

Disorder induced violet/blue luminescence in rf-deposited ZnO films

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In this work ZnO thin films were deposited on different substrates, glass, silicon (100), and MgO (100) using rf-magnetron sputtering at low temperature in order to promote a large defect density, aiming to study a possible correlation with the observed violet/blue emission band. The peak position, width and low energy band shape asymmetry of the violet/blue band was found to be dependent on the deposition temperature and oxygen partial pressure. The structural analysis of deposited films reveals an epitaxial relationship for the *a*-oriented ZnO/MgO while for the *c*-oriented ZnO/Si no epitaxial relation was found with the substrate. The dependence of the violet/blue band on temperature displays always a

shift of the peak position to lower energies, discarding the hypothesis of a free to bound transition. The sublinear dependence of the emission intensity with the excitation intensity suggests that the violet/blue bands on both samples could have a donor-acceptor pair nature. However, the unusually strong shift of the peak position to lower energies for the ZnO/MgO films and the emphasised asymmetric band shape for the ZnO/Si samples suggest that potential fluctuations in the electronic bands, due to disorder induced charged defects, could also be considered as an alternative recombination model for the violet/blue band.

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1 Introduction ZnO is a wide and direct band gap material with 60 meV binding energy for the free exciton (FX), being promising for optical applications such as UV lasers, solar cells, photo-detectors, and surface wave acoustics devices [1, 2].

At cryogenic temperatures besides the FX(A) recombination (at ca. 3.38 eV, [2, 3]) the ability of the neutral donor impurities to trap excitons leads to the donor bound exciton (D⁰X) recombination near 3.36 eV [3, 4]. Most of the ZnO samples processed by different routes, exhibit at low temperatures the D⁰X lines as prominent recombination. Nevertheless, by using above bandgap excitation, the ZnO photoluminescence (PL) is often accompanied by

deep defect-related broad emission bands located in the violet/blue, green, yellow and red spectral regions [5, 6]. Although a significant amount of work has been published till now, the nature of the broad bands is still a controversial topic. The identification of the defects chemical nature as well as the understanding of their recombination models are crucial for further device developments based on this oxide host. Among the mentioned broad bands the violet/blue luminescence bands (also called blue band), with maxima between ca. 2.8 and 3.0 eV have been observed both in single crystals [4] and in thin films deposited on different substrates (glass [7, 8], Si [9], MgO [10] and sapphire [11]). The peak position and band shape are sensi-

tive to excitation density and temperature conditions [11]. The main recombination models for the violet/blue band have been reported as free to bound [10] and bound to bound transitions [4]. In the first case, electrons promoted to the conduction band by photons with energy higher (or equal) to the bandgap energy are able to recombine with photogenerated holes captured by acceptor impurities (e-A transitions). Similarly, free holes in the valence band can recombine radiatively with bound electrons at donors (h-D process). In ZnO these free to bound transitions have been associated with V_{Zn} and Zn_i acceptor and donor levels, respectively [12]. For the bound to bound process electrons bound at the donors can recombine with holes bound at the acceptors leading to the so called donor-acceptor pair (DAP) transitions [4]. Besides these recombination models, alternative explanations have been recently reported by Reshchikov *et al.* [11] with the violet/blue band being assigned to diagonal transitions from the conduction to the valence band due to potential fluctuations induced by a random distribution of charged defects.

In this work ZnO thin films were deposited on glass, silicon (100), and MgO (100) using rf-magnetron sputtering at low substrate temperature in order to promote a large defect density, aiming at their correlation with the violet/blue band emission. The analysis of the PL intensity as a function of the temperature and excitation intensity indicates that distinct disorder induced violet/blue bands occur in the analysed samples

2 Experimental details ZnO thin films were deposited on glass, Si (001) and MgO (001) by rf-sputtering with different deposition parameters (Table 1). The samples structural properties were investigated by X-ray diffraction (XRD) using a Phillips X'Pert diffractometer with the Cu $K_{\alpha 1}$ line. PL studies were carried out by using the 325 nm He-Cd laser line as excitation source. The samples luminescence was dispersed by a Spex 1704 monochromator (1 m, 1200 mm^{-1}) and detected by a cooled Hamamatsu R928 photomultiplier. All the deposited films and the glass and MgO substrates were analysed under the same excitation and detection conditions. For the case of the PL excitation intensity dependence calibrated neutral density filters were used. Temperature dependent PL measurements were acquired in the temperature range between 14 K and room temperature (RT). All the presented spectra are uncorrected to the optics and dispersive system spectral response.

