Correlation of structural properties with energy transfer of Eu-doped ZnO thin films prepared by sol-gel process and magnetron reactive sputtering

Julien Petersen,^{1,2,a)} Christelle Brimont,^{1,4} Mathieu Gallart,¹ Guy Schmerber,¹ Pierre Gilliot,¹ Corinne Ulhaq-Bouillet,¹ Jean-Luc Rehspringer,¹ Silviu Colis,¹ Claude Becker,² Abdelillah Slaoui,³ and Aziz Dinia^{1,b)}

¹*Institut de Physique et Chimie des Matériaux de Strasbourg (IPCMS), UMR 7504 CNRS-UDS, 23 rue du Læss, BP 43, 67034 Strasbourg Cedex 2, France*

²*Department of Advanced Materials and Structure, Centre de Recherche Public Henri Tudor, 66 rue du Luxembourg, Esch/Alzette 4002, Luxembourg*

³*Institut d'Électronique du Solide et des Systèmes (IneSS), UMR 7163 CNRS-UDS, 23 rue du Loess, B.P. 43, 67037 Strasbourg Cedex 2, France*

⁴*Groupe d'Etude des Semiconducteurs, UMR5650, Université Montpellier 2–CNRS, Place Eugène Bataillon, F-34095 Montpellier, France*

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We investigated the structural and optical properties of Eu-doped ZnO thin films made by sol-gel technique and magnetron reactive sputtering on Si (100) substrate. The films elaborated by sol-gel process are polycrystalline while the films made by sputtering show a strongly textured growth along the c-axis. X-ray diffraction patterns and transmission electron microscopy analysis show that all samples are free of spurious phases. The presence of Eu^{2+} and Eu^{3+} into the ZnO matrix has been confirmed by x-ray photoemission spectroscopy. This means that a small fraction of Europium substitutes Zn^{2+} as Eu^{2+} into the ZnO matrix; the rest of Eu being in the trivalent state. This is probably due to the formation of Eu_2O_3 oxide at the surface of ZnO particles. This is at the origin of the strong photoluminescence band observed at 2 eV, which is characteristic of the $^5\text{D}_0 \rightarrow ^7\text{F}_2$ Eu^{3+} transition. In addition the photoluminescence excitonic spectra showed efficient energy transfer from the ZnO matrix to the Eu^{3+} ion, which is qualitatively similar for both films although the sputtered films have a better structural quality compared to the sol-gel process grown films.

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I. INTRODUCTION

Wide band-gap semiconductors, such as TiO_2 ,^{1,2} GaN ,^{3–5} Y_2O_3 ,⁶ and ZnO ,^{7,8} are promising candidates for light conversion due to their excellent luminescent properties at room temperature in the ultraviolet (UV) and visible regions. ZnO ⁹ has a gap of 3.37 eV at room temperature and a large exciton binding energy (60 meV), which makes it as a potential candidate for applications in the field of solar cells,¹⁰ transparent conducting oxide thin film electrodes,¹¹ diluted magnetic semiconductor,^{12–14} nanopiezotronics,¹⁵ and electroacoustic transducers.¹⁶ Doping wide band gap materials with trivalent rare earth (RE) ions is well known to enhance the optical activity. Compared to classical transition metals elements, RE ions are believed to be the best luminescent centers because their 4f intrashell transitions can generate narrow and intense emission lines.^{17,18} Doping ZnO with RE ions, such as Eu and Er ions,^{19–21} should allow a better absorption of photons in the red region and thus enlarge the absorption spectra. Various methods are commonly used to dope II–VI semiconductors nanostructures with RE ions, such as hydrothermal synthesis,²² microemulsion,²³ sol-gel process,^{24,25} spray pyrolysis,²⁶ electrodeposition,²⁷ magnetron

sputtering,²⁸ and vapor-transport and condensation method.²⁹

Among these strategies, sol-gel and magnetron reactive sputtering processes have been considered in this study. The sol-gel process is a low-cost technique and is easy to implement, while sputtering allows to grow on large areas, and to control many parameters such as the surface roughness or the film thickness. We aim in the present work to study the effect of these two elaboration routes on structural and optical properties of Eu-doped ZnO thin films.

