

Zinc Oxide: Soft Hydrothermal Synthesis and Luminescent Characteristics.

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Microcrystalline ZnO powders and polycrystalline films were synthesized by soft hydrothermal methods at temperatures 150-250°C using different types of Zn-precursors and solvents. The luminescent characteristics of ZnO crystalline powders and films were analyzed depending on the growth conditions (type of precursor, solvent, impurity). Polycrystalline films were obtained on the Zn-substrate due to oxidation and precipitation processes. The sizes of crystallites were 100-10000 nm depending on growth conditions. The films and powders were studied using XRD, SEM and ICL spectroscopy. Spectra of ICL were obtained for bulk single crystals, powders (synthesized from various ZnO-precursors) and polycrystalline films. Two characteristic bands of emission (in UV and visible parts of spectrum) were observed in spectra. The ratio of their intensities I_{UV}/I_{VIS} depends on the crystallographic orientation (single crystal) and pre-history of the sample.

Key words: zinc oxide; hydrothermal synthesis; UV luminescence; impulse cathodoluminescence.

1. INTRODUCTION

Wide-gap semiconductor ZnO is very well known compound due to a wide range of its applications in various regions of modern techniques. Zinc oxide is of special interest for low-voltage and short wave length electro-optical device, piezoelectric transducers, chemical sensors, varistors etc, technologies and medicine [1- 4]. One of the attractive properties of zinc oxide is bright luminescence in several regions of spectrum (orange luminescence, $\lambda \approx 600$ nm, green luminescence, $\lambda \approx 520$ nm, UV luminescence, $\lambda \approx 385$ nm). UV luminescence makes zinc oxide a perspective material for manufacture of UV lasers operating at room temperature and display devices.

First observation of ultraviolet stimulated emission and lasing of ZnO at low temperatures have been made many years ago (electron beam excitation [5-7], optical excitation [3, 8]. UV luminescence of ZnO at room temperatures has been mentioned in [9] and has been studied in publications of last decade [10-16].

The violability of light emitting devices, based on ZnO, is clearly demonstrated in these recent publications. It was shown that effective generation in UV region for disordered nanosized polycrystalline powders and films of ZnO is one order higher in comparison with bulk crystals [11]. This fact explains growing interest to manufacture of low-sized powder samples of ZnO.

Ultrathin powders consisting of faceted crystallites of definite shape may be obtained using various techniques (from simple mechanical grinding to plasma spraying). ZnO samples analyzed in [11-15] were obtained by different methods such as the crystallisation from the gas phase, precipitation onto various substrates using pulsed laser deposition, laser molecular epitaxy, laser or plasma spraying, MBE, powder pressing and annealing at temperatures more than 1000°C, precipitation from the solution during the electrophoresis. Among the other techniques, the hydrothermal synthesis is of special

interest because (a) it operates at rather low temperatures, (b) it allows to vary the crystal size and properties in a wide range due to varying the growth media composition, temperature, pressure and (c) hydrothermally obtained crystals have shown much higher efficiency of UV-luminescence in comparison with crystals grown from the gas phase [16].

The first results on hydrothermal growth of ZnO bulk single crystals and optical properties were described in [3, 5]. The lasing in UV range of spectrum was found in hydrothermal ZnO bulk crystals, and also in the films and powders. UV luminescence arises as a result of emission recombination of excitons (interband exciton recombination) and it depends on the quality of the material under study.

We performed the investigations on the synthesis of ZnO (single crystals, powders and polycrystalline films) by soft hydrothermal techniques and on the study of luminescence characteristics of ZnO depending on the growth conditions.

2. EXPERIMENTAL PROCEDURES

Zinc oxide thin powders and polycrystalline films were synthesised by soft hydrothermal chemistry methods at low temperatures. Experiments were carried out under isothermal conditions and under conditions of temperature gradient.

To choice the best conditions for obtaining low-dimensional powder, we carried out the ZnO synthesis at various Zn-precursors, solvents, temperatures.

