



# Gas sensitive luminescence of ZnO coatings obtained by plasma electrolytic oxidation



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## ABSTRACT

The ZnO coatings on Zn substrate were obtained using plasma electrolytic oxidation method. The XRD and SEM methods were used for structural and morphological characterization of obtained coatings. The luminescence of ZnO coatings were studied and compared with luminescence characteristics of ZnO single crystal. It is shown that luminescence intensity in ZnO defect band depends on oxygen concentration in ambient atmosphere. The effect is of interest for oxygen sensing based on ZnO coating luminescence.

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## 1. Introduction

Variety of different types of ZnO is known: single crystals, thin films, powders (including nanopowders), ceramics. ZnO receives huge attention due to its unique properties, for example fast near-band excitonic and donor–acceptor luminescence (DAP) [1,2], intensive “green” luminescence [3–5] and ability to produce transparent conductive films [6]. In recent years, a huge progress was made in development of technological processes for ZnO based nanostructured system synthesis, which is great for various applications used in different devices. Most comprehensive information about the ZnO properties and devices can be found in [7].

At low temperature (12 K) the spectra of near-band photoluminescence in samples with acceptor centres shows emission from the exciton (Ex) bound at neutral donor ( $\text{ExD}^0$ ), its phonon replicas (LO  $\text{ExD}^0$ ) and DAP band. At room temperature (RT) (294 K) the 1LO Ex is the main luminescence band in undoped ZnO crystals. The near-band luminescence decay is fast. For exciton radiative recombination the lifetime estimation in different papers gives biexponential decay function with two time constants: 10 ps–30 ps for the fast component and 100 ps–20 ns for the slow component [1,2,8]. As a general rule, the near band luminescence intensity and defect band intensity are inversely proportional—in high-quality ZnO the near band luminescence intensity is high and phonon replicas are resolved, but the intensity of defect band is low.

The defect band is wide luminescence band in spectral region 450–700 nm. The peak position depends on sample doping and nonstoichiometry. As an example, the luminescence with maxima at 2.45 eV (“green” luminescence) was observed in high-purity undoped ZnO crystals. The different models are suggested for the “green” luminescence: Cu doping and zinc or oxygen vacancies ( $V_{\text{Zn}}$  and  $V_{\text{O}}$ ) [7 and references therein]. The luminescence peak position of Cu centers is at 2.45 eV and it is close to that observed in high-purity ZnO samples. However, there are some characteristics (for example, exponential decay, phonon structure) [9] that allow us to distinguish the Cu associated luminescence and ZnO native defect ( $V_{\text{Zn}}$  and  $V_{\text{O}}$ ) luminescence. Another common model of “green” luminescence is the donor–acceptor pair (DAP) recombination, where the donor centre is  $V_{\text{O}}$ . The origin of 2.45 eV luminescence is not clear up to now despite the fact that the “green” luminescence was extensively studied [3,10,11]. The luminescence intensity of this band depends on the sample stoichiometry, thermal annealing regimes, sample morphology and other factors. It was shown in [12] that the “green” luminescence intensity increases if during sample oxidation process the oxygen partial pressure in atmosphere was decreased, which means that the oxygen vacancy may be involved in luminescence processes. However, the authors do not consider that “green” luminescence is due to  $V_{\text{O}}$ .

Nanostructured materials have high specific surface area and grain boundaries contain several disordered monolayers [13,14]. Thus the defect concentration within grain boundaries is high and could determine the properties of nanostructured material [14,15]. Since the vacancies and the other defects are located mainly near the free surfaces and within boundaries of grains, the luminescence

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of nanostructured ZnO as well as its correlation with ambient atmosphere can be studied. During the gas adsorption the defect luminescence intensity changes since the molecules are incorporated in defect states or bounds near these states. The effect of gas or gas mixture sensing is observed and studied for various metal oxides [16–18]. Not only the resistive type gas sensors are known, but also the optical sensors are studied. However, the mechanism of optical sensing is still unclear and depends on material type and properties.

In present study, the ZnO coatings on Zn substrate were obtained by plasma electrolytic oxidation (PEO) method. The luminescence intensity, spectra and decay kinetic dependence on air pressure was studied

## 2. Experiments

### 2.1. Sample preparation

Different methods are known for ZnO film or coating preparation; for example, magnetron sputtering, spray pyrolysis, laser ablation, Zn oxidation and others. In present study, we use PEO method to prepare ZnO coatings on Zn substrate. 0.5 mm thick, 99.994% Zn foil obtained from Alfa Aesar Company was used in present study. Prior to PEO, the foil was polished, washed in acetone and etched in hydrochloric acid. The PEO method used in present paper was described in details in Ref. [19] and previously applied for alumina coating preparation. Current pulses were used between two electrodes: Pt and Zn foil. The distance between electrodes was 2.5 cm. 1 L KOH (1g/L) electrolyte solution was used and stirred during PEO process. Coating was made in two stages: 250 V 40  $\mu$ s unipolar pulses for 15 min following with 700 V 40  $\mu$ s pulses for 5 min.

