

GROWTH AND CHARACTERIZATION OF ZnO:Eu THIN FILMS FOR SOLAR CELL APPLICATION

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Eu doped ZnO thin films were fabricated on silicon substrates by reactive magnetron sputtering. XRD spectra of the doped samples with different Eu-compositions of 0.5, 1 and 2 wt. %, have been analysed. EDX and AES spectroscopy analysis have been used for determination of Eu concentration and the morphology of the annealed samples are observed by SEM. The analysis show that the average crystal grain size of the 0.5 wt.% ZnO:Eu film is larger than those of the ZnO and 1.0 wt.% films, which is consistent with the narrow FWHM of 0.5 wt.% film and widen FWHM of 1.0 wt.% ZnO:Eu film. It is established, that increasing of concentration of Eu leads to lattice mismatch. The more intense red emission related with Eu³⁺ optical transitions observed for ZnO:Eu films after annealing at 400 °C.

Keywords: thin films, ZnO:Eu, FWHM, PL spectra.

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INTRODUCTION

Zinc oxide (ZnO) thin films have been widely investigated due to their great potential for different types of applications such as gas sensors, transparent electrodes, light-emitting diodes, solar cells, UV photodetectors, among others [1,2]. However, their electrical and optical properties can be improved by doping with different elements. In recent years, the interest in preparing ZnO thin films doped with lanthanide elements (Ln³⁺) has increased due to the interesting properties that can be obtained by using 4f valence electron elements. It is well known that rare-earth (RE) ions (erbium, terbium, europium, thulium, and so on) are a special kind of photoactive centers with narrow emission lines and long emission lifetimes in various semiconductor materials. Europium (Eu) is of particular interest among rare-earth elements because it shows an intense luminescence in the red spectral region around ~ 620 nm [3 - 9].

It has been demonstrated that Eu acts as an optically active center if it is surrounded by oxygen forming a pseudo-octahedron structure [10]. That means that Eu replacing Zn in the ZnO matrix forms Eu₂O₃ and does not act as an optically active center; therefore, an annealing treatment is required to change Eu local structure, forming clusters either in the ZnO matrix or at the grain boundaries.

In the present work, the influence of Eu ions on the structural and optical properties of ZnO films thermally treated at 200 – 600°C was investigated.

1. EXPERIMENT

ZnO thin films were fabricated on silicon substrates by reactive magnetron sputtering of zinc target doped with Eu element in an argon (Ar) atmosphere with oxygen (10% Ar and 90% O₂) at a pressure of 5×10⁻³ Torr. Europium oxide (Eu₂O₃) pellets were placed on the electron race of the ZnO target surface. The films were grown on the substrates kept at 100 °C. Power density applied to the cathode was 2.0 W/cm² and the deposition time was 1 h. Prior to deposition, all substrates were submitted to the cleaning procedure in ultrasonic bath during 5 min to remove mechanical pollution, and then sent to cleaning in propanol for 5 min and drying with nitrogen flow. After cleaning all the substrates were placed in load lock chamber of deposition unit. The thicknesses of the films were about 700 - 1000 nm. The doping concentrations were in the range of 0.0 - 2.0 wt. % and the annealing temperature varied from 200 to 600 °C. The samples have been annealed for one hour in a quartz tubular furnace.

The structural characteristics of ZnO films were analyzed using Ultima IV X-ray diffractometer (Rigaku) in grazing incidence X-ray diffraction (GIXD) geometry. Chemical composition and the depth profile of elements were determined by energy dispersive X-ray analysis (EDX) and Auger electron spectroscopy (AES). Photoluminescence (PL) and photoluminescence excitation (PLE) measurements were carried out by employing a 1000 W Xe lamp as an excitation source combined with a grating

monochromator (600 grooves/mm, focal length ~ 0.3 m).

