Photoluminescence and positron annihilation lifetime studies on pellets of ZnO nanocrystals

Andrzej Karbowski, Kamil Fedus, Jaromir Patyk, Łukasz Bujak, Krzysztof Służewski, Grzegorz Karwasz

Nicolaus Copernicus University, Institute of Physics, 5/7 Grudziądzka Str., 87-100 Toruń, Poland, Tel.: +48 56 611 3291, Fax: +48 56 622 5397, E-mail: kamil@fizyka.umk.pl

Abstract. We explore the interrelationships between the X-ray diffraction patterns, the photoluminescence spectra and the positron lifetimes obtained from circular pellets composed of commercial ZnO nanoparticles. The experimental results are studied as a function of thermal treatment at different temperatures. X-ray diffractograms reveal the temperature-independent wurtzite phase structure of nanocrystals and show huge enlargement of ZnO grains after annealing at temperatures higher than 700°C. Photoluminescence measurements exhibit two emission bands: a near band edge emission in UV (≈378 nm) and a defect-related broad visible peak with a maximum in the green region (≈502 nm). The significant enhancement of the green emission at the expense of UV luminescence is observed after sample sintering at 800 and 1000°C. The positron annihilation lifetime spectroscopy (PALS) is applied in order to study the thermally induced evolution of defects. The lifetime components show a step-like dependence on the thermal treatment, but do not follow exactly the variation in crystallographic phases and only vaguely follow differences in photoluminescence. The positron data indicate therefore some additional structural and/or defect changes. The possible origin of green luminescence from ZnO pellets is discussed.

Key words: photoluminescence (PL) • positron annihilation lifetime spectroscopy (PALS) • X-ray diffraction (XRD) • ZnO nanocrystals

Introduction

Zinc oxide (ZnO) is a material with great potential for a variety of practical applications due to the unique physical and chemical properties such as wide and direct energy band gap (~3.37 eV), large exciton binding energy (~60 meV), high electron mobility, high thermal conductivity, high radiation damage resistance and biocompatibility. The recent progress in nanoscaling of ZnO structures attracts also attention towards the use of ZnO in nanotechnological applications. Therefore, mechanical, electrical and optical properties of nanostructured ZnO crystals are widely investigated in different conditions by many research groups [5, 6, 14]. However, in spite of the numerous studies, not all mechanisms responsible for physical phenomena in ZnO are fully understood. One of the problems concerns the origin of spontaneous emission which has been broadly investigated by photoluminescence (PL) spectroscopy. Typically, the room temperature spectra of ZnO consist of a UV emission and possibly one or more visible bands (violet [21, 33], blue [24, 31], green [4, 8, 9, 11, 12, 19, 22, 28, 27–29, 32, 34] or yellow-orange-red [20, 23]). The origin of the UV peak is well explained because it is related to the near-band-edge
excitonic transitions. Whereas the visible emissions are assigned to defects and/or impurities. However finding the exact explanations for each peak are complicated because their spectral positions and the intensities strongly depend on the fabrication process [18]. Growth procedures determine concentrations of intrinsic and extrinsic defects as well as the spcies of impurities. The created luminescent centres must to be identified as a function of preparation procedure in order to understand and control ZnO properties. Particularly, a number of different hypothesis have been proposed in order to explain the most frequently observed green emission. Propositions include the involvement of Cu impurities [8], Zn vacancies [27, 29, 34], oxygen vacancies [9, 12, 25, 28, 32], oxide antisite defects [19] or surface defects/defects complexes [4, 11]. However, no consensus has been reached and the topic remains controversial. What is worse, there are also huge discrepancies between theoretical models of defects in ZnO. Different studies predict different energy levels for the same type of defect and, consequently, no constructive conclusions can be made (see Ref. [6] and references therein). As pointed out in Ref. [6], the difficulties in identifying the origin of defects bands in ZnO is the fact that the bands are broad and overlapping. In the light of all these problems it is necessary to make as many measurements as possible on different samples using different characterization techniques in various experimental conditions in order to obtain a final reliable picture of phenomenon. The aim of this paper is to add another contribution to studies on green luminescence in ZnO. In particular, we investigated the effect of thermal treatment on spontaneous emission from circular pellets composed of ZnO nanocrystals. The study is supported by two complementary characterization techniques: X-ray diffraction (XRD) and positron annihilation lifetime spectroscopy (PALS). Both methods provide valuable insights into defects, structure and size of nanoparticles. The correlation between results obtained from these different experiments is presented and the possible origin of green luminescence in ZnO is discussed.

