Available online at www.sciencedirect.com

ScienceDirect

Solid State Communications 145 (2008) 321–326

solid state communications

www.elsevier.com/locate/ssc

Temperature dependence and decay times of zinc and oxygen vacancy related photoluminescence bands in zinc oxide

Peter Klason[a,*], Thomas Moe Børseth[d], Qing X. Zhao[b], Bengt G. Svensson[d], Andrej Yu. Kuznetsov[d], Peder J. Bergman[c], Magnus Willander[a,b]

[a] *Department of Physics, Göteborg University, SE-412 96 Göteborg, Sweden*
[b] *Department of Science and Technology (ITN), Linköping University, SE-601 74 Norrköping, Sweden*
[c] *Department of Physics, Linköping University, SE-583 81 Linköping, Sweden*
[d] *Physics Department/Centre of Material Science and Nanotechnology, University of Oslo, P. O. Box 1126 Blindern, 0318 Oslo, Norway*

Received 20 August 2007; received in revised form 16 October 2007; accepted 25 October 2007 by M. Grynberg
Available online 1 November 2007

Abstract

A photoluminescence study was performed at different temperatures on bulk ZnO samples annealed in zinc- and oxygen-rich atmospheres. The different annealing conditions create oxygen and zinc vacancies in a controlled way in the ZnO samples. These defects are both involved in the deep band emission (DBE) that is often observed in ZnO but exhibit different optical characteristics promoting defect identification. In particular, when decreasing the PL measurement temperature the energy peak position of the V_{O}-related band decreases while that of V_{Zn} increases. Secondly, phonon replicas are clearly observed in the DBE spectra in the sample containing V_{Zn}. Finally, the characteristics of the DBE decay time for V_{Zn}- and V_{O}-enriched samples are also different. Specifically, for the V_{Zn}-enriched sample the decay curves show strong wavelength dependence and generally slower decay components as compared to the sample enriched with V_{O}.

PACS: 71.55.Gs; 78.55.Et; 61.72.Cc; 61.72.Ji

Keywords: A. Semiconductors; C. Point defects; E. Luminescence

1. Introduction

Zinc oxide (ZnO) is a wide band gap semiconductor exhibiting many interesting properties making it promising for optoelectronic devices. To mention a few of these properties, ZnO has a direct band gap (3.37 eV at room temperature) and shows more resistance to radiation damage than Si and GaN. In addition, ZnO has the strongest exciton binding energy (about 60 meV) making the excitons thermally stable at room temperature (RT). Accordingly, ZnO has a significant advantage for ultraviolet (UV) lasing applications. Recently, Wei et al. fabricated ZnO blue–violet light-emitting diodes (LED) using p–n homojunctions [1], Ryu et al. demonstrated UV photodiodes [2] and Tsukazaki et al. have also managed to fabricate a UV LED [3]. At low temperature there are 10 prominent photoluminescence (PL) lines observed (I_1–I_{10}) from high quality ZnO layers [4]. Some of them have recently been ascribed to H (I_4), Al (I_6), In (I_9) and Ga (I_8) [5, 6]. It has also been shown that defects in ZnO give rise to the green luminescence band or deep band emission (DBE), literally the emission band between 420 and 700 nm [7–34]. It is surprising that even though the DBE has been intensively studied, its origin is still a matter of discussion. To explain the nature of the DBE in ZnO many different models have been proposed. For example, Reynolds et al. [7] suggested that a deep acceptor is involved, but did not determine its nature. Dingle [8] and also Garces et al. [9] correlated the DBE with extrinsic impurities such as Cu. Studenikin et al. [10] observed a broad green band centered at 2.43 eV and attributed it to an oxygen vacancy (V_{O}) consistent with identification by several other groups [11–24]. Among other candidates assigned to explain the DBE are interstitial Zn and O (Zn_i &

---

[*] Corresponding author. Tel.: +46 317722097.
E-mail address: peter.klason@physics.gu.se (P. Klason).

0038-1098/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ssc.2007.10.036

O_i) [18,24–26], Zn vacancy (V_{Zn}) [27–33] and the O antisite (O_{Zn}) [34]. Theoretical calculations have also been performed to provide the energy levels, formation energy etc. of the different defects in ZnO [19,30,35–37]. Özgür et al. suggested in their review paper that the DBE could consist of several PL bands having different origins placed at similar positions [38]. Indeed, Moe Børseth et al. have recently assigned the V_O, V_{Zn} and Li related PL bands contributing to the DBE preferentially at different wavelength [39]. However, the identification was made measuring PL at RT only and more studies are necessary to support the identification.

In this paper we present decay time and temperature dependent PL measurements of V_O- and V_{Zn}-related bands predetermined by annealing hydrothermally grown single crystal ZnO in zinc- and oxygen-rich atmospheres. It is shown that the V_O- and V_{Zn}-related PL signatures exhibit strongly different temperature dependences. Furthermore, we show that the characteristics of decay times from the emission band related to V_O and V_{Zn} are very different versus detected wavelength. The decay time of the V_O-related emission has negligible effect versus the detected wavelength and the decay time of the V_{Zn}-related emission strongly depends on the detected wavelength. These features promote identification of the V_O- and V_{Zn}-related defects in ZnO.

