

Optical active centres in ZnO samples

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Abstract

In recent years, there has been a resurgence in the interest in the use of ZnO ($E_g \sim 3.37$ eV) as a material for a wide range of opto-emitter applications spanning visible and short wavelengths. Bulk, thin films and nanomaterials obtained using different synthesis methods have been investigated for optoelectronic and biotechnological device applications. Nominally undoped bulk samples typically present a myriad-structured near-band-edge recombination, mainly due to free/bound excitons and donor–acceptor pair transitions. Furthermore, deep level emission due to intrinsic defects and extrinsic impurities, such as transition metal ions, are commonly observed in different grades of bulk ZnO samples. Undoped thin film and ZnO nanocrystal samples also present optically-active centres due to the presence of native and extrinsic defects. Continuing improvement in device performance hinges on improved understanding of the role of these defects present in ZnO samples. In this work a correlation between the optical centres was observed between nominally-undoped bulk, thin films and nanocrystal ZnO. We also observed a correlation between the structural properties and ion optical activation for single crystal samples which were intentionally-doped with rare earth ions (Tm, Er, Eu and Tb) either (a) by ion-implantation or (b) during synthesis. For the doped ZnO nanocrystals, intra-ionic recombination and XRD data suggest that the ions are in a crystalline environment.

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1. Introduction

Due to their application to light emitters, the nature of the observed optical transitions in ZnO is one of the relevant topics for this oxide semiconductor. Bulk ZnO typically exhibit a richly structured near band edge recombination mainly due to free and bound excitons as well as donor acceptor pair transitions. Furthermore, deep level emission due to intrinsic defects and extrinsic impuri-

ties, such as transition metal ions, are commonly observed in different grade bulk ZnO samples. Undoped thin film and ZnO nanocrystal samples also show optically active centres due to the presence of native and extrinsic defects. The low temperature photoluminescence (PL) spectra of the samples grown by different procedures are typically characterized by the presence of several emitting centres both in UV–visible and infrared spectral regions [1–9]. Even in non-intentionally doped samples, besides the free exciton recombination, other optical active centres due to defects and impurities that originate near band edge and deep level emissions are commonly present [1–9]. Improve-

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ments on device performances hinge a deep understanding on the behaviour of defects present in ZnO samples.

In this work we will discuss the PL results obtained using above and below band gap excitation for single crystals (SC), thin films and nanocrystals (nc). The results of the analysed samples clearly indicate that both the growth process and defect/impurities have an important role on the observed optical active centres.

2. Experimental procedures

Non-intentionally doped ZnO thin films grown by pulsed laser deposition (PLD) [10] and metal organic chemical vapour deposition (MOCVD) on sapphire are studied. The observed results are compared with a high quality commercially available non-intentionally doped SC grown by seeded chemical vapour transport that is used as reference sample. The ZnO-nc samples were prepared using an adaptation of the method reported by Gamelin and co-workers [11]. In brief, the method employed here involved the controlled nucleation and growth of ZnO nanoparticles in an organic solution, either in the presence or absence of RE cations. The ZnO-nc were isolated as powders by adding a non-solvent to the as prepared colloids. Intentionally doped SC, thin films and ZnO-nc samples with rare earth (RE) ions were studied in order to investigate the ion optical activation and its site location.

RBS measurements were performed with a 1 mm diameter collimated beam of 2 MeV He⁺ ions. The backscattered particles were detected at 160° and close to 180°, with respect to the beam direction, using silicon surface barrier detectors located in the standard IBM geometry and with resolutions of 13 and 16 keV, respectively.

XRD was performed on a X'Pert MPD diffractometer system, equipped with a curved graphite monochromator and using CuK_α radiation. Sapphire peaks were used as reference for sample alignment.

The PL measurements were carried out using a He–Cd laser line for above band gap excitation. Below band gap excitation was achieved using the 488 nm and 514.5 nm lines of an Ar⁺ laser were used. A cooled photomultiplier tube and a Ge detector were used to detect the emissions in the visible and infrared spectral regions, respectively.

