

Photoluminescence around 1.54 μm from Er-containing ZnO at Room Temperature^{*1}

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The photoluminescence (PL) around the wavelength of 1.54 μm from the Er-containing ZnO specimens was measured at room temperature by the indirect excitation of the He-Cd laser (325 nm). The PL intensity varied greatly with the Er concentration and the specimen preparation conditions as well. The specimens with the Er content of about 2.6 at%, sintered at 1623 K, and cooled quickly to room temperature in air showed the highest PL intensity at 1.534 μm . The local structure of the optically active Er centers in ZnO was also discussed, and the appropriate optically active center might be the Er ions existing in the grain boundaries.

(Received January 6, 2004; Accepted March 5, 2004)

Keywords: ZnO, Er, sintering, photoluminescence (PL), electrical conductivity

1. Introduction

Erbium-doped semiconductors are expected as optoelectronic devices because the Er intra-4f shell transition causes photoemission around the wavelength of 1.54 μm . Numerous studies have been performed on the Er in various hosts such as GaN,¹⁻³⁾ GaAs,^{4,5)} Si,^{5,6)} etc. One of the remarkable results is that the co-doping of Er and O increases the luminescence intensity greatly.⁷⁻⁹⁾ Recently, a new host semiconductor, ZnO, has been proposed.¹⁰⁻¹⁶⁾ The wide band gap (about 3.3 eV) of ZnO can be applied to the excitation of Er, and the controllable electrical conductivity and the varistor characteristics of ZnO may be suitable for the fabrication of the practical optoelectronic devices; moreover, the oxide semiconductor ZnO is easy for the realization of coexistence of Er and O in it. However, the coordination number of O ions and the symmetry around an Er ion also affected the PL intensity very much.¹⁴⁾ It is still not clear what is the most appropriate local structure around Er to provide an optically active center for the PL emission in ZnO.

In this study various Er-containing ZnO specimens were prepared, and the dependence of the photoluminescence (PL) intensity around 1.54 μm was investigated on the Er concentration in ZnO and the preparation conditions, both of which could make the different local structure around Er in ZnO.

2. Experimental Details

The $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powder was mixed with the alcohol solution of the $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in a conventional way,¹⁷⁾ and the Er content ranged from 0.1 at% to 10 at%. The slurry was dried at 323 K for 43.2 ks, and then calcined at 773 K for 7.2 ks to get the Er-containing ZnO powders. The contents of Er were analyzed by an inductively coupled plasma (ICP) spectrometer (SPS 1500VR, SEIKO Instruments, Japan). The

Er-containing ZnO powders were consolidated into the disk-shaped specimens with 1.2 cm in diameter and 2-2.5 mm in thickness by the uniaxial pressing at 30 MPa in a mold, and then isostatically pressed at 150 MPa. Specimens were placed in crucibles and sintered in a muffle furnace. The sintering condition was controlled as follows; specimens were held at 1273 K for 7.2 ks, heated up to either 1473 K, or 1623 K, or 1723 K in 2 h and then kept at each temperature for 10.8 ks, and subsequently taken out of the furnace and cooled down to room temperature quickly in air or quenched into water, or cooled in the furnace slowly at a constant speed. The structure of the sintered ZnO was analyzed with an X-ray diffractometer (XRD, RAD-IIC, Rigaku Co., Japan). The ZnO specimens were observed and analyzed using SEM/EDX (S-3500H, Hitachi, Japan).

The In-Ga alloy was used to make ohmic electrodes for electrical measurements. The dc electrical measurements were conducted through the 3522-50 LCR HiTESTER (HIOKI, Japan) and the Model 2400 SourceMeter (Keithley, USA). The ac impedance was measured with an impedance analyzer (3535 LCR HiTESTER, HIOKI, Japan). All the electrical measurements were conducted at room temperature.

The photoluminescence (PL) spectra were measured at room temperature through the SPEX 1702104 Spectrometer and a Hamamatsu R1387 photomultiplier tube. The photoexcitation source was a cw mode He-Cd laser (325 nm) with a beam diameter of 1 mm and an incident power of 5 mW. The luminescence of the sample was detected with a liquid nitrogen-cooled Ge pin photodiode using a chopper and a lock-in amplifier.

