Physics of the Solid State, 2025, Vol. 67, No. 1

03,07,08

Mechanism of Growth of Ga_2O_3 Epitaxial Layers by Hydride Vapour-Phase Epitaxy on SiC/Si (110)

© *S.A. Kukushkin*[1], *A.V. Osipov*[2], *E.V. Ubyivovk*[1,2], *E.V. Osipova*[1], *Sh.Sh. Sharofidinov*[3]

[1] Institute for Problems in Mechanical Engineering of the Russian Academy of Sciences,
St. Petersburg, Russia
[2] St. Petersburg State University,
St. Petersburg, Russia
[3] Ioffe Institute,
St. Petersburg, Russia
E-mail: sergey.a.kukushkin@gmail.com

Received November 17, 2024
Revised November 24, 2024
Accepted November 25, 2024

The article studies the growth mechanisms of epitaxial films of β, ε and α phases of gallium oxide (Ga_2O_3) grown by hydride vapour-phase epitaxy (HVPE) on the surface of hybrid SiC/Si substrates synthesized by the method of coordinated atomic substitution (MCSA) on the surface (110) of silicon substrates. The growth of Ga_2O_3 layers occurred in a wide range of substrate temperatures from 550°C. The microstructure was analyzed using Raman spectroscopy and high-resolution transmission electron microscopy (TEM). The chemical composition (distribution of chemical elements) was determined using an X-ray spectrometer (EDS), which is an attachment to a scanning electron microscope (SEM). As a result of the studies, it was found that the growth of the Ga_2O_3 film on the SiC/Si (110) surface occurs in two stages. In the first stage, the SiC/Si (110) surface is enriched with carbon and saturated with silicon vacancies as a result of the interaction of chlorine, which is a product of the reaction of gallium chloride and oxygen, with the SiC/Si (110) surface. Only after the formation of a thin, approximately 1.5 nm thick, carbon layer on the SiC surface, the second stage begins, namely, the growth of the Ga_2O_3 layer begins. The growth of Ga_2O_3 begins with the introduction of oxygen atoms into the carbon layer, to which gallium atoms are then attached. After which the growth of the bulk Ga_2O_3 layer begins. Since the reaction between chlorine and SiC begins to occur noticeably only at temperatures above 700°C, then at lower temperatures no carbon layer is formed on the SiC surface, and accordingly, Ga_2O_3 layers do not nucleate. It has been suggested that in order to grow high-quality Ga_2O_3 films, the SiC surfaces must be modified before growth by covering them with either a thin carbon layer or a graphene layer.

Keywords: silicon carbide on silicon, gallium oxide, and α, ε and β polytypes Ga_2O_3, graphene, carbon nanostructures, growth mechanisms.

DOI: 10.61011/PSS.2025.01.60587.309

1. Introduction

We will discuss in this paper the growing of gallium oxide films (Ga_2O_3) of epitaxial quality by hydride vapour-phase epitaxy (HVPE) on the surface of cubic silicon carbide (3*C*-SiC) and, in particular, on the surface of hybrid SiC/Si substrates grown by the method of coordinated substitution of atoms (MCSA) [1–5]. Gallium oxide has a band gap of ~ 4.9 eV and retains transparency in the ultraviolet region of the spectrum up to 260 nm. Crystals Ga_2O_3 have a high electrical breakdown voltage of $\sim 8\,\mathrm{MVcm^{-1}}$ and are easily doped, which makes them very promising for micro- and optoelectronics applications [6–8]. An important feature of Ga_2O_3 is that it can be in several crystalline modifications. Currently, the possibility of the formation of 5 phases (polytypes) Ga_2O_3 has been discovered [6–8]. As the main phases, we would like to note three phases, the formation of which we will study in this paper, namely, the stable β-phase with a monoclinic structure $C2/m$ and two metastable ε-phase with an orthorhombic structure $Pna2_1$, α-phase with a rhombohedral structure $R\bar{3}c$ (corundum structure).

