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Characterization of Optical and Photoelectrical Properties of ZnO Crystals

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We characterized optical and photoelectrical properties of undoped and Ga-doped ZnO layers differently grown on sapphire substrates by using complementary optical methods. Different stimulated emission threshold values for ZnO epitaxial layers grown by pulsed laser deposition and MBE methods were attributed to crystalline quality of the layers and the growth method used. Different carrier lifetimes in various ZnO epitaxial layers are explained by defect-related and intrinsic mechanisms of recombination.

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1. Introduction

ZnO has attracted quite much attention due to its unique optical, piezoelectric, magnetic properties, and potential applications as light-emitting devices [1, 2]. An extremely high exciton binding energy (60 meV) [1–3] allows to observe exciton emission at high temperature. The stimulated emission (SE) in ZnO epitaxial layers was observed not only at room temperature (RT), but even at 550 K and was attributed to exciton–exciton collision (P-line) or electron–hole plasma (EHP) [1, 4].

In this paper, we report on optical and photoelectrical properties of differently grown ZnO heterostructures under strong optical excitation conditions. The photoluminescence (PL), free carrier absorption (FCA), and transient grating (TG) techniques were used to investigate carrier dynamics which revealed various features of recombination processes of these layers.

2. Experimental details

The experiments were carried on a set of ZnO thin layers grown by pulsed laser deposition (PLD) and molecular beam epitaxy (MBE) techniques on a sapphire substrate. PLD growth provided ≈ 1 μm thick n-type ZnO layers with residual electron density of about 10^{17} cm^{-3} or Ga doped ($n_0 = 10^{18}$ cm^{-3}). ZnO layers of ≈ 650 and ≈ 340 nm thicknesses were grown by MBE, depositing the layer directly on sapphire or on GaN buffer layer.

Low excitation PL measurements were carried out using a CW semiconductor laser of few μW power at $\lambda = 340$ nm and a CCD camera, while a picosecond pulsed laser ($\lambda = 266$ nm, pulse duration 25 ps) was used as an excitation source for room temperature PL measurements. In the latter case, maximum excitation energy density was 5.5 mJ/cm^2.

A time-resolved picosecond TG and FCA techniques were used to monitor the injected carrier density decay and determine the carrier lifetime values τ_R. FCA decay in MBE-grown layers was measured under $\lambda = 351$ nm excitation by a picosecond YAG laser. Dependence of carrier recombination rates vs. excitation and direct lifetime measurement in PLD grown ZnO were performed by TG technique. To record the grating, an interference pattern of two $\tau = 7$ ps duration laser beams with wavelength $\lambda = 351$ nm ($h\nu = 3.53$ eV) was used to create a modulated free-carriers spatial distribution (i.e. a transient free-carrier diffraction grating [5]). The grating decay was probed by a weakly absorbed beam at $\lambda = 1064$ nm which propagated through the sample and created a diffracted pattern behind the sample.

3. Results and discussion

Figure 1 shows the typical PL spectra of PLD-grown ZnO layers measured under low excitation regime at RT. The PL spectra consist of two bands: a sharp band related to near band edge (NBE) UV emission and a broad green luminescence (GL) band related to radiative recombination via deep defect/impurity levels. The "blue" shift of NBE band in Ga-doped ZnO layers in comparison with ZnO layers is explained by the Burstein–Moss effect due to higher concentration of free carriers [6, 7]. Lower PL intensity in the doped layer is probably caused by additional centers of nonradiative recombination.

The dependence of NBE band spectra on excitation energy density was investigated in the ZnO layers grown by PLD (Fig. 2) and MBE [8] methods at RT. At the lowest excitation, the emission of exciton–exciton scattering (so-called P-line at ≈ 3.26 eV) was observed. The further increase of excitation energy density revealed EHP emission at ≈ 3.15 eV [9]. We attributed the broadening

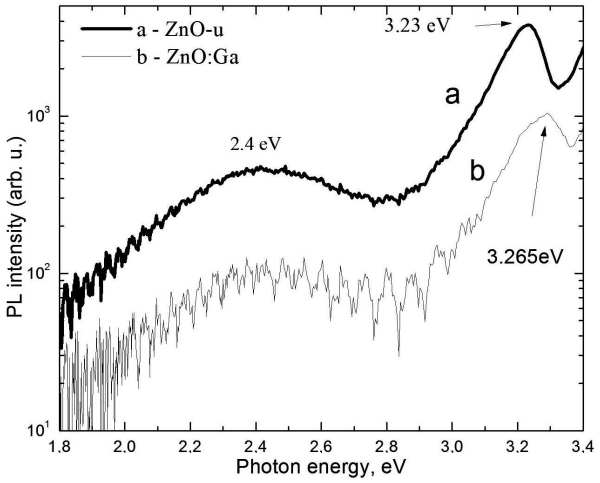

Fig. 1. PL spectra of the undoped ZnO (a) and Ga--doped ZnO epitaxial layers (b).

of the EHP band and shift of the PL spectra maximum to lower energy ("red" shift) with increase of excitation energy density (see Fig. 2b), to band gap renormalization [10].