Table 1 Deposition parameters of the different samples.

Sample	Temp. ($^{\circ}\text{C}$)	PPO ₂ (mbar)	Substrate
A	490	4×10^{-4}	Si (100)
B	390	1.6×10^{-3}	Si (100)
C	480	5×10^{-4}	MgO (100)
D	390	1.5×10^{-3}	glass
E	390	-----	glass

3 Results and discussion

3.1 Structural properties Figure 1 shows the Omega-2Theta scans for the analysed samples. The ZnO samples deposited on silicon (samples A and B) and glass (samples D and E) substrates exhibit the (0002) reflection peak revealing a *c*-axis orientation of the produced films. Contrarily, sample C (ZnO/MgO) displays the reflection corresponding to the (10-10) plane, confirming a preferential growth with the *m*-plane nonpolar orientation.

The epitaxial relation and orientation of these films were investigated by X-ray pole figure measurements, as shown in Fig. 2. Figures 2 a to d compare the ZnO (0002) and ZnO (10-11) pole figures for the ZnO/Si samples, which are *c*-axis oriented (Figs. 2a and 2b). The orbicular intensity belt and the absence of distinct peaks in Figs. 2c and 2d, reveal that the ZnO/Si films have no preferred in-plane epitaxial relation with the substrate.

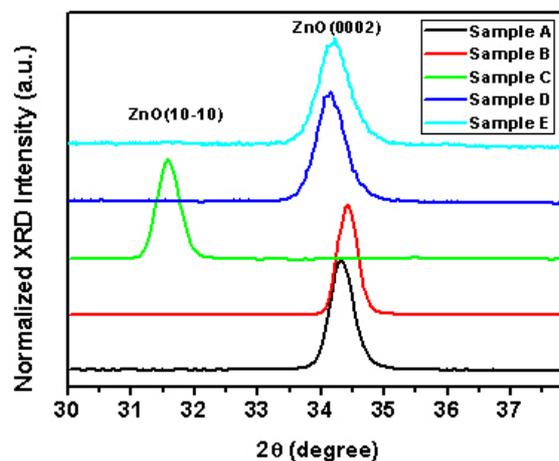


Figure 1 XRD omega-2theta scans for all samples.

The data show that the ZnO has a columnar structure with a random orientation in the azimuthal directions but with the same crystallographic axis (0002) normal to the surface. Similar results were obtained for the samples deposited on glass (Fig. 2e). The broadening of the (0002) peak comparatively with samples deposited on Si indicates poor crystal quality and stronger tilts between columns for the ZnO/glass samples. The absence of epitaxy for the ZnO/Si is likely to be due to the formation of an amorphous SiO₂ layer at the substrate surface. Comparing the ZnO/Si deposited at lower (sample A) and higher oxygen partial pressure (sample B), an improved crystalline quality was found to occur in sample A as sample B evidence a broader (0002) peak and belt associated to the (10-11) plane (Figs. 2a to d).

For the ZnO/MgO (100) sample (sample C) the same analysis was performed for the (10-11) plane (Fig. 2f). In contrast to the results found for the ZnO/Si samples, the ZnO/MgO film displays distinct peaks in line with an epitaxial relationship between the film and the substrate as

observed by others [13]. From Fig. 2f two different domains rotated by $\sim 16^\circ$ can be clearly observed. Due to the promoted epitaxial relationship a lower density of defects is expected at the ZnO/MgO interface.

Symmetric reciprocal space maps of the ZnO/Si samples (Fig. 3a and b) evidence different mosaicity characteristics for samples A and B. The broadening in reciprocal space along Q_x indicates that a small lateral coherence length and/or screw type threading dislocations dominate for the ZnO/Si sample B. For sample A, the broadening in the reciprocal space map is due to a mixture of small lateral coherence length (in less amount than for sample B), and small vertical coherence lengths (the latter seen in the broadening in Q_z direction) [14]. The differences between these samples are associated with different oxygen partial pressure during deposition. These results are in agreement with those obtained by the pole figures.