### 2.2. XRD

Crystalline structure was analyzed using XRD measurements. Measurements were performed by X-ray diffractometer (X Pert Pro MPD) with Cu K $\alpha$  line.

### 2.3. SEM and TEM measurements

The crystallite size verification and morphology studies were made using SEM Lyra (Tescan) operated at 25 kV and TEM Tecnai G20 (FEI) operated at 200 kV, and using a transmission electron microscope (TEM, Tecnai G20, FEI) operated at 200 kV. The powder like TEM samples were prepared by mechanical scraping of ZnO

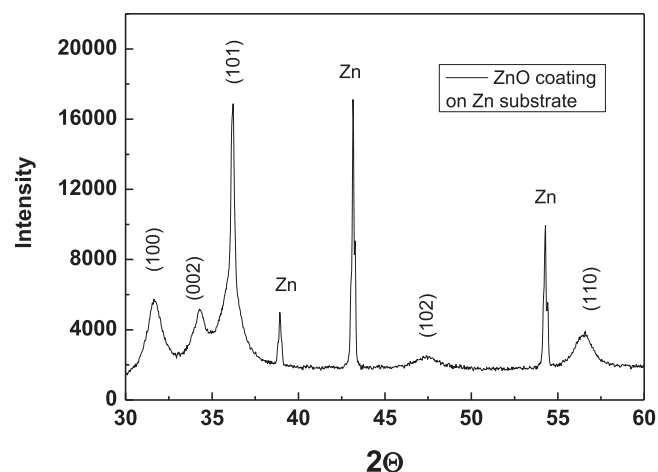


Fig. 1. XRD pattern for ZnO coating on Zn substrate obtained by PEO method.

from coating using diamond cutter and placed on holey carbon film grid S147-4 (Agar Scientific). The samples for SEM were attached to a conductive adhesive carbon tape and coated with gold.

### 2.4. Luminescence measurements

The luminescence spectra and decay kinetics were measured under 266 nm YAG:Nd laser excitation. The FWHM of excitation pulse was 2 ns. The luminescence was measured through monochromator MDR-3 with HAMAMATSU H8259 photon counting head and photon counting board FastComTech module P7887 with 500 channels. The minimal time bins is 250 ps. The laser frequency and time bins can be adjusted. All luminescence experiments are made at RT. Luminescence intensity was measured in air, vacuum or in N<sub>2</sub> gas. The sample was inserted in hermetic chamber and at first the luminescence intensity was measured chamber filled with ambient air. Then the chamber was evacuated or filled with pure nitrogen gas and the luminescence was recorded continuously.

## 3. Results and discussion

### 3.1. XRD

XRD measurements of the obtained ZnO coatings (Fig. 1) confirm the ZnO wurtzite structure. The signals from substrate are

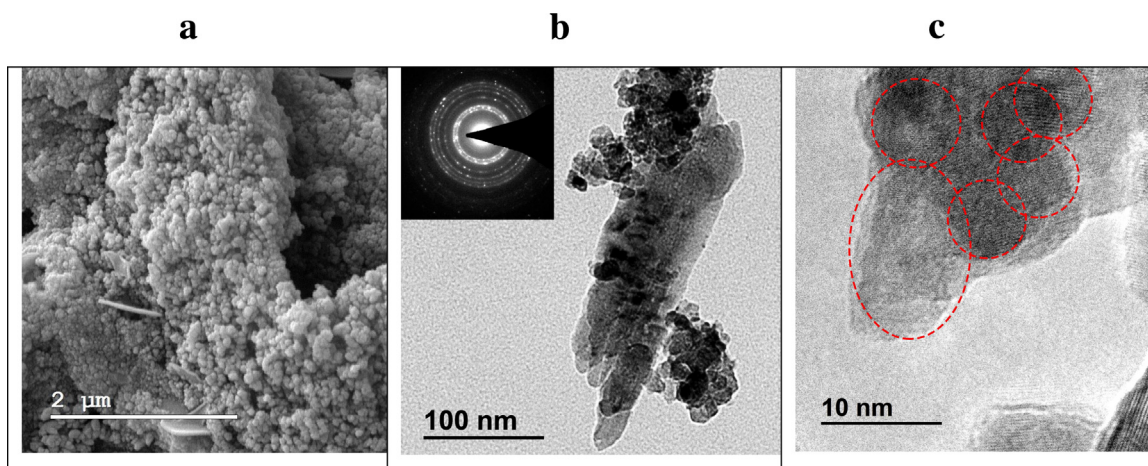


Fig. 2. SEM (a) and TEM (b,c) images of ZnO coating. The electron diffractogram is shown in inset (b).

