Effect of Eu doping on the near band edge emission of Eu doped ZnO

thin films after high temperature annealing

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Abstract

We studied the effect of europium (Eu) doping on the near band edge emission of ZnO thin films, fabricated by sputtering and high temperatures annealing. The doping concentration of Eu in the ZnO films was varied from 0.01 to 0.62 at.%. Photoluminescence (PL) spectra showed that the films ultra-violet (UV) emission was enhanced very much by high temperature treatment and was stronger for the Eu doped ZnO than that for the un-doped ZnO films after 1100 °C annealing. X-ray diffraction showed the films had hexagonal wurtzite structure, the width of the ZnO (002) plane diffraction peak was sensitive to the anneal temperature and also to the Eu doping concentration, and Zn silicates had formed after the 1100 °C annealing. Scanning electron microscopy showed that the surface morphology of the films became more uneven with increasing Eu concentration. The PL decay spectra inferred that the lifetime of the UV PL was correlated with the size of ZnO nanocrystals in the films. The results support that the intensity of the UV PL is primarily influenced by the crystalline perfection of the films which is also influenced by the Eu doping concentration.

Keywords: ZnO films, Eu doping, UV emission, magnetron sputtering

1. Introduction

The reports of room temperature ultraviolet (UV) lasing from ZnO micro-crystalline films [1, 2], have attracted intense interest for potential applications such as UV lasers, diodes and detectors, but to acquire highly efficient UV emission from ZnO films remains a challenge. Normally the UV emission involves recombination near the band edge (NBE) of ZnO and strongly depends on the crystal quality and stoichiometry of the ZnO films, both of which are affected greatly by fabrication technology, doping, post-annealing conditions, and so on.

Rare earths (REs) have unique electronic structures that are interesting for optical applications, and they have been used as dopants in many host materials. REs have therefore also naturally been explored as a dopant in ZnO for potential applications in photonic devices. Nevertheless, the consensus of many reports on RE doping of ZnO is that the material properties are not favorable for RE doping of ZnO, and this has a consequence for crystalline bulk material. The incorporation of a trivalent RE-cation in the wurtzite-like lattice of ZnO is not a favorable process [3]. Further, the lifetime of the exciton in ZnO is more than three orders of magnitude shorter than the radiative lifetime of the RE ion, which makes the energy transfer from ZnO to RE unlikely [4]. However, if defects are introduced, then bulk defects, surface states in nanostructures, or additional compounds that are in close contact with the RE ions, could facilitate an energy transfer [5-10]. It has been considered that states associated with oxygen vacancies in ZnO can facilitate the energy transfer. However, nonradiative pathways are also correlated with oxygen vacancies, therefore other strategies than optimizing the oxygen vacancy concentration might be overall more efficient. There has also been a large effort on producing inexpensive phosphors being more stable than the RE doped II-VI semiconductor powders. Among the oxide hosts that have been

investigated are ZnO-SiO₂ based systems which appear attractive. Inspired by that we have previously studied ZnO films doped with cerium (Ce) and/or ytterbium (Yb) reacting with a Si substrate [11-13]. These films were sputter-grown from RE oxides and ZnO composite targets with an O₂ partial pressure yielding oxygen rich films. This could minimize the oxygen vacancies. For high temperature annealing, silicates were formed in addition to the ZnO crystal quality being enhanced. However, the energy transfer to Ce or Yb was not efficient. Another striking feature of the cases with Ce and Yb doping was a significant increase in the UV NBE emission, in particularly for high temperature annealing and here we explore the hypothesis that europium (Eu) doping will yield similar results.

It has been reported that both Eu²⁺ and Eu³⁺ ions could substitute Zn²⁺ in the ZnO lattice by incorporation of charge balancing point defects or form Eu₂O₃ at the nanocrystal surface [8, 9, 14-16], dependent on the doping concentration. The lattice constant of ZnO was reported to vary slightly, and that was attributed to the difference in ionic radius, and a deteriorated crystallinity of nano-ZnO films. Eu doping will also introduce energy levels within the band-gap of ZnO, which provides an extra recombination/decay route for excitons. With regards to UV emission, Luo et al [17] reported that an enhanced UV lasing and reduced threshold occurred in their Eu doped ZnO films prepared by a sol-gel method, and attributed the lasing enhancement to the significantly reduced concentration of singly ionized oxygen vacancies. Albeit many reports on Eu doping of ZnO have been reported, only very few have considered the effect of Eu doping on the UV emission of ZnO:Eu systems.