2. RESULTS AND DISCUSSION

Figure 1 shows the XRD spectra of the doped samples with different Eu-compositions of 0.5, 1 and 2 wt. %, which have peaks at around 34.5° and correspond to (002) diffraction peak of hexagonal wurtzite ZnO. According to X-ray analysis, ZnO films are polycrystalline and crystallize with a strong preferred orientation along the [001] direction and the c -axis perpendicular to the substrate. The diffraction patterns of ZnO films show reflection of the (002) plane of the first- and second-order reflection (004) at $2\theta = 34.5^\circ$ and 72.4° , respectively. The angular position of both peaks is in good agreement with JCPDS card data for nominally pure ZnO [11]. Experimental data indicate that single phase ZnO:Eu layers without any binary phases (europium-oxygen containing compounds) may be fabricated under technological conditions. The as-deposited ZnO thin films did not show any feature related to the Eu_2O_3 phase, suggesting that Eu atoms are either substitutionally replacing Zn in the ZnO lattice or segregated to the non-crystalline region in grain boundaries [7-9].

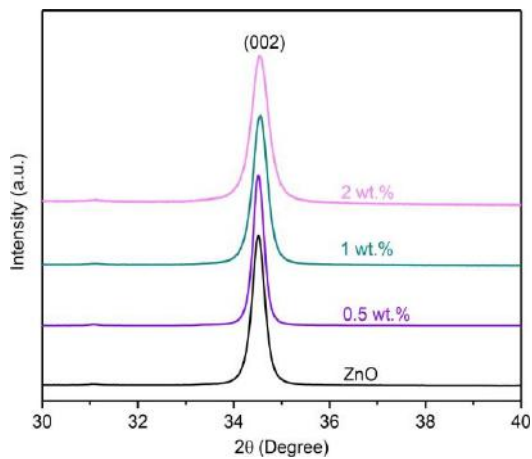


Fig. 1. XRD patterns for ZnO and Eu-doped ZnO films.

On the other hand, when the samples were annealed, the micro-structure of the films was not changed by the plausible oxidation of Eu and presented Eu_2O_3 phase in the XRD patterns (the annealing process was done in an air atmosphere). The presence of Eu_2O_3 phase was not observed in the sample, associated either to the relatively small amount of Eu atoms incorporated into the film (low doping level), or due to the absence of those phases for the employed deposition conditions. The lattice parameter value of films has been estimated from the diffraction peaks related to the ZnO wurtzite structure. All as-deposited films showed c parameter values slightly higher than that of ZnO powder material ($c = 0.521$ nm, $a = 0.325$ nm) [1, 10], indicating that the unit cells of thin films are elongated along the c -axis and the compressive forces were predominant as usual

in RF sputtered ZnO thin films [6-7]. The internal compressive stress in the as-deposited films is assigned to the bombardment of energetic particles during deposition and not to the thermal stress originating from the difference between the thermal expansion coefficients of the film and the substrate [1].

After the annealing, the peaks were shifted to higher diffraction angles and all the films showed lattice parameters (a and c) slightly lower than the ideal values for undoped ZnO films. This suggested that the stress was changing from compressive to tensile. It is possible that such high temperature of 600°C produced tensile stress due to the mismatch between thermal energy coefficients when the films cooled down [7].

It was also observed that the annealing produces variation in the intensity of the main diffraction peak ($2\theta = 34.5^\circ$) and showed an increase in its intensity, which unequivocally indicates an enhancement of the film crystalline arrangement. The average crystallite size in the direction normal to the reflecting planes was increased after the annealing process. The c -axis lattice constant was calculated by the Bragg relation and the average grain size was found by the Scherrer's equation.

The composition of the thin films before and after the annealing was estimated from the EDX measurements and appeared to be invariable after the heat treatment (Table 1). The chemical composition was determined by averaging the concentration values from 10 different points on the surface of the same film. The EDX spectrum of each film shows the signals of Zn, O, Si, where the signal of Si is only from the silicon substrate. Because the Eu concentration is too low, there is no signal for Eu element due to the low doping content.

Table 1. Chemical composition of ZnO thin films fabricated on silicon substrates.

