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Structure of zinc oxide nanocrystals in track templates

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Abstract. In this paper, the results on the electrochemical deposition of zinc in the track templates of α -SiO₂/Si – n are presented. Track templates were obtained by irradiation 200 MeV Xe ions, up to a fluence of 10⁸ ions/cm², 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, α -SiO₂/Si nanoporous template is of interest for nanotechnological applications. Nanoporous α -SiO₂/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 α -SiO₂ on a silicon substrate are investigated in [1-6]. Irradiation of SHI and etching leads to the formation of track templates of SiO₂/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 SiO₂/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/SiO₂/Ni structure as the main element of high-sensitivity sensors in the low-temperature region. In [10] n-Si/SiO₂ (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/SiO₂(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/SiO₂ [11]. SiO₂/Si were irradiated with Au ions (350 MeV, fluence 10⁸ 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 $a\text{-SiO}_2/\text{Si-n}$.

2. Experimental equipment

The structure of $a\text{-SiO}_2/\text{Si-n}$ 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/cm².

Chemical etching of SiO_2/Si samples in 1% HF, $m(\text{Pd})=0.025$ g, $18\pm 1^\circ\text{C}$. Before etching the tracks, ultrasonic surface cleaning of samples in isopropanol was performed for 15 minutes in ultrasound 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 M Ω m). 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 $\text{pH}=3$. The composition of the electrolyte: $\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$ – 360 g/l; NH_4Cl – 30 g/l; $3\text{H}_2\text{O}\cdot\text{CH}_3\text{COONa}$ – 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 2θ $30\text{--}110^\circ$ in 0.01° increments. To identify the phases and study the crystal structure, the software Bruker AXSDIFFRAC.EVA v.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, $(\text{Zn})\text{SiO}_2/\text{Si-n}$, 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).

Table 1. The results of XRD analysis of the sample deposited within 10 minutes at a voltage of 1.5V (figure 1).

Phase and type structure	Spatial group	(hkl)	$2\theta^\circ$ Density	$d, \text{\AA}$	Cell parameters	Degree of crystallinity	Phase content, %	Density, g/cm ³
ZnO, Cubic	F-43m (216)	200	40.275	2.23746	$a=4.47932$	19	100	5.975

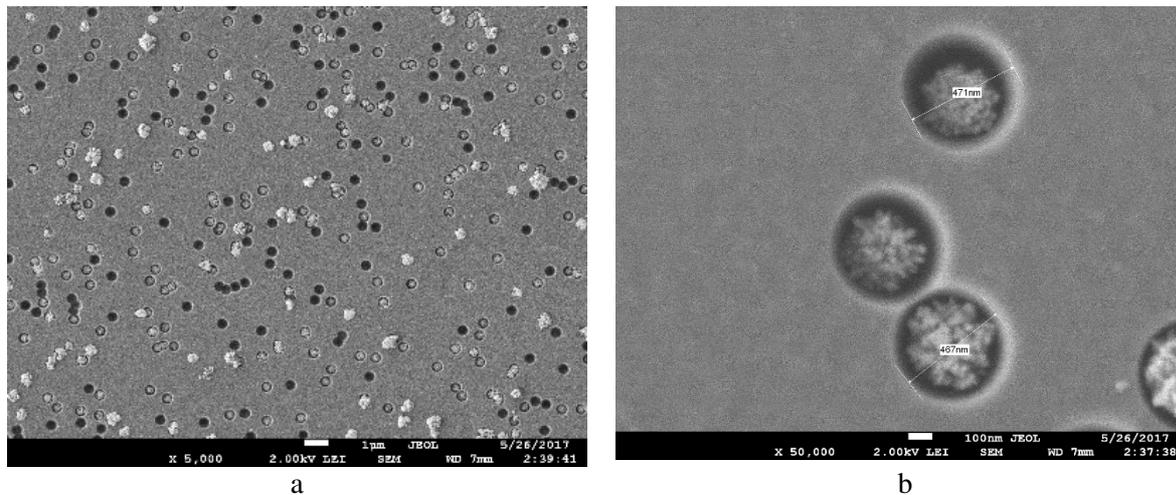


Figure 1. SEM Image of ECD sample for 10 minutes at a voltage of 1.5V.

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)	2 θ	d , Å	Cell parameters	Degree of crystallinity	Phase content, %	Density, g/cm ³
ZnO, Cubic	Pm-3m (221)	111	61.79	1.50003	$a=2.69220$, $c=4.94215$	45	7.5	7.618
Zn 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 $f_i=0.616$ 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].