In this work, we focus on the enhancement of UV emission by high temperature annealing and the effect of Eu doping on the UV emission. We here test the hypothesis, deduced from our previous observations [11-13], that Eu additions to ZnO

sputtered films will have similar effects as we have observed for Ce and Yb doping. The results could be in agreement with the hypothesis if the UV emission enhancement is mainly related to the structure and crystalline perfection of the film. Our hypothesis is that the RE influences the microstructure of the as-deposited film, likely by influencing the atomic mobility of surface atoms and nucleation. Different crystalline quality would then mainly come from grain growth effects of the films upon annealing. It would yield difference in the crystal perfection for the different cases if the as-deposited structures are different, and because of that. It can not be excluded that RE doping also influence the grain growth, and likely will at high doping concentrations. Here we report how the enhancements depend on the Eu doping concentration and also how the structural properties of the films depend upon the Eu doping concentration. Our hypotheses would be false if the trends in crystal perfection and UV intensity with Eu concentration was different that predicted. These observations may pave a new way to acquire strong UV emission from the ZnO films, which have potential application in ZnO-based UV photonics.

2. Experimental details

The Eu doped ZnO (ZnO+EuO) films were deposited on Si single crystal substrates by magnetron sputtering from two targets simultaneously. One target was an Eu_2O_3 +ZnO composite target, made by hot-pressing a mixture of Eu_2O_3 (99.99%) and ZnO (99.999%) powders (1:9 wt.%). The other target was a ZnO target with a purity of 99.99%. A DC bias was applied to the ZnO target and a RF bias was applied to the Eu_2O_3 +ZnO target during the co-sputtering. The Eu concentration in the films was varied for different depositions by applying different sputtering powers on the two targets. During sputtering, the base vacuum pressure was 6.7×10^{-5} Pa, the working

gas was a mixture of argon and oxygen with flow rates of 25.0 and 5.0 sccm, respectively, and the gas pressure was kept at 0.33 Pa. No intentional substrate heating was used, but the Si substrates were rotated during deposition to obtain lateral uniformity. Eight sputtering runs yielding different Eu concentrations were fabricated. The resulting ZnO+EuO films were fabricated and labeled as sample S0, S1, S2, S3, S4, S5, S6 and S7, respectively. The S0 sample function as a reference ZnO film without any Eu. The stoichiometry of the films was characterized by using Rutherford backscattering spectrometry (RBS, NEC 2x1.7 MV Tandem Accelerator in Ion Beam Materials Laboratory in Peking University), and the results are listed in Table I. The films clearly have excess oxygen in the as-deposited samples.

The Si wafers with the films were then cleaved into small pieces and annealed at 700-1100 °C in flowing N₂ (purity 99.999%) ambience for 30 minutes. The microstructure of the films and its evolution was investigated by using X-ray diffraction (XRD) (Rigaku D/MAX-2500). Scanning electron microscopy (SEM) was used to observe the surface morphology of the films after the high temperature annealings. The chemical state of the elements in the annealed films were examined by X-ray photoelectron spectroscopy (XPS) by using a ThermoFisher Scientific ESCALAB 250 system with monochromatic Al K α X-ray radiation (150W). The photoluminescence (PL) spectra were recorded by using a Lab RAM HR800 microscopic fluorescence image system, where the sample was excited using the 325 nm (3.815 eV) line of a He-Cd laser (~ 30 mW) and detected in the range 350-950 nm (3.5-1.3 eV) by a spectrometer employing a charge-coupled device array. The PL decay spectra were recorded with a FLS 920 fluorescence spectrophotometer using a Xe lamp as excitation source. All the measurements were performed at room temperature.

