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X-ray studies on optical and structural properties of ZnO nanostructured thin films

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Abstract

X-ray absorption near-edge fine structure (XANES) studies have been carried out on nanostructured ZnO thin films prepared by atmospheric pressure chemical vapour deposition (APCVD).

Films have been characterized by X-ray diffraction (XRD) and optical luminescence spectroscopy exciting with laser light (PL) or X-ray (XEOL).

According to XRD measurements, all the APCVD samples reveal a highly (002) oriented crystalline structure.

The samples have different thickness (less than 1 μm) and show significant shifts of the PL and XEOL bands in the visible region.

Zn K-edge XANES spectra were recorded using synchrotron radiation at BM08 of ESRF (France), by detecting photoluminescence yield (PLY) and X-ray fluorescence yield (FLY).

The differences between the PLY- and FLY-XANES confirm the possibility of studying the local environment in the luminescence centres and to correlate the structural and optical properties of ZnO nanostructured samples.

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1. Introduction

ZnO is a promising material for short-wavelength light-emitting devices and for a wide range of technological applications (blue lasers, transparent conductive coatings for flat panels and solar cells, surface acoustic wave devices, oxygen sensors,...), due to its wide band-gap (3.3 eV) and peculiar optical, electrical and piezoelectrical properties.

These properties depend crucially on the intrinsic defects concentration, type and amount of impurities and degree of crystallinity. In many cases ZnO shows, under proper excitation conditions, a green photoluminescence band, centred at about 550 nm, and a UV band at about 370 nm. The green band comes from deep defect levels attributed to oxygen vacancies or interstitial zinc ions, whereas the UV band has excitonic nature [1,2]. The relationship between the two luminescence bands depends strongly on the preparation method and post-preparation treatment [3].

ZnO can be prepared in a form of single crystals, powders and films. Thin films have a potentially large number of applications if their properties can be well controlled.

The goal of this work is to develop an experimental method to obtain original information on the local environment around Zn atoms related to different luminescent centres in nanocrystalline ZnO thin films.

In order to do this, we have carried out X-ray absorption near-edge fine structure (XANES) studies, by detecting X-ray excited optical luminescence (XEOL) and X-ray fluorescence (FLY) at room temperature.

The XANES spectra probe the short-range around each absorbing atom, and in particular the local electron density of states in the first empty levels of the conduction band. Hence, X-ray Absorption Spectroscopy (XAS) is more sensitive than XRD in the study of little changes between polycrystalline powders and nanostructured thin films of ZnO, because the information on the long-range order does not allow us to describe local disorder, defects or surface-related states. Moreover, by comparing XANES spectra obtained by different detection techniques (transmission, fluorescence yield (FLY), total electron yield (TEY) or photoluminescence yield (PLY)) [4,5], we want to characterize the absorbing centres that are directly related to the light emission properties. As a matter of fact, while a conventional XAS experiment averages over the whole set of absorbing atoms, in some selected cases by detecting the PLY we have the possibility of studying only the local environment of atoms near the emission centres. Hayakawa et al. [6] have already used the chemical state selectivity of XEOL detection for selective measurements of X-ray absorption fine structure (XAFS) spectra from a mixture of ZnS and ZnO: since the two chemical states have different luminescence wavelengths under X-ray excitation, they have been able to distinguish the zinc environment in the two compounds. However, to our knowledge, the present PLY-XANES measurements are the first performed on ZnO thin films.

The preliminary characterization of films has been performed by luminescence spectroscopy and X-ray diffraction (XRD) measurements at room temperature.

