

The Luminescence Properties of ZnO nanopowders

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Abstract. Pure and Al³⁺ doped ZnO nanopowders were studied by means of time-resolved luminescence spectroscopy. The powders were synthesized by hydrothermal and plasma methods. These powders were used as a raw material for vaporization-condensation process inside the Solar reactor. The commercially available ZnO nanopowder was studied for a comparison. Exciton to defect band luminescence intensity ratio was estimated in different types of ZnO nanopowders. It was found that nanopowders with whiskers morphology show superlinear luminescence intensity depending on excitation density. The observed effect depends on the average nanoparticle size and on the powder morphology.

1. Introduction

ZnO is an II-IV semiconductor with 3.37 eV band gap and exciton binding energy ~60 meV. It is a promising material for optoelectronic applications such as photodiodes, light emitting devices. Various methods such as hydrothermal (HY) [1], plasma (PL) [2], vaporization-condensation in solar reactor (VC) [3] and others are used to synthesize ZnO nanostructures. Nanopowders synthesized by various methods have a different morphology, particle sizes and, correspondingly, spectral characteristics. The yellow or green luminescence associated with defects. The blue luminescence appears due to exciton process is possible for ZnO nanocrystals obtained by appropriate synthesis. Such luminescence bands are usually utilized for a ZnO sample characterization. As a rule the observation of intensive luminescence in blue spectral region is used for the ZnO sample quality characterization. [4]. Various dopants and powder morphology can change the luminescence properties especially the luminescence decay rate in defect related bands [5,6]. The luminescence of donor-acceptor pairs generally are peaking in the blue spectral region and their luminescence decay kinetic are slower if compare with excitonic luminescence [7]. Hence it is important to use time-resolved luminescence spectroscopy for the sample testing.

In this work, we report the time-resolved luminescence properties of pure and Al³⁺ doped ZnO obtained by HY, PL and VC methods and compare the luminescence characteristics in nanopowders with different morphology.

2. Experimental procedures

The ZnO samples were obtained by various methods: HY, PL and VC in solar reactor. The details of sample preparation were described in [1-3]. We use the commercially available ZnO nanopowder (Aldrich 99,99%) for the comparative studies. As a raw material for VC process we used the commercial, HY and PL synthesized undoped powders as well as the PL synthesized powders doped with Al³⁺ ions in different concentrations. It was found that after VC process Al³⁺ concentration are noticeably lower than in the raw material [1]. Some additional impurities (such as nitrides and chlorides) which can be detected in a PL synthesized powders have been removed during VC process. All studied samples are listed in Table 1.

Table 1. Samples description

Sample	Synthesis method	Dopant	Morphology
HY3	HY	-	Spherical nanoparticles
VC HY3	VC HY	-	Whiskers, tetrapods
PL G2	PL	-	Nanowires, nanoplanes
VC PL G2	VC PL	-	Nanowires, tetrapods
Al0.8	PL	Al 0.8 w%	Network of whiskers
VC Al0.8	VC PL	Al (0.8 w% in raw mat.)	Tetrapods
VC Al1.9	VC PL	Al (1.9 w% in raw mat.)	Tetrapods, nanoplanes
VC Al3	VC PL	Al (3 w% in raw mat.)	Nanowires, tetrapods
VC Al5.1	VC PL	Al (5.1 w% in raw mat.)	Nanowires, tetrapods
comm	Commercially available	-	Nanoparticles with regular hexagonal form
VC comm	VC	-	Whiskers, tetrapods

For the sample characterization SEM, X-ray diffraction (XRD) and specific surface area (S_{BET}) methods were applied. The SEM images of powders were obtained using a LEO 1530 field emission scanning microscope. The used experimental equipment for XRD and S_{BET} methods are described in [1,8]. XRD measurements show only the diffraction peaks from ZnO phase in all samples studied, except the PL_Al0.8 sample. In the last sample small contribution (less than 10%) of ZnAl₂O₄ spinel phase was detected [9]. The average grain size (d) of nanopowders was calculated from XRD peaks using the Scherrer's formula. Photoluminescence decay kinetics were measured for all samples in three spectral points where usually main luminescence bands appear: at 2.0 eV – yellow luminescence, which is typical for the HY synthesized powders, at 2.4 eV - green luminescence, which is typical for the commercial powder, the PL powders and for all powders obtained by VC process; at 3.2 eV – the luminescence due to excitonic processes - typical for all samples studied.

For the luminescence excitation we used fourth harmonic (266 nm) of YAG:Nd laser with a pulse duration 8 ns. Excitation pulse energy for the luminescence kinetics measurements was 1 μJ/pulse, the laser beam was focused in 2 mm² spot (50 μJ/cm²). The photomultiplier tube and ultra fast multiscaler (Fast ComTec Communication Technology module P8777-1E) were used for luminescence registration. For the luminescence decay measurements the time resolution was 2 ns.

