

Doping of ZnO thin film with Eu using ion beams

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Abstract

Modification of electric and magnetic properties of ZnO thin films was achieved by low energy Eu ion irradiation. The desired doping levels as well as the depth distribution of the dopant was controlled by the ion energy and the ion flux, following a simulated interaction between the doping ion and the host ZnO matrix of epitaxial ZnO (0001) films of approximately 200nm, grown on c-Al₂O₃ by PLD. The properties of the doped ZnO film depend in a critical way on the homogeneity of the doped ions throughout the entire film. The doping levels and the depth distribution of dopants were measured by elastic recoil detection analysis (ERDA). The results show a uniform depth distribution of Eu, as well as some level of Al diffusion from the substrate and the presence of some low levels of H, N and O.

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1. Introduction

The large potential for use of ZnO thin films for electronic applications is due to its attractive properties, such as a large band-gap (~3.3eV) and high exciton binding energy (60meV) [1], large piezoelectric constant e_{33} (1.3C/cm²) [2], large thermal conductivity (0.54W/cm K) [3], as well as attractive other physical properties such as hardness. ZnO is an intrinsic n-type semiconductor and may become ferromagnetic at room temperature, by small additions of magnetic ions, and therefore be a possible candidate for spintronic applications [4, 5]. Doping of rare earth ions into the structure of ZnO may change its optic properties, and it was shown that optically-active centers can be created in bulk ZnO by Tm, Tb and Er doping at the Zn crystallographic site [6] or by Eu doping of ZnO nanocrystals [7]. Reported magnetic and optic properties of doped ZnO are sensitive to the level and the dispersion of dopants. In Co-doped ZnO, Co segregation was assumed to be at the origin of observed high

values of Curie temperature [8], while in Co-doped ZnO film, nano-scale Co clustering was believed to be responsible for room-temperature spin-glass behaviour [9]. In Eu-doped ZnO nano-powder, the photo-luminescence (PL) intensity was found to be related to the state of defects resulted from the doping and annealing processes [10]. Introducing and homogeneously distributing small quantities of transition metals into ZnO thin films is challenging, but a convenient way to attempt this is by the non-equilibrium ion irradiation technique.

Here we present results on the doping of ZnO thin films with Eu by low energy ion irradiation.

2. Experimental Details

ZnO thin films of grown epitaxially on c-Al₂O₃ (0001) substrates by PLD, with an approximate thickness of 200nm, were irradiated with Eu ions at low energies. Eu ions were produced using a metal vapour ion source, in which the Eu charge distribution during the ionization process was reported to be: Eu⁺¹=2%; Eu⁺²=80%; Eu⁺³=18% [11]. TRIM simulations show that for the above charge distribution, an acceleration voltage of 45kV for Eu, result in a skewed-Gaussian distribution implanted layer, with a tail on the low energy side, deeper into the film.

In order to optimise the process, a number of samples were implanted with Eu at different doses. The equivalent chemical composition of implanted film samples was Zn_{1-x}Eu_xO with x=0.01-0.12. The Eu ions were implanted along (0001) direction of the film (normal to the film surface), using a nominal acceleration voltage 45kV respectively, and a beam current of 20mA. The implantation depth and distribution was simulated using TRIM code, and the depth distribution of elements in the virgin and implanted ZnO films was measured by ERDA, using 33MeV Cl⁺⁵ projectiles and a time-of-flight (ToF) detection system, in a vacuum better than 1x10⁻⁶ Pa. The beam was shaped in a rectangular form, 3 mm high and 1mm wide, and directed onto the sample at an incident angle of 67.5°, between the beam direction and sample normal. The energy of recoils was measured with a time-of-flight detector placed at an exit angle of 67.5° relative to the sample normal, resulting in a scattering angle of 45°. The configuration of the ToF detector used in this experiment was made up by two electrostatic mirrors with the active foils made of diamond-like carbon (DLC) of 2μg/cm², placed 0.5 m apart, and the final rest energy of recoils was measured with a surface barrier detector, placed at the end of the flight path [12]. The time axis projection of the 2D coincidence scatter plot was converted into depth profile using first principle calculations as well as published information on the stopping power of ions [13]. In this

experiment, the total charge collected on each sample during the measurement was $12\mu\text{C}$. The magnetic properties of doped ZnO films were measured using a superconducting quantum interference device (SQUID) magnetometer (MPMS from Quantum Design), and the optic properties were assessed by photo luminescence (PL) and transmission measurements, with a PL mapping system (Rapid PL Mapping System from Accent).

