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Top-down formation of biocompatible SiC nanotubes

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It was found that the synthesis of silicon carbide epitaxial layers on silicon by coordinated substitution of atoms can be accompanied by the formation of silicon carbide nanotubes growing deep into silicon substrates. That is, for the first time discovered a new „top-down“ mechanism for the formation of silicon carbide nanotubes.

Keywords: silicon carbide, nanotubes, vapor-liquid-crystal, nanostructure formation.

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1. Introduction

Silicon carbide (SiC) quasi-one-dimensional nanostructures generate considerable interest because of their unique properties [1]. Such nanostructures have great potential for a number of technological applications, for example, in gas detectors [2–4], transistors [5], and pressure sensors [6]. Typically, quasi-one-dimensional SiC nanostructures, including nanotubes, are synthesized „bottom-up“ via the vapor-liquid-solid (VLS) mechanism using various growth catalysts [7–10]. Also, they can be formed by self-catalytic growth, with the help of masks [11] or by the vapor-solid-solid (VSS) mechanism [12]. In all cases, the growth of SiC nanostructures occurs from the substrate upward, i. e. „bottom-up“.

It should be noted that close attention is drawn to studies not only of the above-mentioned nanostructures, but also of bulk SiC, including layers and thin films. It is well known that films of wide-gap materials synthesized on foreign substrates, such as silicon (Si), can be separated and transferred to other substrates. Therefore, such SiC layers can be of significant interest not only from the point of view of creating various device structures, for example, microelectromechanical systems (MEMS) and nanoelectromechanical systems (NEMS) [13], but also the production of SiC substrates (or sufficiently thick layers of silicon carbide).

To date, various methods have been proposed for the synthesis of SiC layers on silicon [14,15]. However, one of the most promising methods among them is the recently proposed solid-phase epitaxy method [16,17]. It is based on the implementation of a coordinated replacement of part of the atoms of the silicon substrate with carbon atoms when heated to temperatures up to the melting point of silicon of 1410°C in an atmosphere of carbon-containing gases due to the chemical interaction of gaseous carbon monoxide (CO), which takes place according to the following reaction (1) [16–18]:

$$2\mathrm{Si}_s + \mathrm{CO}_g \rightarrow \mathrm{SiC}_s + \mathrm{SiO}_g \uparrow . \qquad (1)$$

As it is shown in [16,17], reaction (1) consists of two stages. At the first stage, an intermediate, metastable structure is formed, consisting of a silicon vacancy resulting from the removal of silicon and carbon in the interstitial position of silicon. This stage is described by reaction (2):

$$\mathrm{CO}_g + \mathrm{Si}_s \rightarrow \mathrm{C} + V_{\mathrm{Si}} + \mathrm{SiO}_g, \qquad (2)$$

where V_{Si} is the silicon vacancy, g subscript indicates the gaseous phase. The silicon vacancy and carbon, according to [16,17], are located in the silicon lattice along the $\langle 111 \rangle$ direction. Only this arrangement ensures that the point defects V_{Si} and the carbon atom elastically attract to each other forming a metastable complex. It is with this arrangement of point defects that the isobaric-isothermal potential of SiC formation [16] has a minimum, i. e. a chemical reaction (1) becomes possible.

In the second stage of the reaction, carbon shifts towards the silicon vacancy

$$\mathrm{Si}_s + \mathrm{C} + V_{\mathrm{Si}} \rightarrow \mathrm{SiC}_s. \quad (3)$$

Here the s subscript indicates the solid phase. Due to the fact that the volume of the SiC lattice cell is almost 2 times less than the volume of the Si lattice cell, shrinkage of the material takes place in the process of reaction (3). As a result of this shrinkage, a SiC layer and shrinkage pores under this layer are formed at the SiC-Si interface.

It should be noted that the formation of channels and pores under the SiC layer was discovered in [19,20], however, their morphology, structure, and properties have not been systematically investigated before. In this study, it will be shown for the first time that during the synthesis of SiC layers on Si using this method, under certain conditions, the formation of biocompatible SiC nanotubes growing deep into the Si-substrate, i. e. „from top to bottom“, can be realized.

