
Proceedings of the XXXIV International School of Semiconducting Compounds, Jaszowiec 2005

Growth and Characterization of ZnO Nanoparticles

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In this work we evaluate structural and optical properties of ZnO nanoparticles grown by wet chemistry method. Light emission properties of these nanoparticles are studied with cathodoluminescence and microphotoluminescence. Even at the room temperature excitonic emission is well resolved, due to high exciton binding energy of ZnO. Decay kinetics of photoluminescence emissions and efficiency of inter-nanoparticles energy migration is evaluated from maps of in-plane variations of photoluminescence decay times measured in microphotoluminescence setup.

PACS numbers: 81.07.Wx, 68.37.Hk, 78.55.Et, 78.47.+p

1. Introduction

ZnO is not “a new semiconductor”. It has a long history of studies of its growth techniques and characterization of its material properties. For example, lattice parameters of ZnO are known from 1935, whereas detailed values of optical parameters were available in mid 50s. Even though good quality thin films (by chemical vapour deposition) were prepared in 1970, only recently ZnO attracts an increasing attention. This is due to a range of predicted applications in elec-

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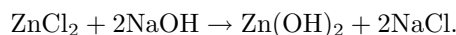
tronics and in optoelectronics. Details of ZnO properties and the predicted ZnO applications are described in the recent reviews [1–4].

Nanoparticles of ZnO also attract an increasing interest, due to their possible use in a range of new nanodevices. Applications in optoelectronics, as blue colour light emitting phosphors [5, 6], as nanorod UV light emitters [7], as fluorescence labels in medicine and biology, in controlling units as UV photodetectors and as high-flame detectors [8], as nanosensors of various gases, but also in cosmetic industry, as a component of sun screens, are envisioned [1–4].

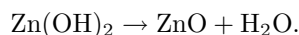
Our interest in the present type of ZnO nanoparticles stems from our recent demonstration of encouraging optical (ZnO) and magnetic (ZnMnO) properties of ZnO and ZnMnO films grown at low temperature (LT) conditions [9, 10]. These studies indicated possibility of producing efficient short wavelength light emitting phosphors by simple LT growth processes. In the present work we discuss structural and optical properties of such ZnO nanoparticles, which were obtained in a wet chemistry process at LT conditions.

2. Sample preparation

ZnO nanoparticles were obtained from wet chemistry reactions using water solution of zinc chloride ZnCl_2 and NaOH as starting precursors



The so-obtained solution was dehydrated in a microwave reactor ERTEC at 150°C and at 1 atm pressure



NaCl was washed out and the so-obtained mixture was diluted in isopropanol. Wet powder was then dried by 24 hours at the temperature of 90°C .

Structural quality of the so-obtained nanoparticles was studied with X-ray diffraction (XRD) and scanning electron microscopy (SEM). In Figs. 1a, b we show

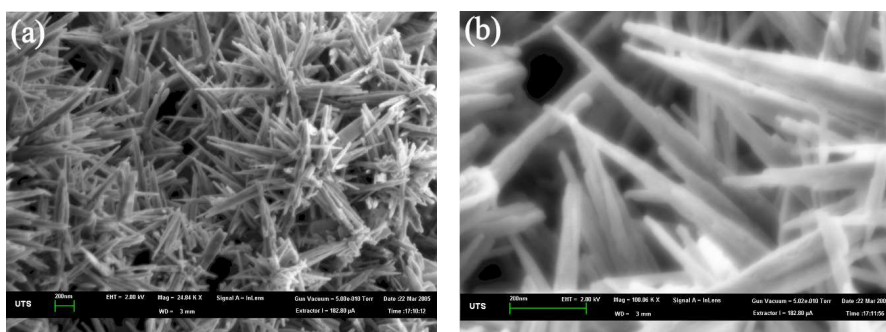


Fig. 1. High resolution SEM images of the LT ZnO nanoparticles taken at room temperature at low accelerating voltage of 2 kV at about $25000\times$ (a) and $100000\times$ (b) magnification.

high resolution SEM images taken with FEG SEM microscope at low accelerating voltage. SEM images indicate that most of the ZnO nanoparticles are in the form of nanorods with about 10 nm radius and 200 nm length. Larger crystallites were also present, but their concentration was low. Other LT ZnO nanoparticles studied by us had shape of small hexagons and were also of nanometer size. XRD examinations confirmed their pure ZnO origin.

3. Optical properties of nanoparticles

As already indicated in Sect. 1, our interest in ZnO nanoparticles stems from their possible use as fluorescence labels and as phosphor materials. For such applications nanoparticles should emit intensively visible light. Thus, we studied their light emission characteristics using cathodoluminescence (CL) and microphotoluminescence (PL) with a time resolution option. Results of these investigations are given below.

