Available online at www.sciencedirect.com
ScienceDirect
Superlattices and Microstructures 42 (2007) 270–277
Superlattices and Microstructures
www.elsevier.com/locate/superlattices

Photoinduced excess carrier dynamics in PLD-grown ZnO

P. Queiroz[a], R. Ayouchi[a], M. Niehus[b,*], E. Morgado[c], A. Fedorov[d], J. Martinho[d], F. Wuensch[e], M. Kunst[e], R. Schwarz[a]

[a] *Departamento de Física, Instituto Superior Técnico (IST), Av. Rovisco Pais 1, 1049-001 Lisbon, Portugal*
[b] *Departamento de Engenharia de Electrónica e Telecomunicações e de Computadores, Instituto Superior de Engenharia de Lisboa, Rua Conselheiro Emídio Navarro 1, 1959-007 Lisbon, Portugal*
[c] *Departamento de Engenharia de Electrónica, IST, Av. Rovisco Pais 1, 1049-001 Lisbon, Portugal*
[d] *Centro de Quimica-Fisica, IST, Av. Rovisco Pais 1, 1049-001 Lisbon, Portugal*
[e] *Solare Energetik, Hahn-Meitner Institut Berlin, Germany*

Available online 1 June 2007

Abstract

ZnO shows a number of similarities with other wide gap semiconductor materials as, e.g., GaN as far as photoluminescence and photoconductivity are concerned. Depending on film quality a broad luminescence band is found in the yellow and/or green spectral region apart from a narrow excitonic line. This study focuses on the observation of non-exponential photoinduced carrier density decay in ZnO.

We have deposited thin polycrystalline ZnO films on sapphire by a cyclic pulsed laser deposition process. We extracted a room temperature band gap of 3.31 eV from absorption spectroscopy measurements, and found evidence for strong sub gap Urbach tails.

Photocurrent transients were measured upon pulsed laser excitation at 532 and 266 nm and compared with transient microwave conductivity decay upon excitation at 355 nm. Both measurements yield power-law decay with an exponent from −0.3 to −0.4. In addition, ps-pulses were used to monitor the initial photoluminescence decay near the bandgap.

We have already observed similar power-law behaviour in polycrystalline GaN films prepared by the same PLD reactor. The interpretation will consider the hypothesis of minority carrier capture and a model invoking thermalization in broad band tail distribution with delayed subsequent recombination during the decay.

Keywords: ZnO; Transient photocurrent; Transient photoluminescence; Thermalization; Recombination

* Corresponding author. Tel.: +351 21 831 7287; fax: +351 21 831 7114.
E-mail address: mniehus@deetc.isel.ipl.pt (M. Niehus).

0749-6036/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.spmi.2007.04.061

1. Introduction

The recent improvement of material quality and in particular the successful p-doping have made of zinc oxide (ZnO) one of the most promising materials to achieve efficient commercial UV LEDs and laser diodes, mainly on account of its large exciton binding energy of 60 meV. The wide gap oxides share with their wide gap nitride "cousins" many of the difficulties that prevented up to now the synthetization of ultra high quality crystals. An important point is that substrate materials exhibit a large degree of lattice and thermal mismatch, resulting in films with a high density of structural defects, increasing hence the density of electronic states in the forbidden band gap and taking part in the ubiquitous yellow–green luminescence (YB) present in most of the deposited ZnO films [1].

Transient measurements of photoluminescence and photocurrent are an important tool to study the excess carrier relaxation dynamic in order to gain insight into the electrical activity of the defects.

In this report, we present results on absorption spectroscopy and transient photoluminescence (TPL) and transient photoconductivity (TPC) of polycrystalline ZnO films deposited by Pulsed Laser Deposition (PLD). The questions addressed include the correlation between TPL and TPC and the importance of carrier trapping on the signal decay.

2. Sample preparation

Polycrystalline ZnO films of thicknesses of about 500 nm have been grown on sapphire by means of a low-temperature cyclic pulsed laser deposition process. The growth of ZnO thin films takes place in a stainless steel deposition chamber, with the substrate fixed "face down" on a grounded Molybdenum (Mo) holder. Radiation heating of the substrate holder is achieved by applying an AC voltage to two tungsten (W) coils. In front of the substrate holder (ground electrode), an R.F. counter-electrode is placed at 3 cm distance. A Mo or ceramic crucible is mounted on top of the RF electrode and filled with ZnO (99.99% purity) to serve as the ablation target. Typical substrate temperatures were between 400–600 °C, at base pressures of about 10^{-7} mbar. We used the fundamental line of a pulsed Nd-YAG at 1064 nm, with a fluence of 15 J/cm^2 at a repetition frequency of 5 Hz. The substrate was pre-treated by plasma etching, and no buffer layer was used.

3. Experimental details

Conventional optical (VIS–UV) reflection/transmission spectroscopy was used to determine the spectral optical absorption coefficient α. The results served as input to calibrate the sub gap absorption found from photothermal deflection spectroscopy (PDS) and photocurrent spectroscopy (PCS). While the former is a measure of the spectral non-radiative recombination rate, the latter measures the optical generation rate to free states times the mobility-lifeime product.

Time-resolved picosecond fluorescence intensity decays were obtained by the single-photon timing method with laser excitation. The apparatus consisted of a mode-locked Coherent Inova 400-10 argon-ion laser that synchronously pumped a cavity dumped Coherent 701-2 dye laser, delivering 5 ps pulses (with about 20 nJ/pulse) at a repetition rate 1.7 MHz. The excitation wavelength was 295 nm (4.2 eV), and the pulse intensity on the sample did not exceed 15 kW/cm^2. Spectral resolution of the detecting system was 30 nm (0.28 eV). The dye laser output beam was frequency doubled in BBO crystal with an efficiency 5% (about