Blue luminescence in ZnO single crystals, nanopowders, ceramic

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Abstract. The luminescence spectra and luminescence decay processes were studied in a ZnO single crystal, nanopowders and ceramic at liquid helium and room temperature under VUV synchrotron radiation as well as under pulsed laser excitation. The exciton-exciton and exciton-multiphonon processes were compared in different ZnO nanopowders (commercial powder, powders obtained by vaporization-condensation technique) and ceramic. The possibility of luminescence decay time modification by Al^{3+} doping was shown.

1. Introduction

ZnO has been widely studied due to its application in optoelectronic devices, including blue light emitters [1,2], transparent electrodes for solar cells [3], piezoelectric sensing [4]. ZnO is unique material for nanostructures preparation. The ZnO nanoparticles, films, nanorings, nanorods, nanotubes, nanowhiskers and tetrapods can be obtained [5]. The studies of ZnO preparation, investigation and application enjoy a wide popularity.

To date arious methods for ZnO synthesizing are known: hydrothermal process (HY) [5], chemical vapor deposition (CVD) [7] and metal-organic chemical vapor deposition (MOCVD) [8], pulse laser deposition [9], plasma process [10] and others.

The luminescence spectra and XRD studies were usually used for ZnO sample testing. At the same time the luminescence mechanisms and processes even in ZnO single crystal is not clear so far. As a rule two different spectral regions were considered: green-yellow and blue luminescence. The origin of yellow and green luminescence is point of discussions for many years [11-13]. These luminescence bands were attributed to different defect states. The different bands distribution was observed, for example, after the annealing of ZnO nanorods in air (or oxygen) atmosphere and in reduction atmosphere [14]. Luminescence spectra and luminescence decay times in defect related peak depends on nanocrystal preparation method and grain sizes [15].

The blue luminescence exhibits in spectral region ~3.0-3.4 eV and it is very intensive at low temperature. The results of low temperature photoluminescence (PL) spectra have been reported in number of publications [16-19]. The luminescence in blue region is very complicated since the free excitons, bound (donor and acceptor) excitons and their phonon satellites are involved [18,19]. The main band observed at liquid helium temperature (LHeT) in a single crystal is peaking at 3.36 eV and has been attributed to exciton bound at neutral donor. The donor-acceptor luminescence peaking at

3.232 eV in nitrogen implanted ZnO single crystal [20].The more intensive luminescence peak at room temperature (RT) at 3.26 eV is due to annihilation of LO-phonon assisted exciton (Ex_LO).

The blue luminescence studies are important from two aspects: for the understanding of fundamental processes in different ZnO structures and for the light emitting devices, fast scintillators and other applications. The purpose of the present work is the study of the blue luminescence mechanisms and its behavior of ZnO samples: a single crystal, nanowhiskers, ceramic.

2. Experimental

2.1. Samples preparation and characterization.

Different synthesis routes were used to obtain pure and doped ZnO nanostructures. The first route is based on hydrolytic precipitation of ZnO (samples denotes HY) using water solution of zinc chloride $ZnCl_2$ and NaOH as starting precursors [6].

The second route is based on plasma chemical synthesis (samples denoted PL) according to the method described in details in [10]. The Al doping was possible directly in plasma reactor and the maximal concentration of Al was 5.1 wt.%.

The third route is the vaporization-condensation (VC) in a solar furnace according to the procedure described in [21]. The commercial ZnO powder (Aldrich 99.99) and nanopowders obtained by HY or PL synthesis was used as precursors for VC process (samples denoted VC_com, VC_HY and VC_PL, respectively). In the VC method the nanostructures grows as a result of vapor condensation ZnO precursors on the cold substrate under controlled air pressure (10-40 Torr) [21,22].

X-ray diffraction (XRD), scanning electron microscope (SEM) and Specific Surface Area (S_{BET}) methods were used for all samples studied. For all samples only ZnO hexagonal wurtzite phase was detected by XRD. The relatively wide distribution of particles size as well as growth of whiskers and tetrapod structures for ZnO prepared by VC has been observed in SEM images.

