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ZINC OXIDE: STRUCTURE, PROPERTIES, METHODS OF OBTAINING, SIGNIFICANCE IN ECOLOGICAL CATALYSIS. REVIEW

Ivanenko I.M.[1], Fedenko Yu.M.[2], Stepanova A.V.[3], Byts O.V.[4]
[1]Igor Sikorsky Kyiv Polytechnic Institute,
Peremogy Ave., 37, 03056, Kyiv
irinaivanenko@hotmail.com;
[2]Igor Sikorsky Kyiv Polytechnic Institute,
Peremogy Ave., 37, 03056, Kyiv
fedenkoyura@ukr.net;
[3]Igor Sikorsky Kyiv Polytechnic Institute,
Peremogy Ave., 37, 03056, Kyiv
st244506@gmail.com
[4]Igor Sikorsky Kyiv Polytechnic Institute,
Peremogy Ave., 37, 03056, Kyiv
byc.olena@gmail.com

The physical properties of crystalline zinc oxide of the "wurtzite" type are considered, namely: the type and characteristics of the crystal structure, possible defects of the crystal lattice. Based on the analysis of literature data, it was found that zinc oxide crystals are most often stabilized in the structure of "wurtzite" in the form of a hexagonal unit cell (spatial group P63mc). Mechanical (using modern equipment – atomic power microscope), electrical and optical properties in terms of the possibility of using crystalline zinc oxide type "wurtzite" as an effective, catalytically stable photocatalyst for removing contaminants of various natures (including azo dyes) from aquatic environments of various origins. Numerous studies of electrical properties indicate that devices based on nanostructures of zinc oxide type "wurtzite" have exceptional potential for use as high-speed electronics. The optical properties of wurtzite zinc nanostructures have been found to be related to both internal and external effects. Internal optical transitions occur between electrons in the conduction band and holes in the valence band, including exciton effects due to Coulomb interaction. Also, the characteristic optical phenomena that can occur in the study of nanostructures of zinc oxide type "wurtzite" include the presence of photoluminescence spectra when applying an excitation source to its nanostructures. The comparative characteristics of the main methods of obtaining crystalline zinc oxide of the "wurtzite" type: «bottom up» and «top down» are analyzed and given. Based on the analysis of literature data, it was found that the key advantage of the method «top to bottom» is that the details are formed on the sample and assembled on site. The bottom-up method, or as it is sometimes called, the «self-assembly» approach, uses chemical or physical forces acting on an extremely small scale (nano-scale) to assemble the basic units into larger structures. Unlike the top-down method, the bottom-up technique starts with small designs and ends with large units. *Key words:* zinc oxide, wurtzite, photocatalyst, exciton effect, nanostructure, photoluminescence.

Цинку оксид: структура, властивості, методи отримання, значення в екологічному каталізі. Літературний огляд. Іваненко І. М., Феденко Ю. М., Степанова А. В., Биць О. В.
Розглянуто фізичні властивості кристалічного цинку оксиду типу «вюрцит», а саме: тип і характеристики кристалічної структури, можливі дефекти кристалічної ґратки. На основі аналізу літературних даних встановлено, що кристали цинку оксиду найчастіше стабілізуються в структурі «вюрцит» у вигляді гексагональної елементарної комірки (просторова група P63mc). Проаналізовано механічні (із застосуванням сучасного обладнання – атомного силового мікроскопа), електричні та оптичні властивості з точки зору можливості застосування кристалічного цинку оксиду типу «вюрцит» як ефективного, каталітично стабільного фотокаталізатора для вилучення забрудників різної природи (зокрема, азобарвників) із водних середовищ різного походження. Численні дослідження електричних властивостей вказують на те, що пристрої на основі наноструктур цинку (ІІ) оксиду типу «вюрцит» мають винятковий потенціал у застосуванні в якості високошвидкісної електроніки. Виявлено, що оптичні властивості наноструктур цинку (ІІ) оксиду типу «вюрцит» пов'язані як із внутрішніми, так і з зовнішніми ефектами. Внутрішні оптичні переходи відбуваються між електронами в зоні провідності та дірками у валентній зоні, включаючи екситонні ефекти внаслідок кулонівської взаємодії. Також до характерних оптичних явищ, що можуть мати місце при дослідженні наноструктур цинку (ІІ) оксиду типу «вюрцит», відноситься наявність спектрів фотолюмінесценції при накладанні джерела збудження до його наноструктур. Проаналізовано та надано порівняльну характеристику основних методів одержання кристалічного оксиду цинку типу «вюрцит»: «знизу вгору» та «згори донизу». На основі аналізу літературних даних встановлено, що ключовою перевагою методу «згори донизу» є те, що деталі формуються за зразком і збираються на місці. В методі «знизу вгору», або, як його іноді називають, підході до «самозбирання», використовуються хімічні або фізичні