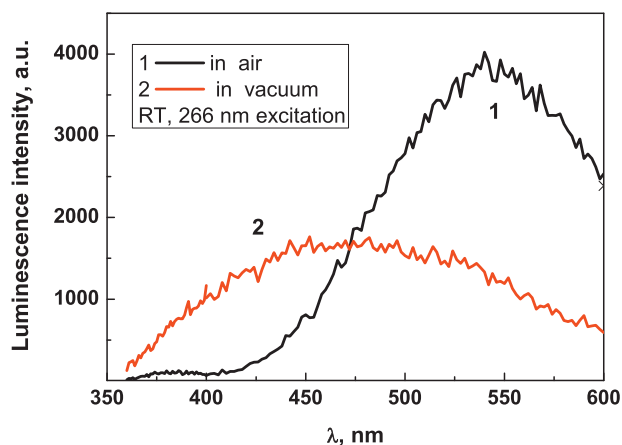


Fig. 3. The luminescence spectra of ZnO coating. 1- in air; 2- in vacuum  $10^{-2}$  mbar. Time gate 125 ns.

identified too. The average grain sizes of coating estimated according the Sherrer's formula gives 35 nm for (1 0 1) plane and 8 nm for (1 1 0) and (1 0 0) planes. This is characteristic for anisotropic systems—some grains with larger average sizes have preferential crystallographic direction. One should note that amorphous phase is not detected; however XRD could not show the disordered layers forming grain boundaries.

### 3.2. SEM and TEM

Fig. 2 shows the SEM and TEM images of ZnO coating on Zn substrate. The sample consists of nanoparticle agglomerates; Mostly the nanocrystallite sizes are less than 10 nm (Fig. 2b and c)—the different orientation of crystalline planes are revealed within areas selected by dotted lines rings. However the degree of agglomeration is very high; besides the small particles also some larger particles are present (Fig. 2b). These particles give the bigger size  $\sim 35$  nm estimated according to Sherrer's formula. Also the select area electron diffraction (Fig. 2b, insert) indicates complete rings with broadening typical for very small nanoparticles and also bright reflection points which belongs to the larger crystals. The obtained coatings have high specific surface area and, respectively, a lot of surface defects that are important for optical gas sensors.

### 3.3. Luminescence spectra

The luminescence spectra measured in air and in vacuum (Fig. 3) shows that the peak position shifts to higher energies and luminescence intensity decreases in spectra measured in vacuum in comparison with spectra measured in air. One part of defects

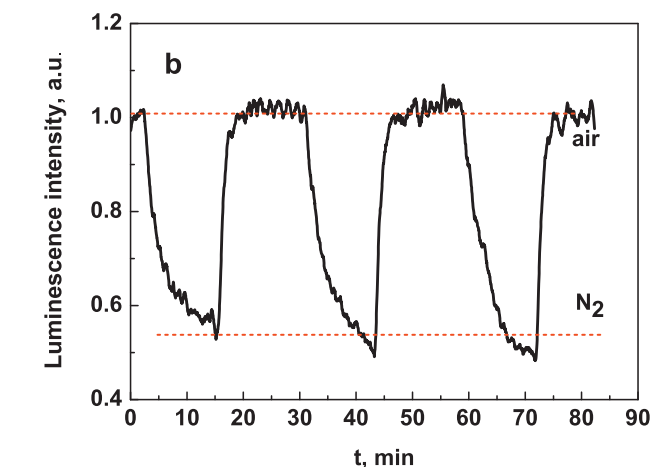
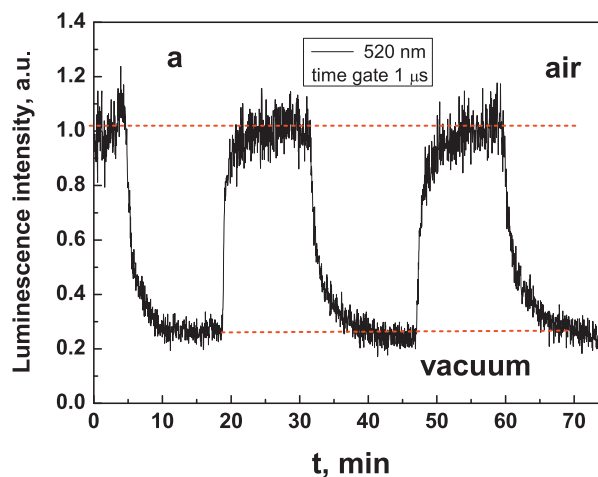
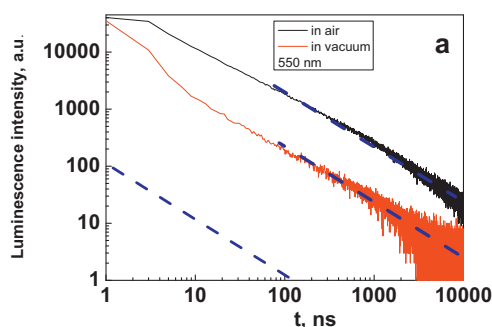


