NEW METHOD OF SYNTHESIS OF $ZnSe_2O_5$ NANOCRYSTALS

A.D. Akylbekova[1)], A.B. Usseinov[1)], Z.K. Baymukhanov[1)], M.V. Zdorovets[2)],
Sh. Giniyatova[1)], L.A. Vlasukova[3)], F.F. Komarov[3)], A.K. Dauletbekova[1)]
[1)]*Eurasian National University L.N. Gumilyov, 010008 Nur-Sultan, Kazakhstan, aiman88_88@mail.ru, useinov_85@mail.ru, giniyat_shol@mail.ru, zeinb77@mail.ru , alma_dauletbek@mail.ru*
[2)]*Astana Branch of the INP, Nur-Sultan, Kazakhstan, mzdorovets@gmail.com*
[3)]*Belarusian State University, 220030 Minsk, Belarus, vlasukova@bsu.by*

The paper presents the results of an experimental and theoretical study of zinc diselenide nanocrystals obtained by electrochemical deposition in a-SiO_2/Si-n track template. The track template SiO_2/Si was obtained by irradiation on a DC-60 cyclotron with Xe ions with an energy of 200 MeV ($\Phi = 10^8$ ions/cm^2) followed by chemical etching in an aqueous solution of hydrofluoric acid (HF). Electrochemical deposition (ECD) in the track template was carried out in potentiostatic mode. The surface of the samples after deposition was examined using a JSM 7500F scanning electron microscope. X-ray diffraction analysis (XRD) was performed using a D8 ADVANCE ECO X-ray diffractometer. According to X-ray diffraction data, electrodeposition of zinc in the a-SiO_2/Si-n track template led to the formation of $ZnSe_2O_5$ nanocrystals with an orthorhombic crystal structure. The experimental parameters of the crystal lattice, the density of the crystal, the effective charge, and the population of the chemical bond are in good agreement with the results of quantum chemical calculations performed in the approximation of linear combinations of atomic orbitals and other literature data.

Keywords: template synthesis; electrochemical deposition; zinc diselenide.

Introduction

A promising method of forming new nanocomposite materials for micro, optoelectronic and nanoelectronic systems is the method of template synthesis. For example, metallic nanoclusters were obtained by this method [1]. Electrochemical metal particles are deposited in tracks formed by irradiation with heavy ions on an accelerator of thin films (templates) SiO_2/Si. So, for example, Sn [2], Au [3] and Cu [4] nanostructures were obtained. By the same method Zinc oxide nanocrystals were obtained [5]. Given method was used to get CdTe nanocrystals [6].

The essence of template synthesis is the creation of nanochannels in the amorphous dioxide layer of a-SiO_2/Si-n structures, irradiating with fast heavy ions and followed by etching in a selective etchant.

In our work, $ZnSe_2O_5$ nanocrystals were obtained using template synthesis. It should be noted that literary sources for this crystal are practically absent, which does not allow revealing the level of research of its structural and optical properties. Against the background of the rapid development of nanotechnology (solar cells, nanodiodes, nanotransistors, gas nanosensors, etc.) in the last decade, it can be stated that there is an increased interest in oxide nanostructures, including $ZnSe_2O_5$ nanostructures. In this regard, we set the goal of our work to study the internal structure and basic physical properties of the obtained nanocrystals in $ZnSe_2O_5$, depending on the growing conditions. To confirm the obtained results, we also conducted a computer simulation of various physicochemical properties and atomic structure with the involvement of modern quantum chemical methods.

Experimental part

The structure of a-SiO_2/Si–n was prepared by thermal oxidation of a silicon substrate (Si –n type) in a humid oxygen atmosphere at 900°C. The thickness of the oxide layer according to ellipsometry was 700 nm. Samples were made in the form of discs with a diameter of 100 mm, and irradiation was carried out on the channel for polymer films. Using the SRIM program [7], electron and nuclear energy losses were calculated for the xenon ion in the a-SiO_2/Si-n structure, as well as the path length. Chemical etching of a-SiO_2/Si-n samples was carried out in 4% aqueous HF solution, the etchant included m(Pd)=0.025 g, etching temperature T=18˚±1°C. Before etching the tracks, ultrasonic cleaning of the sample surface in isopropanol was carried out for 15 minutes in an ultrasonic cleaner 6.SB25-12DTS. After treatment in HF, the samples were washed in deionized water (18.2 MΩ).

