

SYNTHESIS AND STRUCTURAL STUDY OF THE ORDERED GERMANIUM NANOROD ARRAYS

**R. G. Valeev,^{1,2} D. V. Surnin,¹ A. N. Beltyukov,^{1,2}
V. M. Vetoshkin,² V. V. Kriventsov,³ Ya. V. Zubavichus,⁴
N. A. Mezentsev,⁵ and A. A. Eliseev⁶**

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A new approach to synthesis of the ordered germanium nanorod arrays using thermal sputtering on the matrices of porous alumina with the ordered channel arrangement is presented. The synthesized filamentary nanostructures were examined by scanning electron microscopy (SEM), EXAFS and XANES spectroscopy. Data on nanorod geometry in arrays, parameters of the local atomic structure such as interatomic distances and coordination numbers for initial samples and those annealed at 450°C in the argon atmosphere, and data on changes in the electronic states near the absorption *K*-edge were acquired. A comparison was made with the data of EXAFS studies of a continuous Ge film synthesized on a smooth surface of non-porous Al₂O₃.

Keywords: porous Al₂O₃, filamentary Ge nanostructures, Ge films, scanning electron microscopy, XANES spectroscopy.

INTRODUCTION

Although germanium as a material for semiconductor devices has a long history of systematic studies, its nanostructural state is of great interest for researchers. For example, nanocrystalline inclusions of germanium in amorphous matrix of material were obtained quite recently by deposition from the vapor phase [1, 2]. Of interest are also the nanosized inclusions in dielectric matrices such as SiO₂, which are a mixture of amorphous and crystalline structural states [3]. It should be noted that all these nanostructures have a disordered arrangement in the matrices, which strongly limits their practical application in nanoelectronics. Besides, analysis of the literature showed the absence of works devoted to synthesis and examination of the ordered filamentary nanosized germanium structures.

In this connection, we suggest a method for synthesis of the ordered arrays of germanium filamentary nanostructures, which is promising both for physics and chemistry. The method is based on filling the ordered nanopores of anodic aluminum oxide (AAO) with a semiconductor via thermal sputtering. The structure of such films may be represented as hexagonal packing of cylindrical pores that are strictly perpendicular to the film plane. A unique pore structure, which parameters such as diameter (from 3 nm to 160 nm), depth (from 0.1 μm to 10 μm) and distance between adjacent pores (from 3 nm to 300 nm) can be varied during the synthesis, makes it possible to use the highly ordered films of porous Al₂O₃ as

¹Institute of Physics and Technology, Uralian Division, Russian Academy of Sciences, Izhevsk; lasas@fti.udm.ru.
²Udmurt State University, Izhevsk. ³G. K. Boreskov Institute of Catalysis, Siberian Division, Russian Academy of Sciences, Novosibirsk; kriven@mail.ru. ⁴Russian Research Center "Kurchatov Institute," Moscow. ⁵G. I. Budker Institute of Nuclear Physics, Siberian Division, Russian Academy of Sciences, Novosibirsk. ⁶M. V. Lomonosov Moscow State University, Department of Materials Science. Translated from *Zhurnal Strukturnoi Khimii*, Vol. 51, Supplement, pp. S135-S139, 2010. Original article submitted November 5, 2009; revised April 15, 2010.

a templating material for synthesis of the ordered nanostructural arrays with controllable diameter and high geometric anisotropy [4-9]. In addition to the above mentioned arrays of filamentary nanostructures, in the same sputtering cycle we obtained films on a smooth polycor underlayer, which were used as the test objects, and nanorod arrays in the matrix annealed at 450°C in air and in the argon atmosphere. The samples were examined by the SEM and EXAFS methods; data on changes in electronic states near the absorption *K*-edge were acquired by XANES spectroscopy.