3. Results and discussion

Fig. 1 shows the low temperature PL spectra of non-intentionally doped SC, PLD, MOCVD and ZnO-nc samples observed upon band gap excitation. It is observed that PL spectra of the different non-intentionally doped samples is dominated by the presence of high energetic transitions near the semiconductor band edge as well as by the presence of deep broad emission bands. On the high energy side it can be observed that for the SC sample a myriad of optical centres are present [1,2] while for the samples grown by PLD and MOCVD some of the optical centres are nearly absent as for instance the 3.22 eV donor acceptor pair

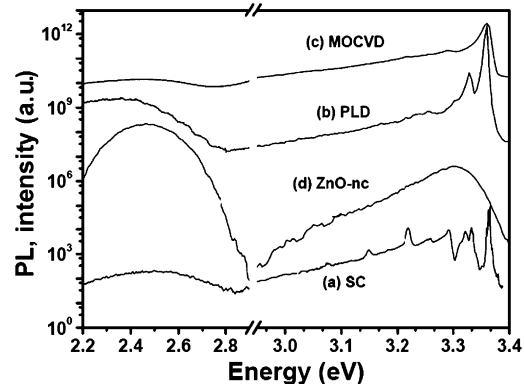


Fig. 1. 10 K PL spectra observed upon He–Cd excitation of (a) single crystal, (b) ZnO/sapphire thin film grown by PLD, (c) ZnO/sapphire thin film grown by MOCVD using DMZN-TEA and *tert*-butanol as described in Ref. [12] and (d) ZnO-nc synthesized as described in text.

recombination (DAP) [2]. Furthermore, within the region of the bound excitons recombination (~ 3.36 eV) the observed lines on the PLD and MOCVD samples are broader and slightly shifted to lower energies than those measured on the SC sample, suggesting that the Al-related bound exciton emission dominates in these samples. Concerning the ZnO-nc sample the near band edge recombination follows closely the same spectral trend as the SC sample but with an expected smearing of the spectral features for an assembly of crystals with different dimensions. All the analysed samples show broad emission bands in the green region indicating the presence of intrinsic defects and/or impurities. While for the SC, MOCVD and ZnO-nc samples the band is unstructured and peaked near 2.45–2.5 eV, for the PLD sample the band is structured and its main maximum occurs nearby 2.4 eV. The unstructured band has been correlated with the presence of intrinsic defects such as oxygen vacancies [1,3] while the structured has been attributed to Cu-related recombination [4].

Due to its interest for light emitters and optical communications rare earth (RE) ions such as Er, Tm, Eu and Tb have been intentionally incorporated in ZnO samples. It is well known that for Tm and Er implanted and annealed SC samples the RE ions occupy the Zn site location [13,14]. However, no noticeable substitutional fraction was founded in Eu and Tb implanted SC samples. ZnO-nc were also intentionally doped during the growth process with Tb and Eu ions.

Fig. 2 shows the chemical and structural analysis of ZnO-nc:Eu and ZnO-nc:Tb samples. Fig. 2(a) shows the Rutherford backscattering spectrum obtained for the Eu-doped ZnO-nc samples. Simulation of the experimental spectrum reveals an Eu content of $23.1 \pm 1.5\%$, which is in relatively good agreement with the 20% nominal value. The X-ray diffraction (XRD) pattern shown in Fig. 2(b) for the ZnO-nc:Tb (20% nominal value) reveals that the ZnO nanocrystals have an hexagonal wurtzite crystal structure. No diffraction peaks related to Tb complexes were