3. Results

3.1 Relationship between the PL intensity and the Er concentration

As described earlier, in this investigation a He-Cd laser (325 nm) was used as the photoexcitation source for the PL spectra measurements. The PL spectra from the wavelength

^{*1}This Paper was Presented at the Fall Meeting of the Japan Institute of Metals, held in Sapporo, on October 13, 2003.

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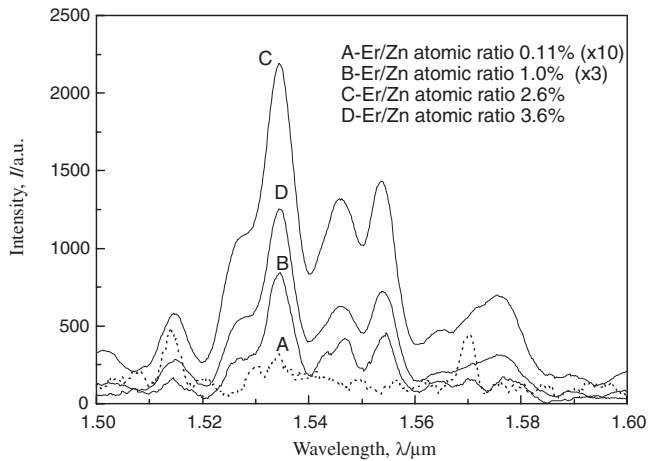


Fig. 1 High-resolution PL spectra of ZnO specimens with various Er contents.

of 1.5 to 1.6 μm were recorded at room temperature for the ZnO specimens with different Er concentrations. Some typical spectra are shown in Fig. 1. It can be seen from this figure that there are several emission peaks appearing in the measured wavelength range, and the strongest emission peak appears around 1.534 μm in the spectra except for the ZnO specimens with the Er content of 0.11 at%. These peaks are attributable to the emission from the excited level $^4I_{13/2}$ to the ground state level $^4I_{15/2}$ of Er. Er in ZnO was not free ion but the ion in solid, so the levels were split due to the Stark effect,¹⁸⁾ and more than one emission peak appeared in the PL spectra.

In Fig. 1 the emission intensity changed greatly with the Er concentration in ZnO. The relationship between the PL intensity at 1.534 μm and the Er content is shown in Fig. 2 in detail. All these specimens were first kept at 1273 K for 7.2 ks, then heated up to 1623 K in 7.2 ks and held at 1623 K for 10.8 ks, and finally cooled down to room temperature quickly in air. When the Er content was lower than 2.6 at%, the PL intensity increased with the Er content. But when the Er content was higher than 2.6 at%, the PL intensity decreased largely, especially when the Er content exceeded 5 at%. The best Er content was about 2.6 at% for the highest PL emission intensity at 1.534 μm in our investigation. Also it was seen clearly from the inset of Fig. 2 that, the PL intensity did not increase linearly with the Er content. This indicates that the Er ions in ZnO could not all act as the optically active centers, and there might be some Er ion sites in ZnO, suitable for the PL emission around 1.54 μm .

3.2 Effects of sintering temperature on the PL intensity of Er in ZnO

Various Er-containing ZnO specimens were sintered at different conditions, and the effects of the sintering temperature on the PL emission intensity were investigated. All the specimens were kept at 1273 K for 7.2 ks, then heated up to either 1473 K, or 1623 K, or 1723 K in 7.2 ks and held at each temperature for 10.8 ks. After the sintering procedure, the specimens were taken out of the furnace and cooled down to room temperature quickly in air. The PL spectra of the above specimens were measured and the results are shown in Fig. 3.

