Effects of Nitrogen Irradiation on Photoluminescence around 1.54 μm from Er-containing ZnO

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The Er-containing ZnO specimens were treated through the N^+ irradiation and the subsequent annealing, and the effect was investigated on the photoluminescence (PL) spectra around 1.54 μm . When the specimens were annealed at 1273 K in air after the N^+ irradiation, the PL spectra changed remarkably. The PL intensity increased by about 35 times after the N^+ irradiation and the subsequent annealing, and there was the attendant shift in the wavelength of the strongest peak from 1.534 to 1.539 μm . Thus, the N^+ irradiation and the subsequent annealing could modify the local structure around Er^{3+} ions in ZnO, resulting in the surprisingly large enhancement of the PL intensity.

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1. Introduction

Erbium-doped semiconductor is one of the promising materials for optoelectronic devices because the Er intra-4f shell transition causes a 1.54 μm photoemission, which lies in the minimum loss region of silica-based optical fibers. One of the remarkable results obtained in this field is that the co-doping of Er and O in GaAs increases the luminescence intensity greatly.¹⁻³⁾ Recently, a new host semiconductor, ZnO, has been proposed,⁴⁻¹⁰⁾ because the controllable electrical conductivity by doping and also the varistor characteristics may be suitable for the fabrication of the practical optoelectronic devices. Moreover, the oxide semiconductor is easy for the realization of the co-existence of Er and O in it. Besides these, it is known that the coordination number and the local symmetry of the O ions around Er^{3+} could affect the photoluminescence (PL) intensity strongly.⁸⁾ In order to modify the local structure around Er^{3+} , the effects of N^+ irradiation and subsequent annealing were investigated on the PL spectra around 1.54 μm of the Er-containing ZnO.

2. Experimental

The Er-containing ZnO powder was prepared by mixing the $\text{ZnC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ powder with the alcohol solution of the $\text{Er}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ in a conventional way, and then by drying and calcining the product.^{11,12)} The Er content in the powder was controlled to be about 2.8 at%. The Er-containing ZnO powder was 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 by the isostatic pressing at 150 MPa. The sintering condition was controlled as follows; every specimen was held at 1273 K for 7.2 ks, heated up to 1623 K in 7.2 ks and then kept at this temperature for 10.8 ks, and subsequently taken out of the furnace and cooled down to room temperature quickly in air. Then the specimens were characterized by using ICP, XRD

and SEM.

The PL spectra were measured at room temperature using the SPEX 1702104 Spectrometer. The photoexcitation source was a cw mode He-Cd laser of 325 nm in wavelength. The luminescence from the specimen was detected by a liquid nitrogen-cooled Ge pin photodiode equipped with a chopper and a lock-in amplifier.

The nitrogen irradiation was conducted with N^+ of 100 keV. The dose was 4.4×10^{15} ions/ cm^2 . The projected range of the N^+ ions with the energy of 100 keV was estimated to be about 160 nm by using TRIM.¹³⁾ Two irradiated specimens were first annealed in an Ar gas atmosphere at 773 K for 7.2 ks, then further annealed in an Ar gas atmosphere at 773 K for 86.4 ks, and finally annealed in air at 1273 K for 18 ks. Hereafter this is called step annealing. Also, one irradiated specimen was directly annealed in air at 1273 K for 18 ks without annealing in an Ar gas atmosphere. Hereafter this is called direct annealing. The PL measurements and SEM observation were conducted for the specimens before and after the N^+ irradiation, and also after each annealing stage.

3. Results and Discussion

3.1 Step annealing in an Ar gas atmosphere and in air

The PL spectra measured at room temperature are shown in Fig. 1 for the Er-containing ZnO specimens before and after the N^+ irradiation, and also after annealing in an Ar gas atmosphere. Before the N^+ irradiation, as indicated by a symbol, A, in Fig. 1, there were apparent emission peaks around 1.54 μm . However, once irradiated, as indicated by a symbol, B, in Fig. 1, such peaks disappeared. In general, it is regarded that the PL intensity is proportional to the concentration of optically active Er and the luminescence quantum efficiency.¹⁴⁾ The luminescence quantum efficiency is inversely proportional to the defect concentration,¹⁵⁾ so that the PL intensity will decrease with the increase of defect concentration.

Since the N^+ irradiation could cause much damage and defect on the surface of the specimens, it was supposed that

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Fig. 1 PL spectra of Er-containing ZnO specimens measured before and also after the N^+ irradiation and subsequent annealing in an Ar gas atmosphere at 773 K. The scales for B, C and D are enlarged by 5 times because of the weaker PL intensity in them than A.

the PL intensity became weak and no apparent emission peaks could be found in the as-irradiated specimens, as shown in Fig. 1. So, to decrease the surface damages and defects, the irradiated specimen was annealed in an Ar gas atmosphere at 773 K for 7.2 ks, and then the PL peaks appeared again in the spectrum, as indicated by a symbol, C, in Fig. 1, indicating that some damages and defects introduced by the N^+ irradiation were eliminated to some extent by annealing. However, the intensity was reduced by only 1/9 of the original one. When the specimen was further annealed in an Ar gas atmosphere for a longer time, the PL intensity decreased, as is indicated by a symbol, D, in Fig. 1. This result might be interpreted as due to the partial loss of oxygen out of the surface or certain damage in the surface. Because, when the Er-containing ZnO specimen without N^+ irradiation was annealed under the same condition in the above, it was found that the PL intensity decreased greatly and the surface appeared to become rough. However, when the specimen was annealed in air again after annealing in an Ar gas atmosphere, the PL spectrum was recovered.