The $\text{Zn}_{1-x}\text{Eu}_x\text{O}$ films were grown on Si (100) substrate. The crystalline structure has been studied by x-ray diffraction (XRD) and transmission electron microscopy (TEM). Rutherford backscattering spectroscopy (RBS) technique was used to evaluate the distribution of Eu in the ZnO matrix. Finally, we investigated the optical properties of our films using photoluminescence excitonic (PLE) spectroscopy. The films deposited by sputtering present a better structural quality than the films prepared by sol-gel process. However, optical measurements do not show any qualitative difference in the energy transfer from the ZnO matrix to the Eu ions when comparing data of sol-gel and sputtered films.

II. EXPERIMENTAL PROCEDURE

$\text{Zn}_{1-x}\text{Eu}_x\text{O}$ thin films were deposited by both sol-gel and sputtering techniques on p-type Si (100) substrates. Prior to deposition, substrates were cleaned using acetone and etha-

^{a)}Author to whom correspondence should be addressed. FAX: +352 42 59 91–555. Electronic mail: julien.petersen@tudor.lu.

^{b)}FAX: (33) 3 88 10 72 49. Electronic mail: aziz.dinia@ipcms.u-strasbg.fr.

zol, followed by a surface oxidation by rf plasma during 5 min. For the sol-gel precursors, solutions (0.3 mol/l) of zinc acetate $[\text{Zn}(\text{COOCH}_3)_2 \cdot 2\text{H}_2\text{O}]$ and europium acetate $[\text{Eu} \cdot x\text{H}_2\text{O}(\text{COOCH}_3)]$ in n-propanol and glycerol, respectively, were stirred at 100 °C for 45 min until complete salt dissolution, and then spin-coated on the substrate at 2000 rpm for 5 min. Organic moieties have been removed by heat treatment at 300 °C for 10 min. This procedure was repeated three times to obtain a thin ZnO layer with the desired thickness. A last deposition step followed by annealing at 700 °C for 10 min yield to a final film thickness of about 180 nm.

The sputtered samples were deposited from a pure (4N) Zn metallic target. The Eu-doping was obtained by sticking small parts of pure europium (3N, Johnson Matthey Co., GmbH) at the surface of the Zn target. To eliminate the native europium oxide, a 15 min presputtering was performed before deposition. During sputtering, the Si substrates were kept at 600 °C to obtain a high crystallinity. The background pressure was around 10^{-8} mbar and the growth was performed under a working gas (a mixture of argon and oxygen) pressure of 5×10^{-3} mbar. The film thickness was about 100 nm as measured by interferometry.

Crystallinity and morphology of the prepared ZnO films were investigated by XRD using a Siemens D5000 diffractometer with a monochromatic Cu $K\alpha_1$ ($\lambda = 1.54056$ Å) radiation and by scanning electron microscopy (SEM) using a JEOL 6700F microscope, respectively. Further structural information was obtained by TEM using a TOPCON 002B microscope. X-ray photoemission spectroscopy (XPS) analyses were performed with a Hemispherical Analyzer PHOIBOS 150 equipped with a monochromated Al $K\alpha$ source (1486.7 eV). An Ar^+ etching (1 keV) was carried out in order to remove a few nanometers of the ZnO superficial layer containing surface contaminants (mainly carbon and oxygen atoms).

In the PLE spectroscopy measurements described here, the emission of a Xenon lamp is spectrally filtered by a monochromator to obtain an excitation bandwidth of 4 meV [full width at half maximum (FWHM)] and a photon energy that can be tuned between 2.75 and 3.5 eV. The filtered light excites the sample and the PL is dispersed in a spectrometer and detected by a cooled charge-coupled device camera. The overall spectral resolution of the PL measurement is about 1 meV.

III. RESULTS AND DISCUSSION

A. Structural properties of Eu:ZnO films

Figure 1 shows the diffraction pattern of ZnO:Eu thin film fabricated by sol-gel process and spin-coated on Si (100) substrate. The ZnO film pattern exhibits typical diffraction peaks of ZnO hexagonal wurtzite structure. Despite the polycrystalline character of the film, the high intensity of the (002) peak at $2\theta = 34.45^\circ$ (in comparison with the other peaks) indicates that the films are preferentially oriented with the c-axis perpendicular to the film surface. After Eu doping the wurtzite structure is conserved and no spurious phase, such as europium oxide, can be detected in the detection limit of the XRD technique. However, the intensity of the

FIG. 1. Diffraction pattern of pure ZnO and Eu-doped ZnO thin films elaborated by sol-gel process.

