

ZnO Nanopowders by a Microwave Hydrothermal Method — Influence of the Precursor Type on Grain Sizes

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Two series of ZnO nanopowders obtained by a microwave hydrothermal method are examined. We used two different zinc precursors (zinc chloride (ZnCl₂) and zinc nitrate hexahydrate (N₂O₆Zn·6H₂O)). Both types of nanopowders show a bright emission in a visible light, including the band edge emission, which indicates their good crystallographic quality. Results of scanning electron microscopy, photo- and cathodoluminescence investigations are presented.

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1. Introduction

ZnO is the intensively investigated material for the range of possible applications in electronics (in cross-bar memories [1]), photovoltaics (as transparent conductive electrodes [2]), spintronics (when doped with transition metal ions [3]). Moreover, ZnO is a wide band gap material emitting in a near UV (band edge emission) or in a visible spectral region (defects related emission). This is why ZnO powders can be used as fluorescence labels [4] and various applications in optoelectronics are discussed. In fact, powders of ZnO (but also of other II–VI semiconductors such as CdS, CdSe, CdTe, ZnS, also when doped with transition metal or rare earth ions) are intensively investigated for the use as luminescence markers in medicine and biology.

For applications in living organisms as fluorescence markers the particles should be of submicrometer sizes [4], i.e. comparable to typical sizes of organs in organism (for example: DNA — 2.5 nm, antibody — 10 nm, cell — 1 μm). This is why we will label them as nanopowders.

At present, organic markers are widely used, which have both efficient luminescence and the required nm size. However, along with these advantages they have three important disadvantages: short stability time, photobleaching (luminescence is deactivated very fast upon photoexcitation), and luminescent signal is rather broad. Thus, it is hard to separate the emission of marker from an autofluorescence of organic tissues, which emit in visible spectral region.

The above mentioned limitations explain a vast interest in light emission properties of nanopowders (quantum dots). First, nanopowders have the required size for medical applications. Moreover, their luminescence is stable in time and efficient, especially in the case of core-shell

systems [5], for which surface states of nanopowders are passivated.

These advantages suggest that nanopowders should be widely used in biology and medicine. This, however, is not the case. Nanopowders showing the brighter emission contain cadmium (CdSe, CdS and CdTe) and thus their use should be limited or even forbidden one due to toxicity. Moreover, emission blinking of luminescence (random changes of emission intensity related to charging of surface states) is the most important barrier for their medical applications [6].

In this work we present results of the technology and characteristics of ZnO nanopowders. ZnO is the biocompatible material for medical applications and can be used as material for biosensors or luminescence markers (if bright emission is achieved) [7]. Highly efficient luminescence of nanopowders obtained by the microwave hydrothermal method is shown.

2. Experimental procedure and the results

Two different precursors (zinc nitrate hexahydrate and zinc chloride) were used for the preparation of ZnO nanopowders with the microwave hydrothermal method [8]. MAGNUM II reactor from ERTEC Company was used.

After the reaction samples were dried and examined as-grown or after annealing at 750 °C for one hour. We measured their photoluminescence (PL) and cathodoluminescence (CL). Shape and size of nanopowders was determined from the scanning electron microscopy (SEM) investigations.

Figure 1 presents the PL spectra of undoped as-grown and annealed samples made with two different precursors. Annealing had an important influence on the PL intensity of our nanopowders. It changed not only the PL

intensity, but also the intensity ratio between the band edge and defect-related PL bands.

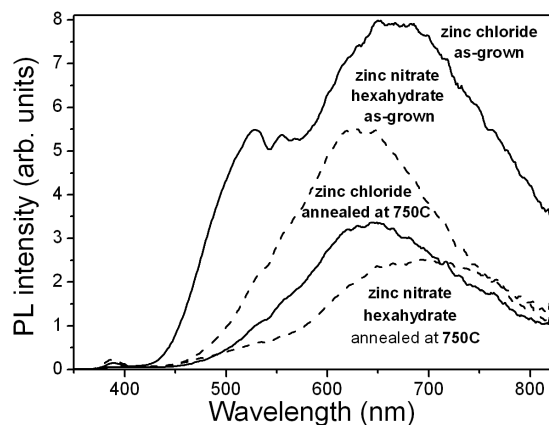


Fig. 1. Photoluminescence of ZnO nanopowders in the visible range. The precursor's type is indicated for each PL spectrum.

We observed a slight enhancement of the band edge PL (PL at 388 nm) upon annealing and a decrease in the intensity of broad “deep PL”. The spectral shift is also seen, indicating some redistribution in concentration of deep defects, such as vacancies, etc. Identity of deep PL in ZnO is given in [9] and reference given there.

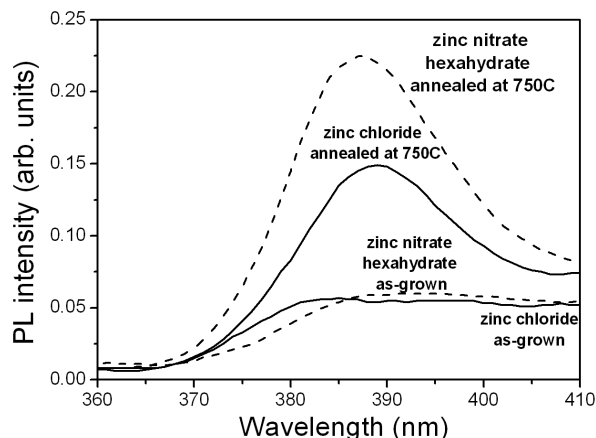


Fig. 2. Band edge PL of ZnO nanopowders.