Sample	Annealing temperature, $^\circ\text{C}$	Zn, at. %	O, at. %	Eu, at. %
i-ZnO	5	50.2	49.8	
ZnO:Eu	400	50.1	49.9	< 1.0
ZnO:Eu	600	49.0	50.0	< 1.0

A similar elemental composition of ZnO thin films has been confirmed by Auger electron spectroscopy method. The AES spectra were analyzed over a range of kinetic energies from 100 to 1400 eV using the primary electron beam of energy 5 keV. The spectrum of each film shows the signals of Zn, O and Si, where the signal of Si is only from the substrate. Because the Eu concentration is too low, there is no signal for Eu element due to the low doping content. The depth profile of elements is shown in Fig 2. As seen, Zn and O atomic concentrations remained fairly uniform through the depth of the ZnO thin film.

The surface morphology and microstructure of ZnO:Eu thin films were found to be dependent on the preparation conditions. As evident from SEM images the large well-faceted grains without any porosity with dense character of the material may be fabricated on silicon substrates (Fig. 3). The difference in the morphology of as-grown and Eu doped ZnO films after annealing are reflected by the size and shape of grains. ZnO films exhibit large-scale grain size about of ~ 0.1 - 0.3 μm . Actually, both films with no doping or doped could present fewer grain boundaries due to the absence of Eu ions at the grain boundaries. The annealing might have helped the grains to grow much bigger, since high temperature annealing stimulates the migration of grain boundaries and causes the coalescence of more grains.

The average crystal grain size of the 0.5 wt.% ZnO:Eu film is larger than those of the ZnO and 1.0 wt.% films, which is consistent with the narrow FWHM of 0.5 wt.% film and wider FWHM of 1.0 wt.% ZnO:Eu film. Therefore, the increasing of Eu content brings about the smaller grain size and a relatively poor crystalline structure in Eu-doped ZnO films due to the mismatch radius of Eu^{3+} (1.09 \AA) to the ZnO lattice (radius of Zn^{2+} is 0.74 \AA).

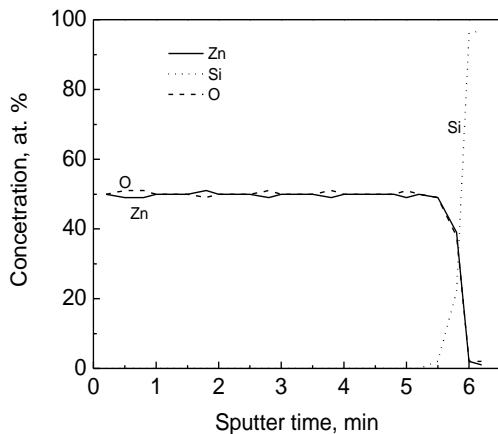


Fig. 2. AES spectra of ZnO:Eu films on a silicon substrate.

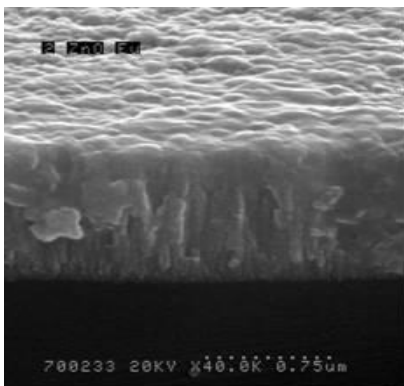


Fig.3. Micrograph of ZnO:Eu film on Si substrate after annealing at 600 °C.

Some attention was concentrated on the photoluminescence and photoluminescence excitation measurements. To determine the nature of the

emission, the experiments with varying excitation and temperature have been performed. Figure 4 shows the typical PL spectra of ZnO:Eu films on silicon substrates for different annealing temperature.