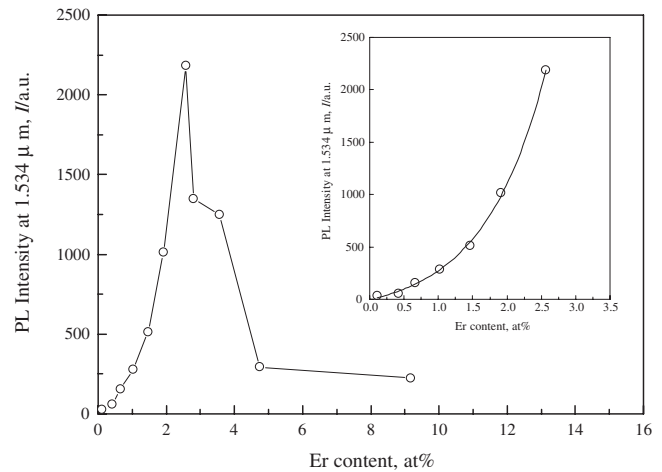


Fig. 2 Variation of the PL intensity at 1.534 μm with Er content. All these specimens were first kept at 1273 K for 7.2 ks, then heated up to 1623 K in 7.2 ks and held at 1623 K for 10.8 ks, and finally cooled down to room temperature quickly in air.

The specimens sintered at 1473 K and 1723 K had the lower emission intensity than the specimen sintered at 1623 K.

3.3 Effects of cooling conditions on the PL intensity of Er in ZnO

In order to investigate the effects of the cooling effects on the PL emission intensity of Er-containing ZnO, the specimens were first kept at 1273 K for 7.2 ks, then heated up to 1623 K in 7.2 ks and kept again at this temperature for 10.8 ks, but the following cooling procedures were quite different among the specimens. One specimen was cooled in the furnace slowly at the speed of 0.05 K/s (slow cooling), the other two specimens were taken out of the furnace and cooled down to room temperature quickly in air (quick cooling), or quenched into water (quenching). The PL spectra of the above specimens are shown in Fig. 4. It can be seen that both the slow cooling specimen and the quenching specimen had the lower PL emission intensity than the quick cooling specimen. The PL intensity at 1.534 μm from the slow cooling specimen was about a quarter of that from the

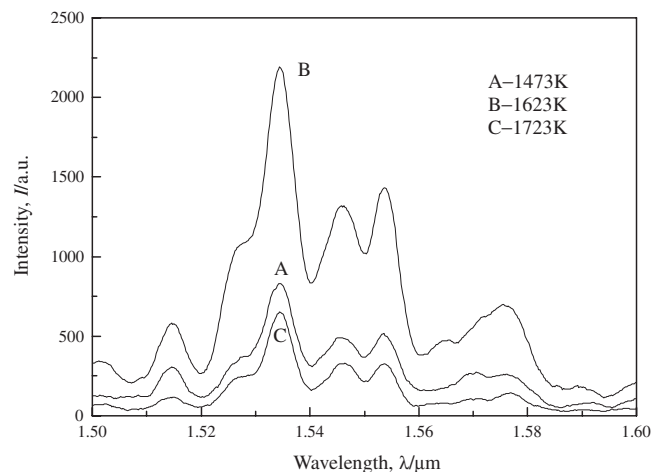


Fig. 3 PL spectra of Er-containing ZnO specimens sintered at different temperatures.

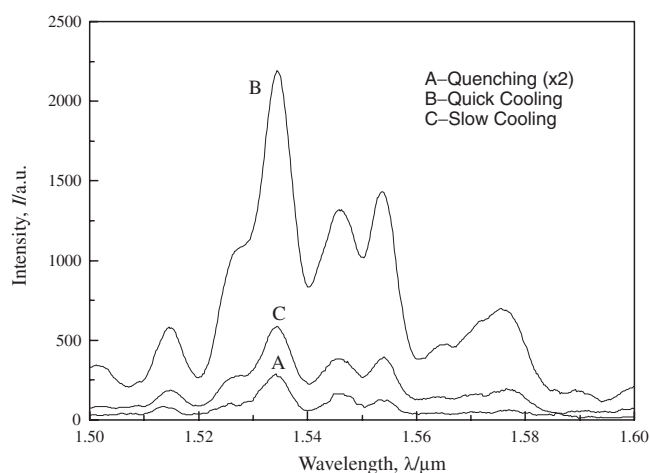


Fig. 4 PL spectra of Er-containing ZnO experienced different cooling procedures.

quick cooling specimen. The PL intensity from the quenching specimen was even much weaker. It was evident that the cooling condition affected the PL intensity of Er-containing ZnO specimens strongly, and the most suitable cooling condition was the quick cooling in air.

