Near-Infrared Light Emissions from Er-doped ZnO Thin Films Induced by an Electrical Field

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We obtained near-infrared (NIR) emissions by applying an electric field to a ZnO thin film containing Er ions. The sample construction was indium tin oxide (ITO) film/Er-doped ZnO film/ITO film on a SiO₂ glass substrate. By applying a suitable alternative voltage to the sample, a broad luminescence in the NIR wavelength range was observed. The intensity of the luminescence increased with applied voltage. The luminescence induced by the electric field had a wavelength of 1.5 μm , which suggests that the light emission is related to the intrashell transition of Er³⁺.

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Various types of optical/electronic devices are required in optical communication fields with a broad-band network system. Among the many types of material, zinc oxide (ZnO) attracts considerable attention as one of the key materials because of its wide band gap of 3.3 eV and large exciton binding energy of about 60 meV at room temperature. Furthermore, ZnO shows the attractive characteristic that its electrical conductivity can be widely controlled from high conductivity to insulator by doping other elements. Recently, Tsukazaki et al. have succeeded in fabricating a stable p-type semiconductive ZnO thin film, which has led to the development of ultraviolet (UV) lasers and various types of light-emitting diodes (LEDs).¹⁾ There has been much research on ZnO films, focusing on the UV emission mechanism and their nanostructures. On the other hand, little research has been reported on the photoluminescence (PL) of ZnO thin films in the near-infrared (NIR) wavelength range.^{2)–4)} According to the results, an intense 1.54 μm emission was obtained by doping Er to the ZnO matrix. The wavelength at 1.54 μm corresponds to a low-loss wavelength of the conventional glass fiber; therefore, such a ZnO thin film has the potential of becoming useful devices in optical communications.

The electroluminescence (EL) technique using a fluorescent thin film has become wide spread for various types of display devices.⁵⁾ Although ZnO powder and ZnO composite phosphor thin films (i.e. ZnGa₂O₄: Mn) have been reported,^{6)–8)} they are mainly restricted in their light emission characteristics to the visible wavelength range. To our knowledge, the EL of ZnO-based thin films in the NIR wavelength range has not yet been reported. If the possibility of NIR emission from ZnO-based thin films is verified, this will be important from the viewpoints of industrial and practical use, particularly for developing new devices.

On the basis of the above background, we demonstrated NIR emission from Er-doped ZnO thin films by applying an electrical field.

A simple construction was selected using a thin-film sample for EL investigation. SiO₂ glass with a thickness of 0.5 mm was selected as a substrate. ITO thin films were used as the electrodes for applying a voltage to the fluorescent film. An ITO thin film was deposited on the substrate by reactive RF magnetron sputtering at 523 K, and under a gas composition of Ar/O₂ (99/1). The Er-doped ZnO thin film having an area of 12 $\times$ 15 mm² was deposited on the ITO film. The Er-doped ZnO thin film was obtained by sputtering zinc metal and

Er₂O₃ targets simultaneously in an ambient gas mixture of Ar/O₂ (4/1) for 1 h at 623 K. The concentration of Er in the ZnO matrix was estimated to be 0.2 at%.⁴⁾ Then, the upper ITO film having an area of 8 $\times$ 8 mm² was deposited on the Er-doped ZnO film. A similar sample using undoped ZnO as a fluorescent thin film was also fabricated.

An AC electrical field (13 Hz) was applied to the Er-doped ZnO thin film, and light emission was measured using a Ge *p-i-n* detector. PL measurements of the thin film sample were also carried out using the 351 nm of an Ar⁺ laser.⁴⁾ The decay time of the specific emission at 1540 nm of EL was measured. X-ray diffraction (XRD) analysis and scanning electron microscopy (SEM) observation were performed to evaluate the structure of the thin-film sample. Infrared absorption measurements were carried out to confirm the IR transmittance of the ITO film.

