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PACS 61.05.Cp, 61.46.Hk, 78.40.Fy

ELECTROLYTIC FABRICATION OF ZINC OXIDE NANOPARTICLES

A possibility of electrolytic fabrication of zinc oxide nanocrystals with the use of zinc electrodes and the aqueous solution of sodium chloride as an electrolyte has been demonstrated. The x-ray analysis of obtained nanoparticles shows that their size is of the order of 30 nm. The researches of the electrolyte transmission spectra registered after the main experiment has been terminated show that the energy gap width in ZnO nanoparticles is 3.35 eV, which agrees with the corresponding value for ZnO single crystals.

K e y w o r d s: ZnO, nanocrystals, wet method, XRD, particle size, optical properties, band gap.

1. Introduction

Nowadays, the search for and the creation of functional materials on the basis of wide-band-gap semiconductors and insulators is a challenging task from the viewpoint of their application in optoelectronics and nonlinear optics. Zinc oxide (ZnO) – a direct-band-gap semiconductor of the n-type with an energy gap of 3.37 eV at room temperature and a large exciton binding energy of 60 meV – is widely applied in optoelectronics [1].

Zinc oxide attracts a special attention in connection with the opportunities of its fabrication in superfine forms such as nanoparticles, rods, and thin films [2]. The reason consists in the presence of quantum-dimensional effects for such objects, which manifest themselves in the growth of the energy gap width and the redox potentials of the valence and conduction bands [3]. Therefore, zinc oxide nanoparticles can be used in solar cells and piezoelectric transducers, as well as in ultra-violet radiation and gas molecular composition sensors. In addition, ZnO is an ecologically safe biocompatible material, which is very important for biomedical applications [4].

The collection of methods applied to fabricating the nanostructure materials is extremely wide. Among them, the vacuum technologies should be emphasized, such as molecular beam epitaxy; gas-transport deposition (including the gas-phase epitaxy of metalloorganic compounds), powder technologies, physicochemical and electrolytic techniques, and hardening from the liquid state [5]. All those methods have their specific advantages and shortcomings.

In this work, the results of the electrolytic fabrication of zinc oxide nanoparticles and their study with the use of x-ray diffraction and optical methods are reported.

2. Experimental Part

We study a fine-dispersed powder of zinc oxide obtained by the electrochemical technique [6, 7]. As an electrolyte, a solution of table salt (NaCl) in distilled water was used. Zinc cylinders 170 mm in length and 9.5 mm in diameter were used as electrodes. The concentration of NaCl in the solution was 500 mg/l. The electrolyte temperature was 98 °C, and the experiment lasted for 4 h. The current density was about 2.8×10^{-2} A/cm^2.

After electrolysis, the electrolyte was filtered through a filtering paper, and the obtained fine-dispersed powder was washed out in distilled water taken in a volume ratio of 5:1. The obtained zinc oxide powder was dried at room temperature. In all experiments, the mass of zinc electrodes was measured before and after the experiment, as well as the mass of the obtained zinc oxide powder. An ionometer I-130M was used to measure the pH index of a solution. The obtained nanocrystals of zinc oxide were studied using the x-ray diffraction method. X-ray researches were carried out on a DRON-4 diffractometer with the help of CuK_α radiation.

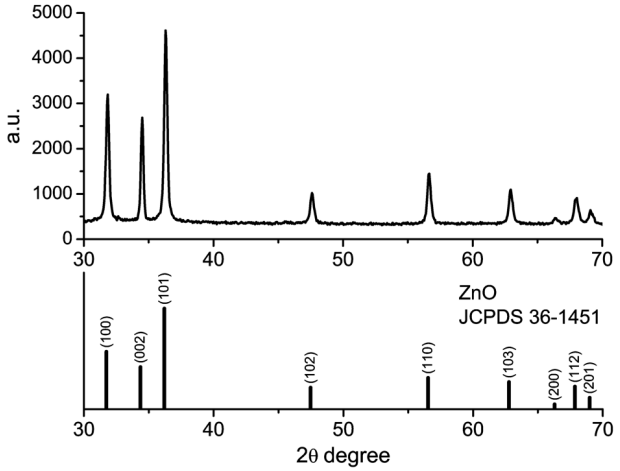

Fig. 1. Diffraction pattern of synthesized zinc oxide

The transmission spectra of the electrolyte were measured after the process of zinc oxide nanoparticle fabrication had been terminated. The spectra were registered on a Carry-50 spectrophotometer at room temperature.