Different compounds have been discussed in literature as precursors for ZnO-based materials [17]. The most widely used precursor is Zn-nitrate although it is very difficult to remove the anion species in the final product. Zn-acetate seems to be a little preferable as ZnO-precursor due to easy decomposition of acetate groups in the gel at heating. We used both Zn-salts for preparing amorphous Zn(OH)₂.

The basic parameters of the experiments were as following:

Zn-precursor	as-prepared amorphous $Zn(OH)_2$, ZnO, Zn;
Solvent	H_2O , KOH, 5-25 wt.%; 5 m KOH+1.2 m LiOH;
Dissolution temperature	150-250°C;
Temperature gradient	0.5 degree/cm;
Fill coefficient	0.85;
Experiment duration	10-48 hours.

The synthesis process consisted of several steps: heating, keeping at high T, slow cooling till room temperature or quenching.

The following series of the experiments were performed:

- A: ZnO-precursor – chemical ZnO; solvent R – H_2O , KOH 5-25 wt.%;
 B: ZnO-precursor – $Zn(OH)_2$ prepared using zinc acetate as a starting Zn-source; R – H_2O , KOH 5-25 wt.%;
 C: ZnO-precursor – $Zn(OH)_2$ prepared using zinc nitrate as a starting Zn-source; R – H_2O , KOH 5-25 wt.%;
 D: ZnO-precursors are variants A, B, C; metallic Zn; R – H_2O , KOH 5-25 wt.%.
 In D-series metallic Zn was served as substrate for precipitation of polycrystalline ZnO-films.

Metallic Zn was introduced into the system to change the red/ox potential and as a result the stoichiometry of ZnO. It is known that hydrogenation of ZnO leads to increase of the efficiency of band edge emission [16]; in our case hydrogen is released as a result of interaction between Zn and KOH.

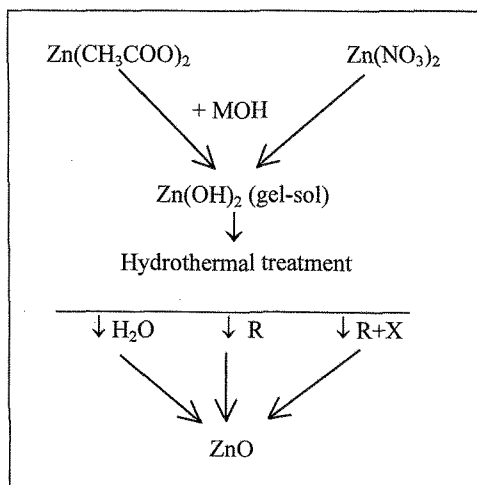


Fig. 1. The scheme of the experiments in the series B, C, D.

The powders and films were analyzed using XRD (Diffractometer Rigaku D-max III-C, $\lambda Cu K\alpha$), SEM (JEOL JXA-840) and impulse cathodoluminescence (ICL) spectroscopy. The spectra of impulse cathodoluminescence were obtained using set-up

"KLAVI-1" constructed in Institute of Electrophysics, Ural Division of RAS (energy of electrons in the beam 180 ± 20 keV, current density 700 ± 100 A/cm², $\tau \approx 2$ ns).

3. RESULTS AND DISCUSSION

3.1 Crystal growth and morphology

ZnO crystalline powders with different form-factors (size and shape of the particles) were obtained in all experiments with output up to 100% depending on growth conditions. Polycrystalline films were formed on the Zn-substrate in the growth zone. ZnO was crystallized as a result of (a) dehydration of starting amorphous Zn-hydroxide at high temperatures; (b) dissolution and recrystallisation of ZnO starting material; (c) oxidation of Zn-substrate. The sizes of crystallites