2. Experiment and discussion of results

As it was noted earlier, layers of wide-gap materials are of significant interest for the creation of various MEMS structures, for example, membrane-type pressure sensors [21]. To manufacture such structures, SiC layers produced by solid-phase epitaxy were used. They were synthesized within 20 minutes. A preliminary study carried out using a JEOL JSM 7001F scanning electron microscope (SEM) showed that the thickness of the resulting SiC layers was ~ 500 nm. To create pressure sensor membranes, it was necessary to carry out a number of technological operations. First, a chromium mask of a certain design was created on the surface of samples with a SiC film using photolithography to form freely suspended beam membranes in the following stages. Then, etching was carried out in the $\mathrm{SF_6}$ plasma, as a result of which fairly deep mesas of the order of several micrometers were formed with layers of silicon carbide located on top. Then, the residual chromium was removed in a $\mathrm{Ce(SO_4)_2}$-based etchant.

The results of the SEM study of the surface morphology of samples with formed mesas unexpectedly revealed (Figure 1) that, in addition to the SiC layer, nanostructures with a maximum length reaching 4 μm were also discovered, growing from the SiC layer deep into the silicon substrate, on which they were formed. It is obvious that the decoration of SiC nanostructures growing „from top to bottom“ — deep into the substrate, in contrast to semiconductor whisker nanocrystals formed within the standard VLS mechanism, i. e. „bottom-up“ occurred during plasma etching operations.

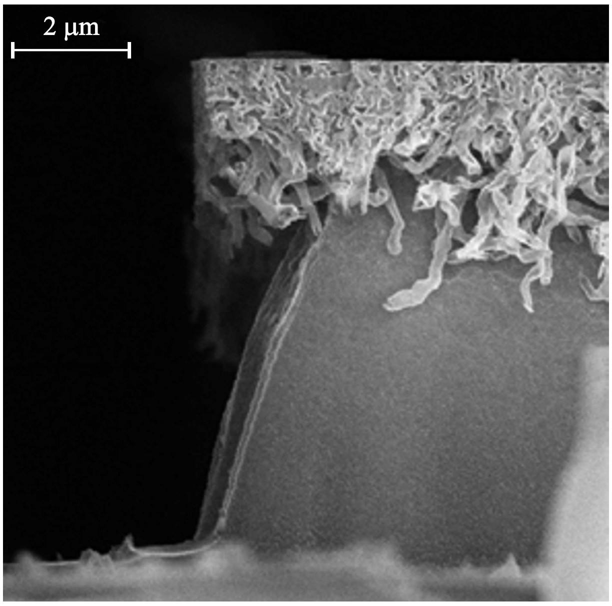

Figure 1. SEM image of the formed SiC nanostructures growing from the SiC layer downwards, i. e. „from top to bottom“.

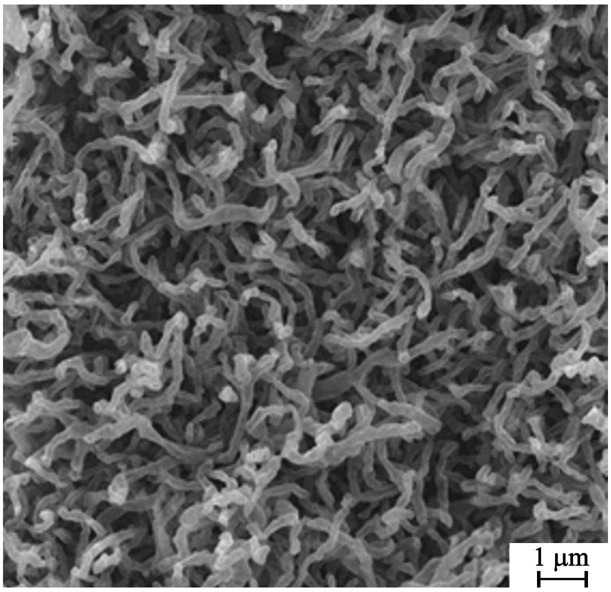

Figure 2. SEM-image of an inverted SiC layer with nanotubes transferred onto a LK5 glass substrate.

In order to study the discovered nanostructures in more detail, steps were undertaken to transfer SiC base layers with the formed SiC nanostructures onto LK5 glass substrates. For this purpose, silicon under the formed layers with nanostructures was partially etched in a

