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# Effect of ultraviolet-illumination and sample ambient on photoluminescence from zinc oxide nanocrystals

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## ABSTRACT

We report an effect of measurement conditions on the photoluminescence intensities of zinc oxide nanoparticles. It was found that in vacuum under UV illumination intensity of near-band edge emission increases while defect related emission intensity decreases. We attribute this effect to a decrease in the depletion region width due to oxygen desorption on the surface of the zinc oxide nanocrystals.

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## 1. Introduction

Zinc oxide (ZnO) is promising for room temperature optoelectronic applications due to its wide band gap (3.37 eV) and large exciton binding energy (60 meV) [1]. The luminescence spectra of ZnO nanomaterials are typically composed of two parts: a near-band edge (NBE) emission at around 380 nm and a defect related deep level emission in the visible range. An emission band at around 500–520 nm (green band) appears in the emission spectrum of ZnO fabricated in oxygen deficient conditions or after a high temperature annealing. It is ascribed to oxygen vacancy defect centers [1,2–4]. It is well known that the high surface-to-volume ratio makes nanocrystals sensitive to the environment. The particle surface of ZnO contains chemisorbed oxygen from air, which makes the surface negatively charged. The nanocrystal surface can also introduce electronic states that dramatically affect the optical properties of ZnO nanoparticles and nanowires. A photoinduced oxygen desorption process has been widely investigated for photoconductivity for several years [6–8]. The desorption of oxygen on the surface of the zinc oxide film induces the change of surface states and results in an increase of photoconductivity. It is believed that the physical processes that are responsible for the photoconductivity increase are also responsible for the photoluminescence increase. Surface defects and impurities have been reported to quench the excitonic luminescence of ZnO [5], since they can act

as trapping centers to compete with the near-band-edge emission. The studies indicate that key properties of ZnO nanostructures may critically depend on their surfaces.

In this work, we have investigated an effect of the emission recording conditions on photoluminescence (PL) spectrum and intensity from ZnO nanoparticles. It is found that depending on ambient (air or vacuum), intensities of the near-band-edge and defect related PL bands are different. In vacuum with decreasing nanoparticle size the relative integrated intensity ratio of the NBE emission to the deep-level emission increases. We attribute the observed effects to the depletion region width variations on the zinc oxide surface due to a photoinduced oxygen desorption process.

## 2. Experimental

The ZnO nanocrystals were fabricated by a chemical solution deposition method as reported previously [9,10]. In the 50 ml conical flask, a 0.6586 g zinc acetate dehydrate ( $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ , 99.999% purity, Aldrich) was dissolved in a 30 ml methanol under vigorous stirring at room temperature. Distilled water (1/10 ml) was then added into the solution under stirring and was ultrasonicated for 5 min. Sapphire and borosilicate glass substrates, previously ultrasonically cleaned in acetone and methanol, were put into the bottom of the conical flask. The conical flask was put into a water tank at constant temperature of 60 °C for 24 h. After the expiration of the ZnO particle deposition process the flask with samples was taken out and cooled to the room temperature. For the next check-up, all samples were

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cleaned several times by methanol. By varying the methanol/distilled water ration the ZnO nanoparticles with an average size of  $\sim 500$  and  $\sim 10$  nm were obtained. The prepared samples were annealed in a tube furnace in ambient air at  $500^\circ\text{C}$  for 1 h.

The morphologies of samples were investigated by using a scanning electron microscope (SEM) (XL-30 PHILIPS). Structural examination of the nanocrystals was performed by using an XRD Bede D1 system. PL measurements were carried out using a SPEX spectrometer equipped with a 0.75 m grating monochromator. A photo-multiplier tube (Hamamatsu R943-02) was used as the photodetector. A 50 mW cw He–Cd laser operating at a wavelength of 325 nm was employed as the excitation source. The samples were placed inside the vacuum chamber of a closed-cycle Janis cryostat. Air could be reintroduced to the cryostat vacuum chamber through a valve.

### 3. Results and discussion

Fig. 1 shows a SEM image of ZnO nanocrystals. The nanocrystals have the regular cone form and the size of 100–1000 nm. The regular cone form is an evidence of crystallinity of ZnO particles. This is also confirmed by XRD measurements. The XRD patterns of the as-prepared particles are shown in Fig. 2. All the diffractive peaks belong to the typical ZnO wurtzite structure and the dominant (002) diffraction peak indicates that the nanoparticles were grown with a *c*-axis preferred orientation. All faces of the annealed nanocrystals contain the randomly distributed speck-like defects, which appear as the dark spots in high resolution SEM

images. The speck-like defects have been correlated to the emission at around 3.311 eV, observed at low temperatures [11].

