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Temperature-dependence of cathodoluminescence of zinc oxide monolayers obtained by atomic layer deposition

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We performed cathodoluminescence (CL) investigations of zinc oxide monolayers obtained by atomic layer deposition. Layers of different thickness were deposited on commercial GaN/sapphire templates. Scanning electron microscopy (SEM) system equipped with CL allows direct comparison of SEM images and CL maps, taken from exactly the same areas of samples. In addition to SEM and CL images, CL profiling was performed by collecting the CL spectra at different accelerating voltages. The CL profiling allows to distinguish the emissions from a surface and volume of samples. An inter-link between samples microstructure and emission properties is investigated. Shifts of emission bands, associated by us with the localization effects, are observed. CL investigations are supported by photoluminescence (PL) measurements, which are characterized by a higher spectral resolution. PL investigations allow determination of the origin of emission bands.

Keywords: zinc oxide, cathodoluminescence, profiling, temperature-dependence, localization.

1. Introduction

Zinc oxide is extensively studied in recent years [1, 2]. It has a direct energy gap of about 3.37 eV at room temperature and high transparency in visible light spectral region [1]. Importantly, modern growth techniques, such as atomic layer deposition (ALD), allow control of ZnO electrical properties in a wide range, which is crucial for many of applications [3]. Due to these properties, ZnO is an attractive material for appli-

cations in photovoltaic [4], electronic [5] and optoelectronic [4] devices. It was already demonstrated that ZnO can be applied in, *e.g.*, solar cells [4], transparent transistors [6], or in chemical sensors [7].

CL investigations of ZnO were performed by several groups (see, *e.g.*, [8]). For example, we recently presented 5 K cathodoluminescence (CL) of ZnO monolayers obtained by the ALD technique at fairly low growth temperature of 300 °C [9]. We compared CL emission of layers obtained on different substrates. These investigations allowed studies of relaxation process observed along the growth direction [10]. Measurements of CL depth profiling were also performed [11].

In this work we analyze new results of CL investigations of ALD-grown ZnO monolayers (grown on GaN templates). Layers of different thickness are investigated. Despite of a fairly low growth temperature ALD-grown samples are characterized by a high quality. Intensive band edge emission is detected, which allows detail CL depth profiling investigations. We study shifts of emission bands, which are associated by us with the localization effects. CL depth profiling allows also determination of dopants distribution.

2. Measurements

In our investigation we used Hitachi SU-70 scanning electron microscopy (SEM) system, equipped with GATAN MONO CL3 system. This allows a direct comparison of SEM images and CL maps, taken from exactly the same areas of samples. The system is equipped with liquid helium cryostat, working in the temperature range of 5 to 300 K. In addition to conventional CL study, we also performed CL depth profiling, by collecting CL spectra at different accelerating voltages (see reference [11] for explanation). From CL depth profiling we can distinguish between the emission bands induced from samples surface and volume. For example, we calculated that for ZnO the accelerating voltages of 5 kV and 15 kV are optimal for excitation of CL emission from a depth of 50 nm and 200–500 nm, respectively. CL depth profiling and temperature dependence of CL spectra allow us to determine an interlink between samples microstructure and emission properties.

Since CL has a limited spectral resolution, CL investigations were supported by low-temperature photoluminescence (PL) measurements, which allow a better spectral resolution.

PL measurements were performed at a temperature of 15 K, with samples mounted in a cryostat Leybold RD580. For excitation we used PLASMA HeCd HCCL-15UM (325 nm) laser. PL was detected with HORIBA Jobin–Yvon FHR1000B system equipped with a CCD detector.

3. Results and discussion

We present here the results for two ZnO monolayers obtained by the ALD technique. Samples were deposited on GaN/sapphire templates at 300 °C. Details on samples

growth are given in [9]. The growth parameters were identical. The only difference was the number of the ALD cycles. Thus, the samples differ only in a thickness – the first sample (labeled here as A) has 1 μm thickness, the second (sample B) – 2 μm thickness.