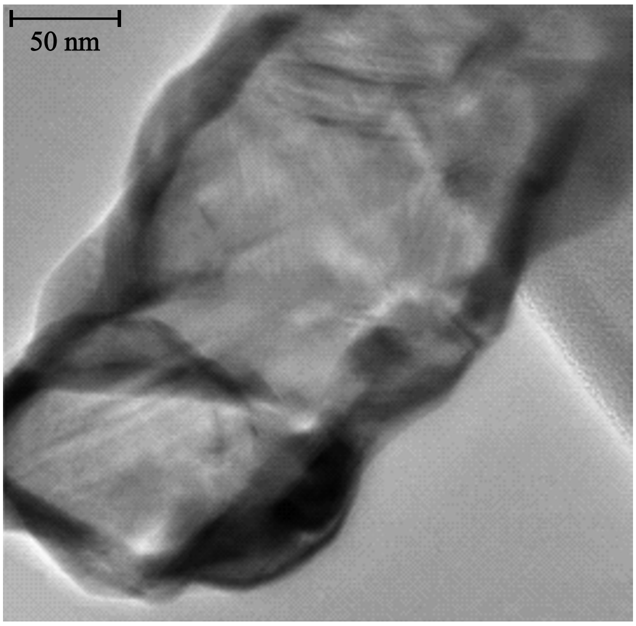

Figure 3. TEM-images of a single SiC nanotube.

$HF:HNO_3:CH_3COOH$ (9 : 2 : 4) selective acid etchant. The etching time ranged from 2 to 30 min and depended on the porosity of the SiC film. Obviously, if the silicon substrate was completely etched, the SiC film could curl up due to internal stresses, which would complicate the transfer process. Therefore, immediately before the start of the etching process, microscopic drops of photoresist were applied to several places on the surface of the SiC layer, which promoted less intense etching of the samples under the areas protected by them. As a result, the SiC layer appeared to be suspended on supporting Si pillars. Then, glass substrates were welded to the front surface of the samples using anodic welding. After breaking off the Si pillars, the inverted SiC layer with nanostructures ended up on the glass substrate.

A detailed study of the obtained samples using SEM (Figure 2) has demonstrated that as a result of the synthesis of layers on silicon substrates with a duration of substitution processes equal to 20 min carried out by solid-phase epitaxy densely-packed arrays of SiC nanostructures, similar in shape to nanotubes, were formed growing in depth („from top to bottom“) of silicon substrates.