EXPERIMENTAL APPROACHES AND METHODS

Sample preparation. Alumina films with a highly ordered pore structure were synthesized by the method of two-step anodic oxidation [10, 11]. An aluminum plate with thickness 0.5 mm (Goodfellow, 99.999%) was used as a starting material. For increasing the size of aluminum crystallites and attaining a better pore ordering, the aluminum underlayers were annealed in air for 10 h at 500°C in a muffle furnace and then mirror-polished with a diamond paste. Anodic oxidation of aluminum was performed in a two-electrode electrochemical cell using a B5-50 constant-current source ($V = 0-299$ V, $I = 0-299$ mA). A Pt wire served as an auxiliary electrode. The electrolyte, which temperature was maintained in the range of 2°C to 4°C, was drawn through the cell by a peristaltic pump during anodization.

Then, an oxide film that formed on the aluminum surface was selectively dissolved in a mixture of 20 g/l CrO₃ and 35 ml/l H₃PO₄ at 70°C. This produced Al underlayers with the ordered surface roughness, which were subjected to anodic reoxidation under the same conditions for 24 h. For film separation from the aluminum underlayer, Al was selectively dissolved in a 10% solution of Br₂ in CH₃OH. After that, the films were washed with methanol and dried in air. The barrier layer was removed by etching of the film with a 5% solution of H₃PO₄ at 60°C for 5 min.

Germanium was sputtered onto the porous AAO surface via resistive evaporation of polycrystalline material from a boat evaporator under high (10⁻⁵ Pa) vacuum [12]. Simultaneously, Ge films were sputtered on a smooth polycor surface to produce a test object. For further SEM studies, the alumina matrix was etched in a 5% solution of H₃PO₄; for EXAFS and XANES examination we used the initial samples, some of them were also annealed at 450°C in air and in argon.

SEM studies. Images of the sample surface synthesized by sputtering onto the AAO matrix were obtained on a Supra 50 VP (LEO) scanning electron microscope equipped with an Oxford INCA Energy+ system for X-ray microanalysis.

EXAFS and XANES studies. The local atomic structure of the films was examined by the extended X-ray absorption fine structure method (EXAFS spectroscopy) with fluorescence yield at the Siberian Center for Synchrotron Radiation, Novosibirsk. A VEPP-3 storage ring with the electron beam energy 2 GeV at the average current of 80 mA was employed as a source of X-radiation. The studies were performed also at the EXAFS spectroscopy end-station at the Kurchatov Center for Synchrotron Radiation both with fluorescence yield and in transmitted rays. Monochromated radiation was obtained using a Si(111) crystal. EXAFS spectra were taken on a *K*-edge of Ge absorption ($E_K = 11\ 103$ eV) with the scanning range of energy 10,880-12,000 eV and step ~1.5 eV; XANES spectra, with the scanning range of energy 11,050-11,250 eV and step ~0.5 eV.

A preliminary processing of EXAFS spectra was made by a standard technique [13, 14]. The correlation functions and their parameters (chemical bond lengths and coordination numbers for the first coordination sphere; in the case of crystalline and annealed samples, for three coordination spheres) were calculated from the normalized oscillating parts of $\chi(k)$ using Fourier fitting in *k*-space from 3.5 Å⁻¹ to 14.5 Å⁻¹ and the Viper software [15]. Analysis of the obtained functions allowed us to acquire the chemical bond lengths and coordination numbers for the first coordination sphere, and in the case of annealed samples — for three coordination spheres.

RESULTS AND DISCUSSION

Figure 1 shows the SEM images of individual filamentary nanostructures (*a*) and an array of the ordered germanium nanorods (*b*). It is seen that the rods with diameter of *ca.* 200 nm and length up to 1 μm have a spatial periodicity of *ca.*