Even at the room temperature excitonic emission is observed (see Fig. 2), due to high exciton binding energy of ZnO [1–4]. In addition to this band edge emission, a broad green-to-red emission band is observed, peaking at about 580–610 nm, depending on a grain size and on excitation conditions. Origin of this

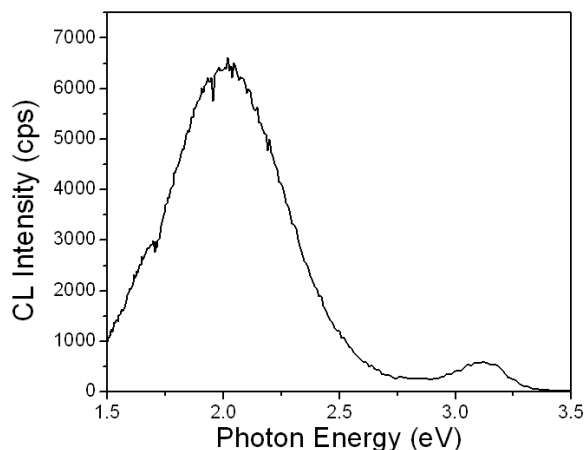


Fig. 2. Low resolution, room temperature CL spectrum measured at 10 kV accelerating voltage, at 20000 \times magnification, and at 16.8 nA excitation current density.

emission is unknown. It is down-shifted in energy, as compared to the spectral positions of the green and yellow ZnO PL bands, but peaks at the higher energy than the red ZnO emission, observed typically at 1.9–2.0 eV, as reported by Nanto et al. [11] and Gomi et al. [12]. Moreover, the yellow and the red PL emissions are usually deactivated at increased temperatures and are replaced by the green ZnO PL band [4], whereas the 580–610 nm PL emission remains strong at the room temperature.

For possible applications co-observation of the band edge and the broad red-to-green PL bands is an attractive property of our ZnO nanoparticles. We have recently observed a similar situation for thin films of ZnSe and we demonstrated that these films are attractive sources of a white light emission [13].

For phosphor applications both emissions should be fairly in-space homogeneous. We studied such characteristics of the PL bands with the CL, by scanning in-plane changes of the CL intensity with detection set at a given wavelength. The relevant results are shown in Figs. 3a, b for the defect-related CL and Fig. 4a, b for the excitonic (edge) CL. Very dispersed powder (dispersed on a copper plate for a good charge collection) was prepared for these CL investigations. Region of a “large” micro-crystal was first selected for the scanning CL investigations. Maps of in-plane changes of both the defect-related and the edge CL emissions show that both these CL emissions are slightly enhanced from edges of crystallites, but otherwise are fairly homogeneous. The effect is more pronounced for the defect-related CL, but is also observed for the edge CL. Origin of such enhancement remains unclear.

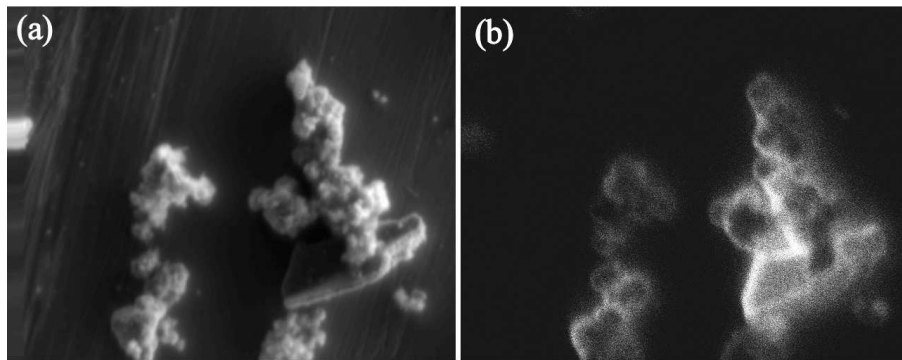


Fig. 3. SEM ((a), left) and CL map ((b), at the defect-related emission) measured at 10 kV, 2000 \times magnification and 16.5 nA.