The luminescence intensity dependence on the excitation density was studied under different excitation densities from 5 to 65 μJ/cm². All experimental procedures were performed at room temperature.

3. Results and discussion

Based on a well known fact that the excitonic luminescence in ZnO lies in a picosecond time range [10] and since the time response of our equipment does not allow to resolve so fast process we used the peak value of intensity in the decay kinetic (for our experimental equipment it is at 10 ns after the excitation pulse starts) for the exciton luminescence intensity characterization. Luminescence decay in the related defect band does not obey the exponential law and it has a slow decay time (hundreds nanoseconds). Since the decay rate depends on the sample morphology and particle size [6] we use the light sum in time gate from 25 to 200 ns ($SumI$) for defect band luminescence intensity characterization.

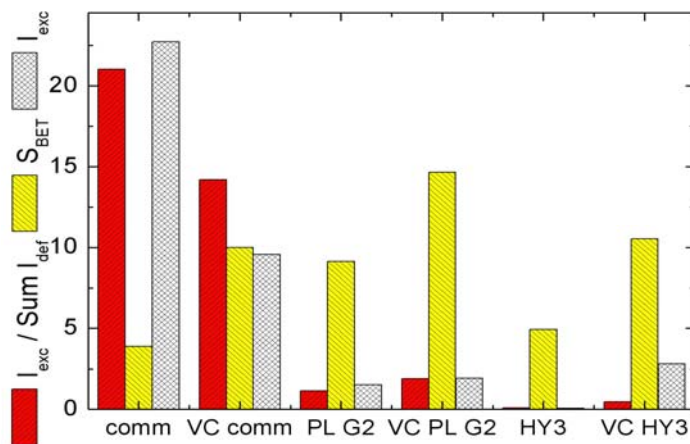


Figure 1. The ratio of the luminescence intensities of exciton to defect band ($I_{exc}/SumI_{def}$), specific surface area (S_{BET}) and exciton luminescence intensity (I_{exc}) for different undoped ZnO powders.

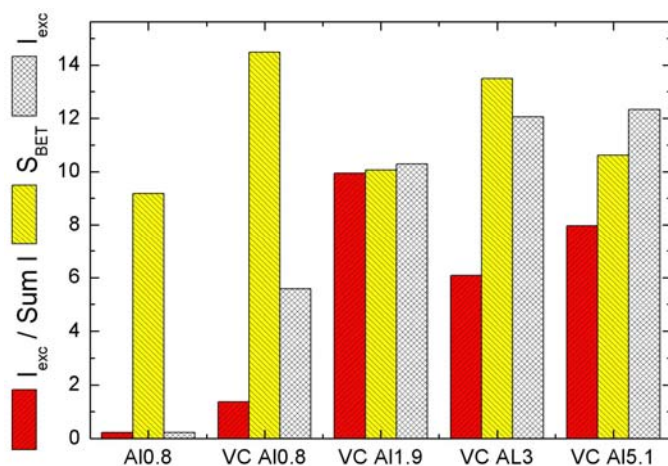


Figure 2. The ratio of the luminescence intensities of exciton to defect band ($I_{exc}/SumI$), specific surface area (S_{BET}) and exciton luminescence intensity (I_{exc}) for PL and VC PL powders doped with Al.

Figure 1 and 2 shows the results of the comparative studies of the defect and the exciton related luminescence bands for all samples. The results of S_{BET} are also shown on these Figures. It can be seen that after VC process the ratio of intensities in exciton to defect bands increases for all samples, except the commercial powder. The reason for this could be due to the changes of powders morphology. For PL synthesized nanopowders it is typical nanowires morphology (Figure 3a). In powders obtained by HY synthesis the spherical grains are observed in SEM images (Figure 3b). After VC procedure, independently of raw material, we obtain nanostructures like whiskers and tetrapods (Figure 3 c,d). Whisker's length and diameter may vary and depend on the synthesis parameters and doping. The S_{BET} values are in region 10-14 m^2/g for all VC powders.

For the commercial powder both exciton and defect related bands intensities decrease after the VC procedure. The commercial powder consists of regular hexagonal nanoparticles with size from 30 to

300 nm. It may be related to the significant morphology changing from regular hexagonal nanoparticles to whiskers. The intensity of the exciton luminescence band increases for PL and HY synthesized nanopowders after VC procedure. The intensity of the defect related luminescence after VC slightly decreases. In HY raw powders the main band was yellow, but after VC the yellow band disappears and only the green band was detected. This intensity growth of the green luminescence is due to defects which appear after VC procedure and previously not observed in the raw material. Al³⁺ doped PL synthesized powders show similar to the undoped samples behavior – after VC procedure the intensity of the luminescence band related to the exciton increases, but the intensity of luminescence band related to the defects decreases.

