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Characterization of luminescent properties of ZnO:Er thin films prepared by rf magnetron sputtering

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Abstract

ZnO:Er thin films were deposited on *c*-plane sapphire substrates by rf magnetron sputtering and annealed at 700 °C under air and H_2 atmospheres for the luminescent improvement. The effects of sputtering parameters and the annealing conditions on visible and 1.54 μm IR emissions were investigated. Structural and luminescent properties strongly depended on the deposition conditions and annealing atmospheres. By tuning the excitation wavelength, ZnO:Er thin films exhibited a strong emission band at around 465 nm and a weak emission at 525 nm originated from the energy transition of $^4I_{15/2}$–$^4F_{5/2}$ and $^4I_{15/2}$–$^2H_{11/2}$, respectively, while 1.54 μm IR emissions due to $^4I_{15/2}$–$^4I_{13/2}$ transition.
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1. Introduction

Numerous works have been carried out for the Er-doped semiconductors, such as GaN, GaAs, Si, etc., in optical applications due to the excellent 1.54 μm infrared (IR) emissions from the intra-4f shell transition in Er^{3+} ions.[1–3] They reported that oxygen co-doping and use of wide band-gap semiconductors are very effective in improving 1.54 μm IR emission properties.

Recently, ZnO has been focused as a new host material for Er-doping, because it has an oxide structure and a wide band-gap of about 3.3 eV, which enable to realize the coexistence of Er and O in the host materials.[3,4–6] It is known that the coordination number and the symmetry of O-ions around Er^{3+} strongly contribute to the luminescent properties, and also a crystal-field by the ligands allowed the intra-4f transition of an isolated Er.[5,7,8] The high-order coordination of O in ZnO:Er decreased the Er-related luminescence. However, post-annealing in O_2 ambient changed the local structure of Er leading to a pseudo-octahedral structure with C_{4v} symmetry, which increased the photoluminescence (PL). Many works were performed to enhance the Er-related emissions in low band-gap semiconductors, but could not solve a significant loss in luminescence efficiency occurred at room temperature due to a trapped electron–hole pair originated from excited Er ions.[9,10] This PL quenching could be diminished by using wide band-gap semiconductors such as ZnO.[3]

In spite of many works on the PL of ZnO:Er powders and films, there are few reports on the correlation between the structural evolution and the optical properties.[11–13] In ZnO:Er powders and films, Er-ions are probably located not only inside the crystalline grains but also at the grain boundaries leading to strong luminescent quenching. However, to investigate the relationship between the structure and the luminescent properties furthermore, it is necessary to obtain the epitaxial ZnO:Er films on sapphire substrates that can minimize the Er segregation at the grain boundaries.

In this work, ZnO:Er films deposited on *c*-axis sapphire substrates by rf magnetron sputtering method. We investigated the effects of growing conditions (O_2 partial pressure and rf power) and annealing atmosphere on the structural characteristics and luminescent properties.

2. Experiment

ZnO:Er films were grown at various oxygen partial pressure and rf powers. ZnO:Er ceramic target was fabricated by pressing the mixture of ZnO (High Purity Chemicals, 99.999%) and Er_2O_3 powders (United International Inc., 99.9%) by 3 tons press in 3 in. diameter molder, and sintering it at 1100 °C for 3 h in air atmosphere. According to the previous work,[14] high PL intensity could be achieved by adding 1 mol% Er to ZnO.

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Thin films were annealed in the tube furnace for 3 h at 700 °C under air and 5% H_2 atmosphere, respectively. All samples had the same thickness of 2 μm by controlling the deposition time. The structural properties of the films were determined using X-ray diffractometer (XRD, SIEMENS-D5005) with Cu Kα radiation (λ = 1.5405 Å). FESEM (field-emission scanning electron microscope, JEOL-JSM 6500F) used to observe the surface morphology. The PL spectra in the visible range were measured by PSI-DARSA5000 PL system. Various excitation wavelengths were refracted by a monochromator with a xenon light source. For measuring IR emissions, Ar laser with a grating monochromator was used as a photoexcitation source.

3. Result and discussion

Fig. 1 shows XRD patterns of ZnO:Er films deposited on *c*-plane sapphire substrates as a function of oxygen partial pressure at 100 W and 150 W. They all exhibited only one characteristic peak of ZnO, (0 0 2) at 34.4°, which meant *c*-axis preferred orientation. As oxygen partial pressure increased, the intensity of (0 0 2) peak increased at both 100 W and 150 W.

