** 1272
[2] Morkoc H et al 1992 *J. Appl. Phys.* **76** 1363
[3] Nakamura S et al 1996 *Appl. Phys. Lett.* **69** 1477
[4] Law K K et al 1996 *Electron. Lett.* **32** 345
[5] Nakamura S et al 1997 *Appl. Phys. Lett.* **70** 1417
[6] Yamamoto A et al 2000 *J. Cryst. Growth* **214/215** 308
[7] Zhang X T et al 2002 *Chin. Phys. Lett.* **19** 127
[8] Egelhaaf H J and Oelkrug D 1996 *J. Cryst. Growth* **161** 190
[9] Bethke S, Pan H and Wessels B W 1988 *Appl. Phys. Lett.* **52** 138
[10] Komuro S et al 1999 *Appl. Phys. Lett.* **74** 377
[11] Komuro S et al 2000 *Appl. Phys. Lett.* **76** 3935
[12] Komuro S et al 2000 *J. Appl. Phys.* **88** 7129
[13] Auzel F and Pllé F 1997 *Phys. Rev.* B **55** 11006
[14] Lozykowski H J, Jadwisienczak W M and Brown I 1999 *Appl. Phys. Lett.* **74** 1129
[15] Birkhahn R, Garter M and Steckl A J 1999 *Appl. Phys. Lett.* **74** 2161
[16] Gouedard C et al 1993 *J. Opt. Soc. Am.* B **10** 2358
[17] Fujii M et al 1998 *J. Appl. Phys.* **84** 4525