3. Results and discussion

Figure 1 shows the results of PL measurements. Fig.1 (a) shows the PL spectra of the undoped ZnO film S0 after various temperatures as indicated. This can be compared with the PL spectra of an Eu doped ZnO film, S4 (0.08 at.% Eu) shown in Fig. 1(b). The spectra have a typical UV emission band in the range of 2.8-3.4 eV and a broad emission band in the visible (VIS) range 1.7 -2.7 eV. The UV band is the near band edge (NBE) emission considered to be associated with exciton recombination and free electron/hole recombination, while the VIS band is due to radiative relaxation through states within the band gap [8]. For increasing annealing temperature from 700 to 1100 °C, both the VIS and the NBE/UV PL band the PL intensities increase greatly (>four orders of magnitude) and reach their maximal values after 1100°C annealing as seen from Fig. 1. The PL spectra of all the films have similar variation with anneal temperature; all the PL intensities showed a significant increase after the 1000-1100 °C annealing, as is shown in Fig. 1(c). Fig.1(d) shows the intensity ratio I_{UV}/I_{VIS} for the films as a function of the anneal temperature, where I_{UV} is the integrated intensity in the range of 350-430 nm (3.54-2.88 eV), and I_{VIS} is integrated in the range of 450-700 nm (2.76-1.77 eV) for each PL spectra (the ratio for S6 is not shown to minimize clutter). The ratios increase with increasing anneal temperature, which has been reported to be correlated with improved crystal quality of the film for some RE doped ZnO films [11-13, 17]. We will in the following see that this correlation also holds for these films. The results then show that a high temperature annealing can enhance the PL intensity greatly by improving the quality of ZnO+EuO films. Moreover, the doped samples have higher I_{UV}/I_{VIS} ratios than that of sample S0.

From the PL spectra of Fig.1(b) no emissions from Eu^{3+} ions nor Eu^{2+} ions are detected for the Eu doped samples. It has been reported for Eu-doped ZnO nanostructures prepared by widely different methods, that Eu is present in both Eu^{3+} and Eu^{2+} states [8, 18-20]. Eu^{3+} ions will in those cases give several characteristic peaks in the range 570-710 nm (~ 2.18 - 1.75 eV) due to transitions $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J=0, 1, 2, 3, 4$) [21, 22]. These are not detected in Fig. 1(b). Emission from Eu^{2+} is expected to also fall in the visible range but the bands are expected to be broader and being more dependent on the local environment of the ion than that for Eu^{3+} [20]. This will make the detection limit worse. From the spectra of Fig.1 no emissions from Eu^{3+} ions nor Eu^{2+} ions are detected. This could be due to that there are too few Eu ions in an optical active state, or that there is no efficient energy transfer to these ions. Since the present films were sputtered from ZnO under an oxygen partial pressure, and thus turned out oxygen rich, they are not likely to contain high concentration of oxygen vacancies which have been reported to facilitate an energy transfer [17]. Thus, the present observation of no Eu PL detected is consistent with the claim that defects associated with oxygen deficiency are needed for energy transfer to RE ions in ZnO [8].

It should be mentioned that the detailed shape of the NBE emission peak of samples S0-S7 after an identical 1100 °C annealing for 30 minutes were somewhat different from each other (not shown). The peak was not symmetric and its position varied in the range 3.22-3.26 eV (385-380 nm) for those samples. This difference could be caused by differences in the weight of contributing emission mechanisms in the samples, but will not be discussed any further since it could also be influenced to an unknown extent by other factors such as interference effects [23, 24], which can be different for the different films because of somewhat different thickness and unknown variation of refractory index associated with the different Eu doping and silicate formation.