The luminescence properties of two ZnO ceramic samples were studied. One of them (Cer_com) was sintered from commercial powder (S_{BET}=3.9 m^2/g, initial grain size 200-300 nm). Sintering conditions was: 48 hours, 1400 ^{0}C, in air. The average grain size in ceramic was ~10 - 15 μm. Second one (Cer_PL) was sintered from PL powder (S_{BET} = 22 m^2/g; nanowires structure; length 1-5 μm, diameter ~ 50 nm). The powder was mixed with 3% solution of oleic acid in alcohol. After drying at 120 ^{0}C the powders were sieved through 200 μm sieve and pressed under pressure of 1.0 MPa. The oleic acid was burn out at 650 ^{0}C and the pressed samples were sintered in air for 2h at the temperature 1150 ^{0}C and the heating rate of 10 degree/min. The density of sintering ceramic was 96% from a single crystal density.

2.2. Experimental procedure

Luminescence properties have been measured using two experimental equipments. At first the pulsed YAG:Nd laser (266 nm, 10 ns pulse duration) was used for luminescence excitation. The luminescence spectra and decay kinetics have been measured using photomultiplier H8256 (HAMAMATSU) and P7888-1(E) multiscaler (FAST ComTec GmbH) for time-resolved measurements. The time gate of the photon counting system was 2 ns; instrumental response 10 ns. The experiments were performed at room temperature (RT).

The second set of experiments have been done using the SUPERLUMI line in HASYLAB at DESY, (Hamburg) [23]. The luminescence spectra and decay kinetics were measured at 8.5-10 K under VUV synchrotron radiation excitation in the range 3.8 – 20 eV. The photomultiplier HAMAMATSU R6358P was used. The luminescence spectra were detected with spectral resolution 0.02 eV (at 3.1 eV). The excitation pulse FWHM was 130 ps, the time gates were 0.051 ns or 0.203 ns; instrumental time response was 2 ns.

3. Results and discussion

The luminescence spectra, luminescence yield and luminescence decay for nanocrystalline materials strongly depends on nanocrystal sintering conditions. The green-yellow spectral region is widely studied at RT. The scope of present work is to analyze the luminescence in blue spectral region. The blue luminescence in ZnO covered wide spectral region from 3.0-3.4 eV and consist from narrow peaks due to different types of exciton annihilation and donor-acceptor pair (DAP) recombination. The luminescence models and peak positions were studied in details for ZnO single crystal [19-20]. In Table 1 the luminescence peak positions and suggested luminescence models are given. The cited data are summarized from [19, 24- 25].

Table 1. Luminescence peak positions and luminescence models in ZnO

Peak position (eV)	Temperature	Luminescence model
3.44-3.37	10K	Ex_A (free exciton)
3.36	10K	Ex_AD^0 (Ex bound at neutral donor)
3.349-3.355	10K	Ex_AA (Ex_A bound at acceptor A)
3.28-3.29	10K	1LO_ Ex_AD^0
3.31-3.32	10K	TES (two electron satellite)
3.25-3.27	10K	1LO_TES
3.22-3.23	10K	DAP (donor-acceptor pair)
3.15	10K	1LO_DAP
3.35	80K	Ex_AD^0
3.3	80K	1LO_ Ex_A
3.225	80K	2LO_ Ex_A
3.33	RT	Ex_A
3.26	RT	1LO_Ex_A
3.18	RT	Ex_A - Ex_A (biexciton)
3.12-3.1	RT	EHP (electron-hole plasma)

The LO phonon energy in ZnO is ~72 meV and 1LO-, 2LO- replicas of the exciton, TES, DAP were observed in low temperature spectra. The excitonic processes in ZnO are very complicate and depend on sample purity, excitation density, temperature, etc. The luminescence decay time of 1LO_Ex at RT is in a range of 400 ps for fast and 3.8 ns for slow components, respectively [25]. Certainly, the photoluminescence technique is very powerful for the exciton processes studying and samples testing, but it is necessary to carry out the fast luminescence measurements at low temperature and with high spectral resolution.