2. Experimental

2.1. Sample preparation

ZnO nanostructured thin films were prepared at atmospheric pressure by chemical vapour deposition (APCVD), as suggested by Yao et al. [7]. We used ZnO powder mixed with graphite (molar ratio 1:1) as source material, without the need for metallic catalysts or of carrying gases. The source material was placed at the centre of a quartz tube, open to the atmosphere at both ends. The quartz tube was inserted in a horizontal furnace heated at 1150 °C at the centre and having a gradient decreasing temperature from centre to side ends. Due to the temperature gradient, the morphologies of the nanostructured thin films depend on the position of the substrate with respect to the centre of the tube. In particular, we will focus our attention on three samples. TEC1 and TEC3 samples were deposited near the centre of the quartz tube. In this way, the evaporation process took place at the same temperature (~900–1000 °C), producing similar ZnO nanostructures on these substrates. On the other hand, TEC5 sample was grown near the tube end, at a much lower temperature (around 100 °C). The effective thickness of the samples was estimated by measuring the edge jump of the XAS spectrum. The average jump for TEC1 and TEC3 samples was about 0.2, corresponding to a thickness of about 1 μm, while the TEC5 sample was much thinner, having an edge jump less than 0.1.

For XAS measurements on polycrystalline ZnO powders used as a reference compound, the sample was prepared by depositing from liquid suspension on a PFTE substrate a thin layer of very fine ZnO powder. The obtained thickness was about 1 μm. Such a thickness allows us to exclude self-absorption effects in detection of the XANES spectra using the FLY and PLY configuration.

2.2. X-ray diffraction

To carry out the X-ray diffraction (XRD) measurements we used an X'Pert Pro diffractometer by Panalytical, equipped with a Cu-anode X-ray tube, a flat crystal monochromator and a proportional detector consisting of a cylindrical chamber filled with a xenon/methane gas mixture. The angle 2θ ranged from 25 ° to 75 °, with a step of 0.05 °. The collection time of each XRD point was 4 s.

2.3. Optical luminescence measurements

The steady-state photoluminescence of our ZnO thin films was studied using two different excitation sources: the 266 nm line of a solid state laser and synchrotron radiation from a bending magnet at BM08 of ESRF (France). In the first case, the detection took place in photon counting mode, using a photomultiplier tube and a monochromator suitable to work in the range 200–3000 nm. In the latter case, the experimental setup is the same used for the PLY-XANES measurements (see below). We also performed time-resolved photoluminescence measurements using the solid state laser as excitation source. The pulse repetition rate and the pulse FWHM were 5600 Hz and ~1 ns, respectively. We used three different time step intervals: 10, 40 and 160 ns. The kinetics was accumulated during 10^5 laser pulses for every photoluminescence energy.

2.4. X-ray absorption measurements

Zn K-edge PLY-XANES and FLY-XANES measurements were carried out using synchrotron radiation from a bending magnet at the BM08 GILDA beamline of ESRF (France). The sample was placed inside a vacuum chamber ($\sim 1.8 \times 10^{-4}$ bar) and positioned vertically at 45° with respect to the incident X-ray beam. The beam size at the sample was less than $3 \times 1 \text{ mm}^2$.

The FLY signal was collected at 45° with respect to the normal to the sample by a 13-element Ge-multidetector, tuned at the Zn K-edge emission lines.

The XEOL detection system was composed of a collection lens coupled with a bunch of 24 optical fibres that directly entered a spectrograph. The collected light was dispersed by a diffraction grating onto a nitrogen-cooled CCD detector (1100×300 pixels), controlled by a dedicated PC. For every energy of the incident X-ray beam, the CCD detector collected the whole XEOL band spectrum, which was successively integrated off-line in a selected range to obtain the PLY-XANES spectra.

In this paper, we will present only PLY-XANES spectra obtained by integrating the broad defect band in the visible range.

3. Results

3.1. X-ray diffraction

The XRD measurements allow us to determine the orientation of the ZnO nanostructures deposited on the Si substrates. The diffraction patterns of the TEC samples are depicted in Fig. 1. We note that, in addition to the huge (201) diffraction peak coming from the Si substrate (not shown in Fig. 1), a very intense and sharp peak appears at around 36° in the spectra of the TEC samples. The comparison of this peak with a *c*-ZnO reference XRD spectrum reveals a highly (002) oriented crystalline structure in all our evaporated films. Hence, the growth direction of the ZnO nanostructures is along the *c*-axis, without a direct relationship with the orientation of the *c*-Si substrate.