3.1. Sample A

Figure 1 shows high resolution PL spectra for the sample A in the band edge luminescence region. Based on the analysis given in work [12], we attribute PL spectra to excitonic emission bands I_1, I_3 and I_8 (related to Ga dopant) and the corresponding two-electron satellite (TES) transitions [13]. In the TES process a donor bound exciton decays at the energy lowered by donor excitation [13]. The experimental lines in Figs. 1 and 4 differ from the Gaussian lines, so we do not expect a good match between

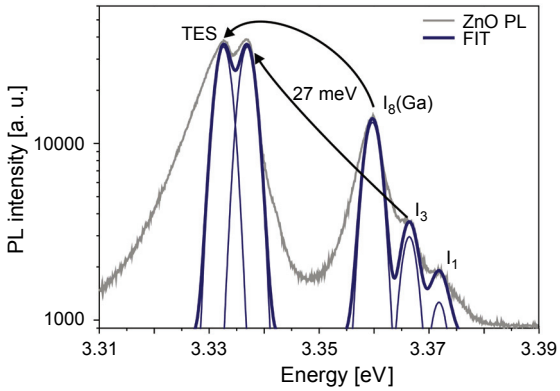

Fig. 1. PL spectra for the sample A of 1 μm thickness.

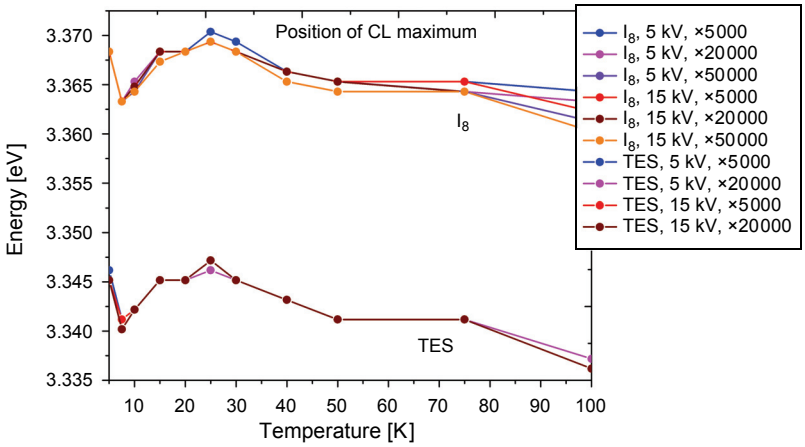

Fig. 2. Temperature dependence of I_8 and TES emission CL maxima for the sample A. Measurements were performed at two different accelerating voltages and three different magnifications.

fits and experimental data. The fits only indicate the peaks positions and should be treated as a guide to the eye. Free exciton emissions are not observed for this sample. Surprisingly, the TES emissions dominate the spectra. Intensive TES transitions were also observed for GaN epilayers [14]. We suppose that this reflects strong localization effects and stress conditions in the layer, but this point needs further investigations.

To verify the strength of localization effects, we looked for temperature dependence of spectral positions of CL lines. The relevant results (from the CL investigations) for the sample A are shown in Fig. 2. We first looked if a typical S-shape dependence is observed and then performed measurements for different excitation densities (by changing magnification ratio).

Figure 2 shows classical S-shape behavior of emissions spectral position, observed at low temperature. At low temperature carriers and excitons are localized by potential fluctuation in a layer. Slight increase in temperature results first in carriers/excitons redistribution to deeper potential wells. Then, for a further increased temperature they gradually redistribute among potential wells (emission shifts towards a higher energy) until fully delocalized carriers and excitons participate in emission processes. Thus, S-shape dependence of PL(T) is commonly explained by strong carriers/excitons localization effects, as discussed previously in many cases, see, *e.g.*, [15]. We also notice that similar shifts of emissions are observed in CL spectra taken at different magnifications, *i.e.*, different excitation densities. This observation supports our statement on a strong localization. The energy difference between I_8 excitonic luminescence and corresponding TES luminescence is approximately 27 meV for each temperature, which proves that it is really two-electron satellite transition.

