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Self-organization of the structure of porous silicon carbide under external influences

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Abstract. This paper presents the results of a study of the effect of external influences on the structure and phase composition of porous SiC layers obtained by anodization. It is shown how carrying out of standard technological operations makes it possible to control the properties of porous structures and significantly expands the variety of their morphological forms. The conditions facilitating the occurrence of phase-structural and polytype transformations in porous SiC structures are determined.

Keywords: silicon carbide, porous structure, external influences, self-organization

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Самоорганизация структуры пористого карбида кремния под внешними воздействиями

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Аннотация. В данной работе представлены результаты исследования влияния внешних воздействий на структуру и фазовый состав пористого карбида кремния. Показано, как проведение стандартных технологических операций позволяет значительно расширить разнообразие морфологических форм пористых структур на основе SiC.

Ключевые слова: карбид кремния, пористая структура, внешние воздействия, самоорганизация

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Introduction

The study of the mechanisms of structural self-organization in solids has undoubted prospects for developing foundations for new technologies of multifunctional materials [1]. Self organization should be understood as a change in the spatial ordering of substructures in multiphase systems under internal factors or external influences and is manifested in large variety of secondary ordered structures. Porous materials obtained as a result of electrochemical processing (anodization) of semiconductors, are a special class of two-phase systems; their functional properties are determined by dimensional and geometric characteristics as the volume of the pore space and pore geometry, as well as by the properties of the crystalline matrix. A high specific surface area and a high proportion of atoms bound to the free surface are important characteristics of porous structures that determine an increase in the probability of the formation of surface nano-sized phases under the action of chemical potential gradients and diffusion mass transfer. This makes it possible to develop new approaches for obtaining materials with functional properties that are unattainable within the framework of traditional technologies. At present, porous silicon, which is used in modern sensor and membrane devices, nanoelectronics, photonics, and bioengineering, remains the most studied porous semiconductor. Porous materials based on binary semiconductor compounds, have not yet found such a wide practical application. This is partly due to insufficient knowledge of the mechanisms of formation and evolution of their structure under external action and the lack of predictive estimates of the stability of their properties in specific applications. At the same time, an urgent task is to obtain materials with a given set of low-dimensional substructures based on wide-gap semiconductors for solving various practical problems. In particular, the unique combination of high corrosion, chemical, radiation, and thermal resistance of the crystalline framework, which is characteristic of porous structures based on silicon carbide, determines the prospects for their use in mobile hydrogen storage systems, where one of the key ways to increase the storage capacity is to create storage elements based on three-dimensional solid-state frameworks with an increased specific surface area [1]. In addition to being used in technical fields and taking into account the fact that SiC does not have a toxic effect on a living organism as well as its ability to maintain its physical properties in a biologically active environment, porous SiC (PSC) can be used as a basis for obtaining structures with a complex architecture for new biomedical technologies [2]. The foregoing determines the relevance of the research topic, some of the results of which are presented in this paper.

Materials and Methods

In this section it is shown how by using standard procedures, such as annealing and ion plasma treatment, one can control the properties of porous structures obtained by anodization of single-crystal 6H-SiC. In (Figures 1, *a*, *b*) shown is an example of significant structural changes, that occurred in the volume of the microporous SiC layer under annealing in vacuum at 1700 °C. As can be seen, the channel microstructure of PSC has been transformed into a structure, formed by isolated faceted pores. The explanation of the observed structural changes can be given based