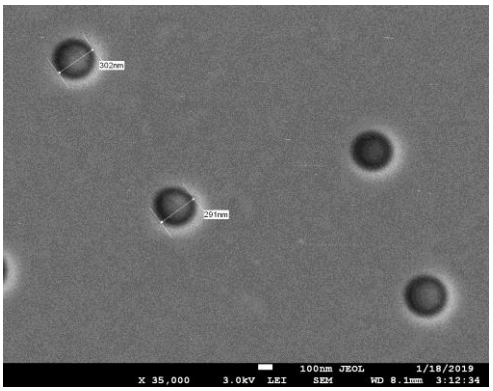
Control over the shape and size of the nanopores was carried out by the etching time. Varying the etching time, nanopore diameters were obtained from 291 nm to 356 nm. For ECD, the following electrolyte composition was used: (Zn - 7.2 g/l, SeO_2 - 0.2 g/l), as well as a standard electrolytic cell, with zinc electrodes, the voltage on the electrodes is 1.25 V, the deposition time is 15 minutes. Analysis of nanopores before and after deposition was carried out on a JSM-7500F scanning electron microscope. X-ray diffraction analysis (XRD) of the samples was carried out on a D8 ADVANCE ECO X-ray diffractometer.

Results and discussion

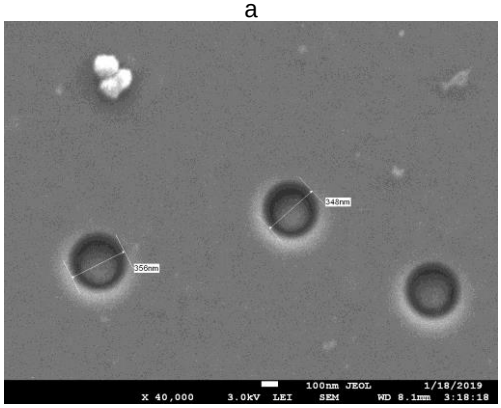
Figure 1 shows the SEM images of the sample surface after electrochemical deposition.

SEM Analysis of Surface Images for six samples of SiO_2/Si, showed that the degree of filling of nanopores at U=1.25 is 5.88%, 20.54%, 30.76%, 81.03%, 3.17% and 94.36%. At such a voltage, a “protrusion” of the precipitated substance from nanopores is observed (Figure 1 b).

In P.G. Meunier and M. Bertaud’s work [8] zinc diselenide was studied by Patterson's method (Heavy-atom method [9]). The analysis of radiographs showed that the structure consists of zigzag strings of ZnO_6 octahedra, sharing edges, parallel to the *c* axis. These $(ZnO_4)_n^{6n-}$ strings are connected by $(Se_2O)^{6+}$ groups. The selenium atoms are coordinated on one-side to three oxygens; the lone pair E occupies the apex of the SeO_3 E tetrahedron.



a



b

Fig. 1. SEM images of the surface of SiO_2/Si (a) before the deposition of the adsorbents, nanopore diameter 291-302 nm; (b) after the deposition of the adsorbents for 15 minutes at a voltage on the electrodes of U = 1.25 V, the diameter of the nanopores is 348-356 nm

Table 1. Results of X-ray analysis for six $ZnSe_2O_5$ samples grown on a SiO_2/Si substrate. All samples correspond to the orthorhombic structure with the space symmetry group Pbcn.

№	(hkl)	2θ°	d, Å	L, nm	Cell parameter, Å
1	113	47.669	1.90623	88.99	a=6.84898
	161	56.573	1.62550	83.15	b=10.40588
					c=6.10726
2	222	43.532	2.07729	30.09	a=6.82438
	161	56.668	1.62301	77.74	b=10.30182
					c=6.08451
3	161	56.605	1.62467	108.20	a=6.83702
					b=10.34424
					c=6.10479
4	161	56.668	1.62301	108.21	a=6.82495
					b=10.30976
					c=6.16404
5	222	43.596	2.07442	35.73	a=6.77276
	115	47.985	1.89442	104.17	b=10.41286
	161	56.637	1.62384	88.38	c=6.18404
6	222	43.564	2.07585	32.22	a=6.71034
	161	56.637	1.62384	80.47	b=10.34140
					c=6.24588

The X-ray diffraction study of the samples established the creation of $ZnSe_2O_5$ nanocrystals (Table 1). A voltage dependence of the type of the crystal structure of $ZnSe_2O_5$ nanocrystals is observed. Only at a voltage of U = 1.25 V the crystalline phase of zinc diselenide is formed, which predominates over the amorphous phase.

The X-ray diffraction data for the templates after ECM showed the creation of $ZnSe_2O_5$ nanocrystals with an orthorhombic crystal structure and a space group, Pbcn. The average values of the $ZnSe_2O_5$ crystal lattice parameters for six samples were: *a*=6.80307 Å, *b*=10.35266 Å, and *c*=6.14842 Å, which agrees well with the literature data [8].