Thus, it is apparent that the PL emission of Er in ZnO is very sensitive to the sintering and cooling conditions, because of the modification of the local structure around Er in ZnO.

3.4 Microstructure of the Er-containing ZnO specimens

The XRD patterns for the Er-containing ZnO specimens are shown in Fig. 5. The lower pattern in the figure was obtained from the specimen with the highest PL emission intensity, whereas, the upper one was obtained from the specimen prepared by the same procedures except for the sintering temperature. The PL intensity of the latter specimen was rather weak as shown in Fig. 3.

It was seen from Fig. 5 that the specimen sintered at 1623 K with the highest PL emission showed stronger Er_2O_3 peaks in the XRD pattern than the specimen sintered at 1723 K. The Er_2O_3 phase could also be observed by the SEM/EDX, as shown in Fig. 6.

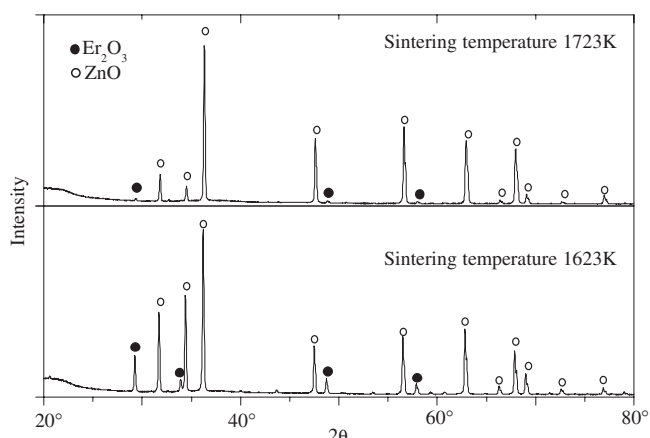


Fig. 5 XRD patterns for Er-containing ZnO specimens sintered at 1623 K and 1723 K.

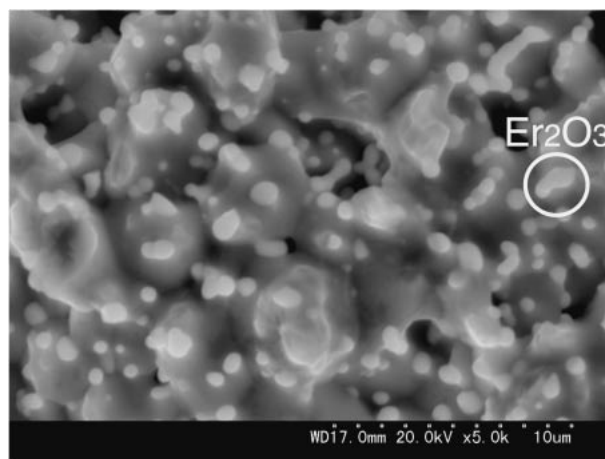


Fig. 6 SEM image for the Er-containing ZnO specimen with the highest PL intensity at 1.534 μm .

4. Discussion

It was evident from the present experimental results that the preparation conditions had great effects on the PL intensity around 1.54 μm of Er in ZnO. The different preparation conditions could cause different sites of Er in ZnO, resulting in the different local structure. It has been reported¹⁴⁾ that the local structure of Er in many hosts relates to the PL intensity, especially the location of the oxygen ions around Er ions would affect the probability of 4f radiation transition through the crystal field effects. The Er concentration, the sintering temperature and the cooling condition were found to affect the formation of Er optically active centers in ZnO.