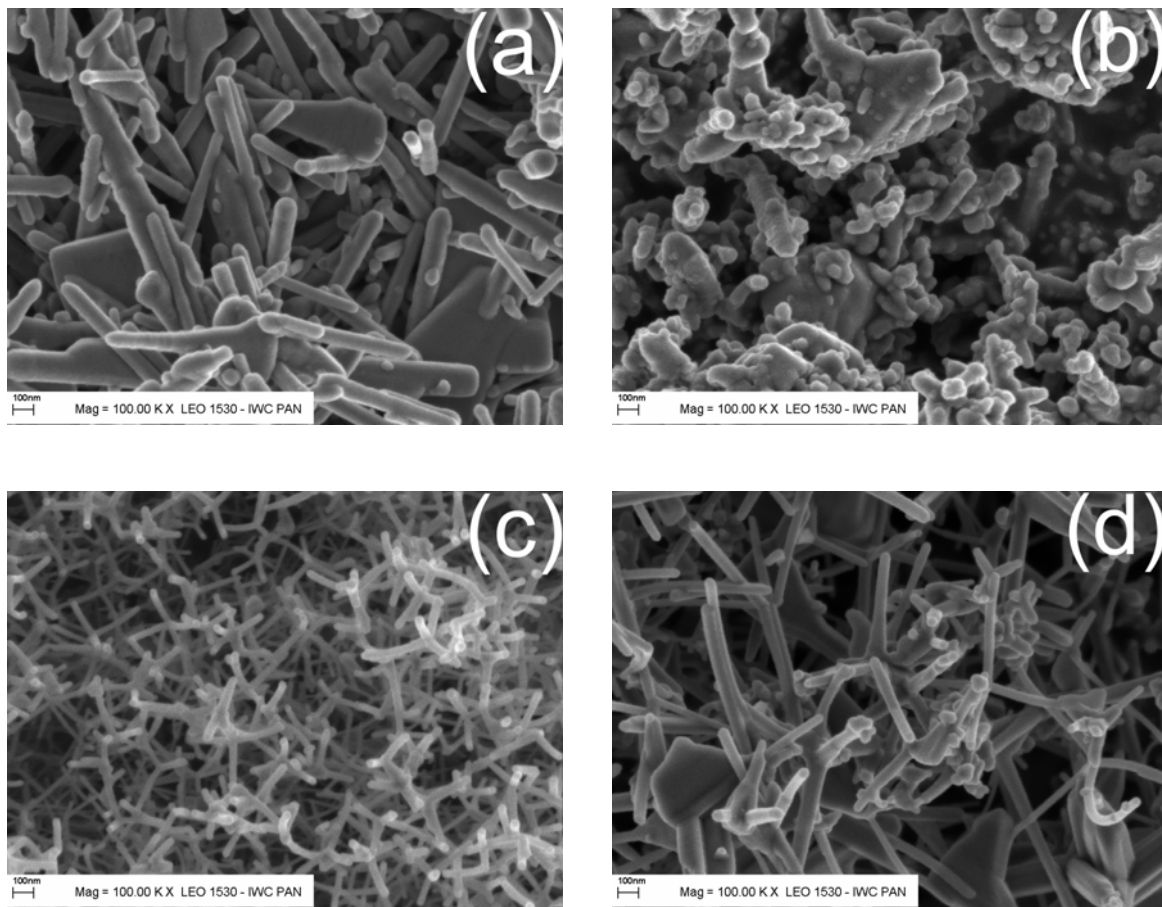


Figure 3. SEM images of ZnO nanostructures: (a) PL G2; (b) PL Al0.8; (c) VC Al0.8; (d) VC Al3; similar to (d) nanostructures have all VC samples with exception of VC Al0.8.

It is observed that the exciton band intensity after VC procedure depends on Al concentration and at concentrations higher than 1.9 wt% Al it is saturated and doesn't noticeably change. Defect band luminescence intensity correlates with specific surface area. It means that for the structures with the lower grain size we obtain higher luminescence intensity of the defect band. We suggest that it is due to higher surface defect centers concentration. Since in VC powders S_{BET} value changes are small the changes of light sum in defect luminescence band are negligible. The highest value S_{BET} (14.47 m²/g) was detected for VC PLAl0.8 sample (see also the SEM image in Figure 3c) and the light sum in defect band is large in comparison with the other VC powders. It is the reason why the low value of the ratio $I_{exc}/SumI$ was observed in this powder (Figure 2). With increasing Al³⁺ concentration in the raw material to 1.9wt% and higher the morphology of powders after VC procedure doesn't strongly

changes. Comparing with the VC AL0.8 sample tetrapods and whiskers become longer and overall size of the nanoparticles increases. That leads to $I_{exc}/SumI$ increase, which is related to exciton luminescence increase and defect luminescence slight decrease. The highest value of $I_{exc}/SumI$ was obtained for VC Al1.9 powder. Possibly 1.9wt% Al^{3+} concentration are optimal for obtaining intense excitonic luminescence and relatively weak defect luminescence.