(002) peak decreases with the increase in the Eu concentration, which creates some disorder in the ZnO structure. This is further supported by the increase in the FWHM of the (002) peak with the europium concentration, indicating a decrease in the crystallite size. Indeed, using the Scherrer formula, the average crystallite size calculated from the (002) peak was initially about 47 nm for ZnO and decreased down to 15 nm for ZnO doped with 5% of Eu. In addition, the XRD pattern shows that the lattice parameters and the volume of the ZnO cell decrease with the increase in the europium concentration (Table I). This result is surprising since the ionic radius of europium (95 pm) is larger than the ionic radius of zinc (60 pm) and therefore its incorporation in the ZnO lattice must lead to an increase in the cell parameters. This is a strong indication of a low solubility of Eu in the ZnO lattice even for 1% Eu content yielding probably to the formation of Eu_2O_3 species at the nanocrystals surface, which are difficult to detect even when using powerful characterization techniques.

The diffraction patterns of ZnO:Eu thin films elaborated by magnetron reactive sputtering deposited on Si (100) substrate are shown in Fig. 2. The thin films are strongly textured on the substrate with the c-axis of the wurtzite structure perpendicular to the film surface. As for the sol-gel films, the diffraction patterns of sputtered ZnO:Eu films show that our samples are free of spurious phases. As shown in the inset of Fig. 2, Eu doping leads to a shift of the wurtzite lines [especially noticed on the (002) peak] to smaller angles. As pre-

TABLE I. Unit cell parameters and crystallite size for ZnO:Eu thin films elaborated by sol-gel process.

Eu concentration (%)	Crystallite size (nm)	Cell parameter a (Å)	Cell parameter c (Å)	Volume (Å ³)
0	49	3.248 ± 0.001	5.204 ± 0.001	47.578
1	25	3.210 ± 0.002	5.15 ± 0.002	46.356
2	21	3.210 ± 0.001	5.152 ± 0.001	45.980
3	17	3.215 ± 0.002	5.143 ± 0.002	46.064
4	17	3.210 ± 0.002	5.148 ± 0.002	45.961
5	15	3.212 ± 0.002	5.144 ± 0.002	45.968

FIG. 2. (Color online) XRD diffraction patterns of ZnO and Eu-doped ZnO thin films elaborated by magnetron reactive sputtering. The inset shows a zoom on the (002) peaks.

viously explained, the difference of ionic size between Eu and Zn ions may lead to an increase in cell parameter highlighting an efficient Eu-doping using this elaboration method (the c parameter of ZnO and ZnO:Eu are of 5.1878 Å and 5.2024 Å, respectively). It should be noted here that the Eu concentration present in the sputtered thin films is much smaller than that in the sol-gel prepared films. This means that this value is probably not far from the solubility limit of Eu in the ZnO matrix.

More information regarding the crystalline structure of the films has been obtained by TEM. The Eu-doped ZnO thin films prepared by sol-gel process exhibited a similar average grain size than those obtained from the XRD data. In fact, the average crystallite size decreases with increasing the Eu content. In addition, SEM observations (not reported here) have shown that the grain size is homogenous and uniformly distributed on the whole surface for both sputtered and sol-gel grown thin films. The selected area electron diffraction (SAED) pattern of Eu-doped ZnO thin films elaborated by sol gel process [Fig. 3(a)] and magnetron sputtering [Fig. 3(b)] evidenced the presence of a series of rings that are typical of a polycrystalline wurtzite structure. There is no indication on the presence of spurious phases.

RBS measurements were performed in order to check the Eu depth distribution in the ZnO films. The energy spectra (2.3 keV/channel) of helium particles backscattered from sol-gel and sputtered Eu-doped ZnO thin films are shown in Fig. 4. The scattering events related to the presence of oxygen, silicon, zinc, and europium can be clearly distinguished. Several differences can be noticed on the RBS spectra of the sol-gel and sputtered samples. For the sol-gel layers, the spectrum reveals an accumulation of Eu at the film surface. In contrast, in the sputtered samples, a slight accumulation of Eu at the Si/ZnO interface is observed. Moreover, the distribution of zinc, oxygen, and europium is more homogeneous for sputtered films than for the sol-gel ones. The RBS measurements allowed also checking the composition of our films. The stoichiometry of the sol-gel films was about $\text{Zn}_{0.40}\text{Eu}_{0.015}\text{O}_{0.585}$ for the 5 wt % Eu doped ZnO. This value

FIG. 3. (Color online) SAED pattern of Eu-doped ZnO thin films elaborated by sol-gel process (a) and (b) magnetron reactive sputtering.

is close to the 1.5 at. % nominal value. For the sputtered films, the stoichiometry is $\text{Zn}_{0.47}\text{Eu}_{0.005}\text{O}_{0.525}$. These results show that the concentrations of both europium and oxygen are smaller for the sputtered films than for sol-gel films. This is of good support for XRD results, which showed that the solubility limit of europium in ZnO is small and, therefore, for higher europium concentration, the later has a tendency to form an oxide at the surface. All these structural analyses suggest that the films prepared by sputtering present a better homogeneity and structural quality than films prepared by

FIG. 4. RBS measurement on Eu doped ZnO thin films elaborated by sol-gel and magnetron reactive sputtering techniques.

