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SPECTRALLY RESOLVED CATHODOLUMINSCENCE CHARACTERIZATION OF ZnO CRYSTALS

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RESUMEN

En este estudio se presentan análisis de cátodoluminiscencia (CL) en cristales de ZnO crecidos por el método hidrotérmico, los cuales se caracterizan por una buena calidad cristalina; sin embargo, presentan una elevada densidad de impurezas. En estos cristales se identifican distintos sectores de crecimiento a través de imágenes de CL. Un análisis espectral detallado demuestra que la incorporación de impurezas y centros de recombinación no radiativos está determinada por el sector de crecimiento. La existencia de estados de cola de banda en la superficie modifica la parte de alta energía del espectro, debido a la autoabsorción de excitones libres.

Palabras claves: ZnO, Catodoluminiscencia, Centros de recombinaciones.

ABSTRACT

In this paper, spectrally resolved cathodoluminiscence (CL) study of hydrothermally grown ZnO crystals is presented. These crystals are characterized by good crystalline quality; however a high density of impurities is present. Different growth sectors through CL images are identified in these crystals. A Spectrally resolved analysis proves that the incorporation of impurities and non-radiative recombination centres depend on the growth sector. The surface termination should introduce band tailing states responsible for the self-absorption of the photons with the higher energy in the luminescence spectrum (free excitons).

Keywords: ZnO, Cathodoluminescence, recombination centres

1. INTRODUCTION

ZnO is emerging as a material with high potential for optoelectronic applications. Its large bandgap (3.4 eV) and large free exciton binding energy (60 meV) make it an excellent candidate for blue and UV devices [1]. ZnO crystals can be grown by different methods, vapour phase transport (VPT) [2], melt [3] and hydrothermal (HTT) [4]. HTT presents some advantages with respect to the other methods, since it allows growth of low dislocation density down to $\approx 10^2$ cm^{-2}. The hydrothermal growth of ZnO requires a mineralizer containing alkaline metals, Li, Na and K, which are known to introduce levels in the band gap affecting to the optical properties of the crystals. The origin of the different luminescence emissions in ZnO remains a matter a controversy. Its understanding is crucial for the control of the impurities in these crystals. We present herein a spectrally resolved cathodoluminescence (CL) study of hydrothermally grown ZnO crystals; the main factors affecting the luminescence emission and its distribution are discussed.

2. EXPERIMENTAL AND SAMPLES

Hydrothermal growth of ZnO crystals is carried out in stainless steel autoclaves. Usually, large HTT ZnO crystals are grown in 2-10 molal alkali solutions at temperatures between 200 and 500ºC and pressures between 500 and 2000 bars. The ZnO seeds are cut in the desired orientation, and then they are drilled and hung in the upper half of the liner. Growth rates up to 0.5 mm per day in the direction perpendicular to the basal planes can be achieved. The crystals were grown using 2cm^2 x0.5 mm (0001) seeds. The liner was filled at 80%, with an alkali solvent composed of 3N NaOH, 1N KOH and 0.5N Li_2CO_3. Crystals with wurtzite structure were obtained. The opposite sides of the basal planes present different surface atomic arrangements. The c^+ basal plane is Zn-rich, while the c^- plane is O-rich. The crystals also present other facets, six prismatic faces (1010) (m planes), which are non polar, and the twelve pyramid faces (1011) (p planes) that are either Zn-rich, p^- planes, or O-rich, p^+ planes, see Fig 1. One should call henceforth the two sides of the samples the upper face (UF) and the back face (BF). The UF is formed by the c^+ basal plane and Zn terminated and BF is formed by the c^- basal plane and is O-terminated. The samples were yellowish to the naked eye, with colourless borders about 1.2mm wide. The samples mechano-chemically polished, show a better surface morphology for the BF surface than for the UF surface, as it will be seen later. CL measurements were performed at liquid nitrogen temperature with a XiCLOne system from Gatan, attached to a JEOL 820 Scanning electron microscope (SEM). The SEM was operated between 5 and 25 kV and 2 nA. The CL spectral images were acquired with a CCD detector.

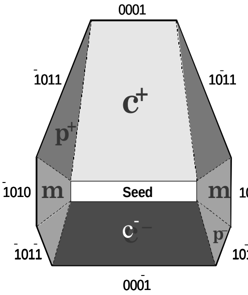

Figure 1. Geometry of the sample.

3. RESULTS AND DISCUSSION

The different facets were first analysed by panchromatic CL images, Fig.2. According to these images one can distinguish three different regions in each face in terms of the CL emission intensity: The first region is coincident with the pale yellow region (YR) seen at the naked eye, which basically corresponds to the c^+ or c^- sector which are either Zn-terminated or O-terminated respectivelyNeighbouring the yellow region a region 0.4 mm wide presents a very bright CL emission (BR): This BR region corresponds to m-sector growth right after the crystal was faceted, forming the prismatic planes. Finally, there is an adjacent region extending from the end of the BR region to the sample edge with lower CL emission (DR), this DR region corresponds to a growth sector boundary where the p^+-prismatic face started forming and p^+-axis growth and m-axis growth simultaneously occurred. Thus, the c^+ (UF) and c^- (BF) planes of three different growth sectors were exposed by the polishing procedure. The strong CL contrast between the different regions gives a major role to the non radiative recombination centers. It has been claimed that the main contribution to non radiative recombination is due to dislocations [5]; however, the presence of crystal defects is not detected by the CL images that show a rather homogeneous distribution in each region. This suggests that point defects acting as non radiative recombination centers should play a major role in the CL contrast and those point defects are not incorporated in the same way in the different facets. In depth CL studies increasing the e-beam energy suggest that excess oxygen could play a relevant role in the non radiative recombination in ZnO [6].

