

Creation of ZnSe nanoclusters in a silicon dioxide track template on silicon

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Abstract: In this work, we study the formation of zinc selenide nanocrystals during chemical deposition into a-SiO₂/Si-n track template. For the first time, zinc selenide nanocrystals were obtained by chemical precipitation in an aqueous alkaline medium using sodium selenosulfate as a source of Se ions. The deposition was carried out at a temperature of $t = 75^{\circ}\text{C}$ for 40 min. The morphology was observed using scanning electron microscopy, and the crystalline phase was studied using X-ray diffraction analysis. To confirm the obtained ZnSe phase by X-ray diffraction analysis, we performed elemental analysis on a TM3030 scanning electron microscope.

The crystalline phase of the sample is a cubic structure (sphalerite) with space group F-43m. The unit cell parameters are: $a = 5.592081 \text{ \AA}$ and corresponds to the results of other works.

Keywords: nanoporous SiO₂/Si, template synthesis, chemical deposition, nanocrystals, sphalerite.

1. Introduction

Semiconductors with a wide bandgap A^{II}B^{VI}, such as zinc selenide, are widely used in the creation of luminescent and laser screens, photodetectors, and in IR technology. In various fields of science and technology, scintillation sensors are needed to detect and record radiation. These areas include, for example, medicine, meteorology, astronomy and nuclear physics.

A^{II}B^{VI} compounds today remain promising materials for optoelectronics, nanoelectronics, and infrared technology. A promising way to integrate A^{II}B^{VI} semiconductors into silicon technology is to grow nanocrystals of the corresponding materials in SiO₂/Si track templates. One of the nanocrystals based on A^{II}B^{VI} chalcogenides is ZnSe, which has a high nonlinear optical susceptibility, which makes it possible to use it as a material for passive optical switches for generating ultrashort laser pulses in the near-IR range.

Zinc selenide (ZnSe) is a semiconductor with a light yellow binary compound (II-VI) with a wide band gap of 2.7 eV [1]. Properties such as wide band gap, high light sensitivity and low resistivity are very attractive for optical devices. ZnSe exists in two crystalline forms; zinc blende (cubic) and wurtzite (hexagonal), in which the cubic phase is considered stable. Due to ZnSe's direct and large bandgap, it is suitable for use in optoelectronic devices as a high power laser window [2], infrared sensors [3], light emitting diodes [4], and blue diode lasers [5]. Due to its high transmission coefficient, ZnSe is also used as a window layer in solar cells [6]. These broad application possibilities of ZnSe have led to the development of zinc selenide thin film research in recent decades.

Thin ZnSe films were obtained by the following methods: RF magnetron sputtering [7], organic metal vapor deposition [8], molecular beam epitaxy, organic metal vapor phase epitaxy [9], and vacuum evaporation [10].

Recently, interest has grown in the study of nanoclusters, which occupy an intermediate position between individual atoms and macroscopic condensed matter. Clusters, as a rule, have properties different from the properties of individual molecules or a massive substance. In this regard, it is of great interest to study the patterns of formation of the geometric and electronic structures of clusters, as well as their chemical and physical properties [11].

The relevance of the study is related to the production of new nanoclusters using track templates.

One of the methods for obtaining nanoclusters is template synthesis. Template synthesis is a relatively simple and easy procedure, thanks to which the fabrication of rather complex nanomaterials has become available to almost any laboratory [12].

The paper [13] presents the results of obtaining nanoporous SiO₂ on a Si substrate (SiO₂/Si, with Zn deposited into nanochannels. Nanoporous SiO₂/Si, obtained by irradiation with fast heavy ¹³²Xe

ions at the DC-60 accelerator (Nur-Sultan, Kazakhstan). Today, ZnSe₂O₅ nanocrystals irradiated with Xe ions with an energy of 200 MeV [14–16] have been obtained using the a-SiO₂/Si-n track template. It is known that ZnSe has two public allotropes: cubic zinc blende (ZB) and hexagonal structure wurtzite (W) (Fig.1).