сили, що діють у надзвичайно дрібному масштабі (нано-масштабі), для збирання основних одиниць у більші структури. На відміну від методу «згори донизу», техніка «знизу вгору» починається з невеликих конструкцій і закінчується великими одиницями. *Ключові слова:* цинку оксид, вюрцит, фотокаталізатор, екситонний ефект, наноструктура, фотолюмінесценція.

Introduction. Much attention is paid to the use of photocatalysts – nanostructured semiconductors for the removal of organic and inorganic substances from water and gas systems in the processes of ecological catalysis, water purification and more in the study of catalytic processes.

Zinc oxide, as a photocatalyst, has recently attracted considerable attention due to its high catalytic stability, cost-effectiveness, and the ability to conduct catalytic processes under environmental conditions.

One of the important problems today is the purification of water from pollutants of various natures, including azo dyes, which are well soluble in water and therefore difficult to remove from it. These dyes can lead to serious environmental problems due to their high resistance to the environment, as well as carcinogenic and mutagenic effects.

Therefore, the development of a photocatalyst based on zinc oxide is one of the possible ways to solve the problem of water pollution by dyes using a new and promising method of photocatalysis.

Many methods of obtaining zinc oxide have been described in the modern literature, including: hydrothermal synthesis, sol gel method, chemical precipitation method, etc. Despite the variety of methods for obtaining nanostructures, there is an urgent need to use such a method of synthesis, which not only guarantees the production of photocatalysts with specified physicochemical properties, but also will be cheap and easy to implement.

Crystal structure of zinc oxide

Zinc oxide (ZnO) is a semiconductor of semiconductor group II–VI. It has a crystalline structure of wurtzite (hexagonal symmetry), zinc mixtures or rock salt (cubic symmetry), as shown in Fig. 1. However, ZnO crystals are most often stabilized in the structure of wurtzite in the form of a hexagonal unit cell (spatial group P63mc). Crystals detect the rock salt phase only at high pressures.

The wurtzite structure of ZnO can be considered to consist of two interpenetrating hexagonal, densely packed (hcp) sublattices of cation (Zn) and anion (O), shifted by the length of the cation-anionic bond in the c direction. The lattice constants of the hexagonal unit cell ZnO are: a = 3.2500 Å, c = 5.2060 Å at 300 K.

The c / a ratio for ZnO is 1.60, which is close to the ratio of 1.633 of an ideal hexagonal densely packed structure. Each hexagonal dense packing (hcp) consists of one type of atom moved relative to each other along the triple axis c by the value u = 3/8 = 0.375 in fractional coordinates (parameter u is defined as the length of the bond parallel to the c axis, in units of c, or the distance of the nearest neighbor b separated by c). α and β are the connection angles 109.070, as shown in Fig. 2.

In this structure each anion is surrounded by four cations at the angle of the tetrahedron and vice versa. The bonds in these materials are usually (sp^3) covalent (tetrahedral), but some ionic characteristics have also been found in this material. In a true ZnO crystal, the wurtzite structure deviates from the ideal location by changing the c/a ratio or the u value. Deviation from the ideal wurtzite crystal is probably due to lattice stability and ionicity.

Point defects, such as zinc antipodes, oxygen vacancies, and extended defects, such as thread dislocations, also increase the lattice constant in the hetero-epitaxial layers of the ZnO crystal, but to a small extent.

There is a high relationship between the coefficient c/a and the parameter u, because when the coefficient c/a decreases, the parameter u increases in such a way that these four tetrahedral distances remain almost constant due to distortion of tetrahedral angles due to distant polar interactions.