At low oxygen partial pressure, weak (0 0 2) peaks were observed due to the deficient oxygen source, while their intensities continuously increased with increasing oxygen partial pressure resulting in strong (0 0 2) peaks. Finally a very strong (0 0 2) peak could be achieved at 50% oxygen partial pressure and 100 W rf power. This indicated that enough oxygen sources had to be provided to form thermodynamically stable and well developed ZnO films during growth.

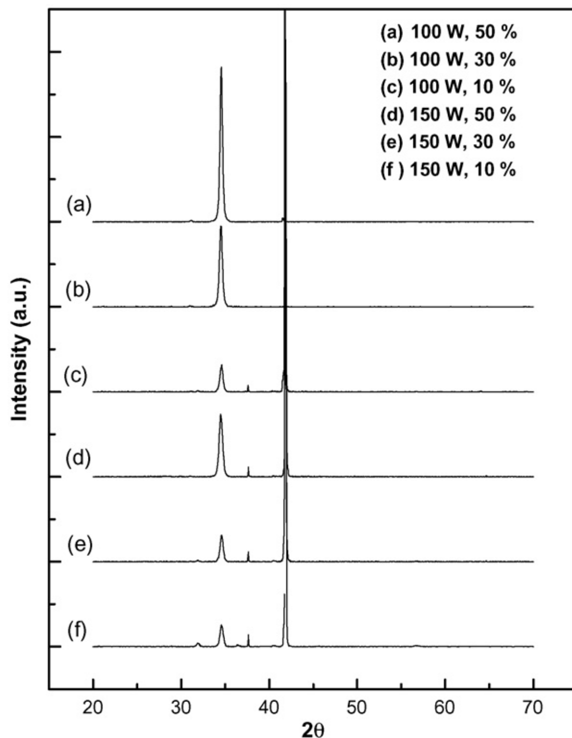

Fig. 1. XRD patterns of ZnO:Er thin films deposited on *c*-plane sapphire substrates as a function of oxygen partial pressure at 100 W and 150 W.

Rf power is a very important sputtering parameter, because it supplies the kinetic energy to the sputtered atoms and increases the growing rate. However, more highly *c*-axis oriented ZnO:Er films were grown at 100 W rather than at 150 W, even though higher kinetic energy could be provided to the sputtered particles at 150 W. Excessive rf powers inversely contribute to the decrease in structural order of the films due to a couple of factors, which are the high deposition rate, the relative number of Zn to ZnO ions arriving at the substrates, and the energy of secondary electrons emitted from the target.[15,16] In our work, it could be concluded that 100 W rf power was an optimal condition, while 150 W was too much for high quality films.

To evaluate the degree of *c*-axis orientation of ZnO:Er films, we measured the standard deviation (σ) of X-ray rocking curve of the (0 0 2) peak, which represented a Gaussian distribution of the *c*-axis of crystallites normal to the substrate. Smaller σ values of *c*-axis preferred films means more perpendicular distribution to the substrates. Fig. 2 shows the standard deviation (σ) of the X-ray rocking curve as a function of oxygen partial pressure and rf power. This result was in well accordance with that of Fig. 1. σ values rapidly decreased with increasing the oxygen partial pressure, and also were apparently lower at 100 W than 150 W. Thirty percent of oxygen partial pressure was estimated as a threshold condition for growing highly oriented ZnO:Er films. At the optimum conditions of 100 W and 50% oxygen, σ value was about 0.65°, which was assumed that an epitaxial ZnO:Er film was grown on the *c*-plane sapphire substrate. This was verified by X-ray pole figure method, which showed the dotted diffraction patterns of ZnO:Er films.

To investigate the correlations between the microstructure and the PL, luminescent properties of ZnO:Er films deposited under various sputtering conditions were observed by changing the excitation wavelength. The PL intensity of as-deposited ZnO:Er films was too low to measure, so as-deposited films had to be post-annealed at 700 °C at air atmosphere. Previous works explained the annealing effects on the PL intensity by

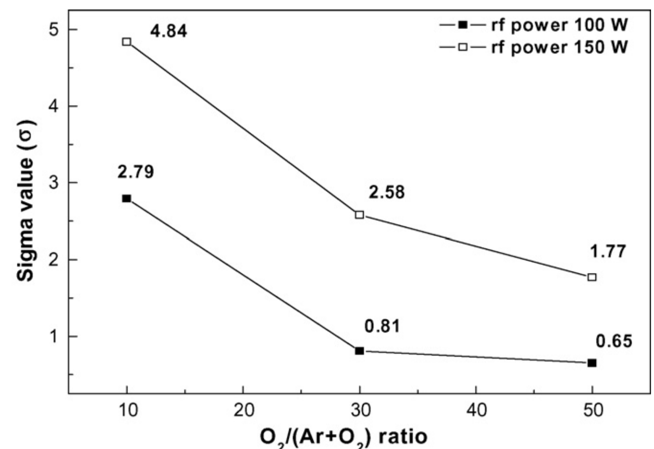

Fig. 2. Variation of the standard deviation (σ) of (0 0 2) X-ray rocking curve of ZnO thin films as a function of oxygen partial pressure at 100 W and 150 W rf power.