FIG. 5. (Color online) Eu 3d regions of XPS spectrum of Eu-doped ZnO films elaborated by sol-gel process (a) and by sputtering (b).

sol-gel technique. We will investigate later if such difference in the crystalline quality has an influence on the optical properties of the studied films.

XPS measurements allow knowing the information on the oxidation state of zinc, oxygen, and europium within the ZnO matrix. The whole spectra (not reported here) are similar for both techniques. In addition to the Zn, Eu, and O peaks, a carbon peak was also observed due to surface contamination such as the one resulting from the acetate and glycerol burning. The energy of the C 1s peak at 284 eV has been used for calibration. The Zn $2p_{3/2}$ peak at 1021 eV is characteristic of Zn²⁺. We will focus on the 1120–1170 eV spectral region in which four peaks of Eu 3d are observed for both sol-gel [Fig. 5(a)] and sputtered [Fig. 5(b)] films. This spectrum can be divided into two groups due to multiple spin-orbit interactions belonging to $J=3/2$ and $5/2$ components of Eu 3d. For the sol-gel films and for the two multiplets structures we observe a dominant peak that corresponds to the Eu³⁺ trivalent ion and a satellite peak characteristic of Eu²⁺ divalent ion. We should also note the presence of a small structure in the region $3d_{5/2}$ corresponding to multiplets. The trivalent and divalent ions come from the $3d4f^6$ and $3d4f^7$ configurations.^{30,31} The presence of two

oxidation states of Eu shows that the insertion of Eu takes place in an oxidized environment. Moreover, the energy difference between the two Eu³⁺ lines is 29.4 eV, which is characteristic of a charge transfer between the energy levels O 2p to Eu 4f.³² The divalent component of Eu is indeed expected and corresponds to europium ions that substitute Zn²⁺ into the ZnO matrix. However, the presence of the trivalent europium means that only a small fraction of Eu atoms has substituted and the rest forms probably europium oxide, Eu₂O₃, at the surface of ZnO. However, it is important to notice here that no direct evidence of such oxide was possible by XRD nor by TEM analyses.

For the film elaborated by sputtering [Fig. 4(b)], the outcome is different, as the intensity of Eu²⁺ is more important than that of Eu³⁺. This is in agreement with XRD data and suggests that the amount of Eu²⁺ is higher than for Eu³⁺. This is not surprising since the europium concentration in the sputtered films is very small and close to the solubility limit of europium in ZnO matrix.

B. Optical properties of Eu:ZnO

In a previous paper,³³ we have demonstrated the possibility to obtain sol-gel ZnO thin films with very good crystalline and optical properties. We observed two emission bands in photoluminescence spectra. The first one is observed near the band gap at 370 nm and is dominated by the radiative recombination of excitons bound on shallow levels like residual donors and acceptors. This emission line is inhomogeneously broadened showing that different types of impurities were unintentionally introduced during the synthesis. The second one is a green luminescence band centered at about 500 nm. The origin of the green luminescence is still a subject of debates but is most often assigned to the presence of ionized oxygen vacancies and zinc interstitial in the ZnO matrix. The intensity of this band is lower for the sputtered ZnO films. For the latter, we can expect a better crystallinity and consequently, fewer vacancies in comparison with the films prepared by sol-gel process. Figure 6(a) shows the visible photoluminescence spectra of ZnO and Eu-doped ZnO sol-gel films obtained for an excitation wavelength of 365 nm. The ZnO spectrum is dominated by a large band characteristic of defects like oxygen and zinc in interstitial position.³⁴ The photoluminescence spectra of the Eu doped films are dominated by sharp lines related to the direct intra-4f transitions in Eu³⁺ ions, in addition to the broad band characteristics of defects in ZnO matrix. The most intense emission is associated to the $^5D_0 \rightarrow ^7F_2$ transition in the red spectral region (612 nm). Moreover, when the Eu concentration increases, the intensity of the Eu³⁺ intra-4f transition increases along with a decrease in the defect band centered at 700 nm. The situation is similar for the sputtered films as shown in Fig. 6(c). It is surprising that Eu²⁺ ions did not show any luminescence peak, while it is well known that they give rise to a broad emission line centered at 530 nm³⁵ and associated to $4f^7-4f^65d^1$ transition. Unfortunately, such peak is not observed at all neither in PL spectrum obtained for sol-gel thin films [Fig. 6(a)] nor in PL spectrum recorded for sputtered thin film [Fig. 6(c)]. The reason of the absence