Figure 1 shows the luminescence spectra of a ZnO single crystal. The peaks due to excitons bound at neutral donor, TES and its phonon satellites were well resolved. The peak positions are in good agreement with data shown in Table 1.

The luminescence spectra obtained for Al doped ZnO nanopowder and ZnO ceramic under excitation with 10 eV photons at 8.5 K are shown at Figure 2a. The luminescence spectrum for single crystal is shown too. The nanopowder was prepared by VC in solar reactor from the nanopowder obtained by PL synthesis. The concentration of Al doping was 1.9 wt.% at raw material. The SEM image of this VC_PL Al sample is shown in Figure 2b. The measurements conditions (excitation energy, temperature, slits, counting time) were the same for all spectra presented in Figure 1 and Figure 2.

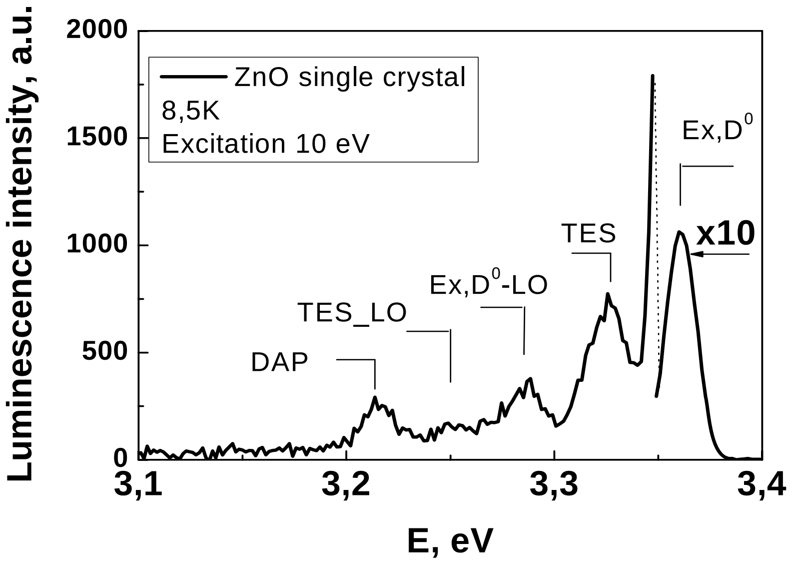

Fig.1. The luminescence spectrum of ZnO single crystal and luminescence models according to [18].

The main luminescence peak is observed at 3.36 eV and is associated with exciton bound at neutral donor (Ex_D^0). Only this luminescence is detected in ZnO ceramic sample. The luminescence intensity in ceramic is lower by factor two in comparison with nanopowder and the TES peak probably should be detected. The intensity of 3.36 eV peak in nanopowder is lower by factor five in comparison with a single crystal. In the nanopowder the intensities of 3.325 eV peak (TES) and 3.36 eV peak (Ex_D^0) are approximately the same. Note, that in a single crystal the 3.36 eV peak is by an order of magnitude higher than the 3.325 eV peak. Therefore, the excitonic processes with creation TES states are more effective in the nanopowders. In the nanopowder the peaks are broader and the 1LO_ExD^0 peak is not resolved (the peak should be hided under TES peak). In the nanopowders exciton-phonon interaction is more effective than that in a single crystal since the 1LO_ExD^0, 1LO_TES and 1LO_DAP peaks were detected in nanopowders. The tentative reasons responsible for observed phenomena are: the processes at nanopowder surface and Al doping. ZnO doping with Al^{3+} require a charge compensator and changes the concentration of neutral donor. These states usually present in ZnO and are involved in the TES state creation. The TES peak is slightly shifted to the low energy side of the spectrum in nanopowders if compare with single crystal (Figure 2a). We suggest that donor concentration near the surface is different in a single crystal and in nanopowder (due to a large surface area in the nanopowders).