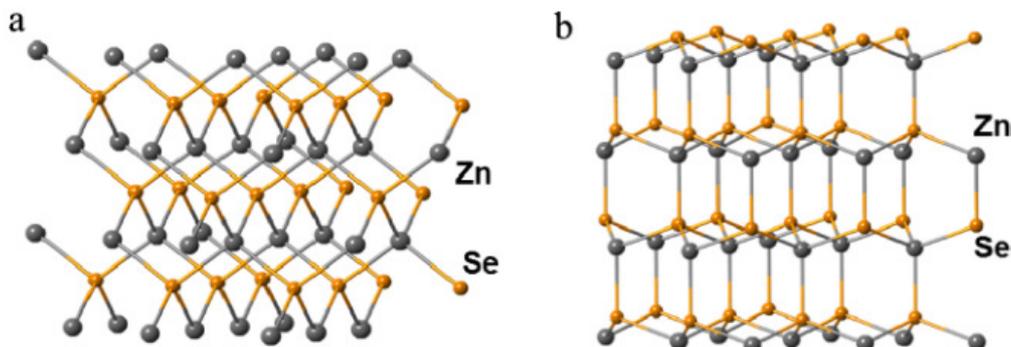


Fig.1. Models showing the difference between the crystal structures of (a) zinc blende (sphalerite) and (b) wurtzite [16].

The main differences lie in the relative two-handedness of the fourth interatomic bond or in their dihedral conformations. Alternatively, ZB is composed of tetrahedrally coordinated zinc and selenium atoms stacked in an ABCABC pattern, while the same building blocks form within the ABABAB block. The ZB lattice parameters are: $a = b = c = 5.68 \text{ \AA}$ (space group F4-3m) and the W structure parameters are: $a = b = 3.98 \text{ \AA}$, $c = 6.53 \text{ \AA}$ (space group = P63mc).

Due to the relatively small difference in total energy between ZB and the W structure (5.3 meV atom⁻¹), ZnSe exhibits the so-called W-ZB polytypism, although ZB is a ground state structure at low temperatures [17].

Our goal is to form and study the main properties, structure and morphology of ZnSe nanocrystals by template synthesis.

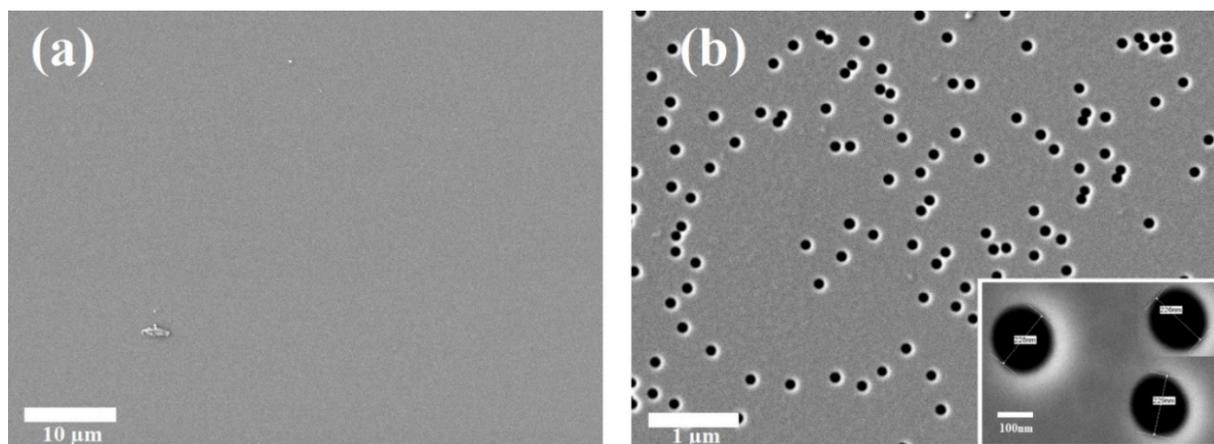


Fig.2. SEM images of the a-SiO₂/Si-n track template surface: a) after irradiation; b) after pickling 10 min.