The luminescence spectrum of ZnO crystals consists of three main spectral regions, the near band excitonic emission (NBE) with energies above 3.32 eV, the bands with energies below 3.32 eV, usually associated with donor acceptor pair (DAP) transitions, and the visible luminescence in the green–orange spectral range. Typical spectra obtained at the three regions in both faces are shown in Fig.3. The emission intensities in the DR and YR are similar; they are more intense in the BF surface. This suggests that the incorporation of non radiative recombination centres is depending on the growth plane.

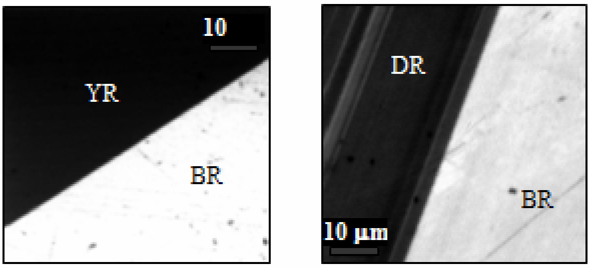

Figure 2. Panchromatic CL images where three different regions are distinguished.

The NBE spectrum consists of several close lying free and bound excitonic transitions. At 80K the bound excitons are not yet free and the NBE spectrum appears as a complex band convolution of several close bands, due to several bound excitonic transitions. However, a clear difference between the spectra of the different regions is observed, mainly between the spectra of the two surfaces. The spectra of the UF surface show a red shift in the high energy side of the NBE spectrum compared to the spectra obtained in the BF surface, Fig.3. The surface termination should introduce band tailing states responsible for the self-absorption of the photons with the higher energy in the luminescence spectrum. A similar effect was observed in ion implanted ZnO [7] and undoped ZnO crystals [5]. The optical absorption edge was also observed to shift to the red with increasing oxygen concentration [8].

The NBE spectrum at 80 K presents two main spectral features, peaking at 3.36 eV and 3.35 eV respectively. The 3.36 eV band is the dominant band in BR and YR of the BF side, while the dominant contribution of the DR region is the 3.35 eV band. On the UF side the 3.36 eV is almost absent, due to the self-absortion of the more energetic part of the spectrum, with the 3.35 eV band dominant. The 3.36 eV band should consist of donor bound exciton emissions, the so-called I_4 band. The emission at 3.35 eV has been associated with either Al impurities (donor bound exciton) or alkali impurities, Li and Na, (acceptor bound excitons) [9], all of them have a relevant presence in our crystals. The dominant presence of this band in the DR region suggests that this growth sector incorporates those impurities with higher efficiency than hydrogen, which balances the dominant luminescence emission towards the 3.35 eV band. The spectral region below 3.32, consists of several bands separated each by ≈70 meV, which is roughly the energy of the LO phonon (72 meV) in ZnO. There is a main band at ≈3.31 eV and several phonon replicas at 3.24, 3.17 and 3.1 eV. The nature of this band is a matter of controversy. It has been associated with a donor-acceptor pair (DAP) transition [10], which the nature of the defects involved is not known. Further investigation is required to elucidate the nature of this band and its relation to impurities or crystal defects.

Finally, the visible luminescence presents a marked distribution among the different growth sectors. The visible CL spectrum consists of a broad band peaking around 2.3 eV, which is composed of at least two bands, the green and the orange bands, typically reported in the literature of ZnO. The origin of the green luminescence has been associated with either V_{Zn} or V_O defects [11]. The visible luminescence is very weak in both basal planes, c^+ and c^-, which suggests that the basal planes incorporate a low concentration of deep centers.

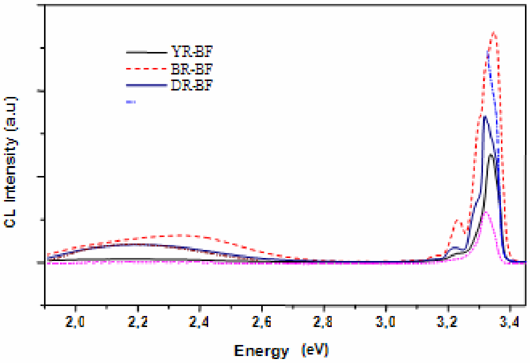

Figure 3. CL spectra for different sectors.

In conclusion, good quality HTT ZnO crystals were grown. Surface represents a real problem concerning the optical properties of the samples. The luminescence analysis shows that the incorporation of impurities and non radiative recombination centers primarily depends on the growth sector.

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