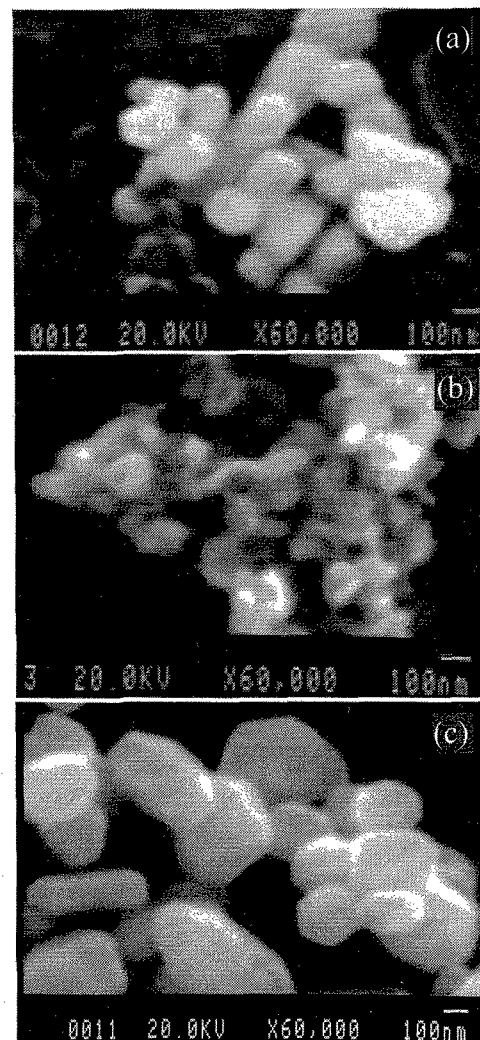


Fig. 2. Typical growth morphology of ZnO crystallites in powder synthesized at 180°C.

- (a) A-series, system ZnO- H_2O ;
 (b) B-series, R = H_2O ;
 (c) C-series, R = KOH 25%.

were 100-10000 nm depending on growth conditions. In accordance with X-ray diffraction data, complete (100%) recrystallization of starting precursors occurs at temperatures about 150°C. Increase in temperature by

50-70°C allows to decrease the duration of hydrothermal treatment in 4-5 times. Increase of the growth process period leads to the appearance of larger size crystals growing due to dissolution of smaller ones.

The powders contain the faceted microcrystallites. Typical simple crystallographic forms are positive monohedron $\langle 0001 \rangle$, negative monohedron $\langle 000 \bar{1} \rangle$, hexagonal prism $\{10 \bar{1}0\}$, hexagonal pyramid $\{10 \bar{1}1\}$. Depending on growth conditions, platelet or prismatic habits of microcrystals are prevalent in powders obtained. The sizes of hexagonal plates and prisms are defined by the growth conditions (type of the solvent, type of ZnO-precursor, presence of the impurities, temperature).

Crystallization in pure water results in weak faceting of the crystallites; faces $\{10 \bar{1}0\}$ and $\{10 \bar{1}1\}$ are forming the crystal habit (Fig. 1 a, b). Prismatic crystallites (maximal c/a ratio) are formed at $R=H_2O$.

Introduction of KOH into the growth system leads to decrease of crystallite growth rate in c -direction due to change of the growth mechanism [18]; crystalline habit changes from prismatic to platy one. The higher is KOH concentration the less c/a ratio is observed for ZnO-platelets (Fig. 2,c).

For crystallites obtained in pure water, faceting is less pronounced in B -series, uniform distribution of crystalline dimensions is characteristic of this series; crystallites are smaller in comparison with C -series. Crystalline powders obtained in C series are characterized by clear faceting with well-developed faces of monohedra.

3.2 Spectra of cathodoluminescence

ICL spectra were obtained for the following groups of ZnO samples:

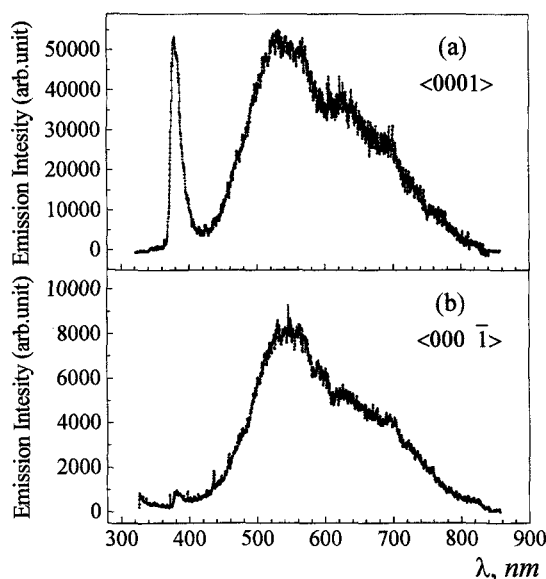


Fig. 3. ICL spectra for ZnO single crystals recorded on the samples cut from growth pyramid $\langle 0001 \rangle$ (a) and $\langle 000 \bar{1} \rangle$ (b).