Luminescence decay at 3.36 eV peak in a single crystal, undoped nanopowder, Al doped nanopowder and ceramic were shown in Figure 3. The decay kinetics were normalized at t=2.5 ns. Since the time resolution of equipment is ~2 ns and decay time of 3.36 eV peak in a single crystal is in ps range [20], it is impossible to correct estimate the decay times. Only the comparison of decay kinetics at t> 5 ns has been carries out. One can conclude from the results shown in Figure 3 that the fast luminescence with close decay time was observed in crystal, ceramic and undoped nanopowder (VC_com). The slower decay was detected in the nanopowder obtained by VC technique from Al doped PL (VC_PL_Al) powder. In ceramic samples the blue luminescence is intensive. The decay time is very fast and this type of luminescence could have a practical application.

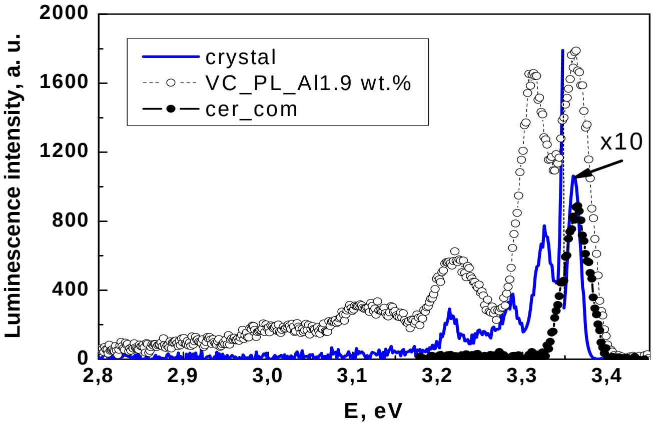

Figure 2a. Luminescence spectra of ZnO single crystal. nanopowder, ceramic. Excitation 10 eV; 8.5K.

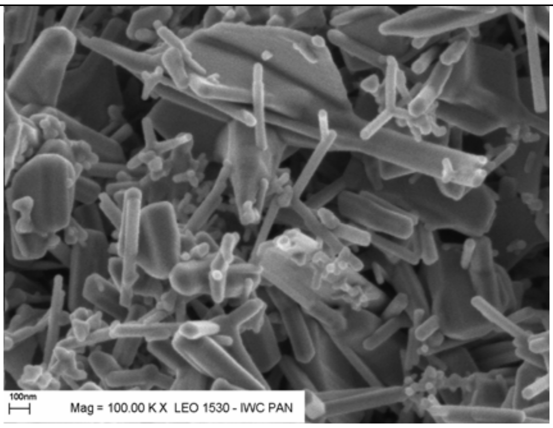

Figure 2b. SEM image of ZnO nanopowder obtained under VC process from Al doped PL powder (VC_PL_1.9 wt.%Al).

The luminescence decay was compared for different peaks in the same VC_com powder (Fig.4). The luminescence decay in TES peak is significantly slower than that in ExD^0 peak. The TES_LO and DAP bands overlap in VC powders. The decay kinetics was detected at two sides of the wide band (3.23 eV and 3.21 eV) and the contribution of slow decay component higher for 3.21 eV peak.

The luminescence decay studies shows that the slower decay rate was observed in luminescence peaks 3.36 eV, 3.32 eV and 3.15 eV in Al doped ZnO nanopowders than that in a single crystal. In ZnO ceramic only one luminescence band (ExD^0) was detected. The decay time in this band coincides with that for single crystal (Figure 3). The study of luminescence properties in ZnO ceramic is important since the ceramic sintering is technically simpler than growth of a single crystal.

The main luminescence peak in blue spectral region in all samples studied at RT is at 3.26 eV. The model of this luminescence is 1LO_Ex annihilation (see Table 1). This band is detected in a single crystal, nanopowders and ceramic. The luminescence is very fast and disappears completely at t<10 ns after excitation pulse start.

The result of time-resolved photoluminescence study of ZnO ceramic is shown in Figure 5. The broad luminescence peaking at ~2.4 eV and luminescence peaking at 3.26 eV were observed. The decay times of these bands are different. The luminescence decay at 3.26 eV peak is fast and decay time is lower than 1 ns. The intensive and fast luminescence at 3.26 eV could find a practical application.