**Results and discussion**

**X-ray diffraction**

Typical XRD patterns of the ZnO pellets prepared from as-purchased powder and powders annealed at 400, 800 and 1000°C are shown in Fig. 1. The ZnO samples exhibit good crystallinity with no obvious indication for the existence of amorphous domains – all diffraction peaks can be readily indexed as hexagonal wurtzite ZnO crystal structure. No phase transition was observed between as-purchased and annealed at 1000°C powders. In addition, the intensity of the peaks increases and the FWHM decreases with the increasing annealed temperature, which indicates a possible change in the grain size. This aspect was analyzed with Bruker Physic TOPAS software [17].

![Fig. 1. XRD patterns for the as-purchased and annealed at 400, 800 and 1000°C ZnO nanocrystals.](image)

Positron annihilation lifetime spectroscopy was used to investigate thermally induced evolution of defects in ZnO nanocrystals. Positron trapping in open-volume defects, such as in vacancies and their agglomerates, causes an increase of the positron lifetime with respect to the defect-free samples. This is due to the locally reduced electron density of the defects. PALS is a powerful method to identify defects since the annihilation characteristics of positrons can be often assigned to particular trapped states. The experiments were carried out using the fast-fast coincidence ORTEC PLS system equipped with plastic scintillators (St. Gobain BC418) and RCA 8850 photomultipliers [16]. The prompt time resolution of the system was 180 ps in full width at half maximum (FWHM). The positron source 22NaCl (10 μCi) in a kapton 7 μm thick foil was sandwiched between two identical ZnO pellets. At least 10^6 total counts were accumulated in each measurement. Several runs were performed for each of the two identical samples. The analysis of lifetime spectra was realized with the LT package created by Kansy [15].
Photoluminescence and positron annihilation lifetime studies on pellets of ZnO nanocrystals

Whole pattern fitting was performed using ZnO structure data (the hexagonal wurtzite phase) with fundamental parameters (FP) profile shape of diffraction reflexes. This procedure allowed to eliminate impact of Kα2 emission line of copper on the registered diffraction data. The average diameters of nanocrystallites were estimated using two algorithms: one Scherrer-like algorithm using a Lorentz shape peak and the second calculated as volume mean weighted using a Lorentz and Gauss convoluted peak shape. The determined sizes are presented in Table 1. Both numerical procedures give results which are in very good agreement. Annealing up to 400°C does not change noticeably the size of ZnO nanoparticles, while sintering at higher temperatures corresponds to a significant increase of nanocrystallites. The particle diameters are enlarged by approximately 180–200 nm after annealing at 1000°C. This can be explained by a thermally-induced agglomeration of grains in the samples [29]. A similar effect has been already observed in Ref. [12] where ZnO pellets have been investigated in the same temperature range.

It has to be highlighted that no quantum confinement effect should be expected for these samples since the sizes are much larger than the exciton Bohr radius in ZnO (approximately 2.34 nm [10]). Hence the quantum effects are expected to have no influence on spontaneous emission spectra presented in the next section.

Photoluminescence

Figure 2a presents the room temperature photoluminescence spectra of ZnO nanocrystals annealed at different temperatures. As typically the spectra exhibit two emission peaks: one in UV with a maximum at 375–380 nm and the second in the visible (green) region peaking at 502–510 nm. Several interesting things can be noticed from the measured data. The luminescence spectrum obtained from the as-purchased powder (RT) consists of approximately equal UV and visible peaks. Whereas the annealing at elevated temperatures to 600–700°C induces continuous quenching of UV emission such that the ratio of heights of the visible-to-UV peaks, shown in Fig. 2b, is increased by a factor of two. Moreover, the shift of the visible peak towards the longer wavelengths is also observed in this range of temperatures. Further increase of sintering temperature up to 800 and 1000°C results in significant enhancement of visible emission and very deep reduction of UV peak. The small shift of the UV emission towards shorter wavelengths is also observed. A plausible explanation of thermally induced quenching of excitonic emission could be the energy band bending due to the chemisorption of oxygen at the ZnO surface as described recently in Ref. [30]. This adsorption can occur in the air in normal conditions and increase with ambient temperature, producing an upward band bending and a surface depletion. A large ZnO absorption coefficient of \( \approx 160 \text{ cm}^{-1} \) at 325 nm corresponds to a penetration depth of \( \approx 60 \text{ nm} \). Therefore, upon excitation, most of the electrons and holes are generated near the surface where they are swept to the opposite directions across the depletion region, thus reducing their chances of recombination through excitonic processes. This model is confirmed by many experiments showing that surface passivation by coating ZnO nanostructures with different materials results in suppressing green emission and enhancing UV luminescence (see Ref. [30] and references therein). Furthermore, the authors of Ref. [30] suggest that the oxygen chemisorption is accompanied by the creation of oxygen vacancies (\( V_o \)) in the depletion region. This can explain the significant enhancement of green luminescence observed in this work after annealing the samples at temperatures higher than 700°C. Nevertheless, this phenomenon requires further investigation, especially the attention should be paid to the obvious correlation of the latter effects with the thermally-induced grain enlargement reported in the previous section as well as in Ref. [29] for similar samples.