Figure 3 compares SEM image and CL maps for the I_8 excitonic emission and corresponding TES band for two temperatures. At 5 K we can see that some of I_8 emission fluctuations do not correspond to a sample microstructure. We believe that such fluctuations of CL intensity are correlated with a nonuniform distribution of Ga dopant. In measurements performed at higher temperatures (*e.g.*, 50 K, see Fig. 2) the emission becomes more in-plane uniform. This reflects carriers delocalization and larger diffusion length. Then, fluctuations of CL intensity gradually disappear and CL maps reflect samples microstructure. Surprisingly, a slightly different behavior shows the TES emission band. In the range of 5–50 K the fluctuations of CL intensity

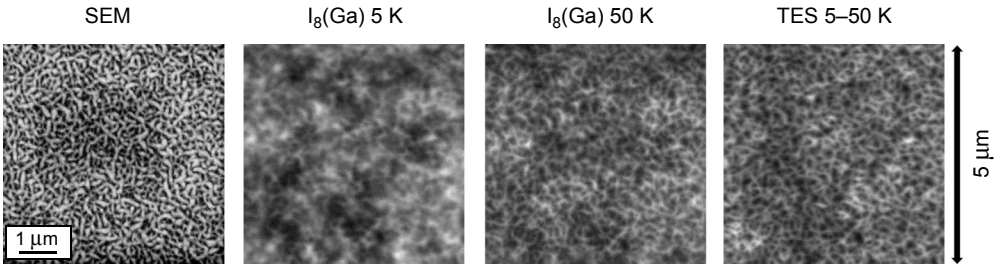

Fig. 3. Sample A, SEM image and CL maps for different measurement temperatures for I_8(Ga) and TES emission bands.

are almost the same. The fluctuations do not exactly correspond to the ones observed for the I_8 emission. This observation indicates that not only dopants distribution affects TES emissions.

3.2. Sample B

The sample B is 2 μm thick ZnO monolayer, grown at the identical conditions as the sample A. The first important difference is already observed in the PL investigations. We observe (see Fig. 4) the free excitonic luminescence, not resolved for the sample A.

Moreover, in the spectra shown in Fig. 4 we identify the I_4 (related to H dopant [12]) band, not seen previously. The I_8 (related to Ga dopant) still dominates the PL spectrum, but corresponding TES emission bands are much weaker. The fact that intensity of TES emission bands is much lower, suggests important influence of stress condi-

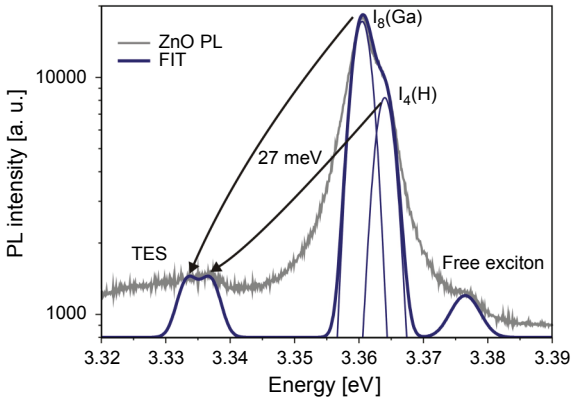

Fig. 4. PL spectra for the sample B of 2 μm thickness.

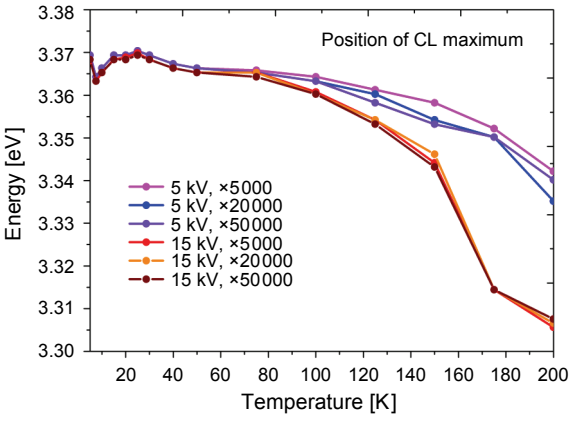

Fig. 5. Temperature dependence of I_8 emission CL maximum for the sample B. Measurements were performed at two different accelerating voltages and three different magnifications.

tions. From our previous investigations [10] we conclude that in the sample B stress is more relaxed. Likely different stress conditions affect intensity of the TES transitions, but this observation needs further investigations.