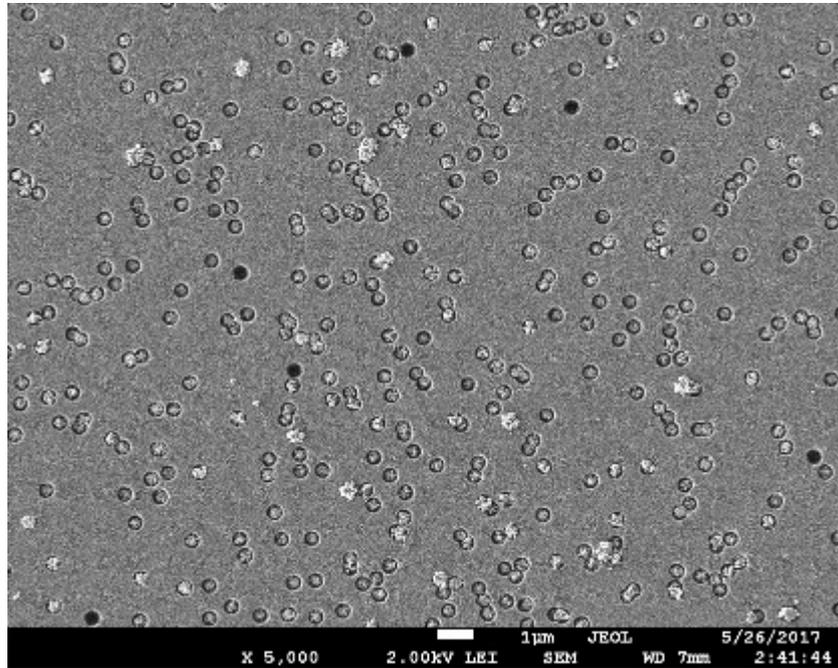


Figure 2. SEM Image of the sample ECHO for 10 minutes at a voltage of 1.6 V.

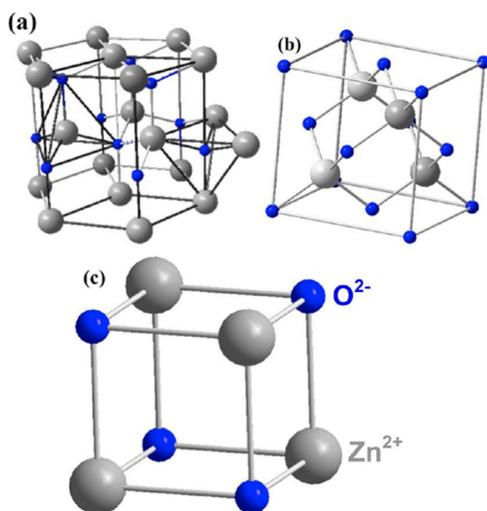


Figure 3. Crystal structure of ZnO crystals: a) hexagonal wurtzite; b) cubic structure of zinc blende type, sphalerite; c) cubic structure of rock salt type [18].

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 $20\ \mu\text{m}$ (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.

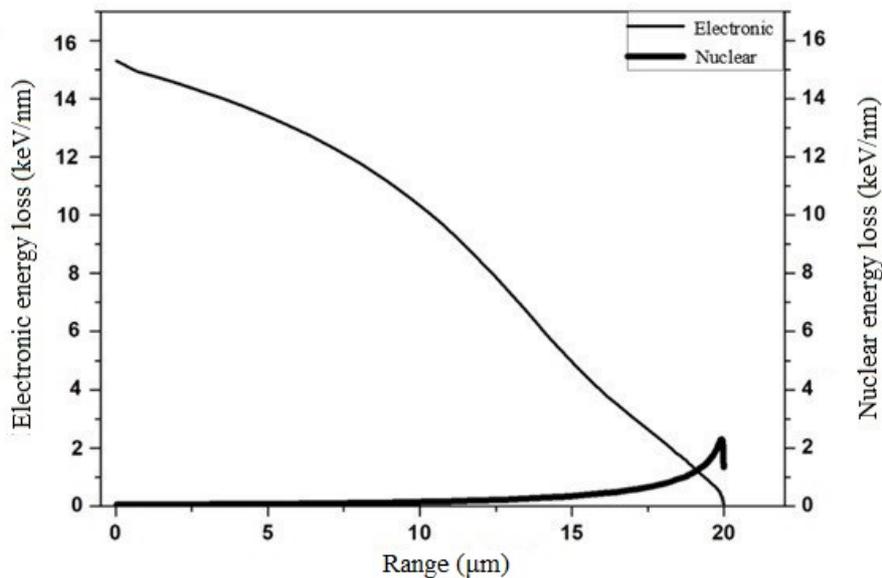


Figure 4. Electronic and nuclear losses of the Xe 200 MeV ion calculated by the SRIM program [27].

4. Conclusion

In the electrochemical deposition of zinc in the track template $a\text{-SiO}_2/\text{Si} - n$, 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

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