Research Article

The Role of Edge Dislocations on the Red Luminescence of ZnO Films Deposited by RF-Sputtering

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Abstract
The existence of extended defects (i.e., dislocations) in inorganic semiconductors, such as GaN or ZnO, responsible for broad emission peaks in photoluminescence analysis remains unresolved. The possible assignments of these luminescence bands are still matter of discussion. In this study, two different zinc oxide samples, grown under different oxygen partial pressures and substrate temperatures, are presented. Epitaxial and structural properties were analysed by means of X-ray diffraction and transmission electron microscopy techniques. They confirm that the layers are single-phase with a good crystalline quality. Nevertheless, a different density of threading dislocations, with a higher contribution of edge dislocations, was found. Photoluminescence spectroscopy has been used to investigate the optical properties. The steady state luminescence spectra performed at 14 K evidenced the donor bound exciton recombination and deep green and red emission bands. The red band with a maximum at 1.78 eV was found to be stronger in the sample grown at lower oxygen pressure which also shows higher density of threading dislocations. From the temperature and excitation density dependence of the red band, a donor acceptor pair recombination model was proposed, where hydrogen and zinc vacancies are strong candidates for the donor and acceptor species, respectively.

1. Introduction

Nowadays ZnO is among other semiconductors, one of the most studied materials, due to the potentialities offered by its wide direct band gap (3.37 eV) at room temperature and high (~60 meV) free exciton binding energy [1, 2]. These characteristics together with the easiness of depositing thin ZnO films by different techniques with a considerable quality make this material a suitable semiconductor for a broad range of applications in optical and electrical devices (light emitting diodes, transparent thin film transistors, and surface acoustic wave systems [2–6]). Despite the increasing interest in this material, a deeper understanding of the role of the structural defects in the oxide host is still necessary, for example, to overcome the difficulties in obtaining p-type conductivity, among others. For instance, line defects, and more specifically threading dislocations (TDs), are known to have effects on photonic and electronic materials behaviours [7, 8] causing a degradation in the semiconductor device. For example, TDs produce undesirable phenomena that lead to the appearance of additional electronic energy levels in the band gap influencing the semiconductor electrical and optical properties [8].

From the luminescence point of view, it is well established that the recombination processes on high quality ZnO layers occur nearby the band gap with the emission due to free and donor bound excitons [9]. Additionally, surface excitons and stacking faults related luminescence effects have also been
reported [10–12]. On the lower energy side, the luminescence has been attributed to donor acceptor pairs (DAP) and recombination’s broad bands to often unknown origin [13]. The latter can occur in distinct spectral regions and have been observed in the blue, green, orange, and red spectral regions, when the samples are excited with photons with energy higher than the band gap [2, 14]. Based on the luminescence behaviour with time, temperature, and excitation density, several models have been proposed for the emitting centres including impurity related [15–18], DAP [2, 13, 19], free-to-bound transitions [14, 20, 21] and potential fluctuations [20, 22]. The observation of the different broad bands is shown to be sample dependent and their assignment to point or structural defects are still under debate.

In this work, ZnO thin films were deposited by radio-frequency- (RF-) sputtering on \([0001] c\)-sapphire substrate using the same RF power. Sample Z1 was deposited in the absence of oxygen and sample Z2 with an oxygen partial pressure of \(4.0 \times 10^{-4}\) mbar. The Z1 and Z2 samples were grown at 664°C and 746°C, respectively. These growth parameters profiles are shown in Figure 1. The distance from the target to the substrate was maintained constant and for the deposition processes a commercial ZnO target with a 99.9% purity was used.

![Figure 1](image)

**Figure 1:** Deposition parameters profiles (substrate temperature, \(O_2\) partial pressure (PPO\(_2\)), and RF power) of sample Z1 (a) and sample Z2 (b).

Structural and optical studies were performed by transmission electron microscopy (TEM), selected area electron diffraction (SAED), XRD, and PL spectroscopy. The structure of the samples was characterised by TEM after samples were prepared in cross sections (XTEM) or for plan-view (PVTEM). They were thinned to reach the electron transparency with conventional methods of mechanical grinding and polishing, dimpling (dimple grinder GATAN TM 656), and ion milling (applied with a GATAN low voltage precision ion polish system, PIPS). Bright field (BF) and dark field (DF) DC-2B-TEM micrographs and SAED patterns were collected with a JEOL-1200EX microscope. The TD density for each ZnO layer was calculated as the average value of 8 different areas sizes ranging between 0.5 and 1 \(\mu m^2\) for PVTEM and 5 different lengths or regions between 0.7 and 3.7 \(\mu m\) for XTEM preparation. The ZnO film thickness and surface roughness were also estimated from the analyses of 10 BF-TEM images, with analysed lengths between 12 and 30 \(\mu m\) depending on the sample.