- bulk single crystals (plates cut from growth pyramid of positive monohedron $\langle 0001 \rangle$ and growth pyramid of negative monohedron $\langle 000 \bar{1} \rangle$);
- powders obtained in series A, B, C with various ZnO-precursors;
- polycrystalline films obtained in series D .

Typical ICL spectra for hydrothermally grown ZnO single crystal are shown in Fig. 3.

Two characteristic bands of emission are observed in spectra. Narrow one in UV region ($\lambda \sim 385$ nm, $\Delta\lambda \sim 15$ nm) is caused by emission recombination of excitons. Wide band ($\lambda \sim 500$ nm, $\Delta\lambda \sim 200$ nm) in visible part of spectrum is explained by the presence of donor and acceptor levels (defects as O -vacancies, interstitial Zn-ions, impurities etc). One can see that the ratios between the intensities of these two band, I_{UV}/I_{VIS} , are different for the samples cut from growth pyramid of positive and negative monohedra $\langle 0001 \rangle$ and $\langle 000 \bar{1} \rangle$. In the first case $I_{UV}/I_{VIS} \sim 1$, while for negative monohedron I_{UV}/I_{VIS} ten times lower. At the same time the shapes of VIS-bands are similar one to another. We consider that this fact may be explained by similar nature, but different quantity of quenching centers in positive and negative monohedra. The difference in the band intensities seems to be pronounced in powder samples not so sharply due to random packing of crystalline particles in powders.

ICL spectra for ZnO powders are shown in Fig. 4 for the three samples obtained at different conditions in D -series. As in the case of single crystal spectra, two basic bands are observed in the spectra. The shape and positions of UV-band are the same for all studied samples, but its intensities are varied depending on pre-history of the sample. Notice that I_{UV} are usually different for ZnO polycrystalline films obtained on the Zn-plates and ZnO powders in the nutrient. This fact may be explained by different growth mechanisms in both cases (recrystallization in nutrient and oxidation-enhanced precipitation on the substrate).

Strong variation of UV luminescence was found depending on ZnO growth conditions: The increase in KOH concentration results in lowering the intensity of UV luminescence ($\lambda \sim 385$ nm) of polycrystalline films; simultaneously the intensity of visible luminescence increases.

For VIS-bands the change in shape and position is characteristic. The VIS-band of luminescence (420-850 nm) consists of several wide overlapping bands. Decomposition of VIS-band shows the presence of more than 3 bands, among them the bands with $\lambda \sim 530$, ≈ 630 , ≈ 700 and ≈ 740 nm are the most intensive. The change of the shapes may be connected with different ratios of quenching centres in the samples obtained under different growth conditions. Thus, the shift of VIS-band maximum (Fig. 3, b) into long-wave part of spectrum is caused by the increase of the numbers of quenching centres with $\lambda \sim 630$ nm.

Analysis of literature and our data on ZnO luminescent properties (partially discussed in [19, 20]) has shown that at least two factors define the efficiency of UV lasing. They are: (a) form-factor of the crystallites (shape and dimensions), their space distribution; (b) spectroscopic properties of crystallites depending on the presence of defects which form the quenching centers.

