Structure of zinc oxide nanocrystals in track templates

A Akilbekov¹, A Dauletbekova¹, Z. Baimukhanov¹, A Kozlovskiy², Sh Giniyatova¹, Zh Karipbayev¹, A Usseinov¹,² and A Seitbayev¹,²

¹Physics and Technology Sciences Faculty, L.N. Gumilyov Eurasian National University, 2 Satpayev Str., Astana, 010008, Kazakhstan
²Astana Branch of Institute of Nuclear Physics, 1/2 Abylaikhan Ave., Astana, 010008, Kazakhstan

E-mail: akilbekov_at@enu.kz

Abstract. In this paper, the results on the electrochemical deposition of zinc in the track templates of \( \alpha \)-SiO\(_2\)/Si – n are presented. Track templates were obtained by irradiation 200 MeV Xe ions, up to a fluence of \( 10^8 \) ions/cm\(^2\), followed by etching in an aqueous solution of HF. As a result of electrochemical deposition, nanocrystals of zinc oxide were obtained in the sphalerite and Zn hexagonal structure. A possible mechanism for the formation of structures is considered.

1. Introduction

At present, \( \alpha \)-SiO\(_2\)/Si nanoporous template is of interest for nanotechnological applications. Nanoporous \( \alpha \)-SiO\(_2\)/Si template can be created by irradiation with swift heavy ions (SHI) followed by etching in selective etchants. The irradiation conditions for the preparation of etched tracks in amorphous thin films of \( \alpha \)-SiO\(_2\) on a silicon substrate are investigated in [1-6]. Irradiation of SHI and etching leads to the formation of track templates of SiO\(_2\)/Si with a controlled nanopore density, shape and sizes from 10 nm to several micrometers. Rows of nanochannels etched in places of latent tracks can be filled with various substances. Nanoporous SiO\(_2\)/Si can find application as template for the creation of metal and semiconductor nanoclusters and nanowires for the development of nanoelectronic devices [5, 6], in the production of active elements of biosensors [7, 8]. In [9], it is proposed to use the Si/SiO\(_2\)/Ni structure as the main element of high-sensitivity sensors in the low-temperature region. In [10] n-Si/SiO\(_2\) (Cu/Ni) systems were created by the electrochemical deposition of copper and nickel in the track template. The layers of copper and nickel metals are deposited, as alternating – 10 layers of 20 nm each. Electrical and galvanomagnetic properties at various temperatures were investigated. Si/SiO\(_2\)/(Cu/Ni) structures can be used as new sensing elements for magnetic field sensors. With the help of track technology, self-assembled silver nanostructures were grown in the template of Si/SiO\(_2\) [11]. SiO\(_2\)/Si were irradiated with Au ions (350 MeV, fluence \( 10^8 \) cm\(^{-2}\)) and etching in 2.5% HCl. Various structures with forms of “sunflowers”, “azaleas” or “corn” were obtained by the method of wet chemical electrolysis. Silver nanostructures, as it turned out, can act as effective surfaces for enhancing Raman spectroscopy, as well as for bio-sensory applications. Another possible application is the transportation of the ion beam in the development of new optical systems based on the interaction of charged particles or quanta with the inner surface of the wall (walls) of the capillaries [12], and the development of track membranes of a new generation with...
suspended thermal and chemical resistance. We see interesting possibilities of using materials based on track templates of SiO$_2$/Si, so it is so important to expand the range of materials introduced into nanopores.

The article is devoted to the investigation of nanoclusters obtained by electrochemical deposition in track templates of $a$-SiO$_2$/Si-n.

2. Experimental equipment

The structure of $a$-SiO$_2$/Si-n was prepared by thermal oxidation of a silicon substrate (Si – n type) in an atmosphere of moist oxygen at 900°C. The thickness of the oxide layer was 700 nm according to ellipsometry. The samples were irradiated at a DC-60 accelerator (Astana, Kazakhstan) with an energy of 200 MeV xenon ions, up to a fluence of $10^8$ ions/cm$^2$.

Chemical etching of SiO$_2$/Si samples in 1% HF, m(Pd)=0.025 g, 18±1°C. Before etching the tracks, ultrasonic surface cleaning of samples in isopropanol was performed for 15 minutes in ultrasonic cleaner 6,SB25-12DTS. A purifier at two frequencies (25kHz/40kHz), provides an intensive cleaning of the surface of the samples. The control range (room temperature) – 80°C. After treatment in HF, the samples were washed in deionized water (18.2 MOhm). The nanopore analysis after etching was carried out on a scanning electron microscope JSM-7500F.

Electrochemical deposition (ECD) of Zn in template Si/SiO$_2$ was carried out in the potentiostatic regime and pH=3. The composition of the electrolyte: ZnSO$_4$·7H$_2$O – 360 g/l; NH$_4$Cl – 30 g/l; 3H$_2$O·CH$_3$COONa – 15 g/l; ascorbic acid –120 g/l. Monitoring the pH level to prevent the formation of hydrogen in the precipitation process, which prevents pore filling, was maintained by the addition of a solution of ascorbic acid. The deposition time is 10–20 minutes.