4.1 Optically active centers of Er in ZnO

The recent XAFS analyses of Er in Si and ZnO thin film indicated the importance of the local structure of Er-O clusters in the Er-related PL emission. It has been reported¹⁴⁾ that according to the XAFS results, the optically inactive Er ion had 4.56 1st-nearest neighbor O ions, and 7.64 2nd-nearest neighbor O ions. However, the optically active Er center in ZnO was at the center of an oxygen octahedron with unequal edge lengths, while showing C_{4v} symmetry. Namely, the octahedron consisted of one 1st-nearest neighbor O ion with the Er-O bond length of 0.2136 nm, four 2nd-nearest neighbor O ions with the Er-O bond length of 0.2378 nm, and one 3rd-nearest neighbor O ion with the Er-O bond length of 0.3028 nm.

If the Er ions in ZnO are located at the Zn sites in the ZnO crystal lattice, the local structure of Er will be an Er-O_4 tetrahedron, shown in Fig. 7(a). This structure is very close to the XAFS results of the optically inactive Er center in ZnO. Thus, it seems that the substitution of Er for Zn in the ZnO crystal lattice is not suitable for the PL emission around 1.534 μm . If the Er ions exist in the segregated Er_2O_3 phase in ZnO, the coordination number of O around Er is the approximately same as that of the XAFS results of the optically active Er center in ZnO, but the Er-O bond lengths and the symmetry of the Er-O_6 cluster are quite different between them, as shown in Fig. 7(b).

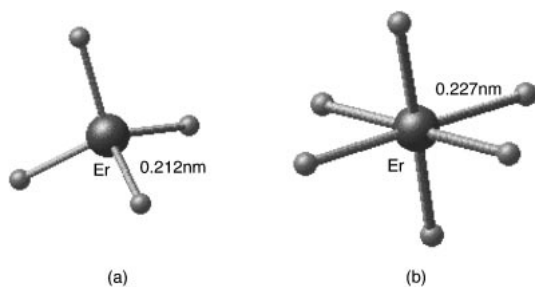


Fig. 7 Local structure of (a) Er at Zn site of ZnO lattice and (b) Er in Er_2O_3 phase.

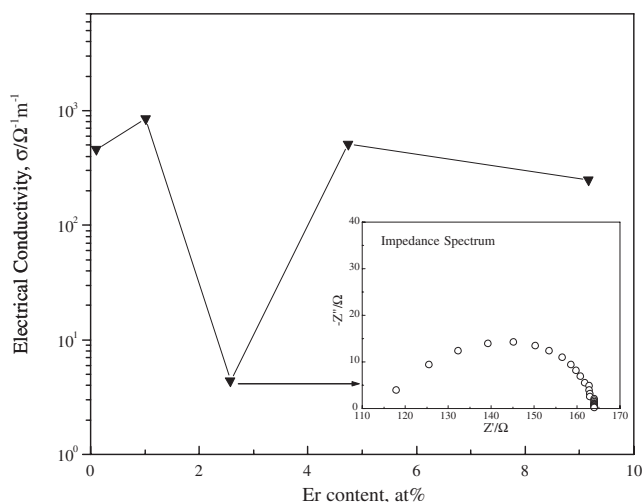


Fig. 8 Variation of the electrical conductivity of Er-containing ZnO specimens with the Er concentration. The inset shows the impedance spectrum of the specimen with the lowest electrical conductivity.

In Fig. 5 the specimen sintered at 1623 K with the highest PL emission showed stronger Er_2O_3 peaks than the specimen sintered at 1723 K. The electrical conductivity of the Er-containing ZnO specimens was also measured, partly shown in Fig. 8. The electrical conductivity of the specimen sintered at 1623 K was about $4.4 \Omega^{-1}\text{m}^{-1}$, but the electrical conductivity of the specimen sintered at 1723 K was much higher, $1.1 \times 10^3 \Omega^{-1}\text{m}^{-1}$. The Er^{3+} ions substituted for Zn^{2+} ions in the ZnO lattice will act as donors ($\text{Er}_{\text{Zn}}^\bullet$), so that the electrical conductivity of ZnO will increase with increasing Er^{3+} concentration. This is the case of the sintering at 1723 K, where Er^{3+} ions tend to substitute for Zn ions without forming a large amount of Er_2O_3 in ZnO, as is observed in the XRD pattern shown in Fig. 5. In such a case, the Er ion will be in the $\text{Er}-\text{O}_4$ tetrahedron in the ZnO lattice, so that the PL emission intensity from this specimen was very weak, in agreement with the XAFS results. However, the Er^{3+} ion has a larger ionic radius than the Zn^{2+} ion, and if the Er^{3+} ion exists in the grain boundary region, it will form the so-called double Schottky barrier region, and will decrease the electrical conductivity of ZnO. That is the reason why rare earth elements can be used in the ZnO varistor.¹⁹⁾ The impedance spectrum of this specimen was also measured, and the result is shown in the inset of Fig. 8. There was an apparent capacitance arc due to the contribution from the grain boundary, and no such an arc was observed in the other