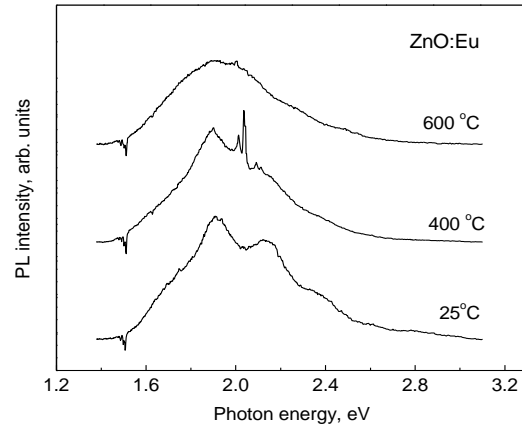


Fig. 4. Room temperature photoluminescence spectra of ZnO:Eu thin films on Si substrates taken for different annealing temperature.

Three broad bands at 2.38, 2.13 and 1.91 eV are presented in photoluminescence spectrum at room temperature for as-grown ZnO:Eu films. A small shift to higher energy about 5 meV is observed for these PL emission bands with increasing measurement temperature in range of 78 – 300 K. No noticeable spectral shifts for these bands were observed when the excitation power was varied from 1 up to 10 W/cm^2 . Therefore, we can conclude that these bands are due to energy band to deep level optical transitions. The experiments show that the relative intensity of these broad bands was depended on the growth process and annealing temperature. In particular, the intensity of green emission band at 2.38 eV decreases with annealing temperature (Fig. 4). The similar behavior of the intensity dependence on annealing temperature has been found for the band at 2.13 eV. Only one broad band at 1.91 eV can be found in PL spectra at annealing temperature higher than 600 °C. The band at 2.38 eV may be related with single ionized oxygen vacancies (V_{O}^-). The bands at 2.13 eV and 1.91 eV probably are due to optical transitions on oxygen atoms occupied Zn positons (O_{Zn}) and oxygen interstitial (O_{i}) [4,5,9]. The most interesting experimental result is an appearance sharp emission peaks at about 2.086, 2.031, 2.006 and 1.894 eV correspond to transitions of Eu^{3+} from $^5\text{D}_0$ to $^7\text{F}_j$ ($j = 1, 2, 3, 4$) electronic states for ZnO:Eu thin films annealed at temperatures in range of 200 – 600 °C. The more intense red emission related with Eu^{3+} optical transitions observed for ZnO:Eu films after annealing at 400 °C. High-resolution PL spectrum of ZnO:Er related red emission is shown in Fig. 5. Photoluminescence excitation spectra show the existence one broad band at 3.28 eV which is respond to the band gap energy of ZnO:Eu material. This band gap value is coinciding with that found from optical absorption measurements for thin films prepared on glass substrates [5,6,9].

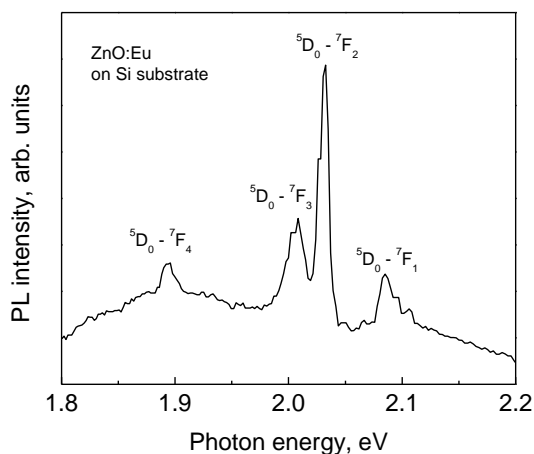


Fig. 5. Room temperature high-resolution PL spectra of ZnO films annealed at 400 °C.

3. CONCLUSION

The structural and optical properties of ZnO:Eu thin films grown on silicon substrates were studied by different experimental techniques. Intense red emission in ZnO films doped by Eu^{3+} is issued by the band-to-band excitation and energy transfer from the host ZnO to europium ions. Thus ZnO:Eu films exhibit bright red emission at low temperature annealing in range of 200 – 400 °C which may be useful for the additional generation of nonequilibrium charge carriers in semiconductor layer under sunlight illumination of thin film solar cells.

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