On the other hand, when the specimens were annealed in air at 1273 K for 18 ks after the N^+ irradiation and annealing in an Ar gas atmosphere at 773 K for 93.6 ks, the PL spectra changed dramatically, as indicated by a symbol, E, in Fig. 2. The intensity became about 16 times as much as that of the specimen before the N^+ irradiation, and the integrated intensity in the wavelength range of 1.52 to 1.56 μm was about 18 times larger than that before the N^+ irradiation. Moreover, the location of the strongest peak was shifted from 1.534 to 1.539 μm after annealing in air. Also, there were no apparent changes in the irradiated surface when the specimens were annealed in an Ar gas atmosphere and further in air, according to the SEM images shown in Fig. 3. For comparison, another PL spectrum is indicated by a symbol, F, in Fig. 2 for the non-irradiated surface of the specimen. In other words, E and F shown in Fig. 2 were obtained from the irradiated and the non-irradiated surface of the same specimen, respectively. The PL intensity at 1.534 μm for F increased by only 55%, as compared to the one before the N^+

Fig. 2 PL spectra of Er-containing ZnO specimens measured before and after the N^+ irradiation followed by step annealing in an Ar gas atmosphere at 773 K for 93.6 ks and then in air at 1273 K for 18 ks. The PL spectra were taken from the irradiated surface, E, and the non-irradiated surface, F, of the same specimen. The scales of A and F are enlarged by 3 times so as to fit the scale of E in the figure.

Fig. 3 SEM images taken from the specimen before the N^+ irradiation (a), and after the N^+ irradiation and annealing in an Ar atmosphere at 773 K for 93.6 ks and further in air at 1273 K for 18 ks (b).

irradiation. Thus, no remarkable enhancement of the PL intensity was observed in the non-irradiated specimen.

3.2 Direct annealing in air

When the specimen was directly annealed in air at 1273 K for 18 ks immediately after the N^+ irradiation, the PL spectra changed more dramatically, as shown in Fig. 4. The intensity

Fig. 4 PL spectra of Er-containing ZnO specimens measured before and after the N^+ irradiation followed by direct annealing in air at 1273 K for 18 ks. The PL spectra were taken from the irradiated surface, G, and the non-irradiated surface, H, of the same specimen. The scales of A and H are enlarged by 10 times so as to fit the scale of G in the figure.

became about 35 times as much as the peak intensity before the N^+ irradiation, and the integrated intensity in the wavelength range of 1.52 to 1.56 μm was about 40 times larger than that before the N^+ irradiation. The location of the strongest peak was also shifted from 1.534 to 1.539 μm after annealing in air. The PL spectrum taken from the opposite surface (*i.e.*, the non-irradiated surface) is indicated by a symbol, H, in Fig. 4. There was no significant increase in the PL intensity for the curve H, as compared to the curve A, measured before the N^+ irradiation.

According to the above results, the effects of the N^+ irradiation and the subsequent annealing may be attributable to the changes in the local structure around Er^{3+} , since there were not only the remarkably large increase in the PL intensity but also the clear shift in the location of the strongest emission peak. It has been reported⁸⁾ that, according to the XAFS results, the optically active Er in ZnO (ErO_6) was at the center of an oxygen octahedron with unequal edge lengths, while showing the C_{4v} symmetry. Also, there have been many reports^{16–19)} on the N-doping into ZnO to explore the p-type conductivity. At this moment, it is however difficult to distinguish a N-doping effect from synergistic oxygen effects, since, in those reports, the N-doped ZnO specimens were also annealed in air or oxygen atmosphere at high temperatures. One of the possible mechanisms of the luminescence enhancement is the formation of an $\text{ErO}_{6-x}\text{N}_x$ octahedron by substituting the N ions for the O ions around the Er^{3+} ion, or the formation of a distorted ErO_6 octahedron or other polyhedrons assisted by the N^+ irradiation. Further experiments are now underway to make clear the mechanism of the enhancement of the PL intensity. It is stressed here that the present N-irradiation combined with annealing causes striking luminescence enhancement with good reproducibility.

4. Conclusion

The Er-containing ZnO specimens were treated through the N^+ irradiation and the subsequent annealing, and the effect was investigated on the PL spectra around 1.54 μm . The PL intensity increased by 16 times when the specimens were annealed first in an Ar gas atmosphere and subsequently in air after the N^+ irradiation. When the specimens were directly annealed in air after the N^+ irradiation, the PL intensity increased by about 35 times. Also, the location of the strongest peak was shifted from 1.534 to 1.539 μm . The remarkable changes may be attributable to the modification of the local structure around the Er^{3+} ion in ZnO.

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