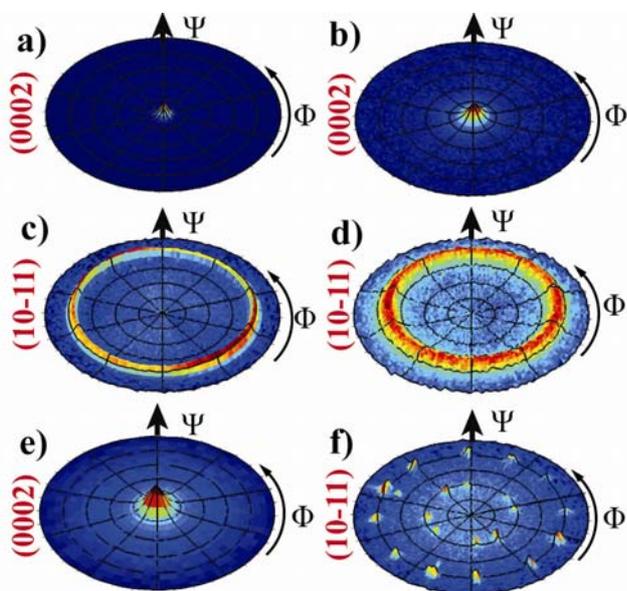


Figure 2 Pole figures of samples: a), c) ZnO/Si sample A; b), d) ZnO/Si sample B; e) ZnO/glass sample D; f) ZnO/MgO sample C.

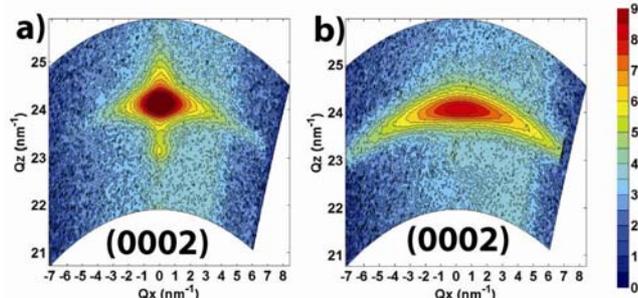


Figure 3 Reciprocal space map around (0002) for the ZnO/Si samples A (a) and B (b).

3.2 Photoluminescence Figure 4 shows the low temperature PL spectra of the analyzed samples obtained with above bandgap excitation. For comparison the PL of the glass and MgO substrates acquired under the same conditions are displayed.

At 14 K the luminescence of the deposited ZnO films showed, on the high energy side, the D^0X lines at ca. 3.36 eV. Besides the deep level defect bands in the green, yellow and red spectral regions all the analyzed films exhibit a wide blue/violet band with a sample dependent maximum arising between 2.96 eV and 3.14 eV. A variable, sample dependent, peak position was also reported by other groups which associate the recombination in the mentioned spectral region as free to bound, DAP and diagonal transitions [4-6]. The intensity of the violet/blue band observed in our deposited films is sensitive to the used oxygen partial pressure and deposition temperature as observed by comparing the spectra of samples A and B (ZnO/Si) and D and E (ZnO/glass). In particular, higher intensity was found for samples with worse crystalline quality (e.g. sample B with lower crystalline quality than sample A shows a stronger violet/blue band). This tendency suggests that the violet/blue band could be related with regions in the material with higher disorder. Focusing our attention on samples B (ZnO/Si), C (ZnO/MgO) and E (ZnO/glass) a closer inspection of the spectral shape of the violet/blue band reveals noticed differences both in the peak position and in their profile. While for the ZnO/MgO sample the luminescence is peaked at ~ 3.12 eV with a near Gaussian band shape, for the case of the ZnO/Si and ZnO/glass the peak position occurs at ~ 3.14 eV and 3.01 eV, respectively, and the band profiles clearly point to an asymmetry on the lower energy side. The band shape asymmetry is more pronounced for the ZnO/Si samples with absence of in-plane epitaxial relationship.

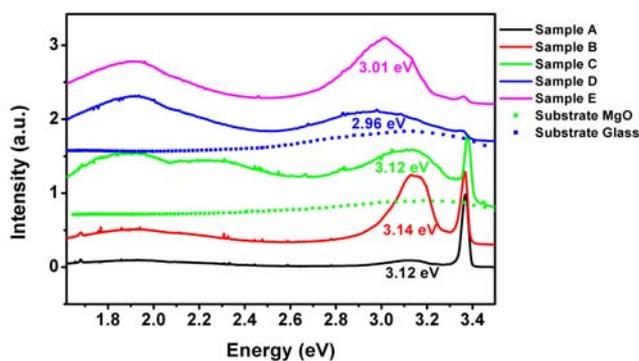


Figure 4 14 K PL spectra of ZnO/Si (samples A and B), ZnO/MgO (sample C) and ZnO/glass (samples D and E) deposited films. For comparison purposes the luminescence of the glass and MgO substrates is displayed (broken lines).