FIG. 6. (Color online) Photoluminescence spectra at 300 K of films elaborated by sol-gel (a) and sputtering (c). PLE spectra at 300 K for detection at 615 nm ($^5D_0 \rightarrow ^7F_2$ transition) for films elaborated by sol-gel (b) and sputtering (d). In all these figures, the horizontal lines correspond to the dark noise level.

of such peak in the PL spectra may be due to the fact that most of europium ions are in trivalent form and that the europium ions in divalent form are not sufficient to give rise to a luminescence that can be easily observed in this spectral region. The PLE spectra of the $^5D_0 \rightarrow ^7F_2$ transition (detection wavelength equal to 612 nm) for the three europium doped ZnO sol-gel films are given in Fig. 6(b). The PLE signal continuously increases when the excitation wavelength varies from ~ 390 to 370 nm. This is related to the photogeneration of electron-hole pairs for photon energy larger than the ZnO band gap and it is the experimental evidence that electron-hole pairs created in the ZnO matrix relax toward the Eu^{3+} ions to recombine radiatively. However, although these data demonstrate the carrier transfer between ZnO and Eu^{3+} exists, a quantitative estimation of the transfer rate cannot be given because only the transferred excitons are detected via the photoluminescence. The maximum at ~ 365 nm is characteristic of the ZnO band gap and the smooth increase starting at 390 nm is probably due to structural disorder. In addition, to this continuum, a sharp line at 3.2 eV is also visible below the band gap. The same kind of spectrum is obtained for the $^5D_0 \rightarrow ^7F_1$ and $^5D_0 \rightarrow ^7F_4$ transitions. This feature is missing on the PLE spectra related to

the background emission due to the ZnO structural defects. Moreover, no photoluminescence signal is observed at 3.2 eV whatever the excitation energy is. The energy transfer of the carriers from the ZnO matrix toward Eu^{3+} ions is efficient but there is also a level at 3.2 eV,^{36,37} below the ZnO band gap, which is nonradiative but connected to Eu^{3+} levels. According to the literature, this level can be interpreted as a trap level related to presence of structural defects in the ZnO matrix. For some reasons, that we are not able to identify yet, the electron-hole pairs, created at 3.2 eV efficiently relax to the radiative Eu^{3+} . Such signal peak is also observed in the PLE spectrum of the Eu doped ZnO sputtered film [Fig. 6(d)]. However, its intensity is very small with respect to the peak observed for sol-gel thin films [Fig. 6(b)]. This is another indication that the sputtered thin films have better crystalline structure and less defects than sol-gel films, since the 3.2 eV peak is interpreted as a $\langle\langle$ trap level $\rangle\rangle$ related to presence of structural defects in the ZnO matrix. Despite the difference in structural properties between the two types of grown films, the photoluminescence spectra are quite similar. Though the PLE experiments do not highlight any fundamental difference in the relaxation scenario of the electron-

hole pair from their creation in the ZnO matrix to their radiative recombination on the Eu^{3+} ions.

IV. CONCLUSION

In this work, the structural and optical properties of Eu-doped ZnO thin films elaborated by sol-gel process and magnetron reactive sputtering have been investigated. In both cases only a small amount of Eu has been successfully incorporated in the ZnO host matrix. Structural studies reveal that films deposited by sputtering have a better structural quality than the films elaborated by the sol-gel technique. XPS measurements showed the presence of trivalent europium probably from Eu_2O_3 that can form at the ZnO particle surface as well as divalent europium substituting Zn^{2+} in the ZnO matrix. The photoluminescence spectra of Eu-doped thin films deposited by sol-gel process and sputtering show different emission lines, as characteristics of the Eu^{3+} ion, but no line corresponding to Eu^{2+} . Finally, we have shown that both sol-gel process and magnetron sputtering were efficient to produce Eu doped ZnO thin films presenting an significant energy transfer from ZnO to Eu ions through a trap level.

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