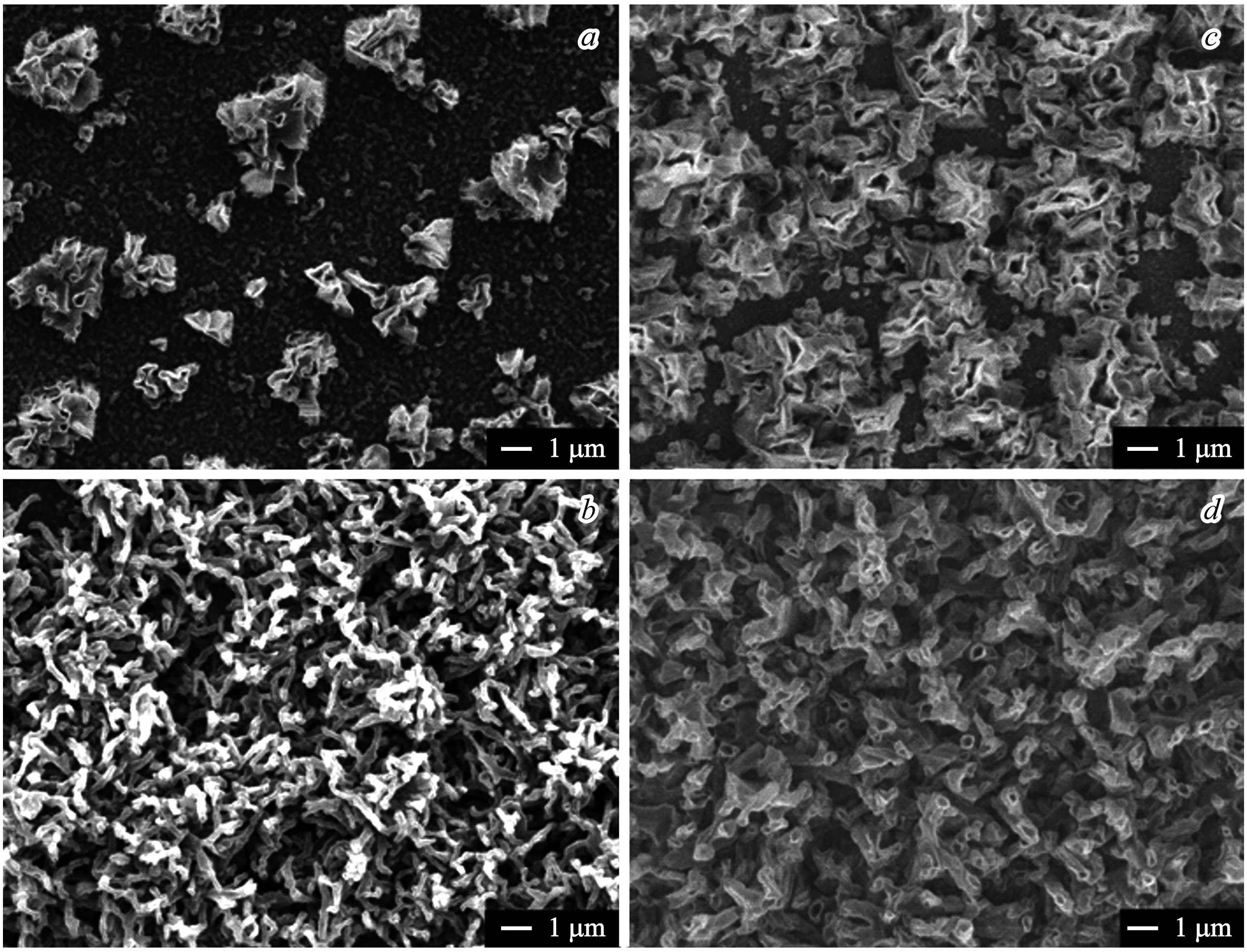

Figure 4. SEM-images of transferred SiC layers with nanotubes produced at: *a*) Si (111), $t = 3.5$ min, *b*) Si (111), $t = 40$ min, *c*) Si (100), $t = 3.5$ min, *d*) Si (100), $t = 40$ min.

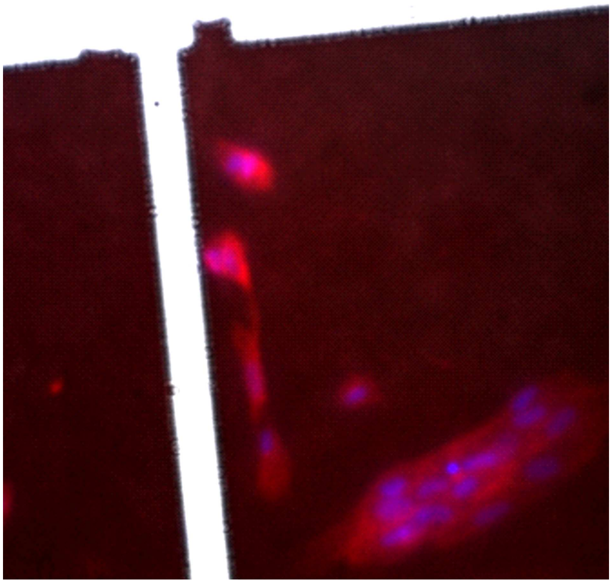

Figure 5. Confocal reflection microscopy of human mesenchymal stem cells after staining with DAPI (4′, 6-diamidino-2-phenylindole) (blue nuclei) and Rhodamine-phalloidin (red staining of the actin cytoskeleton) after 2 h of cultivation on chips with arrays of SiC nanotubes.

In order to verify the assumption made about the shape of the resulting nanostructures, they were studied using a Zeiss Libra 200 FE transmission electron microscope (TEM). The results of the study confirmed (Figure 3) that the detected nanostructures are indeed nanotubes with a cubic crystal structure. Moreover, they have a rather complex shape. Their outer diameter varies from 100 to 200 nm, and the wall thickness is < 10 nm.

It should be noted that such an unusual „top-to-bottom“ formation of SiC quasi-one-dimensional nanostructures was observed for the first time. To study the growth processes of SiC nanotubes, a series of samples with SiC layers was prepared, which differed both in the crystallographic orientation of the silicon substrates, (100) and (111), and in the formation time of the structures themselves (varied in the range from 3.5 to 40 min). In the course of a series of technological operations, SiC layers with nanostructures created on them were transferred onto LK5 glass substrates by the method described above. Figure 4 shows SEM-images of some of the prepared samples with SiC nanotubes, synthesized at different orientations of Si substrates and times of substitution processes.

It can be seen that the crystallographic orientation of the initial substrate has a significant effect on the formation of nanostructures. At the same duration of the substitution process, in the case of (100) type orientation of silicon substrates, the process of growth of nanostructures into the depths of silicon substrates is much more intense compared to substrates with (111) type orientation (Figure 4). Most likely, this is due to the denser packing of the Si(111) substrates. It can be seen that the process of formation of SiC nanostructures also strongly depends on the growth time. At the initial stages, most likely, penetration of carbon atoms occurs along selected crystallographic planes or directions with their subsequent decoration (Figure 4, *a, c*). It was found that the process of nanotube formation begins after times of the order of 10 min. The nanostructures produced with long synthesis times can be called nanotubes, because the images show the presence of internal cavities that were filled with silicon atoms. Thus, during the formation process, carbon atoms penetrated deep into the silicon substrates through some dedicated channels.