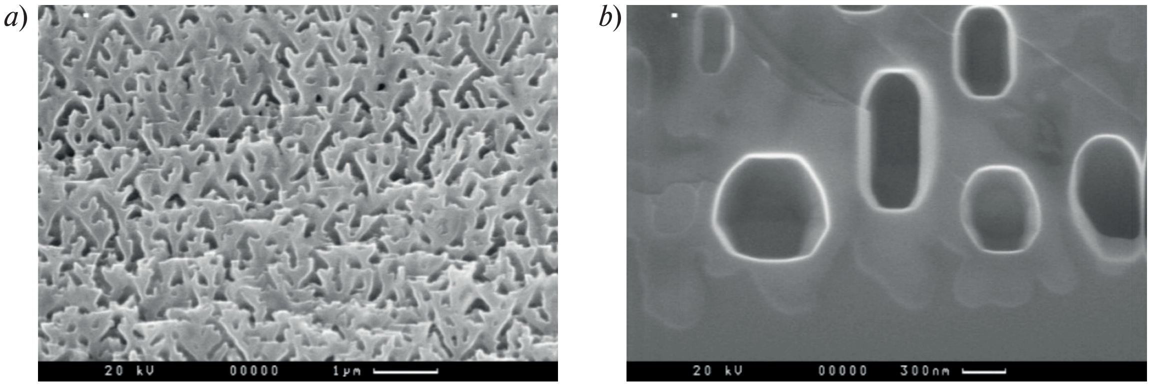

Fig.1. Scanning electron microscopy (SEM) images of transverse cleavages of initial microporous structure (*a*) and the same structure after annealing in vacuum at a temperature of 1700 °C (*b*)

on the known mechanisms of self-diffusion, used in the classical theory of sintering. With regard to two-phase (porous) solids, the term “sintering” refers to the processes of merging of pores (coalescence), leading to enlargement and change in the shape and size of pores under external influences. The driving force behind coalescence processes is the tendency of the two phase system to reduce the free energy, which is realized through a decrease in the proportion of the internal free surface, associated with the presence of pores in the crystalline matrix [3].

Results and Discussion

In the framework of the experiments, the problem of determining the effect of annealing conditions on the change in the chemical composition of porous SiC samples was studied. Annealing was carried out in high vacuum and in an argon (Ar) atmosphere at temperatures 900–1700 °C. Table 1 summarizes the Auger electron spectroscopy (AES) depth profiling data for PSC samples with a microporous structure obtained based on 6H-SiC wafers. Depending on the annealing conditions, a change in the composition was observed towards an increase in the carbon content up to a depth of 400 nm. This was indicative of a significant difference in the behavior of PSC samples and ordinary silicon carbide material annealed under similar conditions; in the latter case, the thickness of carbon-enriched layers was determined to be in order of single units of nanometers. As follows from Table 1, from the point of view of stoichiometry, PSC samples demonstrated thermal stability up to a temperature of 1500 °C, when annealing was carried out in an argon atmosphere. Heating of the samples in vacuum lead to PSC graphitization already at 1200 °C, when taking into account the results of the experiments on annealing 3D-SiC/2D-C hierarchical structures, that were fabricated on the basis of microporous SiC. Such self-organized structures represented a three-dimensional SiC matrix with a two dimensional carbon coating on its free surfaces [4, 5]. Given the proven compatibility of SiC and nanocarbon-based materials with human tissues, the obtained 3D-SiC/2D-C structures have great potential for developing tissue-inducing matrices and for other similar applications.

Plasma treatment can also lead to similar significant changes in the porous structure. Figure 2 shows images of a cleavage of a sample with a microporous structure before and after exposure to radio frequency (RF, 15 MHz, 175 W) Ar^+ ion plasma.

Table 1

AES profiling data for 6H-PSC samples with a micro-porous structure

Depth of AES analysis	*T* (°C)	C/Si ratio (%)
0 nm	900 (Ar)	67.15 32.85
15nm		48.19 51.81
400 nm		45.1 54.9
0 nm	1200 (Ar)	68.45 31.55
15 nm		48.87 51.13
400 nm		44.25 55.73
0 nm	1500 (Ar)	64.24 35.76
15 nm		50.03 49.97
400 nm		45.22 54.78
0 nm	1700 (Ar)	90.08 9.92
15 nm		58.64 41.36
400 nm		50.82 49.18
0 nm	1200 (vac.)	89.87 10.13
15 nm		50.56 49.44
400 nm		48.48 51.52
0 nm	1500 (vac.)	100.0 0
15 nm		92.50 7.50
400 nm		54.00 46.0
0 nm	1700 (vac.)	100 0
15 nm		95.65 4.35
400 nm		69.03 0.97