It should be noted that the ECD has been successfully applied in the deposition of copper, nickel, silver into the track templates of SiO$_2$/Si [8-10]. ECD is widely used in the deposition of various substances in polymeric membranes [15-17].

The surface was examined by a scanning electron microscope JSM 7500F (SEM). X-ray diffraction analysis (XRD) was performed on a D8 ADVANCE ECO X-ray diffractometer using an X-ray tube with a Cu-anode in the range of angles 2$\theta$ 30-110° in 0.01° increments. To identify the phases and study the crystal structure, the software BrukerAXSDIFFRAC.EVAv.4.2 and the international ICDD PDF-2 database were used.

3. Results and discussion

In table 1 the results of XRD analysis of the sample deposited within 10 minutes at a voltage of 1.5V (figure 1) are presented.

Figure 1 shows the SEM image of the sample surface, (Zn)SiO$_2$/Si-n, after the ECD. X-ray diffraction analysis of the sample showed that nanocrystals of zinc oxide were formed in nanopores. With a face-centered cubic structure, the degree of crystallinity is 19%.

An increase in the voltage at the electrodes leads to the formation of nanocrystals of Zn in the hexagonal structure (figure 2 and table 2).

| Phase and type structure | Spatial group | (hkl) | $2\theta$° | $d$, Å | Cell parameters | Degree of crystallinity, % | Phase content, g/cm$^3$ |
|--------------------------|--------------|-------|----------|-------|----------------|--------------------------|------------------------|
| ZnO, Cubic               | F-43m        | (216) | 200      | 40.275| 2.23746        | a=4.47932                | 19                     | 100                    | 5.975                  |
Figure 1. SEM Image of ECD sample for 10 minutes at a voltage of 1.5V.

Table 2. The results of XRD of the sample deposited for 10 minutes at a voltage of 1.6 V (figure 2).

| Phase and type structure | Spatial group (hkl) | θ, Degree | d, Å | Cell parameters | Degree of crystallinity, % | Phase content, % | Density, g/cm³ |
|--------------------------|--------------------|----------|-----|----------------|--------------------------|----------------|--------------|
| ZnO, Cubic               | Pm-3m (221)        | 61.79    |     |                | a=2.69220, c=4.94215      | 45             | 7.5          | 7.618        |
| Zn                        |                    | 111      | 8   | 1.50003        | a=2.69220, c=4.94215      | 45             | 7.5          | 7.618        |
| Hexagonal                | P63/mmc (194)      | 100      | 38.58 | 2.33143 | a=2.69220, c=4.94215      | 45             | 92.5         | 7.050        |

It is known that zinc oxide crystallizes in three phases [19, 20]: hexagonal wurtzite, cubic sphalerite, and a rarely encountered cubic modification of rock salt. The most common form is the wurtzite. The sphalerite phase can be stable when growing ZnO on substrates with a cubic lattice, which is confirmed by our experiment. Track template is an amorphous thin film of SiO₂ on a crystalline Si substrate, silicon has a cubic face-centered structure. This structure is formed at U=1.5 V.

The hexagonal structure and sphalerite structure of ZnO do not possess symmetry with respect to inversion [19, 20]. This leads to piezoelectric properties of these modifications and pyroelectric properties of hexagonal ZnO. As with most materials based on group II-VI elements, the bond in ZnO is predominantly ionic, which explains the strong piezoelectric properties and, therefore, ZnO can be classified as a cross between the covalently bound and ionically bound compound with a degree of ionicity f=0.616 on Phillips ionicity scale [21]. The lattice parameters of the hexagonal unit cell are a=3.2495 Å and c=5.2069 Å, and a density of 5.605 g/cm³ [22].

It should be noted that at a voltage of 1.6 V the hexagonal Zn structure and the cubic primitive coexist, with Zn phase content of 925% and a degree of crystallinity of 45%.

In the ideal Zn crystal, a=0.26649 nm, c=0.49431 nm, the axial ratio c/a=(8/3)¹/²=1.632993. In our experiment for the Zn, c/a=1.835729.

In addition, it is known that ZnO crystallizes in the cubic structures of sphalerite and rock salt (NaCl), which are shown in figure 3. ZnO sphalerite is stable only when growing on cubic structures [22–24], while the rock salt structure is metastable phase with high pressure, formed at ~10 GPa, and cannot be epitaxially stabilized [25]. Theoretical calculations show that the fourth phase, cubic cesium...
chloride, is possible at extremely high temperatures, but this phase must still be experimentally detected [26].

![Figure 2](image)

**Figure 2.** SEM Image of the sample ECHO for 10 minutes at a voltage of 1.6 V.

![Figure 3](image)

**Figure 3.** Crystal structure of ZnO crystals: a) hexagonal wurtzite; b) cubic structure of zinc blende type, sphalerite; c) cubic structure of rock salt type [18].