Figure 2 shows the PL normalized peak intensity for sample S1-S7 after annealing at 1100 °C for 30 min. In order to compare the intensities we have normalized them to the same excitation volume by using an absorption coefficient $\alpha=1.6\times10^5\text{ cm}^{-1}$ at 325 nm (3.815 eV) as reported for ZnO [25-27]. This normalization changes the value by less than 7% so it should not have a large effect on the results. We see that the UV peak height is higher for all the Eu doped samples than it is for the undoped: S1-S7 have about 2.3-3.4 times higher peak than S0. The UV peak heights of the Eu doped samples are different from each other, but there is no clear dependence of the doping concentration among them for the 1100 °C anneal, which is taken to indicate that for this annealing temperature unintentional differences between the individual samples have comparable effect as that of doping concentration differences. It is interesting and assuring to note how the full width at half maximum (FWHM) of the UV peaks of the S1-S7 are narrower than that of the S0 for the 1100 °C annealing also shown in Fig.2. It is common practice among crystal growers to use the width of the UV peak as a quick measure of the quality of the grown layer. We see that the variation of the intensity and the width among the samples are correlated: an increase in the intensity is accompanied by a decrease in width. So this correlation is consistent with that the high UV emission is correlated with good crystalline quality. Note that the width of the UV peak of S6 can be as narrow as 0.10 eV, which is close to that of bulk ZnO (~0.08 eV) [28].

Figure 3 shows the XRD spectra of sample S0-S7 after the above temperature annealings. In Fig. 3(a), we see a major diffraction peak at $2\theta \sim 34.6^\circ$ in the spectra of the S4 corresponding to the (002) plane of ZnO with hexagonal wurtzite structure, indicating that the sample films were highly c-axis oriented. With increasing anneal temperature from 600 °C to 1100 °C, the FWHM of the (002) peaks decrease from

0.392° to 0.175° which means the size of the nanocrystal film has increased from 21 nm to 47 nm according to the Scherrer formula [29]. Similar phenomena were observed for the other samples as is shown in Fig. 3(b). The FWHM can also have contributions from strain, so the Scherrer formula gives a minimum size, but the fact that the FWHM decreases confirms that the crystallinity of the sample films has improved by the high temperature annealing. That is similar to what we have observed for ZnO films sputtered similarly to S0-S7 but doped with Yb and/or Ce [11-13]. The inset of Fig. 3b compares the widths of the (002) peak after 1100 °C annealing. Note that the doped samples have wider (002) peak than that of S0, except for the case of S5. This indicates the average size of ZnO nanocrystals within the S1-S7 vary somewhat and most are smaller than that of the S0 or have more strain broadening. For this high annealing temperature unintentional differences between the individual samples have comparable effect on the FWHM as that of doping concentration differences.

Further analysis of the XRD patterns of Fig.3 reveals that besides the dominant (002) diffraction peak, several small diffraction peaks have emerged in the XRD spectra for the samples after 1100 °C annealing. Fig. 3(c) shows their peak positions at around $2\theta = 25.3^\circ, 30.8^\circ, 43.7^\circ, 47.6^\circ, 52.2^\circ, 54.4^\circ$ and 56.2° , respectively. Among them, the peaks at $2\theta = 30.8^\circ, 34.6^\circ, 47.6^\circ$, and 56.2° correspond to the formations of ZnO crystallites (PDF No. 36-1451), the peaks at $2\theta = 25.3^\circ, 30.8^\circ, 43.7^\circ, 47.6^\circ, 54.4^\circ$ and 56.2° indicate the formation of Zn silicates (Zn_2SiO_3) in the annealed S1-S7 films according to PDF No.37-1485, 40-0007 and 24-1496, while the peaks at $2\theta = 25.3^\circ, 30.8^\circ$, and 52.2° infer the formation of Eu silicate (EuSiO_3) in the samples S1-S7.

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The formation of Zn_2SiO_4 is possibly through the chemical reaction: $2\text{ZnO} + \text{SiO}_2 \rightarrow \text{Zn}_2\text{SiO}_4$, where the SiO_2 could come from the native oxide and/or Si atoms diffuse into the films from the Si substrate [30]. From the above XRD and the PL results, the stronger UV enhancements in S1-S7 than that of S0, should be mainly due to the improved crystal quality for the films by the slight Eu doping.