The room temperature (RT) PL spectrum of the ZnO nanocrystals contains a sharp peak in the UV region at 383 nm (3.24 eV) and a broad emission band at around 500 nm (2.48 eV). According to the conventional classification for the bulk ZnO crystals the UV peak has been attributed to NBE emission. The visible (green) emission band is related to deep-level defects in ZnO, namely to oxygen vacancy defect centers [1]. It is found that the PL spectra depend on the measurement conditions. Fig. 3 shows the room temperature PL spectra of the annealed ZnO nanocrystals recorded in the air (1), in vacuum (2) and after air admission to the cryostat vacuum chamber (3). In both air and vacuum before recording the PL spectra ZnO nanocrystals were continuously exposed to 325 nm ultraviolet laser radiation for 30 min. As seen, pumping out of an air from the cryostat chamber leads to increase in the NBE emission intensity. At the same time the green-band emission intensity decreases. In air the relative integrated intensity ratio of the near-band-gap emission to the deep-level emission is 0.61 and it grows up to 0.69 in vacuum (the percentage increase is  $\sim 13\%$ ). The integration ranges are 360–415 nm for NBE emission and 415–625 nm for the green-band emission, respectively. The intensity of both NBE emission and green-band emission increases after the air admission to the cryostat vacuum chamber and the relative integrated intensity ratio of the emission bands becomes equal to 0.64.

It is found that the effect of the measurement conditions on PL intensity depends on the ZnO particle size. Fig. 4 shows a SEM image of ZnO nanoparticles. An average size of the particles is  $\sim 10$  nm. In contrast to the ZnO nanocrystals presented in Fig. 1,

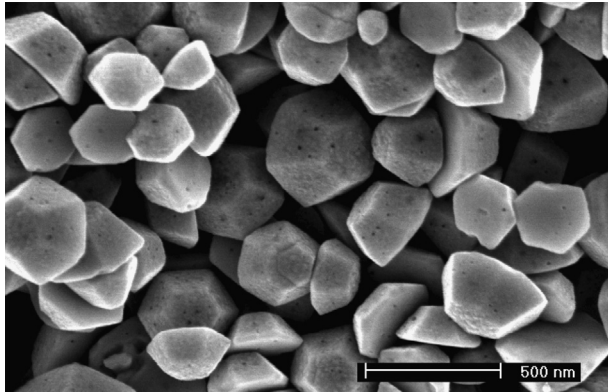


Fig. 1. SEM image of large size ZnO nanocrystals.

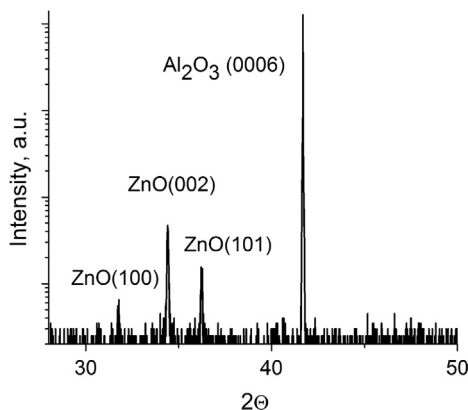


Fig. 2. XRD pattern of large size ZnO nanocrystals.

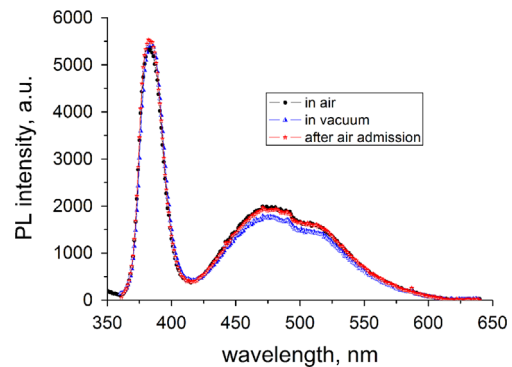


Fig. 3. PL spectra of large size ZnO nanocrystals recorded at 300 K in the air (1), in vacuum (2) and after air admission to the cryostat vacuum chamber (3).

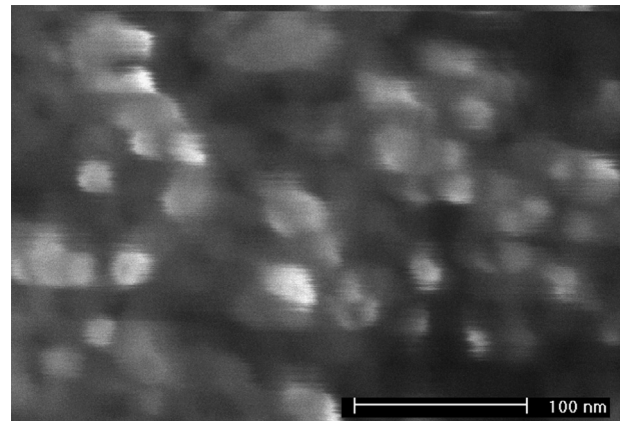


Fig. 4. SEM image of small size ZnO nanoparticles.

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