The XRD measurements were carried out with a Philips XRD X’pert diffractometer with the Cu K\(\alpha\) in out-of-plane configuration for symmetric planes and in skew geometry for asymmetric ones. XRD reciprocal space maps (RSM) were obtained for the symmetric (0002) reflections and \(\phi\)-scans for asymmetric planes (202). The PL studies were carried out using a 325 nm He-Cd laser line as excitation source, and a Spex 1704 monochromator (with a 1200 grooves/mm grating) coupled with a cooled photomultiplier (Hamamatsu R928) was used to disperse and detect the luminescence, respectively. The temperature dependent PL measurements

2. **Experimental**

Two zinc oxide film samples (Z1 and Z2) were deposited by RF-sputtering on \(c\)-sapphire substrate using the same RF power.

Sample Z1 was deposited in the absence of oxygen and sample Z2 with an oxygen partial pressure of \(4.0 \times 10^{-4}\) mbar.
were acquired in the temperature range between 14 K and room temperature (RT) using a closed-cycle-cryostat. For the excitation intensity dependence commercial calibrated neutral density filters were used. All the PL spectra were corrected to the spectral response of the collection and detection system.

3. Results and Discussion

3.1. Structural Properties. TEM was applied to get information about the structural quality and the presence of defects at the ZnO films. The thickness and surface roughness of the layers were analysed from lengths of 12 μm for sample Z1 and 30 μm for sample Z2 (see Table 1). According to a higher growth deposition time (as present in Figure 1), the ZnO layer in sample Z1 is thicker and less rough.

Concerning TD characterization by TEM, the method used in this work is based on the combination (cross-correlation) of DC-2B-BF TEM images from XTEM and PVTEM preparations [23] which allows obtaining on the one hand edge + mixed and screw + mixed TDs and on the other hand density of TDs at different depths of the ZnO layers.

Images of TDs in DC-2B-TEM conditions were obtained when the samples are oriented taking into account the invisibility criterion $g \cdot b = 0$. Therefore, dislocations become invisible if this criterion is satisfied, where “$g$” is the excited reflection and “$b$” is the Burgers vector [24]. Besides, depending on Burgers vector, TDs are classified in three different groups, that is, screw, edge, and mixed, which in the concerned wurtzite system correspond to $b_s = \langle 0001 \rangle$, $b_e = (1/3) \langle 11\overline{2}0 \rangle$, and $b_{s+m} = b_m = (1/3) \langle 11\overline{2}3 \rangle$, respectively.

Table 1: Thickness and roughness of ZnO layers for samples Z1 and Z2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness (nm)</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z1</td>
<td>322 ± 12</td>
<td>38 ± 12</td>
</tr>
<tr>
<td>Z2</td>
<td>195 ± 20</td>
<td>84 ± 20</td>
</tr>
</tbody>
</table>

Table 2: Groups of TDs that can be observed in TEM for each preparation and two-beam conditions.

<table>
<thead>
<tr>
<th>Preparation</th>
<th>Zone axis</th>
<th>Reflection (g)</th>
<th>Type of TDs</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVTEM</td>
<td>[0001]</td>
<td>(11\overline{2}0)</td>
<td>Edge and mixed</td>
</tr>
<tr>
<td>XTEM</td>
<td>[11\overline{2}0]</td>
<td>(0002)</td>
<td>Screw and mixed</td>
</tr>
</tbody>
</table>

Traditionally, dislocations are given in groups (edge + mixed or screw + mixed) because images with only one type of dislocations are not geometrically possible to be obtained. For this reason, in the present work, the TD density data will be given together, that is, screw + mixed and edge + mixed. Table 2 shows the crystallographic direction (zone axis) and the related reflection (g) selected to acquire the TEM images for each preparation, together with the type of TDs that are observed.