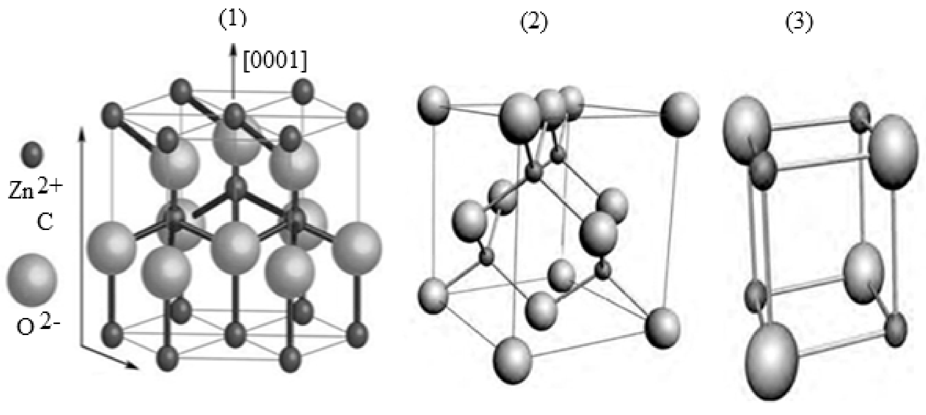

Fig. 1. Different crystalline structures of zinc oxide: (1) – wurtzite, (2) – zinc mixture, (3) – rock salt

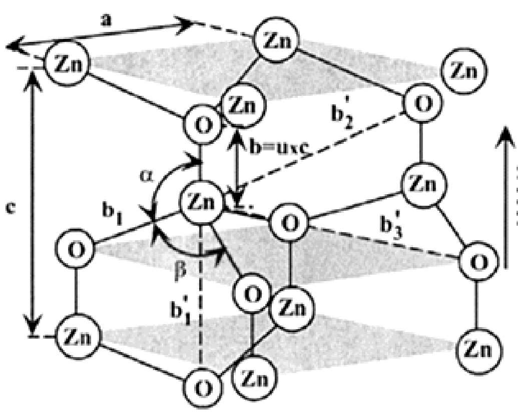

Fig. 2. Schematic diagram of Wurzite structure of ZnO [1]

Physical properties of zinc oxide "wurtzite" structure

Research and understanding of the basic physical properties of ZnO are important for many reasons. For example, they are useful for the rational design of functional devices and for the development of their potential as building blocks for future nanoscale devices. Table 1 shows a compilation of the basic physical parameter for the bulk structure of ZnO.

It should be noted that there is still some uncertainty in these values. For example, several reports mention only physical properties of the ZnO type, and therefore hole mobility and effective mass are still discussed [1; 2]. In addition, because the size of semiconductor materials is continuously decreasing to the nanometer or even smaller, some of their physical properties are changing, known as «quantum size effects.» Quantum restriction increases the band gap of ZnO nanowire, which was confirmed by photoluminescence measurements [3; 4].

Table 1

Physical properties of zinc oxide "wurtzite" structure (300 К) [5]

Property	Value
a_0, nm	0.32495
c_0, nm	0.52069
a_0/c_0	1.602
U	0.345
Density, g·cm^{-3}	5.606
Stable phase at 300 К	Wurtzite
Bond length, Å	1.977
Static dielectric constant	8.656
Refractive index	2.008; 2.029
Restricted area width, eV	3.4
Knupp's hardness, H/cm^2	0.5
Volumetric hardness, GPa	5.0±0.1
Ionicity, %	62
Heat capacity, J/mole·K	9.6
Jung's module, GPa	111.2±4.7
Spontaneous polarization, C/m^2	–0.057

Mechanical properties of zinc oxide "wurtzite" structure

Direct measurement of the mechanical properties of individual ZnO nanostructures is a really difficult task. Therefore, there are very few experimental studies of the mechanical properties of ZnO nanostructures. In fact, the lack of experimental studies of ZnO nanostructures is mainly due to some problems with nanoscale characterization techniques, such as sample manipulation, alignment and capture to achieve desired boundary conditions, and the use and measurement of force and displacement at very high resolutions [6]. According to Table 1, ZnO is a relatively soft material with a hardness of 5 GPa at a plastic penetration depth of 300 nm (for the ZnO-oriented mass of ZnO). Some researchers have tested different techniques for measuring the Young's modulus of ZnO nanostructures. Based on the resonant excitation caused by the electric field, the bending modulus of ZnO nanobands was characterized by a transmission electron microscope (TEM) [7]. In this method, a special TEM sample holder was made to supply an oscillating electric field between the ZnO nanoband and the fixed electrode. This electric field triggered the vibration of the nanoband, and resonant oscillations were achieved by adjusting the frequency of movement. Following the classical theory of elasticity, the bending modulus was calculated, which turned out to be equal to 50 GPa.