2. Experimental details

The ZnO bulk samples used in this investigation were nominally undoped, 0.5 mm thick and 1×1 cm^2 n-type wurtzite (0001) single crystal ZnO wafers. The wafers were highly resistive (~2 kΩ cm), polished on both sides and provided by ZnOrdic AB. In all wafers, Li was the major impurity with a concentration around 5×10^{17} cm^{-3}. All measurements were done on the O face. The as-grown samples were isochronically (1 h) annealed at 500–1050 °C in the presence of ZnO powder, metallic zinc, pure oxygen or air. All annealings, except air, were done in closed quartz ampoules filled with the corresponding gas/powders. In the case of air the annealing was performed in an open furnace. The ZnO powder (grain size ~ 1 μm) as well as the metallic Zn were ~99.9% pure. The sample surface topography and crystalline quality were monitored by x-ray diffraction and atomic force microscopy [40].

Photoluminescence measurements were performed between 27 K and RT using a 350 nm laser line from an Ar$^+$ laser as the excitation source. In order to disperse and detect the ZnO emission a double grating monochromator and photomultiplier detector were used. The laser operated at 150 mW. We estimated the photon penetration depth to ~50 nm for a relative intensity of 1/e, applying an absorption coefficient of $\sim 2 \times 10^5$ cm^{-1} [41]. It was also assumed that the concentration of optically active defects is homogenous throughout the layer of optical interaction. The PL emission decays were measured using two different systems covering decay times from 1 to 10^5 ns. The first is a streak camera in a slow scan mode, using femtosecond excitation pulses with 250 kHz repetition rate obtained from an amplifier after a modelocked Ti:sapphire laser. The time resolution of this system is below 1 ns. The second system uses a frequency doubled diode-pumped YAG laser with a 40 ns pulse width and tunable frequency. This method utilizes photocounting for the detection and the time resolution is limited by the laser pulse width. The repetition rate used was 120 μs.

3. Results

For clarity, we focus our discussion in the present paper only on anneals at $T > 800$ °C because RT measurements were discussed in detail in [39]. The RT measurements showed that for temperatures above 800 °C the DBE peak position strongly depends on the annealing ambients. There are three distinct levels appearing for the DBE maxima, for a Zn-rich atmosphere around 2.53 ± 0.05 eV, for an O-rich atmosphere around 2.35 ± 0.05 eV and for ZnO powder around 2.17 ± 0.05 eV [39]. The samples annealed in air exhibit similar DBE behavior to the samples annealed in O_2. Annealing in O-rich conditions, e.g. in O_2, should increase the concentration of V_{Zn}, O_i and O_{Zn}, decreasing the concentration of V_O, Zn_i and Zn_O accordingly. However, some of these defects give rise to shallow levels, such as Zn_i [42] and O_i [37], whereas others have high formation energy, such as Zn_O and O_{Zn} [30]. Hence, it is unlikely that these defects make a significant contribution to the DBE signal, leaving V_{Zn}-related defects to be responsible for the DBE peak at 2.35 ± 0.05 eV. In a similar manner the 2.53 ± 0.05 eV DBE peak was attributed to emission from V_O-related defects. The defect level at 2.17 ± 0.05 eV, giving rise to the yellow emission, was attributed to Li [39].

Fig. 1(a) and (c) shows typical examples of UV parts of the PL spectra as measured at 27 K for samples annealed at around 900 °C (solid line) and at 1050 °C (dashed line) in an O-rich (a) and Zn-rich atmosphere (c). Both the V_O-enriched samples, Fig. 1(c), exhibit an exciton emission peak located at around 3.35 eV, but only the sample annealed at 900 °C shows some phonon replicas. The exciton emission peak is also present in the V_{Zn}-enriched samples, Fig. 1(a); however, there is an additional peak centered at 3.26 eV. For the samples annealed at 900 °C there is also a peak centered at 3.32 eV. The corresponding DBE emission spectra for the same samples are shown in Fig. 1(b) and (d). The V_{Zn}-enriched samples show well-developed phonon replicas in the DBE part of the spectrum in contrast to the V_O-enriched samples.

Fig. 2(a) shows a comparison of the DBE peak positions measured at 27 K for both the V_{Zn}-enriched (squares) and V_O-enriched (triangles) samples as a function of annealing temperature. The corresponding levels at RT are shown as dashed lines. The DBE peak positions are obtained by fitting gaussian functions to the PL data and take the center position of the sum of the gaussians, in order to reduce the influence of the phonon structures at low temperatures. Otherwise, without phonon structures, the gaussian fitting is not necessary. Firstly, a characteristic trend is observed when measuring V_O- and V_{Zn}-related DBE signatures at 27 K from the samples annealed in Zn- and O-rich conditions (Fig. 2(a)). As seen from Fig. 2(a) the V_O-related band is shifted from 2.53±0.05 eV to around 2.47±0.04 eV and the V_{Zn}-related band is shifted from 2.35±0.05 eV