3. Results and Discussion

The thickness of virgin ZnO thin films was measured by RBS with 1.8MeV He ions, and it was around 1800ML, equivalent to about 200nm, assuming the density of the films was 95% of the density of ZnO single crystal, which is 5.642g/cm^3 . In addition, the out-of-plane orientation of the film was confirmed by $(\theta-2\theta)$ XRD to be c-axis oriented.

The ERDA result for the depth profile of elements present in the virgin ZnO film grown on c- Al_2O_3 substrate is shown in Fig. 1. It reveals, besides Zn, O and Al, small quantities of H and C, as well as some N. The H and C are mostly present at the surface of ZnO thin film, and are most likely due to the handling of the sample in air. However, N appears to be present both at the surface and at the interface between the film and the substrate. The presence of Al throughout the ZnO film, at a level between 5-7at%, is most likely caused by diffusion from the substrate during the high temperature film growth, rather than from an impure PLD target. In addition, the stoichiometry of the Al_2O_3 substrate in the first couple of thousands of mono-layers under the ZnO film appear to be affected, with Al slightly depleted, and with the presence of some N.

The ERDA depth profile results for Eu-doped ZnO film, with an equivalent composition $\text{Zn}_{0.96}\text{Eu}_{0.04}\text{O}$ is shown in Fig. 2. The implanted Eu is located in the top half of the film, with a depth distribution which resembles the TRIM prediction reasonably well. Also, the depth distribution of other elements appears to be similar with their depth distribution in the virgin ZnO films, with the exception of the top layers of the substrate under the film, for which the variation in stoichiometry appears to be more pronounced.

Room temperature magnetization of Eu-doped ZnO film, measured with the external field applied parallel to the film surface and after the subtraction of diamagnetic contribution of the substrate, show that the doped films are ferromagnetic, with a Curie temperature above 300K.

Figure 3 represents the PL results measured at room temperature, for virgin and Eu-doped ZnO/ Al_2O_3 films. For the virgin ZnO film, we note the absence of the commonly observed green emission [14], and instead the appearances of a broad red emission around 1.8eV, which may be caused by Al and N presence in the film, which is consistent with ERDA

result. The PL of Eu-doped ZnO film show the absence of the well documented weak peaks within the red visible range, usually observed in other Eu-doped systems [15], and the exciton peak is smaller and broader than in the case of virgin ZnO film, possible associated with the decrease of the band gap. In order to explore this possibility, four ZnO films were doped with Eu by ion irradiation, to a level of 1at%, 2at%, 3at% and 4at%. Optic transmission was measured for all these samples, including a virgin ZnO film and an Al₂O₃ substrate. In the high absorption region of the transmission spectra were Tauc model [16] is applicable, for ZnO system we can write $\alpha h\nu = D (h\nu - E_g)^{1/2}$, where α is the absorption coefficient, h is Plank's constant, ν is the radiation frequency, D is a constant and E_g is the optic band gap. If we plot $(\alpha h\nu)^2$ as function of frequency, Figure 4, we can get an estimation of the optic band gap E_g . The result shows that as the Eu doping level is increased from 1at% to 4at%, E_g is decreasing.

Finally we performed ground state band structure (BS) calculations on pure ZnO system (space group P 63 m c), and on a similar structure in which Eu⁺² replaced Zn⁺² on the crystallographic site 2b, in a proportion equivalent to 1at%, 2at%, 3at% and 4at%. The BS calculations were performed with the DFT code CASTEP, in the local density approximation (LDA) with a screen exchange correlation. It is well documented that the DFT theory is reproducing well the shape of the bands, but it under-estimates the band gap by 20-40% as compared with angle-resolved photo-emission spectroscopy [16]. Nevertheless, the BS calculation results, Figure 5, show a band gap in the Γ direction of the Brillouin zone of 3.2eV for pure ZnO, and a decrease down to 2.2eV as Zn was replaced by Eu in the above proportions. These calculated results, together with the estimated optic band gap E_g suggest that Eu is replacing Zn in the in the ion irradiated ZnO thin film samples.