Figure 1 shows (a) a photograph of the Er-doped ZnO thin-film sample sandwiched between two ITO films and (b) the cross-sectional SEM image of the sample. The sample was almost transparent. The Er-doped ZnO film was about 1 μm thick and the ITO films were about 200 nm thick. The XRD pattern of the sample confirmed that a ZnO (002) peak was predominant, although the fluorescent film was composed of poly crystals. This indicates that there were many columnar <001>-aligned grains in the Er-doped ZnO film synthesized under the experimental conditions. The undoped ZnO film sample showed results similar to those mentioned above. The transmittance of the ITO film in the NIR range was confirmed to be about 80%.

Figure 2 shows the emission spectra in the NIR range from the Er-doped ZnO thin film induced by various electrical

Fig. 1. Photographs of sample for EL measurement: (a) optical photograph, (b) cross-sectional SEM image.

Fig. 2. EL spectra in NIR range from Er-doped ZnO thin film. The applied field for each spectrum is indicated.

Fig. 4. Typical PL spectrum in NIR range from Er-doped ZnO thin film. Note that the spectral width is sharp compared with that of the EL spectra shown in Fig. 2.

Fig. 3. (a) Emission pattern at 1540 nm under AC bias and (b) typical voltage–current characteristics (AC) of Er-doped ZnO thin film.

fields. Broad emission was observed at ± 15.6 V. With a gradual increase in the applied voltage, the emission intensity increased. The maximum intensity of the emission was obtained at $V = \pm 16.5$ V. When the applied voltage was lower than 14.8 V, luminescent peaks could hardly be observed within the detection sensitivity of the apparatus. On the other hand, there was no emission signal from the Er-doped ZnO sample in another range from 370 nm to 1000 nm under the conditions described above ($V = 16.5$ V). In the case of the undoped ZnO thin film, luminescence was not detectable in the entire range: 370 nm–1800 nm under a similar electrical field ($V = 26.5$ V).

Figure 3 shows (a) a typical oscillograph of the emission intensity at 1540 nm in the direction of applied voltage and (b) the voltage–current characteristics (AC) of the sample. It was found that the EL intensity was independent of the direction of the bias and that the V – I characteristics of the sample were almost linear, this being an intrinsic property of ZnO. These results indicate that the emission obtained in this experiment did not originate from electron-hole recombination in a pn junction or a Schottky barrier but a direct or indirect excitation/transition of ions induced by electrically accelerating electrons.

The decay time of the emission at 1540 nm was measured by applying a short pulse to the sample, and its value was about 2.5 ms, which was in agreement with the reported value for the PL peak in Er-doped ZnO thin film.³⁾ In addition, the luminescence shown in Fig. 3(a) disappeared immediately when the applied voltage was removed. Taking account of these phenomena and the lack of emission from the undoped

ZnO sample, it is thought to be that the emission is not obtained owing to a thermal effect but to an electrical effect and is strongly related to the intrashell transition of Er^{3+} ($^4I_{13/2} \rightarrow ^4I_{15/2}$).

Figure 4 shows a typical PL spectrum in the NIR range from the Er-doped ZnO thin film. A sharp spectral peak having a center wavelength at 1540 nm was observed in contrast to the EL spectrum shown in Fig. 2. It is difficult to interpret the detail of the EL spectrum of Fig. 2; for example, the reason why there are broad spectral shapes compared to the PL spectrum and the identification of the peaks at approximately 1.3 μm are still unresolved. This means such a specific EL spectral shape in the NIR region is thought to suggest that the energy states of Er ions in the ZnO matrix (or ZnO–Er atomic interaction) are complex under a high electrical field.

By applying a suitable alternating electrical field to Er-doped ZnO thin films, a broad luminescence in the NIR wavelength range was observed. The luminescence showed high emission intensity in the vicinity of the wavelength of 1.5 μm , which suggests that the light emission is related to the presence of Er ions.

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