In addition, atomic force microscope (AFM) experiments are popular methods for the mechanical characterization of ZnO nanostructures. Because the stiffness of the AFM tip is very low, the force measurement resolution is very high (nano-newtons). In this technique, a very soft spring (such as a cantilever beam) was used to bend the ZnO nanowire. The researchers used this technique to measure the Young's modulus of ZnO nanowires [8; 9]. They reported different values of the Young's modulus of 29 ± 8 and 97 ± 18 GPa. On a mass scale, the Young's modulus of zinc oxide in the [0001] direction is 140 GPa [10], which is much higher than the modulus value given for ZnO nanostructures.

Electrical properties of zinc oxide "wurtzite" structure

Due to its electrical properties, ZnO is very attractive for optoelectronic and electronic devices. For example, a device made of ZnO material has a high breakdown voltage, lower noise level and can operate at higher temperatures with high operating power. The background concentration of ZnO carrier is usually 1016 cm^{-3}, and the effective electronic mass of ZnO is 0.24 m_0 (m_0 is the mass of free electrons), while the effective mass of the hole is 0.59 m_0 [5]. In addition, studies of electric transport after the configuration of individual ZnO nanowires as field-effect transistors confirm that the grown ZnO nanowires demonstrate n-type behavior [11]. Usually, the mobility of the field effects of grown nanowires is 20–100 cm^2/V · s [12].

Scientists later reported electron mobility of 1000 $cm^2/V{\cdot}s$ after coating nanowires with a polyimide passivation layer to reduce scattering and capture of electrons on the surface. It has recently been found that after coating ZnO nanowires with a layer of SiO_2, followed by Si_3N_4 to passivate surface states, the mobility of ZnO nanowires can be significantly increased to levels above 4000 $cm^2/V \cdot s$ [13]. These results indicate that devices based on ZnO nanostructures have exceptional potential for use in high-speed electronics.

Optical properties of zinc oxide "wurtzite" structure

The optical properties of ZnO nanostructures have been widely studied due to their promising potential in optoelectronics. The optical properties of ZnO nanostructures are related to both internal and external effects. Internal optical transitions occur between electrons in the conduction band and holes in the valence band, including exciton effects due to Coulomb interaction. External properties are associated with additives or defects, which usually create discrete electronic states in the gap, and therefore affect both the processes of optical absorption and radiation. ZnO is usually formed as an n-type semiconductor material in which the electrical conductivity is due to excess zinc, probably interstitially inside the lattice and oxygen vacancies [14]. External defects, such as hydrogen, are more often included as small donors [15]. In general, ZnO has a wide semiconductor band (3.4 eV), which makes it potentially useful for efficient UV laser diodes and low power thresholds for pumping at room temperature. It is also one of the promising materials for high temperature and high-power devices. High temperature operation requires a wide range of restricted areas so that the internal concentration of the carrier remains. High power operation is attractive to semiconductors with wide bands due to large breakdown fields.

Photoluminescence (PL) spectra of ZnO nanostructures have been widely reported experimentally. The PL spectrum of ZnO at room temperature usually consists of a close band of ultraviolet radiation (380 nm) through the transition from band to band and a green-yellow band of radiation associated with the oxygen vacancy [16]. Red emission bands have also been reported, due to vacancies in double ionized oxygen [17]. It was reported that the intensity of green ZnO emissions increases with decreasing nanowire diameter. This indicated that the level of the defect was higher in thinner nanowires due to the increase in the ratio of surface to volume. The constant decrease in the diameter of the ZnO nanowire leads to a quantum size effect, which is manifested in the blue shift of the edge band radiation in the photoluminescence spectra (as shown in Fig. 3) [18].

In addition, the most important advantage of ZnO nanostructures is the high exciton binding energy (60 meV), which is 2.4 times higher than the effective thermal energy (25 meV) at room temperature, which leads to efficient exciton radiation at room temperature.