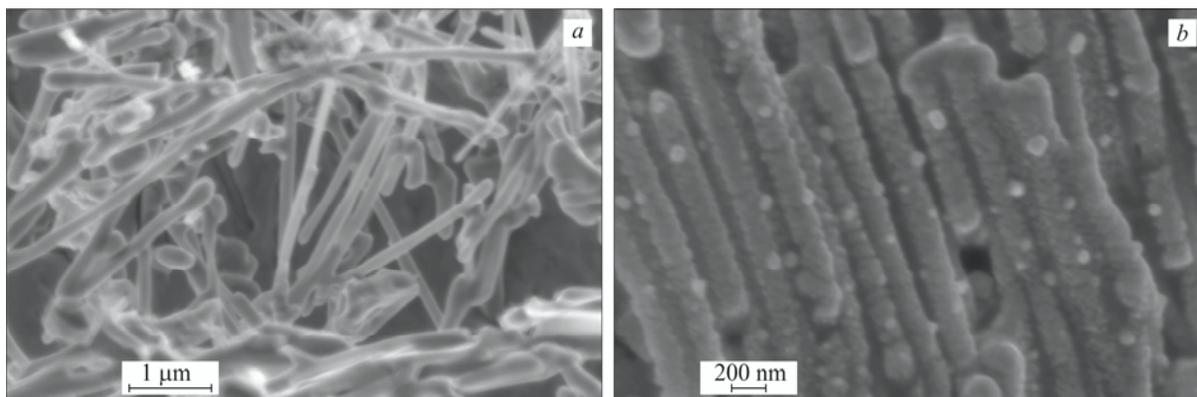


Fig. 1. SEM images of individual nanorods (*a*) and nanorod array (*b*).

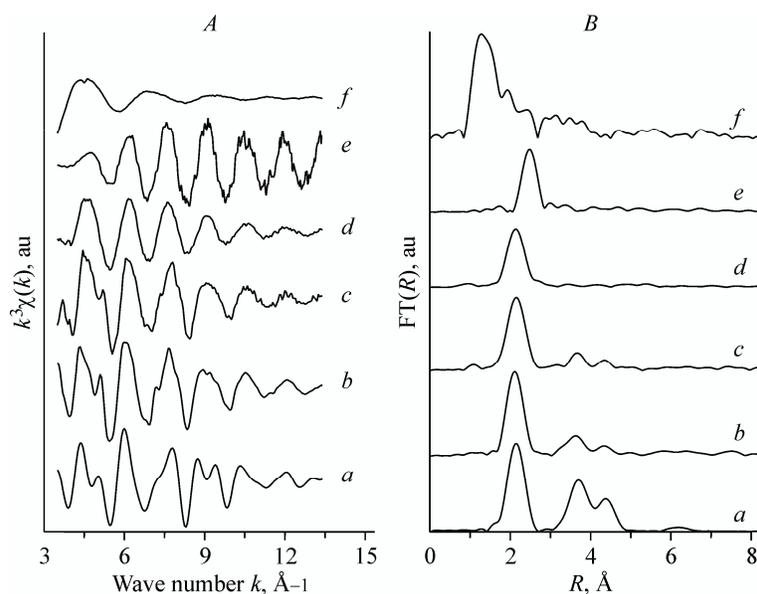


Fig. 2. Normalized oscillating fragments of germanium *K*-edge X-ray absorption spectra (*A*) and their Fourier images (*B*): *a* — data of the model calculation made by the FEFF-8 program, *b* — powder sample, *c* — germanium nanorod array annealed at 450°C in the argon atmosphere, *d* — initial sample of nanorod array, *e* — germanium film on a smooth polycrystalline surface, *f* — germanium nanorod array annealed at 450°C in air.

250 nm. Arrangement of the rods and their diameter are similar to those of the AAO film channels, which indicates the replication of template structure by germanium. At that, the lengths of filamentary nanostructures are virtually identical; however, examination of the chips showed that the matrix pores are filled incompletely with the material. This may be attributed to high adhesion of germanium to the matrix material; germanium clusters stick to the pore walls before reaching the underlayer on which the matrix is fixed, and fill the pores. Note that the rods consist of smaller particles.