the local structure of an optically active center in ZnO:Er thin films compared with Si:Er films.[5,7,8] They suggested that Er is surrounded by first five O-atoms and second nearest neighbors of eight O-atoms, and demonstrated that this high-order coordination of O as well as the low symmetry caused the crystal-field around Er to suppress the 4f-intra transition of Er, resulting in the low PL intensity. However, post-annealing at air atmosphere changed the local structure of Er to form a pseudo-octahedral structure with C_{4v} symmetry by diffusion of excess O, leading to higher PL intensity. We also verified the above suggestions by comparing the effects of post-annealing at air and H_2 atmosphere, respectively. ZnO:Er thin films post-annealed at air ambient exhibited remarkably higher PL intensity and smaller σ values than those post-annealed at H_2 ambient. These results meant that the diffusion of excess O could occur only at air ambient (oxidation), but not at H_2 (reduction) that inversely caused the re-evaporation of oxygen atoms in ZnO:Er films.

PL spectra of ZnO:Er films deposited at 100 W and 50% oxygen partial pressure after annealing at 700 °C at air atmosphere is shown in Fig. 3, which exhibited a strong blue emission band at 465 nm and a weak green-band at 520 nm simultaneously. The excitation wavelength was 385 nm of ultra-violet (UV) region at which PL showed maximum absorption for 520 nm emission. ZnO is a kind of semiconductors with a wide band-gap of 3.1–3.3 eV with the corresponding wavelength ranging from 375 nm to 400 nm. Hence, the UV absorption of the prepared films was caused by the band-to-band or band tail transition.[17] An emission peak at 520 nm of ZnO:Er thin film was not attributed to pure ZnO emission, even though pure ZnO could show the green emission at the same wavelength. It was a radiative transition of $^2H_{11/2} \rightarrow {}^4I_{15/2}$ (ground state) of Er^{3+} ion due to the re-absorption by Er^{3+} ion of the light emitted from pure ZnO powder. The blue emission peak at 465 nm was originated from the intra-4f shell transition of Er^{3+} ions ($^4F_{5/2} \rightarrow {}^4I_{15/2}$).[18]

To characterize IR emission of ZnO:Er thin films, they were pumped with 477 nm and 515 nm using an Ar laser as shown in Fig. 4. We selected two excitation wavelengths that is almost similar to the emission peaks (around 465 nm and 520 nm) shown in Fig. 3. The main peak was located at 1.537 μm originated from the intra-4f shell transition from the first excited state ($^4I_{13/2}$) to the ground state ($^4I_{15/2}$) in the Er^{3+} ions,[4] and there was little difference between 477 nm and 515 nm excitation. This meant that IR emission of ZnO:Er thin films was attributed to the identical Er emission center under 477 nm and 515 nm excitation.

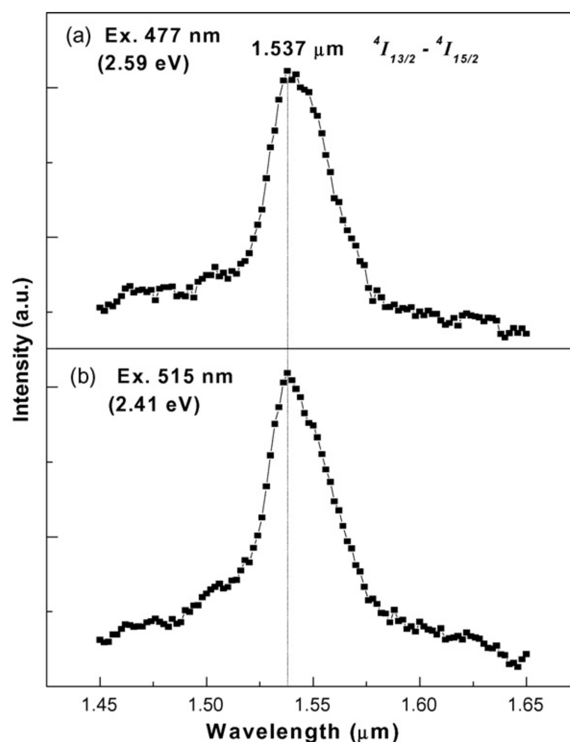

Fig. 4. IR emission spectra of post-annealed ZnO:Er thin films deposited at 100 W and 50% oxygen partial pressure under (a) 477 nm and (b) 515 nm excitation.