Ab-initio calculations of the main properties of $ZnSe_2O_5$

To confirm the obtained experimental properties of $ZnSe_2O_5$ nanostructures, we also performed ab-initio calculations in the approximation of linear combinations of atomic orbitals (LCAO) using the exchange-correlation functional LDA-PZ density functional theory [10, 11]. The calculations were performed in the program CRYSTAL [12]. This program performs calculations of the electronic structure of crystalline systems using the Hartree-Fock methods, density functional (DFT) and various hybrid approximations in combination with the basis (set) of local Gaussian functions for periodic (3D, 2D, 1D) systems and has proven to be a reliable tool to describe the different properties of a wide range of materials. To describe the atomic orbitals of irreducible atoms, we chose the following basic sets of Gauss-type functions: $ZnSe_2O_5$: for the zinc and oxygen atoms, the Jaffe basis was used (Jaffe et. Al.) [13] and Towler basis for the selenium atom [14]. To better describe the crystalline properties in the original Towler basis, the last diffuse sp-orbital was removed. In the calculations of self-consistency (SCF), high accuracy limits of 10^{-7}, 10^{-7}, 10^{-7}, 10^{-7}, 10^{-14} were chosen for the Coulomb and exchange integrals. The effective atomic charges and bond population were calculated using Mulliken's analysis [15].

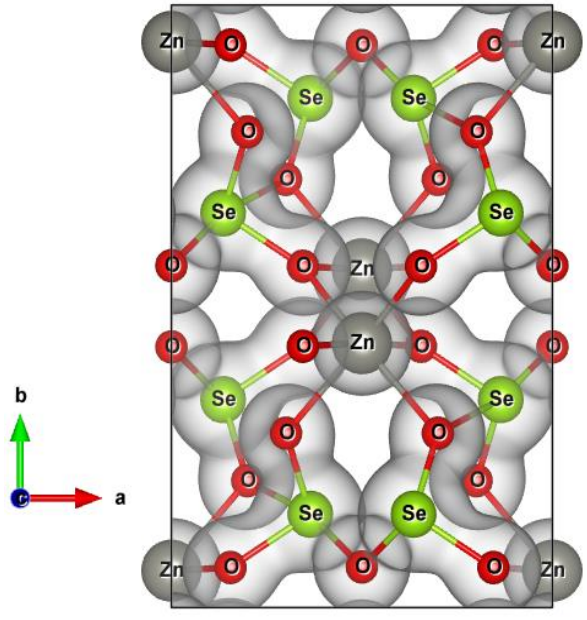


Fig. 2. The crystal lattice of $ZnSe_2O_5$ and the isosurface of the electron distribution. The borders of the primitive cell and the directions of the translation vectors are shown. Large (gray) balls represent Zn atoms, medium (green) mean Se atoms and small (red) atoms are O atoms.

To find various properties of a crystal (physical, mechanical, etc.), a periodic model of a primitive $ZnSe_2O_5$ cell consisting of 32 atoms was used (Fig. 2). The calculated lattice parameters (a, b, c), crystal density (ρ_V), effective charges on atoms (q_{eff}) and density are presented in Table 2 together in comparison with the experimental results.

Table 2. The main properties of $ZnSe_2O_5$ nanocrystals

Parameter	This work, Exper.	This work, Calc.	Exper. [8]
a, Å	6.80307 Å	6.86	6.797 ± 0.002 Å
b, Å	10.35266 Å	10.14	10.412 ± 0.003 Å
c, Å	6.14842 Å	5.77	6.068 ± 0.002 Å
Space group	*Pbcn*	*Pbcn*	*Pbcn*
ρ_V (g/cm^3)	4.69 [16]	4.971	4.69
q_{eff} (Zn/Se/O)	-	+1.23/+1.41/-0.833	-

Conclusions

In this work, six nanocrystalline $ZnSe_2O_5$ samples with an orthorhombic crystal structure were obtained by electrochemical deposition into the a-SiO_2/Si-n track matrix. It has been established that during precipitation a protrusion of a precipitated substance from nanopores is observed. For some samples, a high degree of amorphization is observed, and the crystalline phase of zinc diselenide is formed only at a voltage of U = 1.25 V. The performed *non-empirical* calculations confirmed experimental studies of the atomic structure and the main properties of $ZnSe_2O_5$ nanocrystals. As a result of the simulation, it was shown that the $ZnSe_2O_5$ nanocrystal is direct-gap with the smallest band gap of 2.8 eV at the G-point, and the charge distribution on ions and chemical bonds showed that the crystal is ion-covalent.

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