Figure 2 depicts the normalized oscillating fragments of absorption spectra on the Ge *K*-edge in the form of $k^3\chi(k)$ (*A*) along with their Fourier images for germanium (*B*) synthesized by thermal sputtering in the matrix pores (*d*) and on a smooth surface of Al_2O_3 (*e*), and for nanorod arrays in the matrix annealed at 450°C in air (*f*) and in argon (*c*). For comparison, data of the model calculation performed with the FEFF-8 software [16] (*a*) and data for Ge powder (*b*) are also shown. The Fourier fitting allowed us to calculate interatomic distances and coordination numbers for three (where it was possible) coordination spheres of the local atomic environment of Ge atoms. Results are summarized in the Table 1.

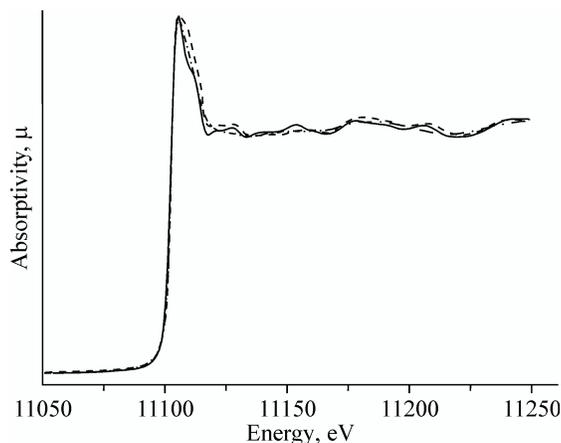


Fig. 3. X-ray absorption near Ge *K*-edge spectra (XANES spectra) for the initial sample of nanorod array (dash line), after annealing (dash-dotted line), and for germanium powder (solid line).

TABLE 1. Parameters of the Local Atomic Environment of Ge

Sample	$R_1, \text{Å}$	N_1	σ_1	$R_2, \text{Å}$	N_2	σ_2	$R_3, \text{Å}$	N_3	σ_3
Model	2.45	4	0.0033	4	12	0.0056	4.69	12	0.0061
Ge powder	2.43	4.03	0.0037	3.96	7.69	0.0085	4.66	7.88	0.0114
Initial nanorod array	2.43	3.92	0.0056	—	—	—	—	—	—
Annealed nanorod array	2.42	4.53	0.0052	3.95	3.83	0.0056	4.62	2.25	0.0045
Ge film	2.44	3.45	0.0061	—	—	—	—	—	—

As seen from the Figures and Table 1, the initial samples of filamentary nanostructures in the matrix and the films on a smooth polycrystalline surface are amorphous. Annealing at 450°C in the argon atmosphere leads to formation of a crystalline structure, whereas annealing at the same temperature in air results in complete oxidation of germanium, which is caused by high reactivity of the small-sized structures. A pronounced decrease of coordination numbers in the second and third spheres for the annealed nanostructural array is related primarily with its much less integral density in comparison with a continuous film; this is caused by the presence of empty space (actually filled with alumina). Thus, the thickness should be corrected when processing the spectra [17].

Figure 3 shows the XANES spectra for the initial sample of nanostructural array (dash line), after annealing (dash-dot line), and for germanium powder (solid line). It is seen that the spectrum of annealed sample essentially differs from that of initial sample, which is close to the spectrum of germanium powder. This is related with changes in the electronic state of germanium atoms and, hence, in the chemical potential. Thus, the annealed germanium rods are more reactive as compared to amorphous rods, which should oxidize faster and at a lower temperature.

CONCLUSIONS

The use of porous alumina as a mask or a template is promising for the formation of spatially ordered semiconductor nanostructures with the size specified by the pore diameter and thickness of the mask.

The electron microscopy study revealed incomplete filling of the matrix pores with germanium. This may be due to high adhesion of germanium to the matrix material; germanium clusters stick to the pore walls, do not reach the underlayer, and thus fill the pores. Besides, according to the SEM study, the rods consist of smaller particles.

The EXAFS spectroscopy study of atomic structure demonstrated that the synthesized filamentary nanostructures of germanium are in amorphous state. Annealing in air results in a fast oxidation of germanium. Annealing in an inert atmosphere leads to crystallization, which increases the chemical activity of germanium (according to XANES data) in comparison with the test sample.

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