SEM images of the as deposited (A.D.) samples indicate the films consist of many small grains that may be agglomerated into larger grains/particles. That is what we have observed before [11-13] for ZnO sputtered similarly but doped by other RE elements. The structure and morphology of the A.D. films are expected to depend strongly on the surface mobility of the atoms. It is expected that the RE atoms can have an effect on mobility and nucleation of particles on the substrate and thereby give a somewhat different morphology for different RE concentrations. That is what we have observed before [11-13]. However, for the present series of Eu doped samples, while there are variations in morphology of the A.D. samples, those variations do not appear to depend systematically on the Eu doping concentration. We interpret that as being due to unintentional variation in fabrication conditions of samples. An example of that can be seen in Figs. 4(a) and 4(b) which compares the A.D. surface morphology of regions of S3 and S4. These have almost the same Eu concentration (0.07 and 0.08 at%), but have different morphology. Thus, we may get better information by considering the correlation of parameters related to structure and PL than by considering their dependence on Eu concentration.

The grains/particles grow larger and the film crystallinity improves greatly with increasing anneal temperatures, which is consistent with the XRD analysis. An example of the evolution of surface morphology upon annealing is shown in the SEM micrographs of Figs. 4(c) and 4(d) for the sample S4 after 700 and 900°C annealing,

respectively. This is qualitatively as expected from general nucleation and growth mechanism models for sputter deposited thin films of ZnO [31].

Fig. 5 shows the SEM images of the S0 and S1-S7 films after annealing at 1100 °C for 30 minutes. The most striking morphological differences between the samples become systematic with the Eu doping concentration for the highest annealing temperature. In Fig. 5(a), the S0 film appears composed of particles with a size of hundreds of nanometers and with different shapes. From the XRD analysis, the particles should consist of smaller nanocrystallites with sizes in the dozens of nanometers range aggregated together during the high temperature annealing. One interpretation is that these do not give sufficient contrast difference to be resolved under the imaging conditions used. For the S1 film with 0.01 at.% Eu doping, Fig. 5(b) the film surface appears very smooth and flat, and the particles of the film appears larger than that of S0, giving some indication that the quality of the latter film is better. The most striking feature is that there are small nanoscale voids within the film. Similar phenomena were reported in our previous work on Ce and Yb doping [11, 13], which could result from diffusion processes (Kirkendall-voids). Fig. 5(c) shows the surface morphology of the S2 film with a Eu concentration of 0.04 at.%. The surface of the film is less smooth and flat than S1, and many nano-pits appear on the surface of the film. By increasing the Eu doping concentration up to 0.07 and 0.08 at.%, as shown in Figs. 5(d) and 5(e), the surface morphology of S3 and S4 films have become more uneven, and many nanostructures stand out on the surface of the films. By increasing the Eu doping concentration further, Figs. 5(f)-5(h) show that the surface morphology of the S5, S6 and S7 films have become more and more holey with many nano-hole structures existing in the films. If the holes are related to reactions involving Eu, it would be natural that there are more holes for larger Eu concentrations. More silicate

formation with increasing Eu concentration was also observed by XRD. From the SEM observations, we find that the change of the films mechanical openness increases with Eu concentration.

The chemical states of the elements in the samples have been investigated by XPS. Fig. 6 shows the XPS spectra of S7 after annealing at 1100 °C for 30 minutes. The spectra were collected before and after etching by Ar sputtering for five minutes giving an indication of the valence state of elements close to the film surface vs inside the film respectively. The binding energy scale has been calibrated by using the adventitious carbon peak (C-1s) at 284.6 eV as reference. In Fig.6 (a), the Zn 2p spectra in both cases show a doublet with binding energies at 1022.15 eV and 1045.15 eV, respectively. The energy difference is 23.0 eV which is lying close to the standard reference value of ZnO [25], i.e the Zn atoms are in the Zn^{2+} oxidation state in both cases. Fig. 6(b) shows the O 1s spectra of the film. The O^{2-} peaks are not completely symmetric, both have a small high-energy added feature. There is less high-energy content in the etched case relative to the lower energy, and the peak position slightly shifts to the low energy side. For simplicity, the spectra were curve-fitted using two Gaussian peaks with peak position at around 531.3 eV and 532.6 eV, respectively. The 531.3 eV component is commonly attributed to O^{2-} ions surrounded by zinc atoms with the full supplement of nearest-neighbor O^{2-} ions (here we do not consider the oxygen from Eu_2O_3 [16] because of the high temperature annealing), while the 532.6 eV component can be attributed to defects and chemisorbed oxygen [8]. The stippled curves in Fig.6(b) are decomposed fits for the etched sample (Those for the un-etched are similar).