3.2. Optical luminescence measurements

Time-resolved PL measurements have been performed in order to study the kinetics of the process and to compare the optical properties of our samples with data available in the literature. Typical time-resolved photoluminescence spectra are shown in Fig. 2. The obtained spectra show a very fast excitonic luminescence, not visible after about 200 ns, and a slower defect-related luminescence, visible up to 12 μs . Actually, the second defect band at 2.4 eV and the excitonic band at 3.2 eV appear together but, as expected, their decay times are different. Our results are in agreement with the ones presented in literature [8,9].

While the excitonic peak does not appear to change in energy for all three TEC samples, a significant shift may be observed by analysing the slow defect band in the visible range, presented in Fig. 3(a). Results are very similar either by detecting steady state laser excited luminescence or XEOL. Fig. 3(a) shows the X-ray excited optical luminescence at the Zn K-edge (9659 eV) for TEC1, TEC3 and TEC5 samples. Since the films are not homogeneous, the photoluminescence intensity strongly depends on the position of the

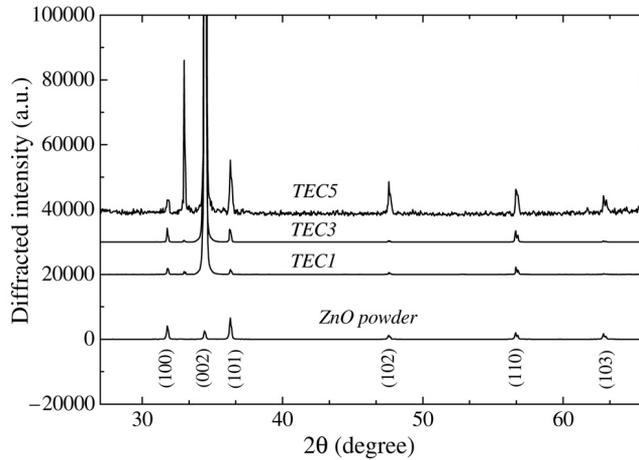


Fig. 1. XRD patterns of TEC1, TEC3 and TEC5 samples. The diffraction peaks of a ZnO reference powder are also presented. Intensity has been scaled to allow comparison of the lowest peaks.

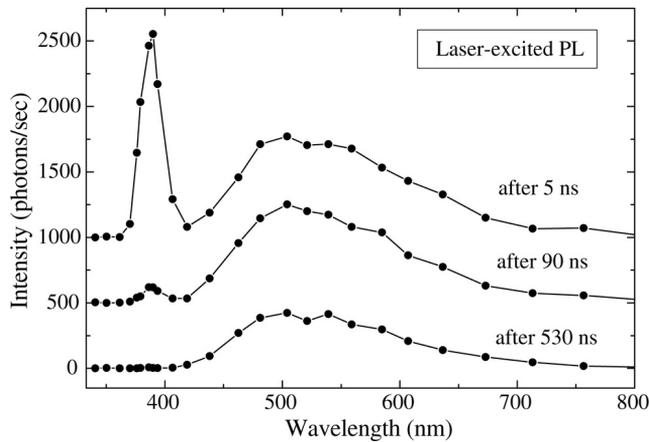


Fig. 2. Typical laser-excited optical luminescence of TEC samples. The three spectra were recorded 5, 90 and 530 ns after the laser pulse. The relative intensity changes between the excitonic and defect-related peak are evident.

incident beam on the sample. That is why the presented spectra are normalized at the maximum. Once the position of the X-ray beam is maintained fixed on the ZnO thin film, we can study the PL intensity as a function of the X-ray beam energy. As expected, the photoluminescence exhibits a strong increase when the Zn K-edge is reached.