### Table 1. ZnO nanocrystallite size depending on temperature of sintering

<table>
<thead>
<tr>
<th>No.</th>
<th>Sample</th>
<th>Lorentz diameter (nm)</th>
<th>Volume diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>powder</td>
<td>94.9 ± 0.6</td>
<td>84.4 ± 0.54</td>
</tr>
<tr>
<td>2</td>
<td>400°C</td>
<td>95.3 ± 0.6</td>
<td>84.8 ± 0.6</td>
</tr>
<tr>
<td>3</td>
<td>800°C</td>
<td>246.8 ± 4.2</td>
<td>220 ± 4</td>
</tr>
<tr>
<td>4</td>
<td>1000°C</td>
<td>293 ± 7</td>
<td>261 ± 6</td>
</tr>
</tbody>
</table>

Fig. 2. (a) Photoluminescence spectra of ZnO pellets annealed at different temperatures for an excitation wavelength of 325 nm; (b) the ratio of heights of visible to UV emission peaks (\( I_{\text{VIS}}/I_{\text{UV}} \)) in function of annealing temperature.
Vacancies (luminescence). Indeed, the reduction of thermal grown ZnO [29]. The sudden fall in 220–230 ps (see Fig. 3a), an intermediate lifetime τ2 of about 430–440 ps (see Fig. 3a) and very long lifetime τ3 of about 60 ns (see Fig. 4a) obtained in the sample prepared from as-purchased powder. The existence of three components is in very good agreement with positron lifetime data published on ZnO nanoparticles by other research groups [21, 26, 29].

According to the most popular hypothesis, the shortest lifetime (τ1) corresponds to positron trapping in zinc vacancies (VZn) [2, 3, 21, 29, 30] located either in the bulk or/and on the particle surface referred to as grain boundary. This assumptions is based on experimental and theoretical works showing that VZn together with oxygen vacancy (VO) are dominant in ZnO because they are characterized by low formation energies [13]. However, only the negatively charged VZn is visible to the positrons since the positively charged VO has too low positron binding energy [3, 27]. Additionally, it is expected that the most efficient trapping occurs on the grain boundaries. This is because the average positron diffusion length could be as large as 150–200 nm [1], so it is usually enough to let positrons reach the grain boundaries during thermalization inside nanocrystals. Moreover, theoretical calculations [7] predict that the formation energy of zinc vacancy is lower at grain boundaries than in the bulk, hence the surface of ZnO nanoparticles is rich in vacancy defects. This experimental work shows that after sample treatment at 150–700°C, τ1 keeps relatively constant (230–240 ps, see Fig. 3a). It means that the grain growth does not influence noticeably on positron annihilations centres responsible for this component. But after annealing at 1000°C, τ1 decreases rapidly to 184 ps. The latter value is close to the positron bulk lifetime reported in hydrothermal grown ZnO [29]. The sudden fall in τ1 value can be explained by a thermally induced recovery of both, grain boundary and bulk located Zn vacancies. Consequently, most positrons annihilate in the bulk and/or in other kind of defects or imperfection left in the sample. If this interpretation is correct, one could conclude that zinc vacancies (VZn) are not responsible for a green luminescence. Indeed, the reduction of VZn concentra-

**Positron annihilation lifetime spectroscopy**

The LT analysis of measured positron lifetime spectra reveals three components: a short lifetime τ1 of about 220–230 ps (see Fig. 3a), an intermediate lifetime τ2 of about 430–440 ps (see Fig. 3a) and very long lifetime τ3 of about 60 ns (see Fig. 4a) obtained in the sample prepared from as-purchased powder. The existence of three components is in very good agreement with positron lifetime data published on ZnO nanoparticles by other research groups [21, 26, 29].