Fig. 5. Defect band luminescence intensity measured in air/vacuum ( $10^{-3}$  mbar) (a) and in air/dry  $N_2$  gas.

involved in luminescence process disappears in vacuum. Results give an evidence to believe that the defect centre model is very complex.

### 3.4. Luminescence intensity and decay kinetics dependence on air pressure

Luminescence decay kinetics was used to understand the physical models responsible for the luminescence dependence on air adsorption in ZnO. The luminescence decay kinetics measured in air and in vacuum is shown in Fig. 4. One can see that the lumines-

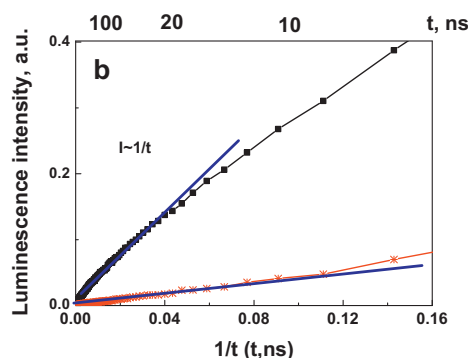


Fig. 4. The luminescence decay kinetics measured in air and in vacuum in coordinates  $\lg I/\lg t$  (a) and  $I/(1/t)$  (b).

cence decay kinetics measured in air and in vacuum are not simple exponential and are not the superposition of two exponents. Such complex decay processes are difficult to interpret physically and similar kinetics were observed previously [4,18,20]. We analyze the last stage of decay kinetic (Fig. 4a) in logarithmic coordinates  $\lg I/I_0$ . The straight line with the slope 1 was observed in luminescence decay for both air and vacuum, which means that the last stage of decay process can be described using the model of tunnelling recombination within donor–acceptor pairs [21]. The main difference in decay process observed in air and in vacuum was in 10–100 ns region. This stage perhaps is due to recombination of close donor acceptor pairs and these defect pairs are responsible for gas sensing in studied ZnO coating.

The luminescence intensity was measured in air for as prepared samples and during the vacuum pumping. It is shown that during the vacuum pumping the intensity decreased and recovered when exposed to air. The time diagram is shown in Fig. 5. For the as prepared coatings the ratio  $I_{air}/I_{vacuum}$  was  $\sim 3$ , if measured at wavelength 550 nm. The relative slow reaching of luminescence stationary value in ambient air and in vacuum (Fig. 5) could be due to the migration of gas molecules before localization, including migration along the grain boundaries. The same intensity was achieved in air and in vacuum after multiple cycles.

No intensity change was observed even after multiple pumping/venting cycles. The luminescence intensity decreases also if the sample chamber was filled with  $N_2$  gas. Therefore, obviously the oxygen defects are responsible for luminescence intensity dependence in gas sensing.

#### 4. Conclusions

The ZnO coatings on Zn substrate were successfully prepared using PEO method. The XRD results confirm that the ZnO nanograined coatings with wurtzite structure were obtained. The grain sizes as estimated from TEM images are  $\sim 8$  nm although some large microcrystals with sizes 30–50 nm were observed too. The nanoparticle agglomerates and coatings have high effective gas adsorption–desorption activity on surface area. It is shown that the photoluminescence intensity of these coatings is sensitive to oxygen adsorption since the defect states on surfaces play a big role in the luminescence processes. The luminescence intensity for the obtained coatings drops three times when sample was in vacuum. The luminescence decay kinetics in defect band (550 nm) was analyzed. We suggest that the tunnelling recombination within the donor–acceptor pairs is responsible for the luminescence process in the last stages of decay process. The defect luminescence of coatings is sensitive to air pressure and good intensity reproduction during multiple cycles was observed.

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