4. Conclusions

The depth profile of elements present in ZnO thin films grown by PLD on c-Al₂O₃ and implanted with Eu was measured by heavy ion ERDA. The presence of Al and N was detected in the virgin and Eu-doped ZnO films, suggesting a reason for the broad red emission around 1.8eV observed in PL spectra of the virgin ZnO film. We also show that ZnO film doped with Eu show an increase in the Curie temperature. However, Eu doping between 1at% and 4at%, leads to a decrease of the optic band gap, and by comparing this result with band structure calculation in the ground state we showed the possibility that Eu is replacing Zn in the ZnO structure of the film.

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Figures Captions

Fig.1: ERDA-ToF depth profile of as grown ZnO/Al₂O₃ thin film

Fig 2: ERDA-ToF depth profile of Eu-implanted ZnO/Al₂O₃ thin film

Fig. 3: PL spectra at room temperature for virgin and Eu-doped ZnO/Al₂O₃ thin films

Fig.4: Plot of $(\alpha h\nu)^2$ as function of frequency for transmission spectra of virgin ZnO film, and ZnO film doped with 1at%, 2at%, 3at% and 4at% Eu

Fig. 5: Ground state BS calculation on ZnO, and ZnO where Zn was replaced by Eu in a proportion of 1at%, 3at% and 4at%