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The change of the O²⁻ peak before and after the Ar etching, could be mainly due to change of chemisorbed oxygen rather than the variation of defects. The defects here are considered to be caused by the formation of Zn- and Eu-silicates. These defects may not contribute to energy transfer to Eu in the PL process. Fig. 6(c) shows the Eu 3d spectra of the S7 film. The peaks with energy at 1125.25 eV and 1154.9 eV are from Eu²⁺ ions 3d_{5/2} and 3d_{3/2} core levels, while the peaks with energy at 1135.3 eV and 1164.8 eV are from Eu³⁺ ions 3d_{5/2} and 3d_{3/2} levels. This confirms that the Eu ions exist both in +2 and +3 valence states. Note that the amount ratio of Eu²⁺/Eu³⁺ is higher inside the film than that at around the film surface. The higher Eu²⁺ amount within the film possibly corresponds to the formation of EuSiO₃ as suggested by the XRD analysis.

Fig. 7(a) compares the time resolved PL decay spectra of the NBE emissions for the S0 and S1-S7 samples after identical 1100°C annealing. The curves themselves are not single exponentials. For many cases in the literature the decay curves from ZnO thin films have been fitted by a bi-exponential function [32, 33]. However the decays reported for ZnO are faster than the curves here. Özgür et al. [32] summarize the decay behavior for high quality epitaxial ZnO layers by referring to the longest time constant in the bi-exponential being less than 1 ns while for single crystal ZnO values up to 10 ns are referred to. The short time constant have been related to nonradiative recombination while the long time constant have been related to radiative excitonic recombination and the exciton lifetimes will vary with crystal quality, becoming longer as the quality improves. The slow decaying component(s) in Fig. 7(a) is interpreted

quite differently, also because the time constants of the slow decay may exceed what has been considered to represent intrinsic recombination times of free excitons [32]. Here we will parameterize the curves of Fig. 7(a) using their average time constant given by: [34]

$$\tau_{ave} = \frac{\int t * I(t) dt}{\int I(t) dt} \quad (1)$$

where $I(t)$ is the luminescence intensity of the UV PL as a function of time t . The value of τ_{ave} for the S0-S7 samples lie in the range 17-28 ns. The long tail could arise from trapped carriers that become (thermally) excited back into the conduction (and/or valence band) and then give off a UV photon by radiative recombination. The thermal excitation from a trap is a slow process dependent upon the energy position of the trap. The trap levels are likely on the surface of the grains or in the grain boundaries. We can then take the intensity of the decay curve as a measure of the concentration of trap states. In Fig.7(b) we have plotted the average lifetime for S0 to S7 as a function of Eu doping concentration. That there is a variation among the samples indicate that they are not equal. If the difference seen here for τ_{ave} is associated with surface traps, one would expect it to be correlated with the structure of the films. To test that expectation, we have in the same graph plotted the FWHM of the (002) diffraction peak, which is taken as a measure of the nanocrystal size. The figure indicate there is a correlation. The larger widths of the (002) diffraction corresponds to smaller nanocrystals size, i.e., more surface states (grain boundary or dislocation) of the film [12, 35, 36]. The similarity of the variation of the two experiments can be understood qualitatively for surface traps. These surface traps

may not have a large direct effect on the PL intensity in steady state (however the origin of the states could be similar to that of defects providing recombination). The variation seen indicate a variation among the samples, and also here the variations induced by unintentional variables in the fabrication of samples may be as large as the direct effect of Eu doping.