3. Results of Measurements and Their Discussion

The monitoring of the nanoparticle fabrication process showed that the electrolyte was transparent at first, but turned milky-colored in due course. A gas was produced at the anode during the electrolysis process, and white-colored associates of nanoparticles moved over the electrolyte volume. After the electrolysis had been terminated, the most part of the nanopowder settled on the electrolyzer bottom. A smaller part settled on the electrolyzer walls and electrodes or floated in the volume or on the electrolyte surface. In the first experiments, samples were taken from the electrolyzer bottom and walls, from the electrodes, and from the electrolyte volume. Their x-ray diffraction analysis showed that zinc oxide nanoparticles were obtained in all cases.

In Fig. 1, the x-ray diffraction pattern of nanoparticles obtained for 4 h of the electrolysis with a current direction reversal in every 30 min is depicted. To analyze it, we preliminarily calculated the angular positions of reflections for ZnO.

Zinc oxide is known to crystallize into a hexagonal wurtzite structure (space group C_{6v}^4–$P6_3mc$) [8]. The elementary cell contains four atoms (two ZnO molecules). The oxygen atoms form a dense hexagonal structure, and the zinc ones are located at the centers of tetrahedra formed by oxygens. According to the quenching rules for space group C_{6v}^4–$P6_3mc$ [9], the diffraction patterns have to include reflections (100), (002), (101), (102), (110), (103), (200), (112), and (201). The diffraction angles were calculated with the help of Bragg's formula [10]

$$2d\sin\theta = \lambda,$$

where d is the distance between the crystal planes, θ the diffraction angle, and λ the wavelength of x-ray radiation. The distance d between the planes with Miller indices (hkl) in the hexagonal system was calculated by the formula [9]

$$d^2 = \frac{1}{\dfrac{4(h^2+hk+k^2)}{3a^2} + \dfrac{l^2}{c^2}},$$

where a and c are the parameters of the elementary cell. In single-crystalline zinc oxide, those parameters are $a = 0.32469$ nm and $c = 0.52069$ nm [11].

To obtain x-ray diffraction patterns, we used radiation of an x-ray tube with a copper anode filtered with the help of a nickel filter. It is known that, in our case, characteristic x-ray radiation consists of two components, Cu$K_{\alpha 1}$ and Cu$K_{\alpha 2}$, with the intensity of the former component being twice as large [12]. The x-ray diffraction pattern demonstrates that the main reflections are located in the small-angle interval $2\theta < 70^\circ$, and the lines are not resolved into two components. Therefore, the x-ray radiation wavelength was calculated by the formula

$$\lambda = \frac{2\lambda_1 + \lambda_2}{3},$$

where λ_1 and λ_2 are the wavelengths of components Cu$K_{\alpha 1}$ and Cu$K_{\alpha 2}$, respectively. In our case, $\lambda_1 = 0.1540562$ nm and $\lambda_2 = 0.1544398$ nm [13], so that $\lambda = 0.1541841$ nm. The results of diffraction angle calculations are quoted in Table.

A comparison between the theoretical and experimental values obtained for 2θ (see Table) and between the experimental reflection intensities and the data of international standard JCPDS No. 36-1451 confirms that zinc oxide was obtained in our case. To determine the size of nanoparticles, we the used the

Debye–Scherrer formula [14]

$$D = \frac{k\lambda}{\beta \cos\theta},$$

where k is a coefficient with specific value depending on the particle shape, λ the wavelength of x-ray radiation, β the half-height width of a diffraction peak, and θ the diffraction angle. For cubic particles, P. Scherrer obtained the value $k = 0.94$. For spherical particles and close to them (an equivalent ellipsoid), $k = 0.89$ [14]. To determine the nanoparticle sizes, we used the reflection (101) and obtained a value of about 28 nm.

The variation of the time interval between reversals of a dc current direction did not substantially affect the dimensions of zinc oxide nanoparticles. For instance, while varying the reversal time interval from 5 min to 1 h 30 min, the nanoparticle sizes changed within the limits from 28.3 to 29.2 nm. The change of NaCl concentration in the electrolyte solution from 50 to 500 mg/l also did not bring about substantial modifications in the dimensions of ZnO nanocrystallites. The measurements of pH gave the following results: for the solvent (distilled water), pH = 5.90; for the as-prepared electrolyte, pH = 6.07; and for the electrolyte after the electrolysis, pH = 7.81.