2. Experimental part

The a-SiO₂/Si-n structure was obtained by thermal oxidation of a silicon substrate in a humid oxygen atmosphere at 900°C. According to ellipsometry, the thickness of the oxide layer is 700 nm. The samples were in the form of disks 100 mm in diameter and irradiated with Xe ions with an energy of 200 MeV up to a fluence of 10⁷ ions/cm². Samples were cut out in size 5×5 mm and 10×10 mm.

To determine the surface morphology of the SiO₂/Si structures irradiated with Xe ions, the oxidized silicon substrate was subjected to chemical etching.

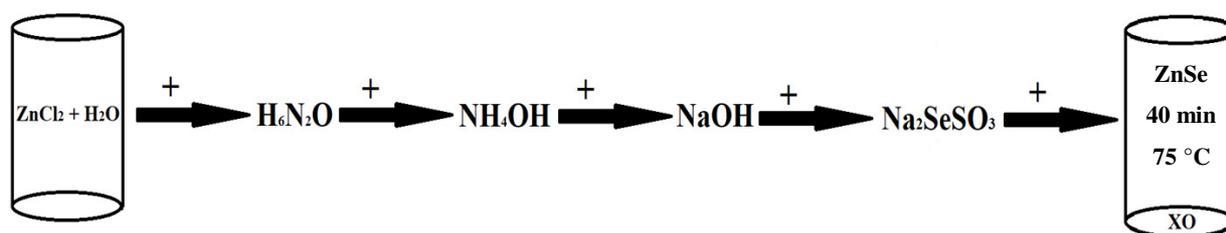


Fig.3. Scheme of synthesis of ZnSe NCs.

Chemical etching of the samples was carried out in a 4% aqueous solution of HF with the addition of 0.05 g of palladium at room temperature for 10 min. Before etching the tracks, the surface of the samples was cleaned with isopropanol for 15 minutes in an ultrasonic cleaner 6.SB25-12DTS. Analysis of the n-type template surfaces after irradiation (Fig.2a) and after etching (Fig.2b) was carried out on a JSM-7500F SEM.

By varying the etching time, nanopore diameters were obtained from 226 to 229 nm. After trawling, the test samples were washed in deionized water (18.2 MΩ) and dried in air.

The chemicals used to precipitate ZnSe were ZnCl₂, hydrazine hydrate (H₆N₂O), ammonia (NH₄OH), sodium hydroxide (NaOH), Na₂SO₃ (sodium sulfite), Se (selenium), (sodium selenosulfate) Na₂SeSO₃ (25 mmol/L).