The number of TDs is directly measured from DC-2B-BF TEM micrographs (a couple of examples are shown in Figures 2 and 3). Thereupon, as indicated in Table 2, edge + mixed dislocations were calculated by using the $g = (11\overline{2}0)$ excited reflection near the [0001] zone axis of ZnO from PVTEM preparations. Likewise, screw + mixed dislocations were calculated by using the (0002) excited reflection near the [11\overline{2}0] zone axis of ZnO from XTEM.
Table 3: TD densities at ZnO surface and annihilation for samples Z1 and Z2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface dislocation densities</th>
<th>Annihilation of screw + mixed TDs (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Edge + mixed</td>
<td>Screw + mixed</td>
</tr>
<tr>
<td></td>
<td>(10^8 \text{ cm}^{-2})</td>
<td>(10^8 \text{ cm}^{-2})</td>
</tr>
<tr>
<td>Z1</td>
<td>84.9 ± 10.3</td>
<td>12.1 ± 0.7</td>
</tr>
<tr>
<td>Z2</td>
<td>31.7 ± 3.9</td>
<td>4.5 ± 0.3</td>
</tr>
</tbody>
</table>

Figure 3: PVTEM DC-BF micrographs of Z1 (a) and Z2 (b) samples where edge + mixed dislocations are visible. They were taken using the \(g = (11\overline{2}0)\) excited reflection.

Since it is well known that TD density values measured from PVTEM preparations are more accurate than those estimated from XTEM [25], the screw + mixed TD density on the ZnO surface has been determined through the edge + mixed TD density. In order to do that, we have relied on previously reported results [26, 27] that claim that edge + mixed dislocations are about 80–90% of the whole, while screw + mixed dislocations range between 10 and 20 per cent. Consequently, the edge + mixed TD density (directly calculated from the PVTEM preparation) is assumed as 85% of the whole, whereas the remaining percentage belongs to the screw + mixed TD density. The thickness of each XTEM preparation is evaluated by equalling the screw + mixed TD density directly measured value at the ZnO surface, to that calculated from the PVTEM. Once the thickness is determined, the density of TDs propagating from the sapphire/ZnO interface towards the ZnO surface (TD density) can be evaluated, and therefore the annihilation rate can be estimated (see Table 3 and Figure 4). Additionally, data of TD density at ZnO surface obtained by using the aforementioned method are shown in Table 3. The errors in this table were calculated through the minimum square method (for the directly measured densities) and the well-known statistical formula for mean value errors.

Evaluating the TEM results, it is found that sample Z1 has a higher TD density than sample Z2 (Table 3). This can be also seen in Figure 2, where pictures for Z1 and Z2 samples have the same scale marker and a higher number of screw + mixed TDs are predicted for sample Z1 at first glance. Besides, it has been evidenced from Figures 2 and 3 that the main structural defects observed in the ZnO layers correspond to TDs (screw + mixed and edge + mixed) with densities ranging from \(10^8\) to \(10^9\) cm\(^{-2}\) from the interface to the surface (Table 3). These values have a good agreement with previously reported results on good quality state of the art ZnO layers [3, 28–30]. For the analysed samples no stacking faults were identified.

Figure 4: Density of screw + mixed (s + m) dislocations for Z1 (red) and Z2 (green) samples in dependence on the distance from sapphire/ZnO interface. The densities of TDs were measured at different height rate (20%, 50%, and 70%) of the ZnO layer, where 0% belongs to sapphire/ZnO interface and 100% refers to ZnO surface.
and the TD density was found to be dependent on the depth inside the film. Attending to the screw + mixed annihilations, the results reveal that about 44% for sample Z1 and 51% in the case of sample Z2 annihilate when they reach the ZnO surface.

SAED patterns for XTEM preparations were also recorded giving indications of the good single-crystallinity of ZnO in regions around the Al$_2$O$_3$ and ZnO interface and at ZnO surface and of its heteroepitaxial placement on the whole heterostructure. Figure 5 shows well-defined characteristic reflections of ZnO wurtzite and $\alpha$-Al$_2$O$_3$. Therefore, the following heteroepitaxial relationships can be concluded: $[11\bar{2}0]$ ZnO//$(01\bar{1}0)$ $\gamma$-Al$_2$O$_3$ and $(01\bar{1}0)$ ZnO//$(11\bar{2}0)$ $\gamma$-Al$_2$O$_3$.

Figure 6 shows the 2 theta-omega ($2\theta$-\(\omega\)) scans for Z1 and Z2 samples. The data indicate that only one diffraction maximum attributed to the (0002) ZnO reflection is observed for the investigated layers. This result specifies that the crystallites grow preponderantly oriented with the $c$-axis normal to the substrate. To evaluate the samples structural quality, the RSM for the reflection (0002) were carried out as shown in Figure 7. The shape and broadening of the symmetric RSM are very similar for both samples, indicating that the type of defects should be similar. The broadening can be accounted by stoichiometry/strain gradients, tilt, and the limited size [31]. In the investigated layers the stoichiometry/strain gradients should be one of the major effects on the broadening, as suggested by the TEM measurements. We also
performed $\phi$-scans in order to evaluate the azimuthal rotation of the crystallites by calculating the twist angle, $\alpha_t$ [32].