In our case, the cubic environment is associated with a silicon crystalline substrate. Crystal lattice of silicon; cubic face-centered, diamond type, parameter \(a=0.54307\) nm. This makes it possible to explain the formation of the structure of zinc oxide in the forms of sphalerite and rock salt, that during the growth process, at least the onset of formation takes place in a cubic medium can be explained by the depth of penetration of the 200 MeV xenon ion, the range is 20 \(\mu m\) (figure 4), which significantly exceeds the oxide layer. It should be noted that the oxide layer is amorphous, but usually short-range order is conserved in amorphous structures. The crystalline structure of silicon dioxide is a trigonal crystal system.
Figure 4. Electronic and nuclear losses of the Xe 200 MeV ion calculated by the SRIM program [27].

4. Conclusion
In the electrochemical deposition of zinc in the track template $a$-SiO$_2$/Si – n, nanocrystals of zinc oxide were obtained in crystalline phases: sphalerite and rock salt structure and nanocrystals of Zn with hexagonal structure. We assume that the cubic structures of zinc oxide (sphalerite and rock salt) are formed in the environment of the cubic structure of silicon nanopores. The Zn structure is formed together with ZnO in rock salt structure. The stabilization effect on a substrate with a cubic structure is not always dominant, and the dimensional effect also makes its contribution. The dimensional effect occurs when epitaxial growth begins only when critical dimensions of the nanocrystals formed are reached. As a result, different cubic phases of zinc oxide appear in the cubic environment at different positions of the Pd catalyst atom.

Acknowledgements
Authors acknowledge the GF 4 AP05134367 of the Ministry of Education and Science of the Republic of Kazakhstan.

References
[1] Jensen J, Razpet A, Skupiński M and Possnert G 2006 Nucl Instr. 241 119
[2] Jensen J, Razpet A, Skupiński M and Possnert G 2006 Nucl Instr. 245 269
[3] Dallanora A, Marcondes T, Bermudez G, Fichtber P, Trautman C, Toulemonde M and Papaleo R 2008 J. Appl. Phys. 104 024307
[4] Benvagoub A and Toulemonde M 2015 J. Mater. Res. 30 1529
[5] Hoppe K, Fahrner W, Fink D, Dhamodoran S, Petrov A, Chandra A, Saad A, Faupel F and Zaporotchenko V 2008 Nucl. Instr. Meth. B 266 1642
[6] Kaniukov E, Ustarroz J, Yakimchuk D, Petrova M, Terryn H, Sivakov V and Petrov A 2016 J. Nanotechnology 27 115305
[7] Fujimaki M, Rocksthul C, Wang X, Awazu K, Tominaga J, Koganezawa Y., Ohki Y and Komatsubara T 2008 Opt. Exp. 16 6408
[8] Ferting N, Blick R and Berhends J 2002 Biophys. J. 82 3056
[9] Demyanov S, Kaniukov E, Petrov A, Belonogov E, Streltsov E, Ivanov D, Ivanova Yu, Trautmann C, Terryn H, Petrova M, Ustarroz J and Sivakov V 2014 J. Surf. Invest. 8 805
[10] Demyanov S, Kaniukov E, Petrov A and Sivakov V 2014 Sens. Actuators A 216 64
[11] Sivakov V, Kaniukov E, Petrov A, Korolik O, Mazmanik A, Bochmann A, Teichert S, Hidi I, Schlesener A and Gialla D 2014 J. Crystal Growth 400 21
[12] Fleischer R 1975 Nuclear Tracks in Solids (Berkeley: Univ. California Press)
[13] Alzhanova A, Dauletbekova A, Komarov F, Vlasukova L, Yuvchenko V, Akilbekov A and Zdorovets M 2016 Nucl. Instr. Meth. B 374 121
[14] Ivanova Yu, Ivanou D and Fedotov A 2007 J. Mater. Sci 42 9163
[15] Toimil-Molares M, Buschmann V, Dobrev D, Neumann R, Scholz R, Schuchert U and Vetter J 2001 Adv. Mater. 13 62
[16] Kadyrzhanov D, Zdorovets M, Kozlovskiy A, Kenzhina I and Petrov V 2017 Mater. Res. Express 4 125023
[17] Rusakov V, Kadyrzhanov K, Kozlovskiy A, Fadeev M and Luk’yanova E 2017 Bull. Russ. Acad. Sci. Phys. 81 831
[18] Coleman V and Jagadish C 2006 Zinc Oxide Bulk, Thin films and Nanostructures Processing, Properties and Applications, (Amsterdam: Elsevier Science)
[19] Klingshirn C 2007 ChemPhysChem. 8 782
[20] Porter F 1991 Zinc Handbook: Properties, Processing, and Use in Design (Publisher: CRC Press.)
[21] Phillips J 1973 Bonds and Bands in Semiconductors (New York: Academic)
[22] Kogure T and Bando Y 1993 J. ElectronMicrosc. 47 7903
[23] Ashrafi A. B, Ueta A, Avramescu A, Kumano H, Suemune I, Ok Y and Seong T 2000 Appl. Phys. Lett. 76 550.
[24] Kim S, Seong S and Cho C 2003 Appl. Phys. Lett. 82 562
[25] Bates C, White W and Roy R 1962 Science 137 993
[26] Jaffe J, Snyder J, Lin Z and Hess A 2000 Phys. Rev. B 62 1660
[27] Ziegler J 1985 The stopping and range of ions in solids (New York: Pergamon)