We may observe that the visible band has a considerable blue shift from ~ 590 to ~ 510 nm, passing from TEC5, to TEC1 and TEC3 samples. Moreover, we note that the emission band of the ZnO powder (thinner solid line) is centred at an intermediate position

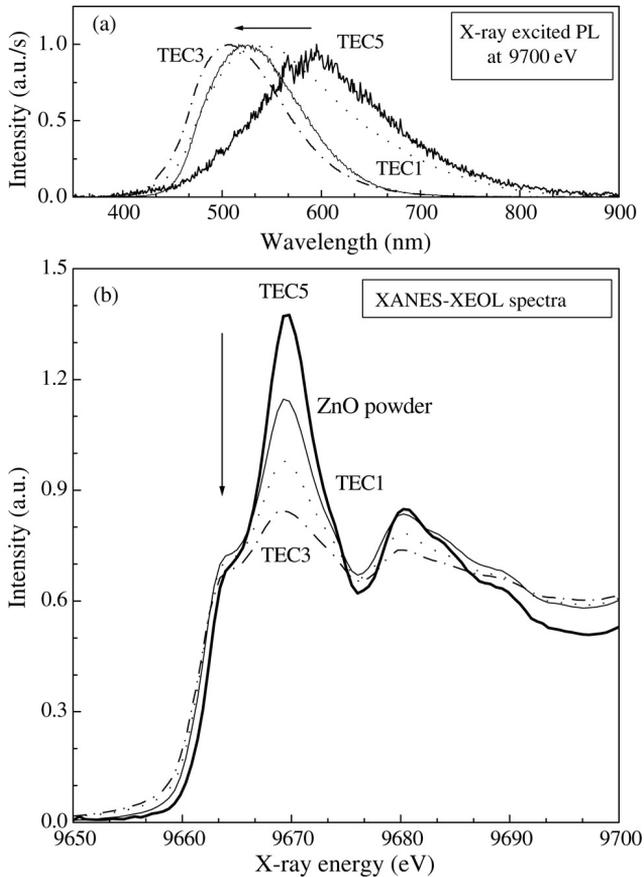


Fig. 3. (a) X-ray excited optical luminescence (visible band) and (b) PLY-XANES spectra for TEC1, TEC3 and TEC5 samples at the Zn K-edge. For comparison, in both panels we also present the measurements performed on a ZnO reference powder (thinner solid line).

(~ 520 nm) with respect to the thermally evaporated thin films. As we will see in the following section, a similar trend is also present in the XANES spectra.

3.3. X-ray absorption measurements

The comparison between the absorption spectrum of ZnO polycrystalline powders and the FLY- and PLY-XANES of the TEC samples shows important modifications in the local electron density of states of our nanostructured films. As a matter of fact, the XANES spectra may be described in terms of a direct transition from the inner shell level to the lowest unoccupied states near the conduction band that are, in the present case, mainly Zn 4p-levels [10–12].

Changes between different TEC samples might be due to quantum confinement (QC), related to the reduced dimensions of nanostructures present in the samples, or to local

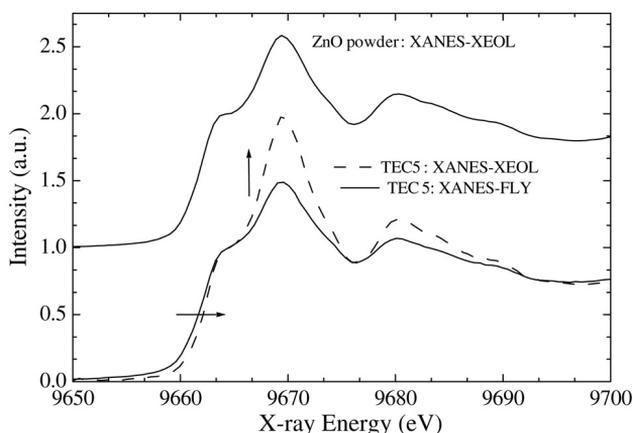


Fig. 4. Comparison between XANES spectra recorded in different detection modes (FLY and XEOL) for TEC5 sample and a ZnO reference powder.

distortions mainly related to defects or surface states. On the other hand, changes between PLY- and FLY-XANES spectra of the same sample should be attributed to the peculiar sensitivity of PLY-XANES, which monitors only the absorbing atoms near the light emitting centres.