After the electrolysis, we measured the transmission spectra of the electrolyte solution on a Carry-50 spectrometer at room temperature. In Fig. 2, the results of measurements are exhibited. One can see that the transmittance first drastically grows to exceed 75% in the visible spectral range. The coefficient of optical absorption is calculated according to the Bouguer–Lambert law

$$I = I_0 e^{-\alpha d},$$

where I and I_0 are the intensities of absorbed and incident light, respectively; and d is the electrolyte layer thickness (in our case, $d = 1$ cm). Single-crystalline zinc oxide is known to be a direct-gap semiconductor [8]. For the allowed direct transitions, the dependence of the absorption coefficient on the energy gap width is described by the equation

$$(\alpha h\nu)^2 = A(h\nu - E_g),$$

where A is a constant, h Planck's constant, and ν the photon frequency.

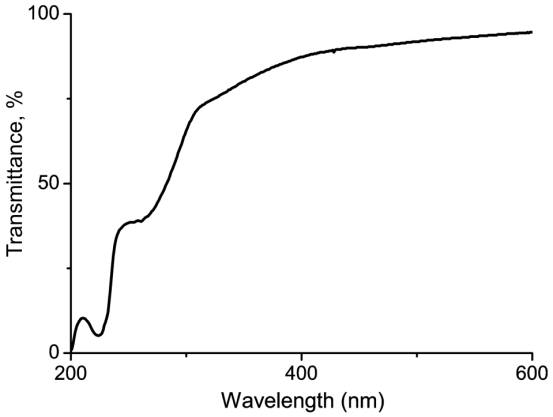

Fig. 2. Light transmittance spectrum of the electrolyte solution after the electrolysis

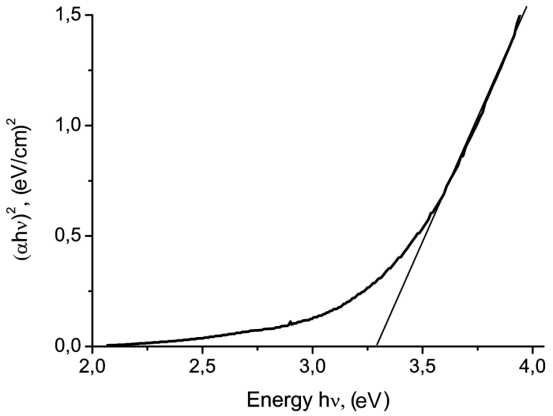

Fig. 3. Dependence of the quantity $(\alpha h\nu)^2$ on the photon energy $h\nu$ and the linear extrapolation of its section

Theoretical and experimental values of angles 2θ for ZnO

Reflection	Theory, $2\theta°$	Experiment, $2\theta°$
100	31.8243	31.85
002	34.4487	34.55
101	36.3098	36.35
102	47.6000	47.60
110	56.7010	56.70
103	62.9291	63.00
200	66.5045	66.55
112	68.0597	68.00
201	69.2167	69.15

In Fig. 3, the dependence of the quantity $(\alpha h\nu)^2$ on the photon energy $h\nu$ is plotted. The energy gap width was calculated, by linearly extrapolating a plot

section to the value $\alpha h\nu = 0$. The same procedure was carried out for a number of specimens, and the averaged value for the energy gap width turned out to equal 3.35 eV, which correlates satisfactorily with the literature data [1–4].

4. Conclusions

1. It is demonstrated that zinc oxide nanoparticles can be fabricated using the electrolytic method at temperatures of about 98 °C.
2. As follows from the results of x-ray structural analysis, the size of obtained nanoparticles is about 28 nm and does not depend on the time interval between the current reversals.
3. The transmission spectra of a NaCl aqueous solution with ZnO nanoparticles are measured to determine their energy gap width, which turns out to be 3.35 eV at room temperature.

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Received 29.05.12.
Translated from Ukrainian by O.I. Voitenko

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ЕЛЕКТРОЛІТИЧНИЙ МЕТОД ОТРИМАННЯ НАНОЧАСТИНОК ОКСИДУ ЦИНКУ

Р е з ю м е

Показана можливість отримання нанокристалів оксиду цинку електролітичним методом з використанням цинкових електродів і розчину кухонної солі в ролі електроліту. Отримані наночастинки досліджувалися методом рентгеноструктурного аналізу, який показав, що їх розміри становлять величину порядку 30 нм. Дослідження спектрів пропускання електроліту після проведення експерименту, показали, що ширина забороненої зони наночастинок становить величину 3,35 еВ, що узгоджується з її значенням для монокристалів.