specimens. It was clear from Fig. 8 that the specimen with the Er content of 2.6 at% had the lowest electrical conductivity, which exhibited the highest PL intensity. The specimens with the higher Er concentration showed the electrical conductivity similar to those of the specimens with the lower Er concentration. According to the SEM observation, more segregated Er_2O_3 phase appeared in the specimens with the higher Er concentration. It seems that the segregated Er_2O_3 phase will not affect the electrical conductivity of ZnO greatly, but the Er ions in the grain and in the grain boundary of ZnO will have much effects on the electrical conductivity of ZnO specimens.

According to the present results of the microstructure and the electrical conductivity, the optically active Er centers in ZnO must be neither the Er ions substituted for Zn ions in ZnO crystal lattice nor the Er ions in the segregated Er_2O_3 . Besides the Er ions in the grain of ZnO and the segregated Er_2O_3 , Er ions would exist in the grain boundary region. These Er ions could appear either as isolated Er ions to decorate the grain boundary or as a thin amorphous Er_2O_3 -layer in the grain boundary. These Er ions will act as optically active centers, by changing the local structure to some extent to the one expected from the XAFS experiment.¹⁴⁾ Further investigation is necessary to understand the PL behavior of Er in ZnO in a fundamental manner. For this purpose, the theoretical calculations of the multiplet electronic structures are now underway.

4.2 Effects of preparation conditions on the PL intensity

On the basis of the above discussion, it is easy to understand the effects of the preparation conditions on the PL intensity of the Er-containing ZnO specimens. Under the appropriate sintering temperature and cooling conditions, the $\text{Er}-\text{O}_6$ optically active centers could easily be formed in ZnO. Because the optically active center might exist in the grain boundary region, so it is not true that the higher Er concentration can form more optically active centers in ZnO. This is because, Er ions in the specimens with much higher concentration (>2.6 at%) will form more segregated Er_2O_3 phase in ZnO, which may not act as optically active centers. Sintered at higher temperatures, more Er^{3+} ions will substitute for Zn ions in the ZnO lattice, so the number of the optically active centers decreases and the PL emission becomes weak. The quenched specimen showed very low PL intensity, which may result from the fact that the water inhibited the complete contact of the specimen with the oxygen in air. It is well known that the grain boundary structure of ZnO is very sensitive to the atmosphere and cooling speed.

5. Conclusions

The photoluminescence (PL) around $1.54 \mu\text{m}$ of the Er-containing ZnO specimens was studied at room temperature by the indirect excitation of the He-Cd laser (325 nm). The PL intensity around $1.54 \mu\text{m}$ varied greatly with the Er concentration and the preparation conditions. The highest PL intensity around $1.54 \mu\text{m}$ was observed in the specimen with the Er content of about 2.6 at%, which was sintered at 1623 K, and cooled quickly to room temperature in air.

The Er^{3+} ions located at the Zn ion sites in the ZnO crystal lattice could not be the optically active centers in the Er-O_4 tetrahedral cluster. The segregated Er_2O_3 phase in ZnO would not act as optically active centers either, although the Er ion is in the Er-O_6 octahedral cluster. There is a great possibility of locating Er ions in the grain boundary region in order to make optically active centers in ZnO.

Acknowledgements

This study was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology of Japan. One of the authors (Zhen Zhou) also thanks the financial support from the Japan Society for the Promotion of Science (JSPS).

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