Effect of post-annealing on structural and optical properties, and elemental distribution in heavy Eu-implanted ZnO thin films

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The effect of post-annealing on ZnO thin films implanted with Eu at 1×10^{17} ions/cm² was studied to characterize the structural and luminescent properties, and the distribution of Eu in thin films. After post-annealing at 600°C, the broadening of the ZnO(002) diffraction peak was the same as that of the as-implanted sample. The sample showed orange luminescence due to Eu³⁺. After post-annealing at 900°C, a sharp diffraction peak of ZnO(002) was observed. The orange luminescence due to Eu³⁺ had disappeared, and instead, the intense luminescence of the band-edge of ZnO was observed in the sample. Ion images of Zn and Eu indicated that the Eu separated from the ZnO during the post-annealing. It is thought that the difference in luminescence is due to the separation of Eu from ZnO.

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1. Introduction

Ion implantation plays an important role in the semiconductor field, and has been applied to oxide materials as a doping and surface modification method, as this technique offers high repeatability. Recently, a new method of producing a dose library for implantation has been developed.¹⁾ The above approaches are useful in the scientific and technological fields because determining the dose library of implants in the substrate makes it possible to suppress unintentional factors introduced by contamination during annealing. We utilized the above method to study the optical properties of ZnO,²⁾ because ZnO is considered to be a promising luminescent material using low-energy electron beam irradiation.³⁾ ZnO shows luminescence in the visible region due to several origins: the transition from shallow donors to deep acceptors;⁴⁾ a singly charged oxygen vacancy;⁵⁾ and Cu phosphor.⁶⁾ In order to obtain other luminescence colors, rare-earth elements such as Eu and Tb are well known as a phosphor for blue, green, and orange luminescence, although the luminescence color also depends on the ionic state of the materials.^{7),8)} It is well known that Eu³⁺ is a phosphor for producing orange luminescence. The luminescence by Eu³⁺ was observed in ZnO⁹⁾ and GaN.¹⁰⁾ Recently, we showed the orange luminescence of Eu³⁺ in ZnO thin film implanted with Eu, and determined the optimal dose of Eu for intense luminescence.¹¹⁾ However, the ZnO thin films implanted with Eu were not characterized in terms of surface morphology, crystallinity, and Eu distribution. In the previous paper, it was suggested as additional evidence that the Eu-related luminescence disappeared by increasing the annealing temperature. In this paper, we report the effect of annealing temperature on the structure and optical properties and the elemental distribution in thin films and explain the reason for the disappearance of the Eu-related luminescence.

2. Experimental procedure

ZnO thin films on Si substrates were synthesized by electron cyclotron resonance (ECR)-assisted chemical vapor deposition (CVD). The reaction chamber containing the ECR source was pumped using a turbo-molecular pump to 2×10^{-8} Torr. The Zn source was zinc acetylacetonate [$\text{Zn}(\text{CH}_3\text{COCHCOCH}_3)_2$: Zn(acac)₂], which was vaporized at 90°C and transferred to the reaction chamber at an H₂ gas flow of 5 standard cubic centimeters per minute (sccm). The gas containing the Zn(acac)₂ vapor was blown out to the substrate using a ring injector. The substrate temperature was fixed at 600°C during the deposition.

After thin film synthesis, Eu ion implantation (accelerating voltage of 150 keV and dose of 1×10^{17} ions/cm²) was carried out using a modified ion implantation system. After the Eu implantation, the ZnO thin film implanted with Eu (ZnO:Eu) was annealed at 600 and 900°C for 10 and 40 min in air atmosphere using an infrared furnace.

The thin films were characterized *ex situ* by several techniques. The surface morphology of ZnO thin films was examined by atomic force microscopy (AFM). The structure of the films was studied by X-ray diffraction (XRD), employing an X'pert diffractometer (Panalytical Co. Ltd., Almelo, Netherlands). Room-temperature photoluminescence (RT-PL, ACCENT Technology Co. Ltd., rpm-2000) was measured using laser irradiation ($\lambda = 266$ nm). Finally, the elemental distribution of Zn, Eu, and impurities in the ZnO films were analyzed by means of secondary ion mass spectroscopy (SIMS, Cameca, NanoSIMS 50).