The aforementioned results suggest that the violet/blue band is due do distinct disorder-induced defects in the different samples. In order to test this hypothesis we have per-

formed temperature and excitation intensity dependent PL measurements on the ZnO/Si and ZnO/MgO selected samples to investigate the nature of the observed optical transitions (Figs. 5 and 6). Under continuous excitation the PL internal quantum efficiency (defined as $W_{\text{rad}}/(W_{\text{rad}}+W_{\text{nr}})$, where $W_{\text{rad,nrad}}$ stands for the radiative and nonradiative transition probability) can be evaluated calculated by using the classical model described by Eq. (1) where only one thermally activated nonradiative recombination channel was considered. I_0 is the integrated PL intensity assuming negligible nonradiative channels (by extrapolation to $T=0$ K), k_B the Boltzmann constant and a a constant pre-factor. Typically, the nonradiative recombination rate for a single thermally activated channel is described by the thermal activation energy, E_a .

$$I(T) = I_0 [1 + a \cdot \exp(-E_a / k_B T)]^{-1} \quad (1)$$

The evolution of the PL spectra with increasing temperature for the ZnO/Si and ZnO/MgO samples is displayed in Fig. 5. In the measured temperature range, the integrated PL intensity of the violet/blue emission is found to decrease as the temperature increases, due to nonradiative competitive processes. Between 14 K and 80 K the luminescence thermal quenching is well fitted by using Eq. (1), with activation energies (E_a) of 7.2 ± 0.2 meV, 12 ± 2.2 meV and 7.9 ± 1.0 meV for samples A, B and C, respectively. The observed different thermal quenching mechanisms agree with the aforementioned hypothesis of distinct disorder-induced defect luminescence.

Figure 6 shows the dependence on the excitation intensity of the violet/blue peak position and intensity for ZnO/Si (sample B) and ZnO/MgO (sample C). In both cases a shift to lower energies of the violet/blue band (peaked at ~ 3.14 eV for the ZnO/Si and ~ 3.12 eV for the ZnO/MgO samples) was found to occur with decreasing excitation intensity. However, while for the ZnO/Si a 26 meV shift was observed, for the ZnO/MgO sample a large 160 meV shift can be identified. For a DAP transition a shift to lower energies with decreasing excitation intensity is expected, where the luminescence from the long-lived distant pairs prevails [15]. Nevertheless, if the semiconductor material exhibits potential fluctuations, e.g. due to a random distribution of charged defects, a similar behaviour for the luminescence could occur [6, 16, 17]. The intensity dependence of the violet/blue band in both samples (I_{PL}) on the excitation intensity (I_{exc}) (Fig. 6d) is described by a power law model, $I_{\text{PL}} \propto I_{\text{exc}}^\beta$, with the exponent close to 1 or below 1 as expected for defect-related processes such as free-to bound or DAP transitions [18]. In a free to bound transition is expected to observe a shift of the peak position to higher energy with increasing temperature. However, from the spectra shown in Fig. 5 no such shift is observed.

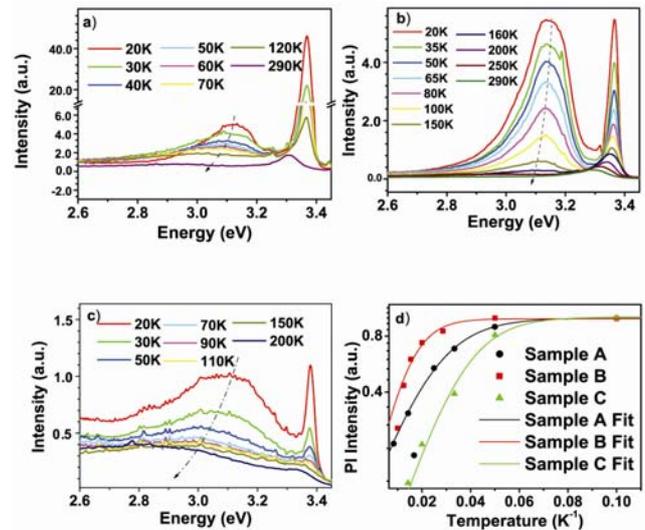


Figure 5 Temperature dependent PL spectra for a) ZnO/Si (sample A), b) ZnO/Si (sample B), c) ZnO/MgO (sample C). d) Temperature dependence of the integrated PL intensity for the violet/blue emission observed in the different samples in the temperature range from 14 K to 80 K. Full lines correspond to the fits using Eq. (1) as described in the text.