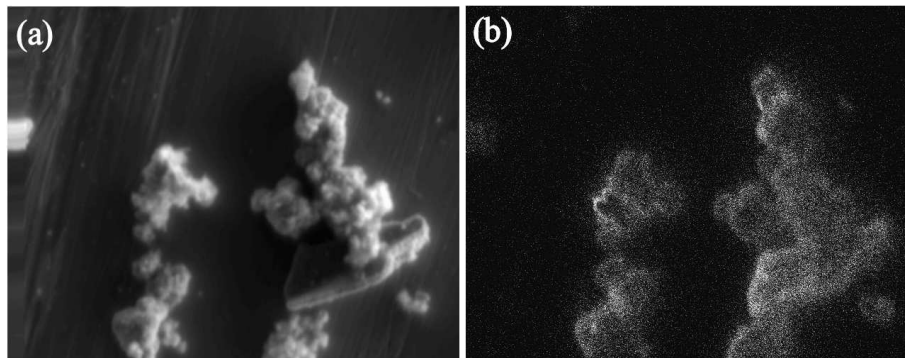


Fig. 4. SEM ((a), left) and CL map ((b), at the edge emission) measured at 10 kV, 2000 \times magnification and 16.5 nA.

At increased density of excitation the edge emission remains still weak, as compared to the defect-related CL, but remains fairly in-space homogeneous, as we also conclude from the spot-mode CL investigations. Interesting new feature observed in the spot-mode CL is the appearance of a weak green emission band from some areas of nanoparticles.

The PL kinetics and efficiency of inter-nanoparticles energy migration were evaluated from maps of in-plane variations of the PL decay times measured in micro-PL setup. These investigations were performed on the Leica confocal microscope with 100 picoseconds time resolution, using a pulsed 405 nm laser diode for the PL excitation. Only the defect-related emission band could be studied at such excitation conditions.

For these measurements diluted powder was prepared by dispersing small amount of the powder in a glycol. First of all we looked for inhomogeneities in intensity of the defect-related emission, by comparing intensity of the emission excited from small areas (from 40 to $280 \mu\text{m}^2$) of dispersed powders.

The PL decay time and its distribution were then measured for selected regions of nanoparticle agglomerations. We first studied in-plane distribution of the mean PL decay time. This experiment was first performed for a large crystallite. Multi-component PL decay was observed, with the fastest one of about 600 ps and with a long decay time component of about 50 ns. We noticed that the distribution of the PL decay time reflects microdetails of a crystallite structure, with a similar dependence to that observed in the scanning CL investigations.

The PL decay time and its distribution were then measured for dispersed nanoparticles. In Figs. 5a–c we show the lifetime distribution of the mean PL decay time measured from 7×7 (a), 25×25 (b) and 39×39 (c) μm^2 areas of dispersed ZnO nanoparticles. Fluctuations of the short component of the PL lifetime are surprisingly large in these regions, indicated by changes in contrast in Fig. 5. The fast PL decay component varies from 200 to 700 ps, depending on excitation point and on excitation density. In our opinion this observation indicates a crucial role of intra- and inter-particles energy transfer processes.

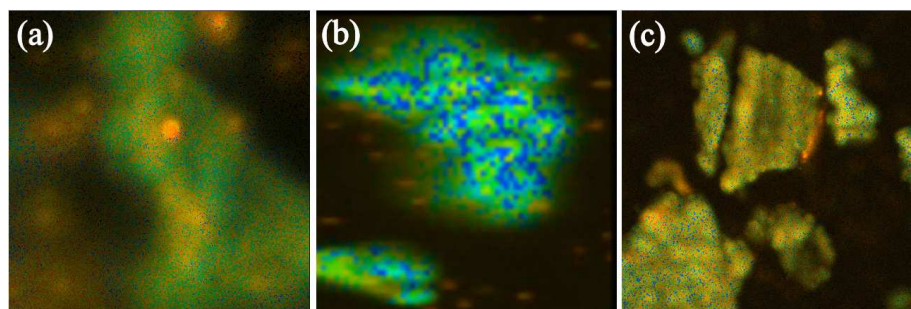


Fig. 5. PL lifetime distributions (mean PL decay time) measured from the 7×7 (a), 25×25 (b), and 39×39 (c) μm^2 areas of the dispersed LT ZnO nanoparticles (red colour means a fast decay (about 200 ps), blue colour means a slow one (about 700 ps)).

Multicomponent PL decays were observed for dispersed nanoparticles, with the fastest one in the range of 280 ps at the room temperature, i.e., nearly three times shorter than the one measured for a large crystallite. We relate such shortening of the PL decay time to intensive inter-grains energy migration processes, which significantly shorten PL decay times measured for a given micrograin.

4. Conclusions

Despite of a simplicity of a wet chemistry procedure, low reaction temperature and lack of post growth annealing at high temperature we obtained high quality ZnO nanoparticles, suitable, in our opinion, for further efforts towards applications as fluorescence labels, as white colour phosphors, and to study their magnetic properties after doping with magnetic impurities. First attempts of doping of these nanoparticles are on the way.

Acknowledgments

This work was partly supported by the grant number PBZ-KBN-044/P03/2001 of the State Committee for Scientific Research (Poland).

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