IV. Summary and Conclusions

In summary, the effect of Eu doping on the NBE emission of ZnO films have been investigated. After high temperature annealing the strength of the UV PL has increased much (4 orders of magnitude) for all films. The UV PL of ZnO+EuO are 2.5-3.5 times stronger than that of un-doped ZnO after 1100 °C annealing. The Eu^{3+} PL is not efficient for the present sputter conditions. If Eu related emission is desired one should probably aim for reducing conditions or oxygen deficient conditions. XRD analysis indicates that the ZnO+EuO samples have hexagonal wurtzite structure, the FWHMs of the (002) plane diffraction peak are sensitive to anneal temperature as well as the Eu doping concentration, and Zn silicates have formed after the 1100 °C annealing. SEM analysis shows that the surface morphology of the sample films become uneven and holey with the increase in Eu concentration. XPS spectra indicate that both Eu^{2+} and Eu^{3+} ions exist in the samples, and Eu^{2+} ions have higher content inside the films possibly in the form of EuSiO_3 . The results suggest that a low concentration of Eu doping [~ 0.04 at. %] followed by high temperature ($\sim 1100^\circ\text{C}$) annealing, is beneficial to enhance the UV emissions of ZnO thin films. The strong enhancement of the UV PL is correlated with increased quality of the films.

Acknowledgments

This work is supported by the National Natural Science Foundation of China No. 61775016. The author (Dr. Wenyong Su) would like to acknowledge the financial support from the National Nature Science Research Foundation of China No. 11374033.

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Table I The stoichiometry of the films

Samples	Zn (at.%)	O (at.%)	Eu (at.%)	Thickness (nm)
S0	46.50	53.50	0	268
S1	48.01	51.98	0.01	160
S2	44.00	55.96	0.04	370
S3	47.00	52.93	0.07	197
S4	46.5	53.42	0.08	345
S5	44.00	55.70	0.30	400
S6	44.00	55.5	0.50	330
S7	44.85	54.53	0.62	248

Figures Caption

Fig. 1 The PL spectra of (a) S0 and (b) S4 ([Eu] 0.08 at.%) after annealing in N₂ for 30 minutes at the temperatures as is indicated. Fig. 1(c) shows the UV PL intensity of the S0-S7 as a function of anneal temperature, and 1(d) shows the ratios of I_{UV}/I_{VIS} of the samples, where the I_{UV} is integrated in the range of 350-430 nm, and the I_{VIS} is integrated in the range of 450-700 nm of the spectra.

Fig. 2 The variation of normalized UV PL intensities and FWHMs of the UV peak after annealing at 1000 °C in N₂ for 30 minutes. The variation of these two measured parameters appears correlated among the samples having different Eu concentrations: An increase in PL is correlated with a decrease in the FWHM. The intensity is higher for all the Eu doped samples than it is for the undoped sample. There are no other obvious trends with Eu concentration.

Fig.3 (a) The XRD spectra of S4, (b) the FWHMs of (002) diffraction peak of S0-S7 after annealing in N₂ for 30 minutes at the temperatures as is indicated. The spectra are vertically shifted for clarity, and 1(c) the magnified XRD spectra of S0-S7 after the 1100 °C annealing. The inset of 1(b) shows the magnified widths of the (002) peak for the samples after the 1100 °C annealing.

Fig. 4 SEM micrographs of Eu doped ZnO films. (a) S3 as deposited (A.D.), (b) S4 A.D., and (c) S4 after 700 °C and (d) 900 °C annealing. See Table I for Eu concentrations.

Fig. 5 (a)-(h) SEM micrographs showing the surface morphologies of the S0-S7 samples after annealing in N₂ at 1100 °C for 30 minutes.

Fig. 6 The XPS spectra of S7 after annealing at 1100°C for 30 minutes. The sample film was examined before an Ar sputtering vs after an Ar sputtering for five minutes. The core energy levels are (a) Zn 2p, (b) O 1s, and (c) Eu 3d. The O 1s spectra can be curve-fitted by using two Gaussian peaks with peak positions at around 531.3 eV and 532.6 eV, respectively.

Fig. 7 (a) The PL decay spectra of S0-S7 samples after annealing at 1100 °C in N₂ for 30 minutes. (b) The variation of the average lifetime (τ_{ave}) and the XRD FWHM. The variation of these two measured parameters appears correlated among the samples having different Eu concentrations. See the text for further discussion.

Figs.1 (a)-1(d)

Figs. 2

Figs. 3(a)-3(c)

Figs. 4(a)-4(d)

Figs. 5(a)-5(h)

Figs. 6(a)-6(c)

Figs. 7(a) and 7(b)