On Figure 4 exciton type luminescence intensity dependence on the excitation pulse energy is shown. All samples with whiskers morphology show superlinear dependence on the excitation pulse energy ($I \sim P^2$). Such dependence sometimes is called lasing effect [11]. In commercial powder superlinear intensity dependence from excitation pulse energy was not observed (Figure 4a). It can be explained by morphology and by size effects. The superlinear dependence is due to exciton coupling effect [12]. For the process characterization we choose the angle of slope (α) of straight line ($I \sim P^2$) (Figure 4 a). The same dependence on excitation pulse energy was obtained for PL powders before and after VC process. In Al doped samples the angle of slope increases with Al concentration growth. It means that exciton coupling are more efficient in samples with higher Al concentrations. This is in a good correlation with the excitonic luminescence intensity dependence on Al concentration (Figure 2).

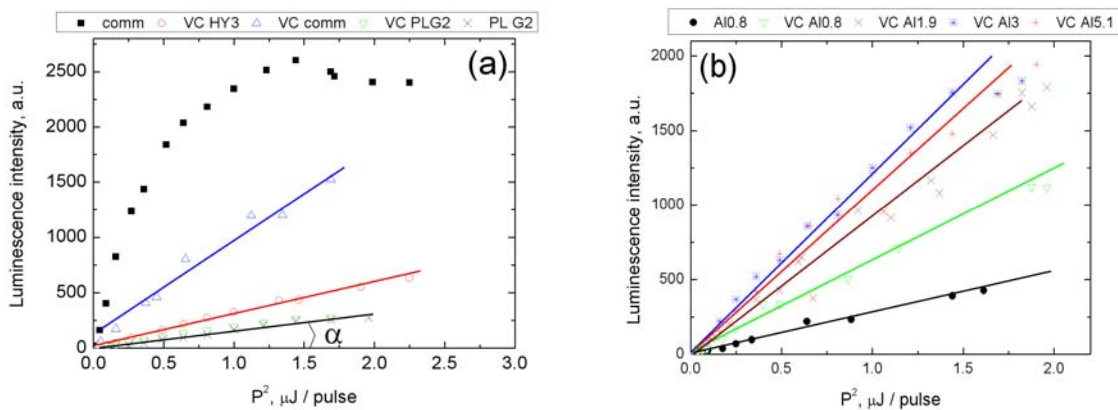


Figure 4. Luminescence intensity (at 3.2 eV) dependence on laser excitation pulse energy: (a) undoped samples; (b) Al doped samples

Figure 5 shows the angle of slope and average grain size dependences on Al concentration. The grain size was estimated from XRD measurements. The good correlation was found and it means that the efficiency of superlinear luminescence process depends on average grain size of nanostructures under investigation.

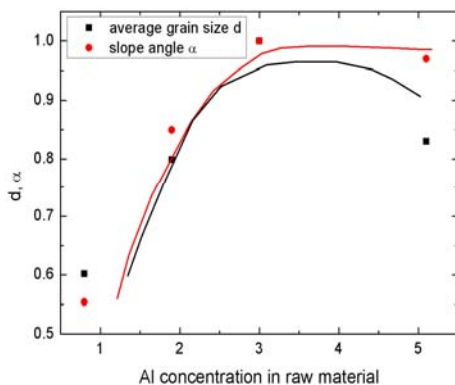


Figure 5. Slope angle (α) and grain size (d) dependence on Al concentration for VC ZnO powders.

Thus, two characteristics of samples are very important: the size of nanotetrapods or nanowires and the intensity of excitonic luminescence. For the studied samples the best powder is VC Al₃. The present investigation gives validation for the estimation of optimal dopand concentration and technology of nanopowders preparation for the obtaining the light emitting materials.

4. Conclusions

The studies of luminescence kinetics in typical points of spectrum in different doped and undoped ZnO nanopowders using time-resolved photoluminescence were presented. It was found that after VC procedure for most samples the ratio of exciton to defect luminescence intensity increases. This ratio together with luminescence intensity in excitonic band can be taken for the surface defect concentration characteristic. For Al doped samples it is found that the luminescence intensity in the excitonic band region is higher than that in the undoped powder. The intensity of the excitonic band increases with Al concentrations and saturates. Defect band luminescence intensity strongly depends on the nanopowders morphology and powders specific surface area.

For all samples with tetrapods and nanowires morphology we observed superlinear luminescence dependence on the laser excitation pulse energy. This fact shows that lasing effect in nanostructures with nanowires and tetrapods morphology obtained by VC in Solar reactor can be observed. Lasing effect are more effective in long, but small diameter nanowires and whiskers.

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