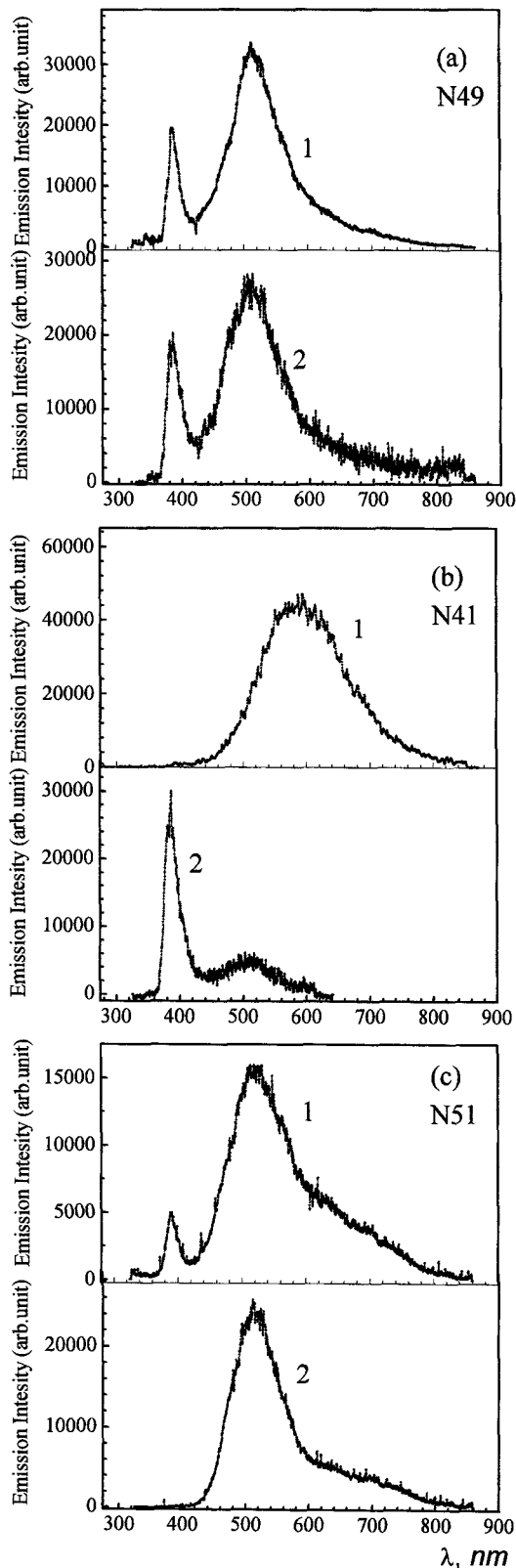


Fig. 4. ICL spectra for ZnO synthesized under different conditions in *D*-series.

- (a) precursor *A*, system ZnO-H₂O-Zn;
 (b) precursor *B*, R=H₂O;
 (c) precursor *A*, R=KOH 15%.
 1 - powder, 2 - polycrystalline film.

4. CONCLUSIONS

1. Crystalline ZnO powders with different form-factors were obtained under soft hydrothermal conditions at temperatures 150-250°C. Increase in temperature by 50-70°C results in the increase of the rate of synthesis processes in 4-5 times.
2. The powders consist of faceted microcrystallites with size 100 nm - 10 μm depending on growth conditions. Crystallites are faceted with the faces of monohedra (0001) and (000 $\bar{1}$), hexagonal prism {10 $\bar{1}0$ }, hexagonal pyramid {10 $\bar{1}1$ }. The development of these faces is defined by the growth conditions.
3. When Zn(OH)₂-precursor was prepared by nitrate technology, crystallites synthesized demonstrate the best faceting. The increase in KOH concentration leads to the decrease of *c/a* ratio in ZnO platelet-like crystallites.
4. Spectra of ICL were obtained for bulk single crystals, powders synthesized from various ZnO-precursors and polycrystalline films. Two characteristic bands of emission (in UV and visible regions) were observed in spectra. The ratio of their intensities I_{UV}/I_{VIS} depends on the crystallographic orientation of the sample. For the samples cut from growth pyramid <0001> and <000 $\bar{1}$ >, $I_{UV}/I_{VIS} \sim 1$, while for negative monohedron I_{UV}/I_{VIS} ten times lower.
5. For ZnO polycrystalline films, the increase in KOH concentration results in lowering the intensity of UV luminescence ($\lambda \approx 385$ nm) of films. Simultaneously the intensity of visible luminescence increases followed with the shifting into long wave-region. Maximal intensity of UV-band was observed in the samples synthesized in H₂O and in the samples obtained using acetate precursor.

Acknowledgments

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