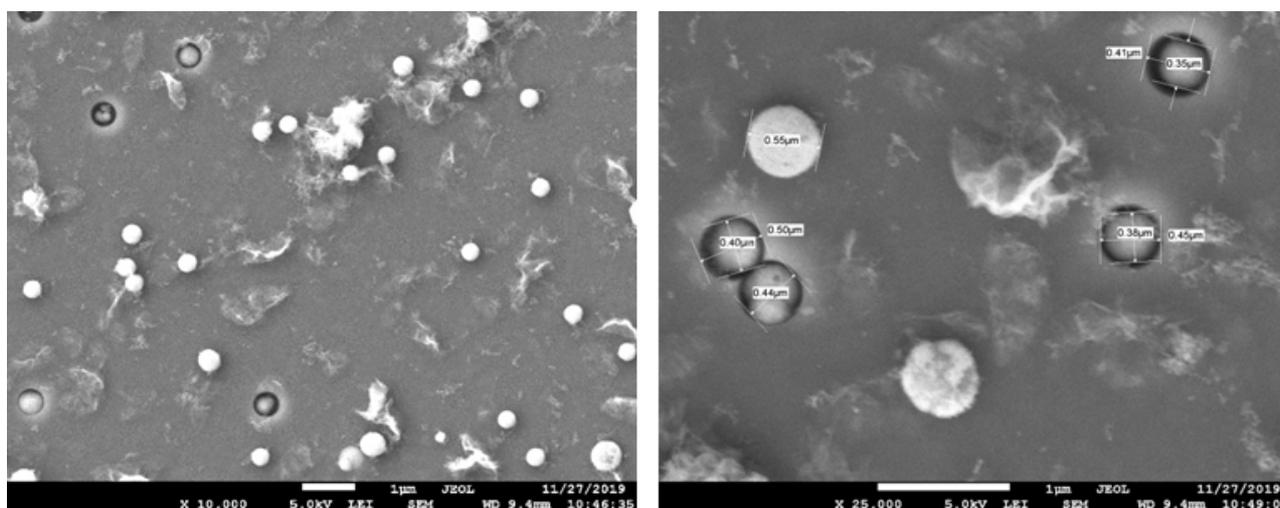


Fig.4. SEM images of the surface after CD of ZnSe for 40 min, at a temperature of $t = 750^{\circ}\text{C}$, on average, the nanopore diameter is from 410 nm to 550 nm.

To precipitate ZnSe, 6.75 g of zinc chloride ZnCl₂ was taken per 100 ml of distilled water, then 45 ml was poured into a 150 ml glass beaker and 2 ml of hydrazine hydrate was added with constant stirring, 25 drops of ammonia were added. The pH = 11 solution was adjusted by adding NaOH solution (5M). The temperature of the solution was then slowly raised with constant stirring. After reaching the required temperature of 75 °C, 45 ml of freshly prepared Na₂SeSO₃ was added with constant stirring. The deposition time of ZnSe on the substrate is 40 min at a temperature of 75 °C. The obtained samples were washed with distilled water and dried in air. On Fig.3 shows the scheme for the synthesis of ZnSe nanoclusters (NCs).

3. Results

Fig.4 shows the surface of the templates after CD of ZnSe.

X-ray diffraction studies are presented in Fig.5, of the ZnSe-deposited template, which was carried out on a Rigaku SmartLab X-ray diffractometer (XRD).

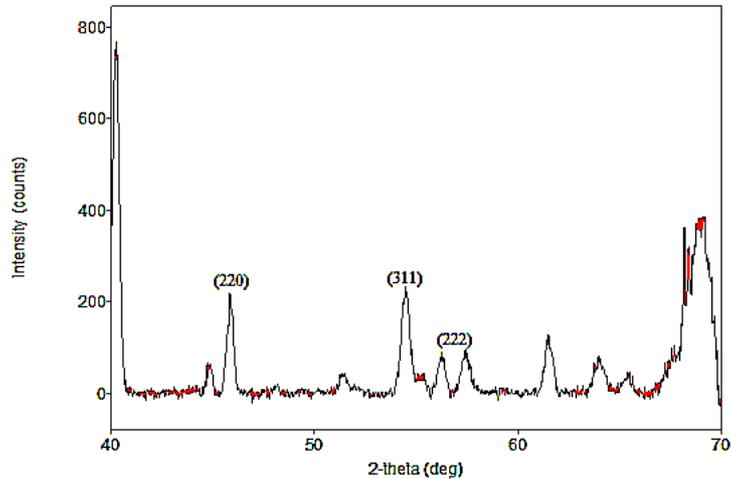


Fig.5. X-ray diffraction pattern of the test sample after deposition.

According to the data obtained, the sample under study is a crystal structure with a cubic phase (sphalerite), spatial syngony F-43m (216). For the sample, planes with Miller indices (220), (311), (222) are observed. Based on the obtained X-ray diffraction patterns, the main crystallographic characteristics of the sample under study were calculated. The data are presented in Table 1.