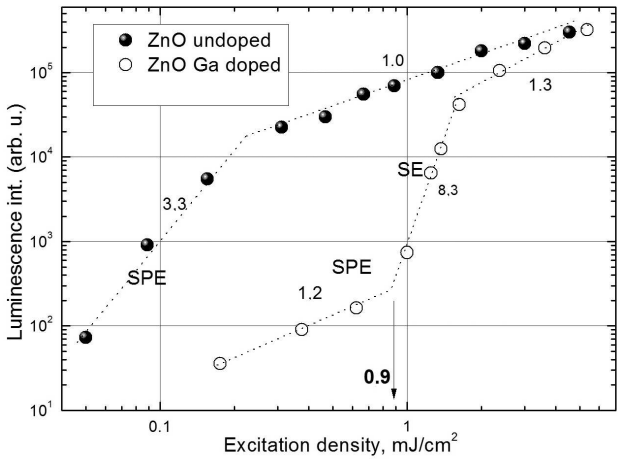

Fig. 3. NBE PL intensity dependence as a function of the excitation energy density in PLD ZnO layers.

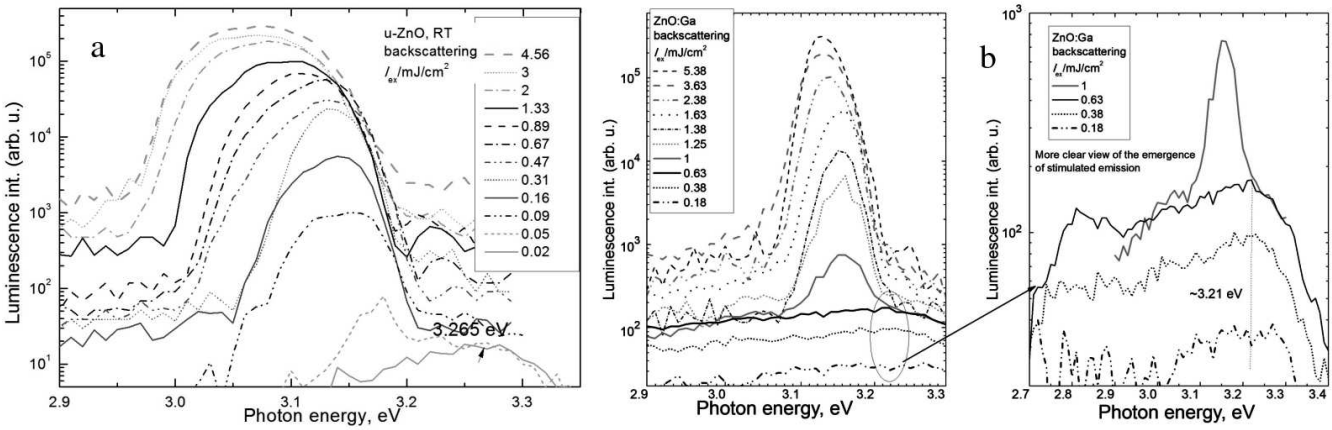

Fig. 2. PL spectra of undoped ZnO (a) and Ga-doped ZnO (b) layers grown by PLD method as a function of excitation energy density. A zoomed section of the part (b) shows the spontaneous PL emission with more details.

A wide PL band located at 2.4 eV is known for decades and is called as GL band, however, its specific interpretation still remains controversial. The most probable mechanisms of radiative recombination are noticed impurities related with copper or oxygen vacancy [2] however we concentrate our attention on NBE emission.

Dependence of the NBE PL intensity on excitation energy density in ZnO layers grown by PLD is shown in Fig. 3. It can be seen that within a certain excitation energy density interval PL intensity of both doped and undoped PLD ZnO layers increases superlinearly with further saturation tendency when excitation energy density is increased. However, in the undoped PLD ZnO layer the contribution of SE is not so clearly expressed showing lower value of the dependence index (3.3 in undoped and 8.3 in Ga-doped ZnO, see Fig. 2a and Fig. 3). Besides, undoped ZnO exhibits considerably lower threshold (≈ 0.05 mJ/cm^2) in comparison with doped sample (≈ 0.9 mJ/cm^2). We explain this feature by a possibility to inject higher density of carriers in undoped ZnO in comparison with Ga-doped ZnO due to higher nonradiative recombination rate in the latter case. The NBE PL band broadening under high excitation (see Fig. 2a) can be explained by accumulation of higher densities of carriers and strong saturation of optical gain [9] in this sample, as well. Let us note that the threshold of SE at 3.15 eV in the MBE-grown layers is around 0.2 mJ/cm^2 which is lower in comparison with Ga-doped ZnO due to lower concentration of intrinsic defects in MBE-grown ZnO layers.