Figure 8 shows the $\phi$-scans of the asymmetric (20$\bar{2}$1) reflection, corresponding to a plane with an inclination angle of 74.8$^\circ$ with respect to the [0001] direction. A distinct broadening can be clearly identified for both samples. This result evidences that dissimilar twist angles (estimated as 0.290$^\circ$ and 0.109$^\circ$, for samples Z1 and Z2, resp.) occur among the crystallites. Assuming that the twisted angle is proportional to the density of the edge dislocations [31, 32], these results suggest that a high density of edge dislocations is present in the sample Z1.

3.2. Optical Properties. Figure 9 shows the 14 K PL spectra of the two ZnO layers obtained with above band gap excitation. On the high energy side, the samples luminescence of the two ZnO layers obtained with above band gap excitation. On the high energy side, the samples luminescence of the two ZnO layers obtained with above band gap excitation. On the high energy side, the samples luminescence of the two ZnO layers observed. The LO-phonon assisted green luminescence ($\sim$2.4 eV) and an unstructured red band ($\sim$1.78 eV) are observed. The LO-phonon assisted green luminescence has been ascribed as a Cu-impurity related defect [37]. Copper impurities are known to be trace contaminants in low purity commercial ZnO targets, as the ones used in this work. Intrinsic defects such as Zn$_i$, O$_i$, V$_{O}$, and their complexes have been reported in the literature as being responsible for the unstructured broad emission bands in ZnO [38, 39]. When the growth conditions are performed under oxygen deficiency, as the case of Z1 sample, V$_{O}$ and Zn$_i$ are expected to be the main intrinsic point defects. However, first-principles calculations have shown that these defects have a high energy formation; consequently their occurrence is unlikely [40]. According to Janotti and Van de Walle [40] the neutral V$_{O}$ leads to a deep donor level located at $\sim$1 eV below the conduction band, V$_{Zn}$ are deep acceptors, and Zn$_i$ are shallow donors. The latter is also known to form unstable defects due to their low energy migration [40]. Nowadays, it has been widely accepted that V$_{Zn}$ (and their aggregates) are the most likely acceptors in ZnO [41–44], introducing energy levels between 1.6 and 2.1 eV below the conduction band [44].

Previous studies have also shown a strong correlation between the screw dislocations and the near band edge PL intensity [45]. Namely, the generated strain fields around screw dislocations leading to heterogeneous spatial distribution of the carriers are known to disturb the density of states reducing the PL recombination efficiency. On the other hand, it has been pointed out that the edge dislocations assume an important role on the deep level emission in semiconductors by trapping point defects and impurities in their strain fields [3, 46].

As can be seen in Figure 9 (in logarithmic scale), besides the already stated transitions, a broad red band of unknown origin was detected in both samples, however, with a stronger emission in sample Z1, which is the sample with the highest estimated value of the TD density ($\sim$10$^9$ cm$^{-2}$). In order to establish a coherent interpretation of the 1.78 eV emission, band temperature and excitation dependent PL studies were carried out for Z1 sample, presented in Figures 10 and II.

The evolution of the red band PL intensity with temperature depicted in Figure 10(a) evidences a decrease in the overall intensity when the temperature increases. Furthermore, a shift to lower energy of the band maximum is observed for temperatures above 40 K (Figure 10(b)). By assuming a Gaussian band shape to fit the deep level recombination, the evolution of the integrated intensity of the red band can be established as shown in Figure 10(c). Considering a classical model to describe a single thermally activated nonradiative recombination channel, the evolution of the integrated intensity, $I(T)$, with temperature follows a Mott law according to

$$I(T) = I_0 \left[1 + a \cdot \exp \left(\frac{E_a}{k_B T}\right)\right]^{-1},$$  

where $I_0$ stands for the low temperature intensity when the nonradiative processes are neglected; $a$ is a temperature independent effective degeneracy, $E_a$ is the activation energy for the nonradiative processes, and $k_B$ is the Boltzmann constant. The best fit is achieved for an activation energy of 14 ± 2 meV.