The enhancement of the band edge PL is better seen in Fig. 2, which presents the PL in the spectral range from 360 nm to 410 nm.

PL investigations shown in Figs. 1 and 2 were performed under a very low excitation density. We also performed the CL investigations (see Fig. 3) to get information on emission upon more intense excitation. We observed that the defect related emission saturates with increasing excitation density, indicating relatively low concentration of these defects. The band edge emission dominates in the CL spectrum for the nanopowders grown with zinc nitrate hexahydrate.

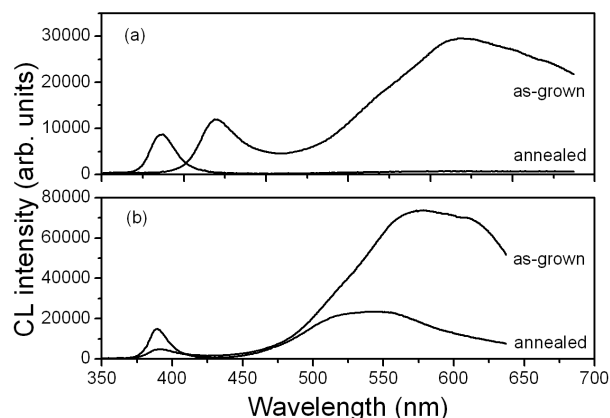


Fig. 3. Cathodoluminescence of ZnO nanopowders obtained from zinc nitrate hexahydrate (a) and zinc chloride (b). CL spectra for as-grown and annealed samples are shown.

For most of Cd–VI nanopowders the PL intensity strongly fluctuates in time (due to so-called blinking) limiting their use [6]. Thus, we have tested time stability of emission of the presently investigated ZnO powders. For this we measured time dependence of samples PL and CL (Fig. 4). In PL (not shown) we traced time dependence of intensity of the PL bands. In turn in the CL study we collected total intensity of the visible emission recorded every 10 s. In both cases we observed that emission is stable in time and there is no blinking. This is very encouraging result, likely related to some specific properties of ZnO surface states.

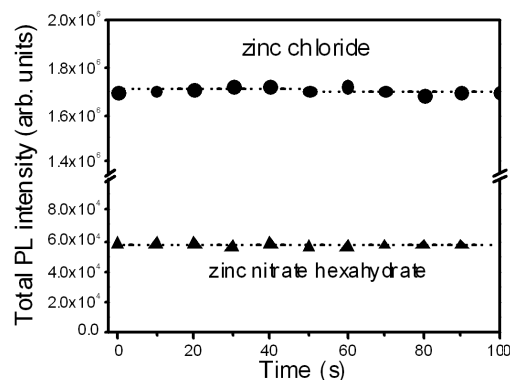


Fig. 4. Time dependence of the CL emission intensity (integrated intensity of the visible emission) measured every 10 s upon a constant excitation density.

Figure 5 presents SEM results for the annealed samples. The annealing procedure has no influence on the size and shape of nanopowders. The results of SEM investigations are as follows:

- ZnO powders made using zinc nitrate hexahydrate are twice larger than made with zinc chloride.
- n nanopowders obtained from zinc nitrate hexahydrate

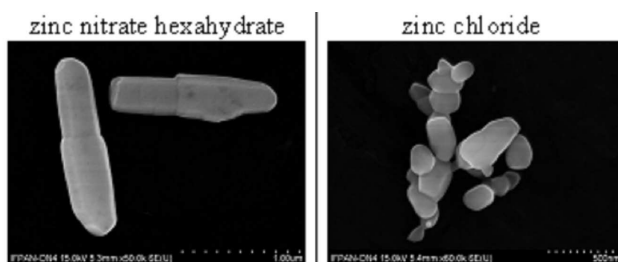


Fig. 5. SEM of ZnO nanopowders.

are nanorod-like and are granular in the case of ZnCl_2 precursor used.

Using SEM and CL we could determine the spatial origin of the observed light emission. We observed that the emission in the 350–650 nm range comes from the whole volume of a given nanoparticle, with only some small variations in the ratio between band edge and deep defect related emissions. No emission quenching was observed from areas of nanopowders close to the surface.

The present results are the starting point for further optimization of material properties and selecting of suitable doping methods.

For future applications it is necessary to search for the appropriate doping methods to get a bright emission in a visible spectral region, excited by e.g. blue light excitation, since the UV excitation should be avoided for applications in living organisms. For this we dope ZnO nanopowders with rare earth ions.

3. Summary

ZnO is the biocompatible material. We demonstrate that it can be used as a luminescence marker since the bright visible emission and no emission blinking can be

achieved. We also demonstrate a possibility to decrease the defects related luminescence of ZnO by a post growth annealing. These properties are very attractive for practical applications of ZnO nanopowders.

Acknowledgments

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