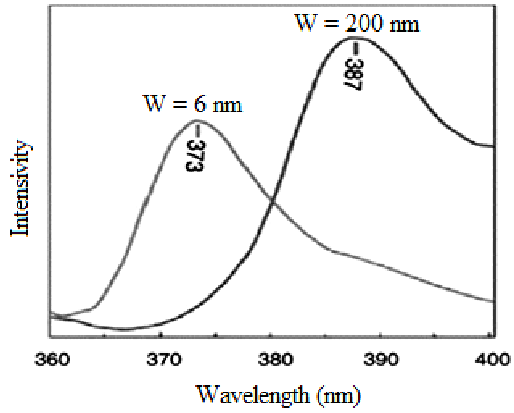

Fig. 3. Photoluminescent spectra of ZnO nanobands of wide 6 nm and 200 nm [18]

This is one of the key parameters by which ZnO exhibits lasing generation at room temperature. An additional advantage of ZnO nanowire lasers is that exciton recombination lowers the lasing threshold, and quantum constraint gives a significant density of states at the edges of the band and increases radiation efficiency. Moreover, due to its almost cylindrical geometry and high refractive index (~2.0), ZnO nanostructures are a natural candidate for optical waveguides [19].

Production of nanosized zinc oxide

There are two main methods used in the synthesis and production of ZnO nanostructures. These techniques are called top-down and bottom-up. Top-down technique refers to the manufacturing technology by which an object is created by carefully removing pieces of a larger object, essentially cutting out the desired object. In this technique, it starts with a bulk material and then breaks it into smaller pieces using mechanical, chemical or other forms of energy. The top-down approach often uses traditional workshop or micro-production techniques, where externally controlled tools are used to cut, mill and shape materials into the desired shape and order. A key advantage of the descending approach is that the parts are molded and assembled on site, so assembly is not required. The bottom-up approach, or sometimes called the self-assembly approach, used chemical or physical forces acting on a nanoscale to assemble the basic units into larger structures. Unlike top-down technology, bottom technology starts with small designs and ends with large units.

Ball grinding. Spherical milling is an example of top-down technology, and it is used to obtain nanocomposites and establish the basic parameters of the mechanochemical reaction and mechanical doping process. It can also be used to obtain alloys that are ultimately more useful than individual elements, because composite alloys are more homogeneous than metals, less corrosive, have higher melting points and hardness. In fact, the technique of ball milling is more environmentally friendly than the modern method of chemical synthesis, generating much less chemical waste. On the other hand, ZnO nanoparticles obtained by abrasion have a fairly wide size distribution and a variety of particle shapes or geometries. In addition, they may contain a significant number of impurities from the grinding medium and defects arising from grinding.

Synthesis from solutions. Solution-based synthesis (SBS) is determined by any chemical reaction that requires a liquid. As a general method of synthesis, SBS is vital for the production of a variety of materials that are often difficult to produce using other methods. As a rule, decision-based methodologies are low cost and provide control materials with high yield and homogeneity. However, growth is complicated, and many defects are formed during the reaction. The most important and common methods of ZnO synthesis are hydrothermal and sol-gel synthesis, both of which will be discussed below.

Sol-gel synthesis. The sol-gel technique is a long-established industrial process for obtaining colloidal nanoparticles from the liquid phase, which has been further developed in recent years for the production of advanced nanomaterials and coatings. Sol-gel processes are well adapted for the synthesis of oxide nanoparticles and composite nanopowders. The main advantages of sol-gel methods of material preparation are low processing temperature, versatility and flexible technology.

Hydrothermal synthesis. The hydrothermal process has been carried out to obtain crystalline structures since the 1970s. As defined, hydrothermal fusion is a subset of solvothermal fusion that includes water under elevated conditions. The basic principle is that small crystals are uniformly formed and grow out of solution under the action of high temperatures and pressures. Usually, a temperature of 100 °C to 300 °C is used and the pressure exceeds 1 atm. During the processes of nucleation and growth, water is both a catalyst and sometimes a solid-phase component. In extreme conditions of the synthesis vessel, water often becomes supercritical, thereby increasing the dissolution force, diffusion and mass transport of the liquid by reducing its viscosity. In addition, the ability to regulate the pressure of the vessel provides a way to adapt to the density of the final product. Compared to other methodologies, hydrothermal synthesis is environmentally safe, inexpensive and reduces free energy for different equilibria [20; 21].

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