We also verified if localization effects in the sample B are similar as the ones in the sample A. For this we performed CL investigations in the temperature range of 5–150 K.

The classical S-shape behavior, similar as for the sample A, is seen in Fig. 5. This means that strong carrier localization effects are also present for this monolayer. However, localization is now weaker that in the sample A. This we conclude from quite different temperature dependences observed in the CL spectra taken at higher magnifications (different excitation densities). Figure 5 indicates that for increased excitation densities (CL taken at higher magnification) a much stronger temperature dependence of CL position is observed, the one expected for delocalized carriers/excitons. Thus, from CL measurements at different magnifications (*i.e.*, different excitation density) we conclude that localization is weaker in the thicker sample. This is indication that lattice mismatch and strain relaxation affect strength of localization in ZnO layers.

Moreover, we observe that CL position at 5 kV is shifted relative to CL observed at 15 kV accelerating voltage, independently of the magnification. This observation indicates that stress is not fully relaxed in depth of the sample and that the stress conditions vary in depth of the sample. This is observed, despite of good quality of a sample, confirmed by a presence of free exciton emission band.

SEM image (Fig. 6) confirms a columnar growth of a sample, as we observed from SEM cross-sections not shown here. The comparison of SEM and CL maps indicates a direct link between the microstructure of the sample and CL intensity fluctuations. The CL map for I_8(Ga) emission band reflects a microstructure of a sample. We do

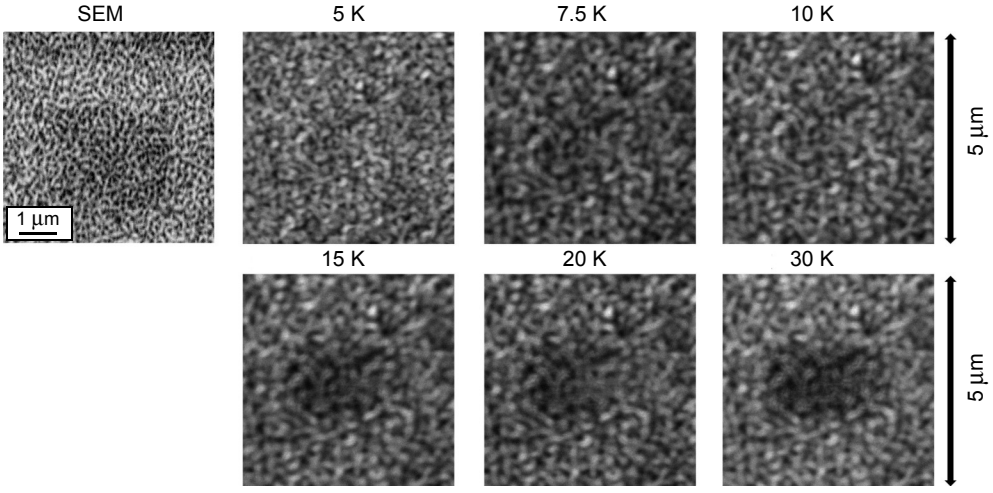

Fig. 6. Sample B, SEM image and CL maps of I_8(Ga) emission band measured at different temperatures. Maps were taken at 5 kV accelerating voltage.

not observe large intensity fluctuation, which indicates that Ga is more uniformly distributed in the thicker film.

4. Conclusions

The CL studies show a very strong interlink between samples microstructure and optical properties. Good quality of the ALD-grown films is confirmed by observation of intensive band edge emissions of excitonic origin, followed by phonon replica and two-electron satellite transitions. Importantly deep defect related emissions are not observed. CL maps at 5 K show high influence of local potential fluctuations on emission bands, which was confirmed also by the presence of S-shape behavior in temperature-dependence measurements. This effect disappears at higher temperatures. TES emission band dominates PL in the sample A, but is weak in the sample B. We tentatively propose that the intensity of this emission band is connected with the stress conditions in the ZnO layer. CL depth-profiling shows that localization effects are also present in the sample B, which is not totally relaxed despite of its thickness of 2 μm.

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