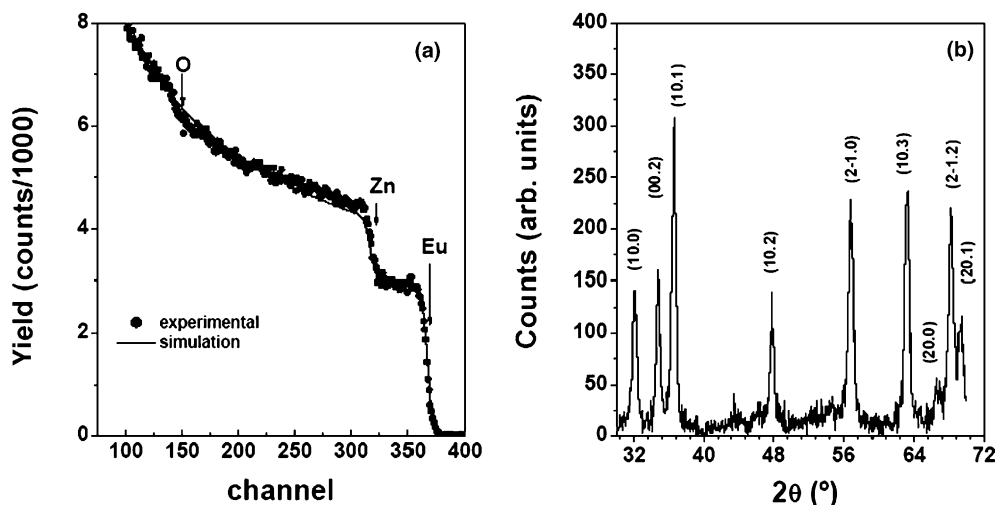


Fig. 2. (a) Random and simulated RBS spectra from ZnO-nc:Eu nanocrystals. Vertical arrows indicate the scattering energies of the different chemical elements at the surface. (b) XRD spectra for ZnO-nc:Tb sample.

found, hinting that the Tb is incorporated in the ZnO lattice. From analysis of diffraction line broadening one can estimate an average size for the ZnO nanocrystals of about 30 ± 10 nm.

Typically, in the ion implanted SC samples, the RE ions (Tm and Er) occupy the Zn site location and a high defect density is needed to achieve ion optical activation [13]. Er^{3+} emission has been observed both in the infrared and visible spectral range for intentionally implanted and annealed samples [14]. So far, no intraionic luminescence was detected in SC samples intentionally implanted with Tb and Eu. However, as shown in Fig. 3, for intentionally Tb and Eu doped ZnO-nc samples intraionic Tb^{3+} and Eu^{3+} luminescence is clearly identified using both above and below band gap excitation. The analysis of the Eu^{3+} and Tb^{3+} intraionic recombination demands the knowledge of the ion site location in the matrix. While the results for the SC samples suggest that the RE's ion optical activation is due to in a large extent to substitutional sites, in the

doped ZnO-nc samples case, a larger fraction of RE's ions was expected to be located at the nanocrystals surface. However, the XRD data and PL behaviour observed in the analysed nanocrystals suggest that the RE ions are in fact in a crystalline environment; probably surface RE's ions have been efficiently removed when collecting the ZnO-nc as powders. In order to clarify these aspects more work is underway, including EXAFS measurements on the doped samples.

4. Conclusions

We have discussed the optical centres observed in nominally undoped bulk, thin films (PLD and MOCVD growth) and ZnO nanocrystals of size 30 ± 10 nm, where no confinement effects are expected. Furthermore, we have studied ZnO samples intentionally doped with rare earth ions (Tm, Er, Eu and Tb). RE ion optical activation was observed in intentionally doped ZnO materials either by

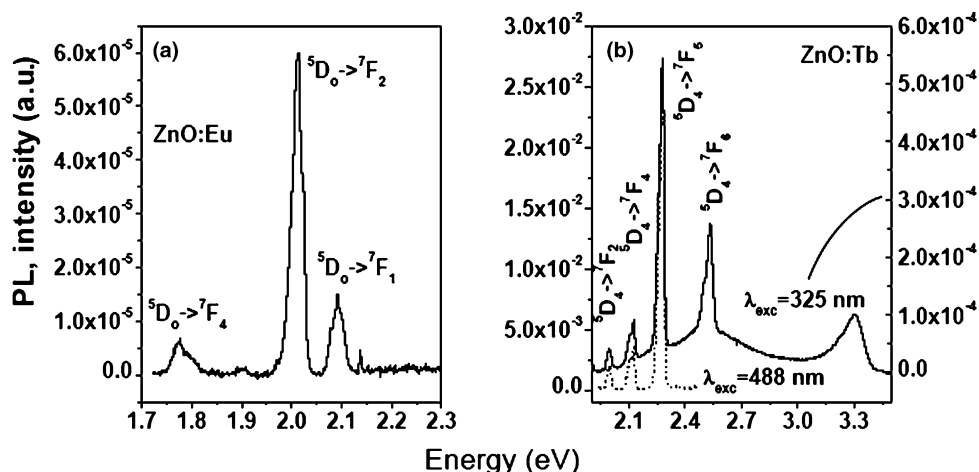


Fig. 3. 10 K PL spectra observed with below band gap excitation of ZnO samples synthesized by colloidal methods doped with (a) Eu^{3+} and (b) Tb^{3+} .

ion implanted or during the synthesis. A correlation between the structural properties and ion optical activation was established for the SC samples. For the doped ZnO nanocrystals the observed intraionic recombination and XRD data suggest that the ions are probably in a crystalline environment.

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