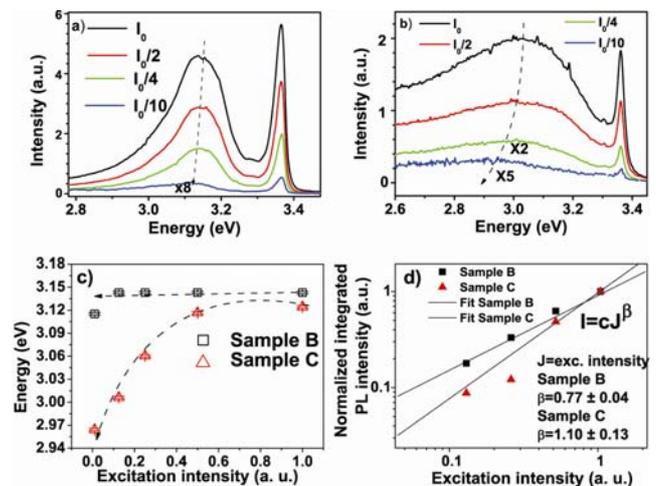


Figure 6 14 K PL spectra as a function of the excitation intensity for ZnO/Si sample B (a) and ZnO/MgO, sample C (b). Evolution of the blue luminescence peak position (c) and normalized integrated PL intensity with the excitation intensity (d).

For the case of the violet/blue emission detected in the ZnO/MgO sample the measured β exponent close to 1 suggests that a DAP transition could be involved on the recombination process. However, the anomalous large shift detected with decreasing excitation intensity is similar to that observed by Reschnikov *et al.* in ZnO/a-Al₂O₃ [11] who consider a model involving Coulomb potential fluctuations leading to a local perturbation in the electronic band structure due to a random distribution of charged defects. For the case of the ZnO/Si sample the violet/blue

band is narrower than for the ZnO/MgO film (see Fig. 4). In addition the small energy shift of the peak position with decreasing excitation intensity together with the sublinear dependence of the intensity suggest DAP transitions as a possible recombination mechanism [4]. Nevertheless, the pronounced band shape asymmetry observed on the lower energy side is consistent with the presence of a high degree of structural disorder evidenced by the strong mosaicity found and small lateral coherence length. At this stage, we cannot rule out that threading dislocations and/or charged defects induced by the disorder could generate potential fluctuations on the band edges for the ZnO/Si sample responsible for the measured violet/blue band.

4 Conclusions ZnO thin films were deposited on different substrates at low temperatures in order to promote a high density of defects. Besides the donor bound exciton luminescence the deposited films exhibit broad unstructured emission bands. In particular, all the samples display violet/blue emission bands with a peak position, width and band shape asymmetry at the low energy side dependent on the deposition temperature and oxygen partial pressure. The structural analysis of deposited films reveals an epitaxial relationship for the *a*-oriented ZnO/MgO while for the *c*-oriented ZnO/Si no in-plane epitaxial relation with the substrate was found.

The dependence of the violet/blue band on temperature, studied for the ZnO/MgO and ZnO/Si samples, reveal always a shift of the peak position to lower energies with increasing temperature discarding the hypothesis of free to bound transitions. The evidenced dependence of the emission intensity with the excitation intensity suggests that the violet/blue bands on both samples could have a DAP nature. However, the atypical 160 meV large low energy shift of the peak position for the violet/blue band observed in the ZnO/MgO implies that another possible explanation should be considered invoking the model of Coulomb potential fluctuations on the electronic band structure due to a random distribution of charged defects. Similarly, while the violet/blue band observed in the ZnO/Si samples could be described by a DAP model; the accentuated asymmetry of the band shape suggests that the influence of potential fluctuations cannot be ruled out. The structural analysis suggests that structural defects assume a significant role on the generated potential fluctuations.

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