A whole interpretation of the XANES spectra will be done in a forthcoming paper. Here we limit ourselves to a qualitative description.

At first, we may note in Fig. 3 that the spectrum of the TEC5 sample is characterized by a very sharp first peak centred at about 9670 eV. The peak, as the other XANES main features, decreases in intensity for TEC1 and TEC3 samples, respectively. A comparison with ZnO powders shows that the TEC3 sample is characterized by a very strong attenuation of all XANES features. A similar trend is shown by FLY- and PLY-XANES, and in general we observe that the PLY-XANES structures are more pronounced than the FLY ones, as documented for TEC5 in Fig. 4. The strong decrease in intensity shown by TEC3 (the nearest to the crucible in the furnace) is probably due to a reduction of the ZnO particle sizes, originating also the blue shift of the photoluminescence band due to QC [4,5]. Another important observation may be made by analysing the position of the main absorption edge of the PLY-XANES spectra: Fig. 3 shows a red shift passing from TEC5 to TEC1, ZnO and TEC3 samples respectively, while Fig. 4 shows that a blue shift is clearly present for the PLY spectra compared with the FLY ones. The origin of these changes is at present not clear because, from QC theory, we expected a blue shift in Fig. 3. However, other interpretations are possible, because the edge shape and energy position are very sensitive to small changes near the Fermi level that may be due either to the presence of localized states within the forbidden gap or to changes in the electron density of states in the conduction band.

In summary, we have shown significant differences in the local structure of samples prepared by APCVD, which may be correlated to their light emission properties. Moreover, these first XAS experiments on nanostructured ZnO samples, performed using PLY and

FLY detection, confirm that it is possible to study the local environment only of those Zn atoms that are in the proximity of or directly related to the light emitting centres.

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References

- [1] A. van Dijken, E.A. Meulenkaamp, D. Vanmaekelbergh, A. Meijerink, *J. Lumin.* 87–89 (2000) 454.
- [2] A. van Dijken, E.A. Meulenkaamp, D. Vanmaekelbergh, A. Meijerink, *J. Lumin.* 90 (2000) 23.
- [3] X.L. Wu, G.G. Siu, C.L. Fu, H.C. Ong, *Appl. Phys. Lett.* 78 (2001) 2285.
- [4] G. Dalba, P. Fornasini, R. Grisenti, N. Daldosso, F. Rocca, *Appl. Phys. Lett.* 74 (1999) 1454.
- [5] G. Dalba, N. Daldosso, P. Fornasini, M. Grimaldi, R. Grisenti, F. Rocca, *Phys. Rev. B* 62 (2000) 9911.
- [6] S. Hayakawa, T. Hirose, L. Yan, M. Morishita, H. Kuwano, Y. Gohshi, *X-Ray Spectrom.* 28 (1999) 515.
- [7] B.D. Yao, Y.F. Chan, N. Wang, *Appl. Phys. Lett.* 81 (2002) 757.
- [8] V.V. Travnikov, A. Freiberg, S.F. Savikhin, *J. Lumin.* 47 (1990) 107.
- [9] M. Anpo, Y. Kubokawa, *J. Phys. Chem.* 88 (1984) 5556.
- [10] H. Yoshida, T. Shimizu, C. Murata, T. Hattori, *J. Catal.* 220 (2003) 262.
- [11] J.W. Chiou et al., *Appl. Phys. Lett.* 84 (2004) 3462.
- [12] T. Mizoguchi et al., *Phys. Rev. B* 70 (2004) 045103.