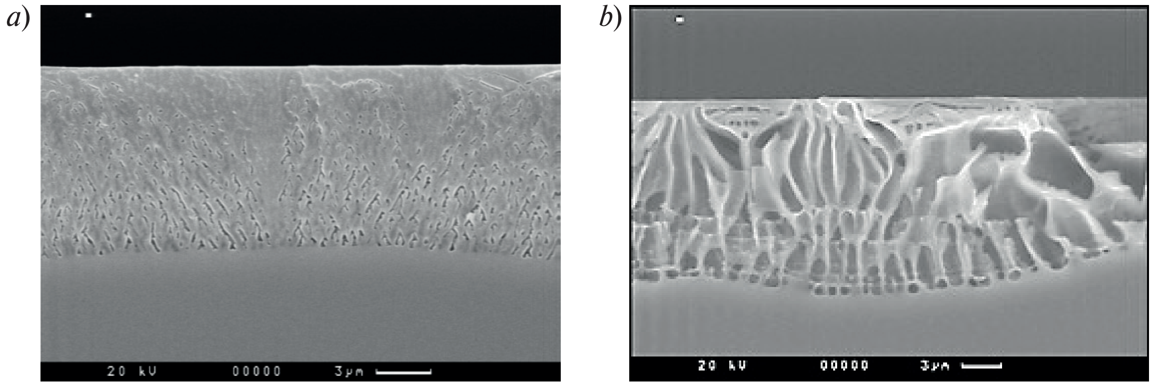

Fig. 2. SEM images of transverse cleavages of the original sample with a layer of microporous SiC, formed on the basis of a 6H-SiC wafer (*a*) and the microporous SiC layer exposed to RF Ar-ion plasma (*b*)

In contrast to thermally stimulated pore growth through coalescence proceeding according to a purely vacancy mechanism, i.e., due to the diffusion “pumping” of vacancies from smaller pores to large ones through the crystalline matrix of the porous structure, radiation-stimulated growth occurs due to the fact that small pores intensively absorb interstitial atoms that are generated under such exposure, and, as a result, disappear, while the remaining pores become larger due to the influx of excess vacancies formed in this case [6]. As follows from the results obtained in this study, changes occur not only in the pore volume, but also in the crystalline matrix of porous structures. The latter include polytype transformations in SiC. Earlier we have shown that low-temperature (2 K) photoluminescence (PL) spectra of the initial 6H-SiC and PSC samples after plasma treatment could be significantly different [7]. Namely, PL spectra of the original sample represented a set of lines in the infrared range with maxima in 1.20–1.50 eV energy range. This luminescence is associated with defects in SiC. On the contrary, the treated porous material was dominated by luminescence in the visible range with photon energy 2.40–3.30 eV. The observed lines were attributed to exciton recombination in the corresponding SiC polytypes: 3.30 eV (6H), 3.28 eV (4H), and 2.86 eV (24R) [8]. Along with that, it was proved that the anodization modes used to obtain porous SiC did not lead to a change in the polytype of the initial material. The observation of excitonic luminescence in the plasma treated material, which is characteristic of nanostructured semiconductors, indicates the appearance of crystallites with a lateral size of a few nanometers. At the same time, it is known that free surfaces in nanostructured materials contribute to a decrease in the activation energy of solid-state processes much more significantly than in the case of their bulk counterparts [9]. Thus, the formation of a multi-polytype substructure in PSC may be an evidence of the occurrence of solid-state transformations in the crystalline matrix of porous SiC.

Conclusion

We discussed selected results of the comprehensive study of effect of external influences on the structure and phase transformations in porous SiC. The proposed approaches open up new possibilities for the formation of complex hierarchical and hybrid structures formed from the atoms of a three-dimensional crystalline matrix of the porous material. Such structures are promising for a wide range of possible applications that go beyond the traditional application of orthodox semiconductors to the modern interdisciplinary scientific areas.

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