3. Results and discussion

Figure 1 shows AFM images of several ZnO thin films, and reveals that the Eu implantation and post-annealing are effective in changing the surface morphology. It is obvious that the as-deposited thin film in Fig. 1a was covered with grains of about 500 nm in diameter. The following images indicate the effect of Eu implantation and the post-annealing on the surface morphol-

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Fig. 1. AFM images of ZnO thin films: (a) as-deposited ZnO, (b) as-implanted ZnO thin film, (c): ZnO:Eu annealed at 600°C, (d): ZnO:Eu annealed at 900°C. Scanning area of all images is $5 \times 5 \mu\text{m}^2$.

Fig. 2. XRD patterns of ZnO thin films: (a) as-deposited ZnO, (b) as-implanted ZnO thin film, (c): ZnO:Eu annealed at 600°C, (d): ZnO:Eu annealed at 900°C. Open circles show the peaks of the substrate. The FWHM of ZnO(002) peaks are also shown in the figure.

ogy. Figure 1b indicates the surface of the as-implanted ZnO:Eu. This image shows that the density of the thin film changed and the smoothness of the surface improved. The ZnO:Eu annealed at 600°C shown in Fig. 1c shows quite a different surface morphology: round grains with a size of about 300 nm were observed. Figure 1d shows the result of ZnO:Eu annealed at 900°C. The grain size is obviously smaller than those of ZnO:Eu annealed at 600°C. Because of this, the surface smoothness has been lost. From the above, the post-annealing causes a significant change in the surface morphology.

Figure 2 shows XRD patterns of several ZnO thin films. All diffraction peaks were assigned as the ZnO and Si substrate. The diffraction peak corresponding to ZnO(002) is observed in all thin films, which is evident in *c*-axis oriented ZnO thin films. The Eu implantation causes the broadening of the ZnO(002) peak: the full width half maximum (FWHM) of ZnO(002) peak in the as-deposited (a) and as-implanted sample (b) is 0.107 and 0.224°, respectively. After the annealing at 600°C, the FWHM of ZnO(002) peak is 0.206°. The ZnO:Eu annealed at 600°C

Fig. 3. Room-temperature photoluminescence spectra of ZnO thin films: (a) ZnO:Eu as-implanted, (b) ZnO:Eu annealed at 600°C, (c) ZnO:Eu annealed at 900°C. The dashed lines indicated the luminescence centers of ZnO.

contains the defects introduced into the lattice by Eu implantation. The ZnO(002) peak in the samples of as-deposited (a), as-implanted (b) and annealed at 600°C (c) are at 34.425, 34.404, and 34.466°, respectively. The XRD pattern of ZnO:Eu annealed at 900°C was shown in spectrum (d). This shows the following feature: the FWHM of ZnO(002) peak of 0.108° and the shift of ZnO(002) peak to 34.536° and the appearance of the weak (004) peak. The above features imply that the crystal quality of ZnO:Eu thin film recovered by a sufficient reaction during the post-annealing temperature of 900°C. Additional peaks, such as due to Eu-related materials, were not observed in the Eu implanted and post-annealed thin films.