The measurement of diffraction efficiency $\eta \propto I_0^2$ as a function of excitation energy density I_0 in ZnO lay-

ers revealed linear carrier recombination rates at $I_0 < 1$ mJ/cm^2, while above this value the diffraction efficiency exhibited a tendency of its saturation. The latter effect is due to essential decrease of carrier lifetime at reaching the SE threshold of ≈ 1 mJ/cm^2 (a similar effect was seen in GaN, see Fig. 2 in Ref. [5]). Time-resolved kinetics of TG decay directly provided carrier lifetimes in the undoped and doped PLD ZnO layers (Fig. 4). We note that lifetime in the undoped layer decreased at higher excitation (from ≈ 38 ps to ≈ 12 ps), while in the doped layer the lifetime was comparable (or even shorter) than the duration of the laser pulse (≈ 7 ps).

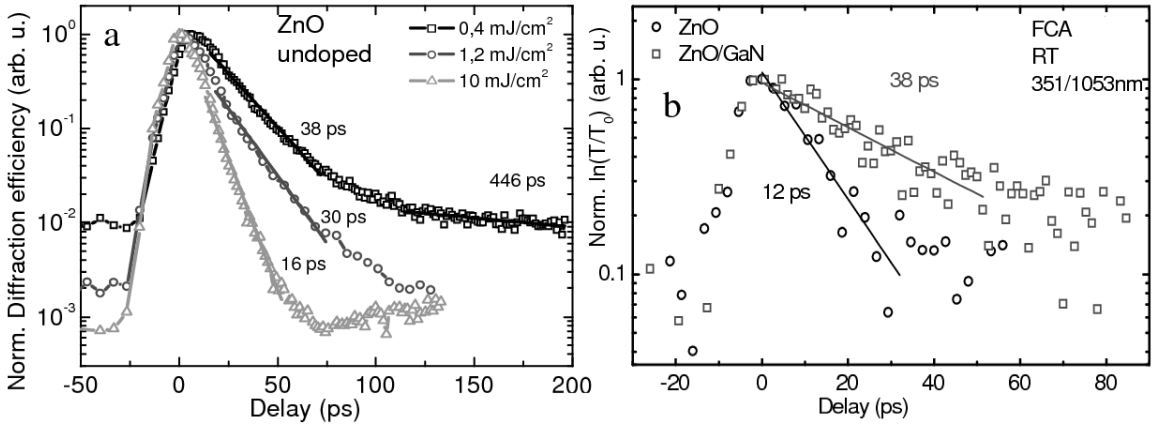

Fig. 4. Transient grating decay kinetics in PLD-grown undoped ZnO layer (a). FCA decay for two MBE-grown ZnO layers (with and without GaN buffer layer) (b).

Free carrier absorption decay in MBE-grown ZnO films with and without the buffer layer are shown in Fig. 4b at $\approx$ 1–2 mJ/cm^2 excitation energy density. The film without buffer layer exhibited shorter lifetime than the other one with the GaN buffer. It is known that a big lattice mismatch between the ZnO and the sapphire (18%) introduces structural defects as misfit dislocations and twin domains. On the other hand, the smaller lattice mismatch due to GaN buffer reduces the density of interface defects. Moreover, XRD measurements have shown that the layer with the buffer has four times smaller FWHM value than the layer grown directly on sapphire [8]. Consequently, we can attribute 4-fold longer carrier lifetime of the buffered ZnO layer to lower concentration of carrier trapping defects.

4. Summary

Using complementary optical methods, we investigated ZnO layers growth by PLD and MBE techniques. The lower stimulated emission threshold in undoped ZnO layers (≈ 0.05 mJ/cm^2) and in the MBE-grown ZnO layers (≈ 0.2 mJ/cm^2) in comparison with the PLD-grown Ga-doped layers (≈ 0.9 mJ/cm^2) is explained by higher density of intrinsic defects in the latter case, as confirmed by the directly measured carrier lifetimes. The determined threshold value of stimulated emission in the PLD-grown ZnO layer correlated well with the essential decrease of carrier lifetime reaching the SE threshold. Presence of the GaN buffer layer in MBE-grown ZnO thin films exhibited increase of free carrier lifetime up to ≈ 40 ps due to smaller lattice mismatch.

Acknowledgments

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