According to the most popular hypothesis, the shortest lifetime (τ1) corresponds to positron trapping in zinc vacancies (VZn) [2, 3, 21, 29, 30] located either in the bulk or/and on the particle surface referred to as grain boundary. This assumptions is based on experimental and theoretical works showing that VZn together with oxygen vacancy (VO) are dominant in ZnO because they are characterized by low formation energies [13]. However, only the negatively charged VZn is visible to the positrons since the positively charged VO has too low positron binding energy [3, 27]. Additionally, it is expected that the most efficient trapping occurs on the grain boundaries. This is because the average positron diffusion length could be as large as 150–200 nm [1], so it is usually enough to let positrons reach the grain boundaries during thermalization inside nanocrystals. Moreover, theoretical calculations [7] predict that the formation energy of zinc vacancy is lower at grain boundaries than in the bulk, hence the surface of ZnO nanoparticles is rich in vacancy defects. This experimental work shows that after sample treatment at 150–700°C, τ1 keeps relatively constant (230–240 ps, see Fig. 3a). It means that the grain growth does not influence noticeably on positron annihilations centres responsible for this component. But after annealing at 1000°C, τ1 decreases rapidly to 184 ps. The latter value is close to the positron bulk lifetime reported in hydrothermal grown ZnO [29]. The sudden fall in τ1 value can be explained by a thermally induced recovery of both, grain boundary and bulk located Zn vacancies. Consequently, most positrons annihilate in the bulk and/or in other kind of defects or imperfection left in the sample. If this interpretation is correct, one could conclude that zinc vacancies (VZn) are not responsible for a green luminescence. Indeed, the reduction of VZn concentra-

**Fig. 3.** (a) Positron lifetimes τ1 and τ2 and (b) relative intensities I1 and I2 as a function of annealing temperatures in ZnO samples.

There is common agreement that the longest lifetime component τ3 should be assigned to the annihilation of ortho-positronium formed in large voids in the intercrystalline regions [21, 29]. Figure 4 shows that when the annealing temperature increases from 150 to 1000°C, τ3 decreases very fast from 60 to 2 ns and the relative intensity I3 changes from 5.5 to 0.8%. This drop is particularly rapid between 400 to 500°C. These results are in very good agreement with the data reported in Refs. [21, 29] and are to be attributed to the sintering process. Namely, the gradual decrease of τ3 suggests the reduction of intercrystalline free volume concentration due to the thermally induced agglomeration of grains in the samples.
measurements. These studies are in progress.

To investigate the influence of oxidation on PL and P ALS in oxygen-poor environments should be considered in order to account for the atmospheric conditions. Particularly, oxygen-rich and/or defect variations in this temperature range of 150–1000°C should be carried out in order to identify the kind of structural and/or defect variations in ZnO. Moreover, PALS measurements show no correlation between zinc vacancies (V\text{Zn}) and defect-induced green emission – the drop in the intensity of the intermediate component (about 450 ps) occurs rapidly between 500 and 700°C, distinctly below the temperature (800°C) where the green photoluminescence starts to dominate. More studies should be carried out in order to identify the kind of structural and/or defect variations in this (500 to 800°C) range of temperatures and to exclude ultimately V\text{Zn} as green luminescence centres. Since it is expected that the green emission originates mainly from the surface of ZnO nanocrystals, thus PL and PALS should be measured and compared in samples treated thermally in different atmospheric conditions. Particularly, oxygen-rich and oxygen-poor environments should be considered in order to investigate the influence of oxidation on PL and PALS measurements. These studies are in progress.

**Conclusions**

The disc-shape pellets composed of ZnO nanoparticles were prepared and annealed at different temperatures in the range of 150–1000°C, and then subsequently studied by X-ray diffraction, photoluminescence and positron lifetime annihilation methods. All techniques reveal significant changes in properties of nanoparticles with annealing temperatures. In particular, the large enhancement of green luminescence at the expense of near-band-edge UV emission is observed after thermal treatment at temperatures higher than 700°C. Moreover, PALS measurements show no correlation between zinc vacancies (V\text{Zn}) and defect-induced green emission – the drop in the intensity of the intermediate component (about 450 ps) occurs rapidly between 500 and 700°C, distinctly below the temperature (800°C) where the green photoluminescence starts to dominate. More studies should be carried out in order to identify the kind of structural and/or defect variations in this (500 to 800°C) range of temperatures and to exclude ultimately V\text{Zn} as green luminescence centres. Since it is expected that the green emission originates mainly from the surface of ZnO nanocrystals, thus PL and PALS should be measured and compared in samples treated thermally in different atmospheric conditions. Particularly, oxygen-rich and oxygen-poor environments should be considered in order to investigate the influence of oxidation on PL and PALS measurements. These studies are in progress.

**Acknowledgment.** One of the authors (Ł. Bujak) would like to acknowledge the support by the WELCOME pro-gramme “Hybrid nanostructures as a stepping-stone towards efficient artificial photosynthesis” from the Foundation for Polish Science. Fluorescence measurements were carried out at the facilities of National Laboratory FAMO in the Institute of Physics, NCU in Toruń. The ORTEC PLS system has been purchased within the NLTK laboratories (grant no. POIG 02.02.00-00-003/08) at NCU in Toruń.

**References**

18. Li D, Leung YH, Djurisic AB et al. (2004) Different origins of visible luminescence in ZnO nanostructures