Glass chips with transferred base layers and arrays of SiC nanotubes produced at substitution times of the order of 30 min were used for studies with cell cultures. We used the non-transformed FetMSC line from the collection of vertebrate cell cultures (Institute of Cytology, Russian Academy of Sciences) as a human mesenchymal stem cell (MSC) line. The morphological features of cells after 1 day of cultivation were assessed using confocal microscopy. It can be seen in Figure 5 that after just 2 h of cultivation, the cells are spread out on the arrays of SiC nanotubes and stained actin filaments become visible. Thus, it was demonstrated that the resulting arrays of SiC nanotubes do not have a toxic effect and therefore can be considered not only as a basis for various detectors, but also as biocompatible materials.

3. Conclusion

During the research activities, a conceptually new mechanism for the formation of SiC nanotubes — „from top to bottom“ was discovered and studied. The results obtained open up broad prospects for the relatively cheap production of SiC nanotube arrays, which could potentially be used for a number of instrumental applications, for example, for various gas sensors and detectors. The study of samples with human cells cultured on them showed that they do not have a toxic effect. This greatly expands the potential use of newly developed materials.

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Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] S. Chen, W. Li, X. Li, W. Yang. Progr. Mater. Sci., **104**, 138 (2019).
[2] D. Ruixue, Y. Yintang, L. Lianxi. J. Semiconductors, **30** (11), 114010 (2009).
[3] X. Wang, K.M. Liew. J. Phys. Chem. C, **115** (21), 10388 (2011).
[4] R.S. Singh. Diamond Relat. Mater., **124**, 108932 (2021).
[5] M. Ollivier, L. Latu-Romain, B. Salem. Mater. Sci. Semicond. Process., **29**, 218 (2015).
[6] K. Nakamura, T. Toriyama, S. Sugiyama. Jpn. J. Appl. Phys., **50**, 06GE05 (2011).
[7] S. Chen, P. Ying, L. Wang, F. Gao. RSC Advances, **4**, 8376 (2014).
[8] A. Bouravleuv, G. Cirlin, V. Sapega, P. Werner, A. Savin, H. Lipsanen. J. Appl. Phys., **113**, 144303 (2013).
[9] A. Bouravleuv, I. Ilkiv, R. Reznik, K. Kotlyar, I. Soshnikov, G. Cirlin, P. Brunkov, D. Kirilenko, L. Bondarenko, A. Nepomnyaschiy, D. Gruznev, A. Zotov, A. Saranin, V. Dhaka, H. Lipsanen. Nanotechnology, **29**, 045602 (2017).
[10] Y. Berdnikov, I. Ilkiv, N. Sibirev, E. Ubyivovk, A. Bouravleuv. Nanotechnology, **37**, 374005 (2020).
[11] H. Ye, N. Titchenal, Y. Gogotsi, F. Ko. Adv. Mater., **17** (12), 1531 (2005).
[12] V.C.S. Tony, Ch.H. Voon, Ch.Ch. Lee. Mater. Res., **20** (6), 1658 (2017).
[13] M. Mehregany, C.A. Zorman. Thin Sol. Films, **355–356**, 518 (1999).
[14] Y. Hirano, T. Inada. J. Appl. Phys., **77**, 1020 (1995).
[15] J.U. Hassan, P. Bergman, A. Henry. Mater. Sci. Forum, **556**, 53 (2007).
[16] S.A. Kukushkin, A.V. Osipov. J. Phys. D: Appl. Phys., **47**, 313001 (2014).
[17] S.A. Kukushkin, A.V. Osipov. Inorg. Mater., **57** (13), 1319 (2021).
[18] S.A. Kukushkin, A.V. Osipov. Condens. Matter and Interphases, **24** (4), 407 (2022).
[19] S.A. Kukushkin, A.V. Osipov, A.V. Red'kov. Semiconductors, **51** (3), 396 (2017). doi: 10.1134/S1063782617030149
[20] S.A. Kukushkin, A.V. Osipov. Physica B, **512**, 26 (2017). http://dx.doi.org/10.1016/j.physb.2017.02.018
[21] R. Rusinek, M. Molenda, J. Horabik. Powder Tech., **190** (3), 410 (2009).

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