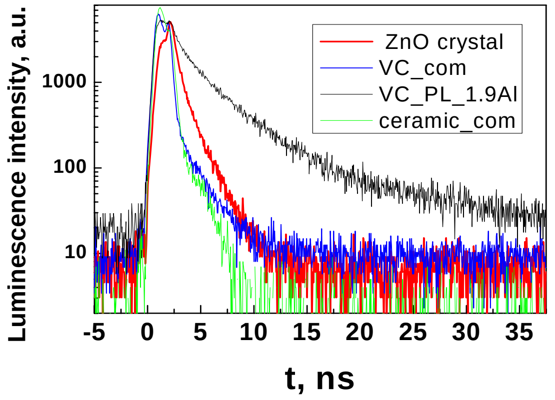

Figure 3. Luminescence decay kinetics for 3.36 eV (ExD^0) peak; T=8.5 K, excitation 14 eV

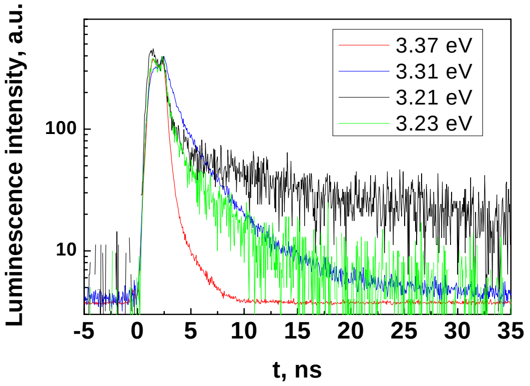

Figure 4. Luminescence decay kinetics for VC_com nanopowder in 3.36 eV (ExD^0), 3.31 eV (TES), 3.23 eV (TES_LO) and 3.21 eV (DAP) peaks; T=8.5 K, excitation 14 eV

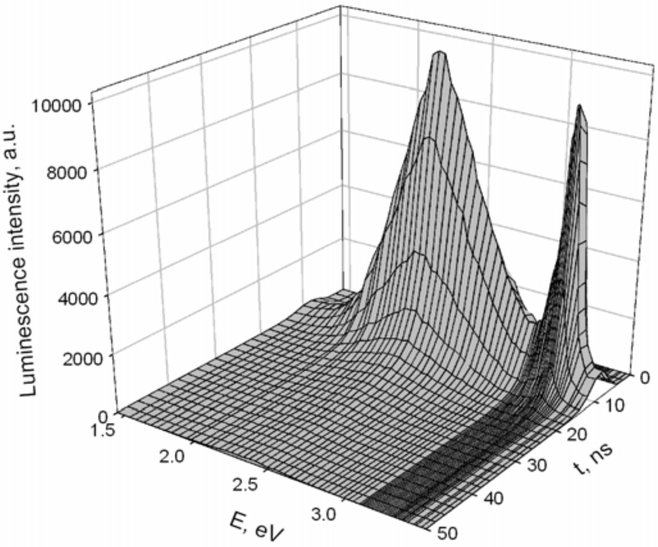

Figure 5. Time-resolved luminescence of ZnO ceramic (cer_PL); excitation 266 nn, RT

Conclusions

The luminescence properties different type ZnO: crystal, VC nanopowders (undoped and Al doped) and ZnO ceramic were studied in spectral region 2.8-3.4. The luminescence spectra at LHeT were presented and identification of observed luminescence bands was made. It is shown that in nanopowders the exciton–phonon interaction processes are more effective. In ceramic sample only luminescence due to annihilation of exciton bound at neutral donor was detected in blue spectral region; the phonon satellites were not detected. The luminescence decay rates in ceramic and single crystal are comparable. The luminescence decay in Al doped ZnO nanopowders was studied. The slower decay rate was observed in luminescence bands 3.36 eV, 3.32 eV and 3.15 eV in Al doped nanopowders in comparison with a single crystal.

The TES band is shifted to the lower energy side of spectrum in VC nanopowders. Relative contribution of this band is significantly larger than that for a single crystal. These changes were supposed to be due to donor center symmetry and/or concentration of donor centers in nanocrystals.

The intensive fast luminescence in blue spectral region was detected under 266 nm excitation at RT in ZnO ceramic. The decay time of this luminescence band is <1 ns.

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