Fig. 5 shows IR emission intensity of ZnO:Er thin films as a function of oxygen partial pressure at different rf power of

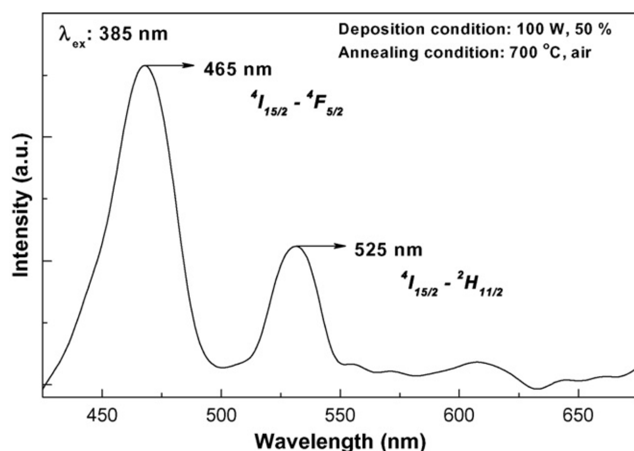

Fig. 3. PL spectra of post-annealed ZnO:Er thin films deposited at 100 W and 50% oxygen partial pressure under 385 nm UV excitation.

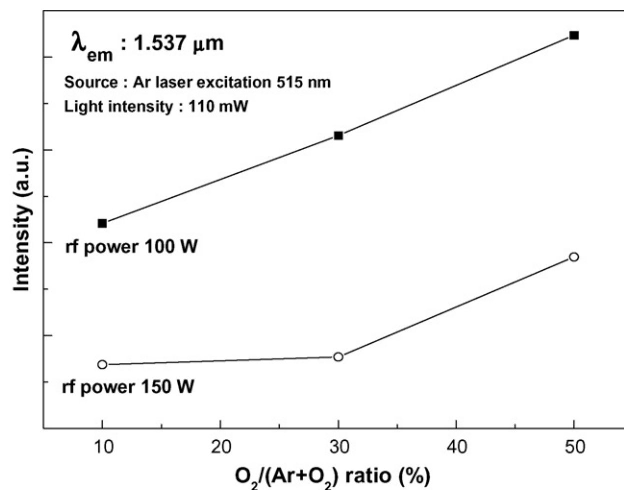

Fig. 5. IR emission intensity of post-annealed ZnO:Er thin films as a function of oxygen partial pressure at 100 W and 150 W rf power under 515 nm excitation.

100 W and 150 W under 515 nm excitation. IR emission intensity increased with increasing oxygen partial pressure at both 100 W and 150 W, while the films deposited at 100 W exhibited much higher emission intensity than those deposited at 150 W. These results were well consistent with those of X-ray rocking curve of Fig. 2. The films of small σ values were superior to those of large σ values in IR emissions. This indicated that IR emission was very closely correlated to the microstructure of films. Especially, epitaxial ZnO:Er thin films deposited at 100 W and 50% oxygen partial pressure showed remarkably high IR emission intensity compared with other films. It can be assumed that epitaxial ZnO:Er films lead to well arranged crystal-field surrounding Er-atoms in ZnO matrix and also to a minimization of the Er segregation at the grain boundaries, resulting in strong emissions. Doped Er-atoms can be located inside the grains and/or at the grain boundaries.[13] The latter case causes the strong luminescent quenching leading to low PL intensity. In our experiment, epitaxial ZnO:Er thin films had no grain boundaries except for low angle ones, and accordingly they could eliminate almost the Er segregation at the grain boundaries. This could partly explain stronger 1.537 μm Er emissions of epitaxial ZnO:Er thin films.

4. Conclusion

Structural properties of ZnO:Er films strongly depended on the deposition conditions and annealing atmospheres, and then optical emissions were closely correlated to the microstructure. Under UV excitation of 385 nm, ZnO:Er thin films exhibited a strong emission band at around 465 nm and a weak emission at 525 nm originated from the energy transition of $^4I_{15/2}$–$^4F_{5/2}$ and $^4I_{15/2}$–$^2H_{11/2}$, respectively. With increasing oxygen partial pressure, (0 0 2) peaks of XRD became stronger and the standard deviation (σ) of X-ray rocking curve of the (0 0 2) peak decreased, resulting in higher IR emission due to $^4I_{15/2}$–$^4I_{13/2}$ transition. Epitaxial ZnO:Er films deposited at 100 W and 50% oxygen partial pressure showed the strongest 1.537 μm IR emissions by minimizing the Er segregations at the grain boundaries as well as providing the well arranged crystal-field surrounding the Er-atoms in ZnO.

Acknowledgement

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