Figures

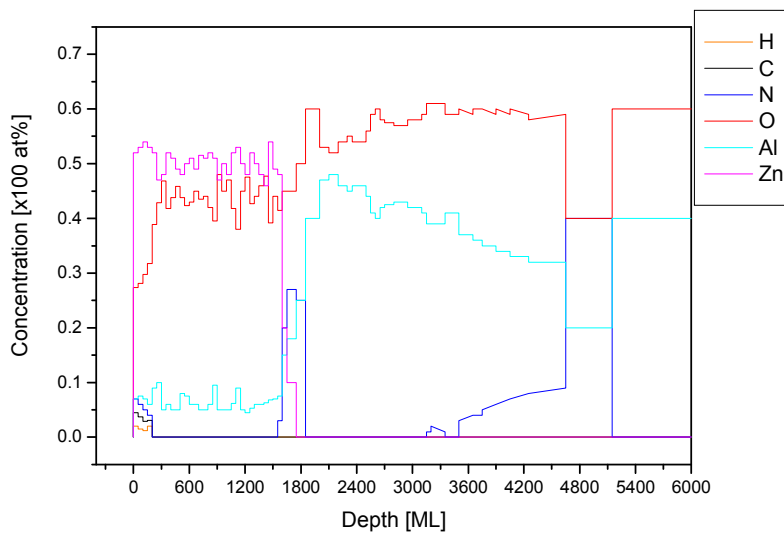


Fig. 1

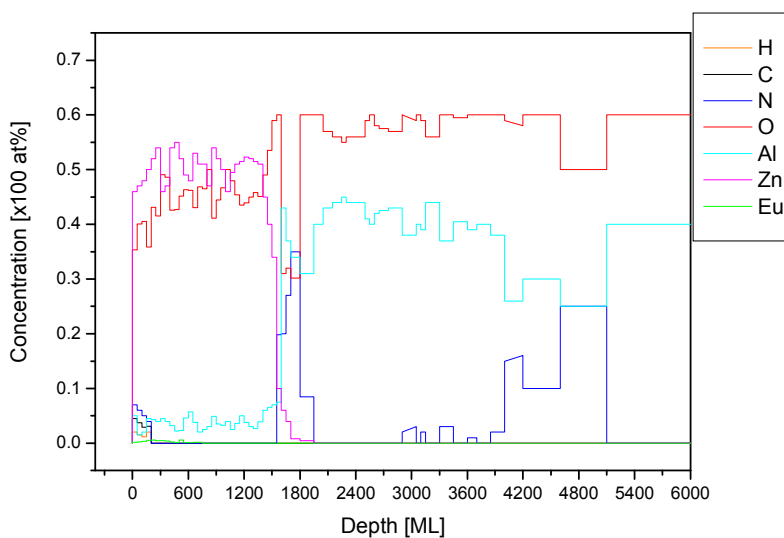


Fig.2

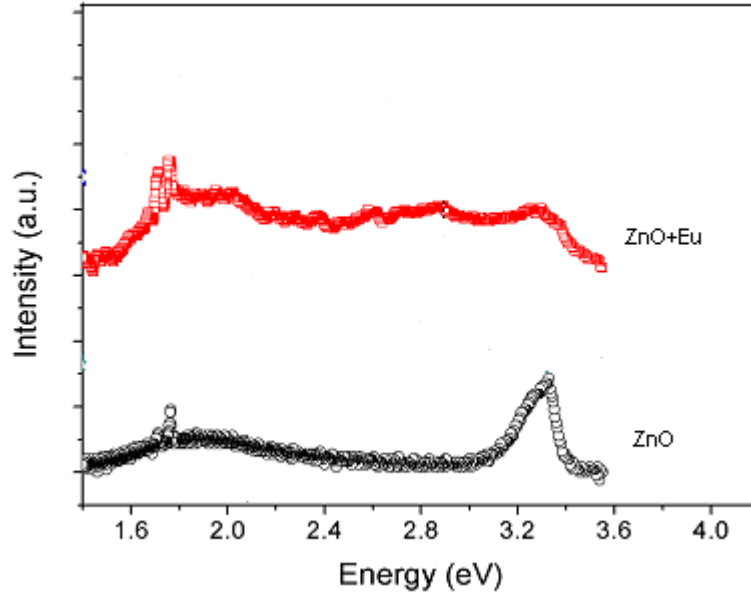


Figure 3

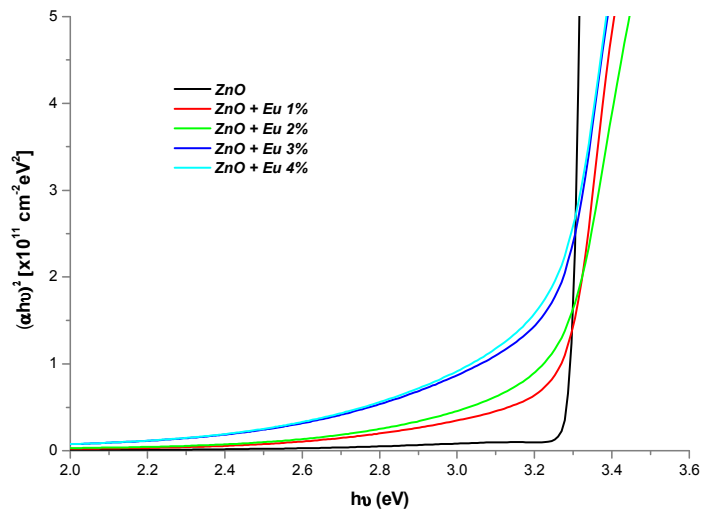


Figure 4

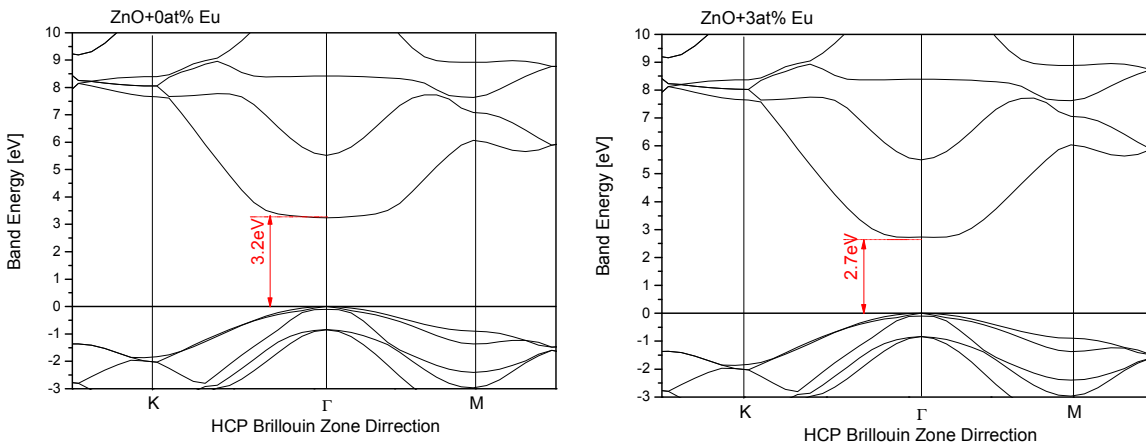


Figure 5