Table 1. Data of crystallographic characteristics of ZnSe

No	Phase	Structure type	Space group	(hkl)	2θ	$d, \text{\AA}$	$L, \text{\AA}$	Cell parameter, \AA	FWHM
1	ZnSe	Cubic	216: F-43m	(2,2,0) (3,1,1) (2,2,2)	45.81(3) 54.46(3) 57.37(4)	1.9790(10) 1.6834(9) 1.6047(11)	4	$a = 5.592081$	0.366(18) 0.42(4) 0.51(3)

The lattice parameters of the ZnSe orthorhombic unit cell obtained by us coincide with the literature data [18, 19].

The elemental composition of the nanocrystals was formulated using EDA spectroscopy. As a result of the analysis of the EDA spectra, the atomic metal structure corresponds to: Zn-42.5% and Se-57.5% (Fig.6).

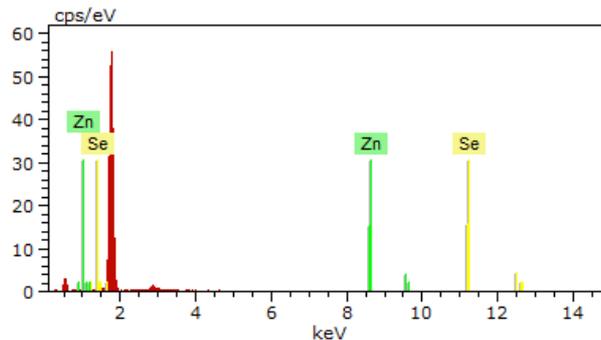


Fig.6. Energy dispersive analysis spectroscopy.

To confirm the obtained ZnSe phase by X-ray diffraction analysis, we performed elemental analysis on a TM3030 scanning electron microscope.

4. Conclusion

This paper presents the results of the formation of nanosized zinc selenide crystals irradiated with Xe ions with an energy of 200 MeV in silicon dioxide layers by chemical deposition. Morphology was studied using scanning electron microscopy. X-ray diffraction analysis showed that the structure of ZnSe nanocrystals is a cubic (sphalerite) crystal structure with space group F-43m. Using the method of energy dispersive analysis, the elemental composition of the sample under study was determined. Analysis of EDA spectra revealed that ZnSe nanocrystals consist of Zn-42.5% and Se-57.5%.

Thus, zinc selenide nanocrystals were successfully obtained by chemical deposition on a silicon substrate in an aqueous alkaline medium.

Acknowledgements

The article was performed as part of the implementation of the scientific project of grant funding for young scientists under the “Zhas Galym” project for 2022-2024 of the Science Committee of the Ministry of Science and Higher Education of the Republic of Kazakhstan AP13268607 “Features of the formation of semiconductor nanostructures in a track template SiO₂/Si”