Figure 3 shows the RT-PL spectra obtained from the ZnO:Eu samples. Spectrum (a) was obtained in the as-implanted ZnO:Eu thin film. The luminescence was not observed. Such results were certainly obtained in the as-implanted ZnO samples.²⁾ The reason is thought to be that the defects, such as dangling bonds, point defects, and dislocations, introduced by the ion implantation act as non-radiative defects in as-implanted ZnO. In our studies, the luminescence property of the implanted ZnO could be obtained after post-annealing.^{2),11)} The broadening of the ZnO(002) peak reflects the damage as well as the implants introduced by the ion implantation. In Fig. 2, the broadening of the ZnO(002) peak shows the maximum value in as-implanted ZnO:Eu, and decreases with increasing post-annealing temperatures. This supports the above consideration. In ZnO:Eu annealed at 600°C, spectrum (b) were characterized by the sharp luminescence lines in the wavelength range of 580–706 nm, originating from the Eu^{3+} .⁹⁾ The main peak of Eu^{3+} at the 618 nm-wavelength and weak peaks at 580, 592, 657, and 706 nm-wavelengths were observed. The assignment of these peaks is shown in the figure. Additionally, weak luminescence peaks at 380 and about 530 nm-wavelength originating from the ZnO were also observed. Spectrum (c) obtained in ZnO:Eu annealed at 900°C shows that the intense luminescence of band-edge emission at the 380 nm-wavelength of ZnO is the main contribution in the spectrum, which is evidence of the recovery of crystal quality. The luminescence originating from Eu^{3+} disappeared. Additionally, a weak, broad peak around the 530 nm-wavelength was also observed.

Fig. 4. Secondary ion images obtained in ZnO:Eu annealed at 900°C. The detected ions are also shown in the figure.

In ZnO:Eu annealed at 600°C, the degree of broadening of ZnO(002) peak is larger than those in the as-deposited and the annealed sample at 900°C in Fig. 2. The broadening of ZnO(002) diffraction peak is evidence of Eu in the ZnO lattice. The surface morphology after the post-annealing changed in Fig. 1b and 1c. This sample shows the luminescence peaks originated from Eu^{3+} and ZnO in Fig. 3a. From above results, the Eu diffused through the implantation damage and occupied the active site to appear as luminescence in the ZnO lattice. On the other hand, in the ZnO:Eu thin film annealed at 900°C, significantly different results were obtained compared with those of ZnO:Eu annealed at 600°C. The surface morphology indicates the changes to the rough surface in Fig. 1d. ZnO:Eu thin film annealed at 900°C shows that the improvement of the broadening and shift to the high angle of the ZnO(002) peak was observed in Fig. 2. The luminescence due to Eu^{3+} disappeared, and the intense luminescence of band-edge of ZnO was observed. However, there is no evidence of Eu in the thin films. In order to show evidence of Eu in the thin film, we carried out measurements of the high-resolution ion image using a SIMS. **Figure 4** presents the scanning ion images of Zn and Eu obtained from the ZnO:Eu annealed at 900°C. These reveal the heterogeneous distribution of Zn and Eu intensities in the images. The high intensity regions of Eu shown as arrows in Fig. 4b are observed as the low intensity regions of Zn in Fig. 4a, indicating that the Eu separates from ZnO during the annealing. From Fig. 4, the grain size of Eu related phases were estimated to be about 200 nm, which is in good agreement with those in Fig. 1d. The diffraction peak related with Eu was not detected, indicating that Eu related phases seem to be random orientations and/or amorphous. Here, after the Eu implantation of the dose of 1×10^{17} ions/cm², ZnO thin film becomes metallic. The post-annealing causes reactions such as the oxidation of Eu and separation from the ZnO lattice. The rate of reaction depends on the temperature. In particular, considering the melting temperature of Eu metal ($T_{\text{mp}} = 822^\circ\text{C}$), it is considered that the results in ZnO:Eu annealed at 900°C are caused by the partial melting of a large amount of Eu in the ZnO thin film.

4. Conclusions

ZnO thin films were grown on Si substrate by ECR-assisted chemical vapor deposition. The thin film was then used as the substrate for heavy Eu implantation (accelerating voltage of 150 keV and dose of 1×10^{17} ions/cm²). Eu implanted ZnO thin films were annealed at 600 and 900°C. In the ZnO:Eu sample annealed at 600°C, luminescence due to Eu^{3+} was observed. On the other hand, the luminescence of Eu^{3+} disappeared in the ZnO:Eu sample annealed at 900°C. The difference in the luminescence of Eu^{3+} can be explained as resulting from the separation of Eu from ZnO. The above results indicate that the temperature of the post-annealing is an important factor in incorporating Eu in the active sites in ZnO.

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