It should be mentioned that similar broad red bands have been reported in bulk, films, and nanostructures of ZnO and GaN materials [38, 47]. Particularly, Reschikov et al. [38] found in bulk material of ZnO an emission band (denoted as RLI) with the maximum near the same energy and a thermal quenching described by similar activation energy. However, while in the latter case no shifts of the RLI band maximum were identified between 14 K and the RT, in our work the red luminescence maximum shifts following the band gap shrinkage (Figure 10(b)). This behaviour suggests that the defect related with the 1.78 eV band should involve electronic energy levels sensitive to the band gap reduction, described by the effective mass theory.
Increasing the excitation density, the measured 14 K PL spectra (Figure 11(a)) promote a high energy shift of the band maximum. This is a common behaviour in DAP transitions due to the saturation of distant pairs, which have low transition probabilities [48]. In our case a ~20 meV shift can be observed among the low and high excitation intensities (Figure 11(b)). An additional indication that the red 1.78 eV band behaves as a DAP transition is provided by the sublinear dependence (Figure 11(c)) of the integrated PL intensity with the excitation intensity ($I_{PL} \propto I_{exc}^{\beta}$) expected for this type of recombination processes [49]. The emission energy of a DAP ($E_{DAP}$) with a separation $r$ is given by [48]

$$E_{DAP} = E_g - E_d - E_a + \frac{e^2}{4\pi\varepsilon_0\varepsilon_r r},$$

(2)

where $E_g$ stands for the band gap energy, $E_d$ and $E_a$ stand for the donor and acceptor binding energies, and the $1/r^2$ term corresponds to the Coulomb interaction among the ionized species.

Considering that under the low excitation intensity conditions an infinite pair separation is reached, the Coulomb term could be neglected, and an ($E_d + E_a$) ~1.68 eV is estimated by assuming a band gap energy of 3.437 eV at 14 K. If the 14 meV determined from the red band quenching corresponds to the binding energy of an exciton bound to the donor ($E_{bd}$), by using the Haynes rule derived by Meyer et al. [9] for shallow donors, $E_{bd} = 0.365E_d - 3.8$ (meV), a donor binding energy of ~49 meV is estimated. This energy value suggests that H participate in DAP [9]. The acceptor

**Figure 7:** RSM of the (0002) symmetric reflections for (a) Z1 and (b) Z2 samples.

**Figure 8:** $\phi$-scans for (2021) reflection obtained in skew geometry for samples Z1 (red) and Z2 (green).

**Figure 9:** The PL spectra of the Z1 (red) and Z2 (green) samples obtained by the He-Cd excitation at 14 K (the spectra are presented in logarithmic scale).
level should be placed at ∼1.75 eV above the valence band, if in agreement with the expected energy level for zinc vacancies [44]. Taking into account the discussion provided on the nature and energy level location of the intrinsic defects referred to above, the red emission band could be associated with a DAP involving the hydrogen shallow donor and zinc vacancies as deep acceptors. Consequently, the stronger intensity of the red emission for sample Z1 (with the higher TD density) suggests that higher amount of point defects could be induced in samples with the highest threading dislocations density.

4. Conclusions

In this work, ZnO films have been deposited on c-Al₂O₃ substrate under presence and absence of oxygen. These different oxygen pressures have strong effects on the structural and optical properties of ZnO layers. The films are monocrystalline with a highlighted quality. However, the TEM characterization has revealed that the sample grown without oxygen atmosphere presents a higher density of TDs, the majority of them being edge dislocations type. Moreover, it was found that both samples evidence heterogeneity in depth, displaying a decrease of the TD density from the sapphire/ZnO interface to the sample surface. In agreement with the TEM results, the asymmetrical ϕ-scans for (2021) reflection reveal a high value of twist angle for the sample process with null oxygen pressure, indicating high density of edge dislocations. In addition by optical characterization, a green band at ∼2.4 eV and a red band at ∼1.78 eV are observed. The green structured band is similar to the one previously assigned to the presence of Cu₆Zn acceptor due to copper impurities likely due to trace contaminants in
the precursor target. The red luminescence is more pronounced in the sample with the uppermost density of TDs. Hence, this red band has been analysed in detail, in order to find a correlation with the different amount of edge dislocations. From the temperature and excitation dependence of the red band, a donor acceptor pair recombination model has been proposed, where hydrogen and zinc vacancies are strong candidates for the donor and acceptor species, respectively. These results suggest that such optically active point defects are promoted in the sample with higher amount of edge dislocations.

**Conflict of Interests**

The authors declare that there is no conflict of interests regarding the publication of this paper.

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