5. References

- [1] Venkatachalam S., Mangalaraj D., Narayandass Sa.K., Kim K., Yi J., *J. Phys. D. Appl. Phys.*, **39**(22), 4777, 2006; doi: 10.1088/0022-3727/39/22/007
- [2] Deutsch T.F., *J. Phys. Chem. Solids*, **34**, 2091, 1973; doi: 10.1016/S0022-3697(73)80057-5
- [3] Masetti E., Montecchi M., da Silva M.P., *Thin Solid Films*, **234**, 557, 1993; doi: 10.1016/0040-6090(93)90331-I
- [4] Bedir M., Oztas M., Bakkaloglu O.F., Ormanci R., *Eur. Phys. J. B*, **45**, 465, 2005; doi: 10.1140/epjb/e2005-00207-3
- [5] Samantilleke A.P., Darmadasa I.M., Prior K.A., Choy K.L, Mei J., Bacewicz R., Wolska A., *J. Mater. Sci. Mater. Electron.*, **12**, 661, 2001; doi: 10.1023/A:1012854101987
- [6] Nouhi A., Stirn R.J., Hermann A., *Proc. 19th IEEE Photovoltaic Specialists Conf. IEEE*, New York, USA, 1461, 1987.
- [7] Liu Q., Lakner H., Taudt W., Heuken M., Mendorf C., Heime K., Kubalek E., *J. Cryst. Growth*, **197**, 507, 1999; doi: 10.1016/S0022-0248(98)00802-1
- [8] Noda Y., Ishikawa T., Yamabe M., Hara Y., *Appl. Surf. Sci.*, **113**, 28, 1997; doi: 10.1016/S0169-4332(96)00811-2
- [9] Kim T.W., Jung M., Lee D.V., Oh E., Lee S.D., Jung H.D., Kim M.D., Kim J.R., Park H.S., Lee J.Y., *Thin Solid Films*, **298**, 187, 1997; doi: 10.1016/S0040-6090(96)09323-6
- [10] Rizzo A., Tagliente M.A., Caneve L., Scaglione S., *Thin Solid Films*, **368**, 8, 2000; doi: 10.1016/S0040-6090(99)01104-9
- [11] Mazalova V.L., Kravtsova A.N., Soldatov A.V., *Nanoclusters: X-ray spectral studies and computer simulation*. (Moscow: PHIZMATLIT, 2012).
- [12] Paolo Ugo, Ligia Maria Moretto, *Handbook of Electrochemistry*, 2007; doi: 10.1016/B978-044451958-0.50030-6
- [13] Dauletbekova A.K., Alzhanova A.E., Komarov F.F., Vlasukova L.A., Akilbekov A.T., Mashentseva A.A., Zdorovets M.V., *Bulletin of ENU. L.N. Gumilyov. Series Physics. Astronomy*, **113**(4), 148, 2016.
- [14] Akilbekov A., Akylbekova A., Usseinov A., Kozlovskiy A., Baymukhanov Z. Giniyatova Sh., Popov A.I., Dauletbekova A., *Nuclear Instruments and Methods in Physics Research Section*

- B: Beam Interactions with Materials and Atoms*, **476**, 10, 2020;
doi: 10.1016/j.nimb.2020.04.039
- [15] Kozlovsky A.L, Giniyatova Sh.G., Dauletbekova A.K, Baimukhanov Z.K., Baizhumanov M., Akylbekova A.A., Useinov A., Shayamanov B., Popov A.I., *Bulletin of ENU. L.N. Gumilyov. Series Physics. Astronomy* , **130**(1), 34, 2020; [In Russian];
url: <https://bulphysast.enu.kz/index.php/physast/article/view/77>
- [16] Zhang Qi., Huiqiao Li., Ying Ma., Tianyou Zhai, *Progress in Materials Science*, **83**, 472, 2016; doi: 10.1016/j.pmatsci.2016.07.005
- [17] Yeh C.Y., Lu Z.W., Froyen S., Zunger A., *J. Phys Rev B*, **46**, 10086, 1992;
doi: 10.1103/PhysRevB.46.10086
- [18] Krylov P.N., Zakirova R.M., Kobziev V.F., Kostenkov N.V., Fedotova I.V., Khamidullin R.R., Dedyukhin A.A., *Journal of Technical Physics*, **86**, 7, 2016;
doi: 10.1134/S1063784216070173
- [19] Sofronova E.M., Sofronov D.S., Starikov V.V., Kurbatov D.I., Opanasyuk A.S., Mateichenko P.V., *Journal of Nano – That Electronic Physics*, **4**, 4, 04016(5), 2012;
url: <http://jnep.sumdu.edu.ua/>
- [20] Continenza A., Massidda S., Freeman A.J., *Phys. Rev. B*, **38**, 12996, 1988;
doi: 10.1103/PhysRevB.38.12996