The growth of β-Ga_2O_3 films by methods of molecular beam epitaxy, epitaxy from organometallic compounds, chloride epitaxy and other methods has been described in a large number of publications. One of the effective methods to grow epitaxial layers of β-Ga_2O_3 is the HVPE method, which allows growing high-quality films with a high growth rate [9]. Sapphire plates (Al_2O_3) are the main substrates for the growth of epitaxial layers of β-Ga_2O_3 [8,10]. However, sapphire is a dielectric and reduces the potential of electrical devices made on the basis of layers β-Ga_2O_3 on Al_2O_3. The most effective for the production of electrical devices is the coupling of epitaxial layers β-Ga_2O_3 with silicon Si, which is the main material of electronics. However, traditional methods of growing of β-Ga_2O_3 films do not allow them to be integrated with silicon substrates due to the chemical instability of the latter under conditions under

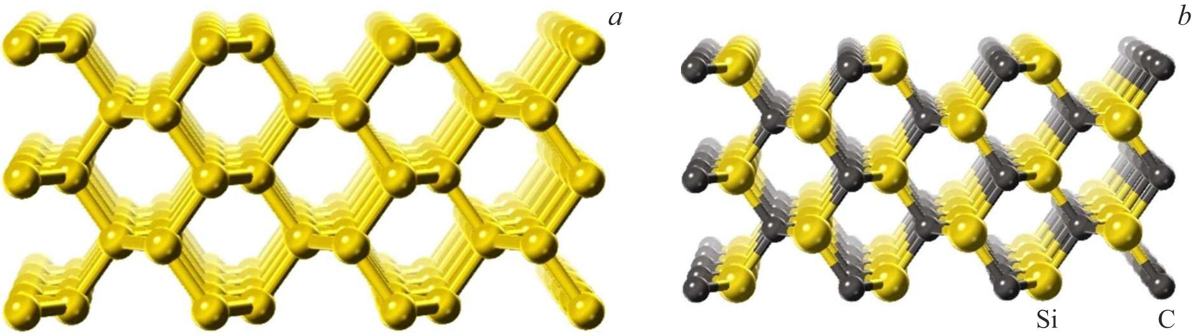

Figure 1. Surfaces (110) Si and 3*C*-SiC: *a* — original surface (110) Si; *b* — surface (110) 3*C*-SiC; large yellow balls conventionally, silicon atoms are depicted; small dark balls correspond to carbon atoms.

which layers β-Ga_2O_3 of epitaxial quality. A method was proposed in [9] for growing films β-Ga_2O_3 films on silicon substrates with a pre-synthesized buffer layer of silicon carbide SiC, which was formed by chemical substitution of atoms with silicon surfaces. This approach makes it possible to integrate epitaxial layers β-Ga_2O_3 with silicon substrates for the production of electrical devices. Later, a method was developed [11] for obtaining Ga_2O_3 on SiC/Si (111) not only of β-phase of Ga_2O_3, but also two other phases that are very attractive for microelectronics applications, namely α- and ε-phases of Ga_2O_3. Layers of various phases of Ga_2O_3 with a high degree of crystalline perfection are needed to create a material suitable for use in instrument structures. Layers of Ga_2O_3 α-, β- and ε-phases grown on SiC/Si hybrid substrates(111) contained a large proportion of polycrystalline phase, the obtained films of α-phases on SiC/Si were least perfect [11]. The reasons leading to the growth of such structures have not been clarified since that time.

Layers of β-phase of Ga_2O_3 were obtained in Refs. [12,13] not only on hybrid SiC/Si substrates grown on the surface of Si orientation (111), but also on the surfaces of SiC films grown on the surfaces of Si (100) and (110). However, these studies did not examine the mechanism of growth of Ga_2O_3 films. All attention in Refs.. [12,13] was paid to the study of only the mechanical properties of films of β-phase of Ga_2O_3. In this regard, it is proposed in this paper to study the features of the nucleation and growth of β-phase layers Ga_2O_3 on hybrid SiC/Si (110) substrates. It is also proposed to establish the possibility of formation of metastable α- and ε-phases on substrates of this type.

The motivation for using this type of substrate is the following. A distinctive feature of the atomic substitution method (MCSA) according to Refs. [1–5] is that the plane (111) is necessarily formed as one of the planes regardless of the initial Si crystallographic plane on which SiC was synthesized. The nature of this phenomenon is described in detail in the reviews in Refs.. [1–5]. This effect means that if the SiC layer grows on the surface of Si (111), then the resulting SiC film forms a face (111) on its surface. If the original Si surface has a different orientation, then this surface, minimizing its surface energy, will be covered with a family of facets (111). Thus, the initial surface of Si (100), after its transformation into SiC, is transformed into a surface covered with pyramids with faces (111). It resembles a sawtooth structure. The surface (110) Si also changes its morphology after the synthesis of SiC. The initial surface of Si, shown in Figure 1, *a*, turns into the cubic surface 3*C*-SiC (110), which is shown in Figure 1, *b*. Figure 2 shows a section of the surface (110) 3*C*-SiC, covered by the faces (111) and $(11\bar{1})$.

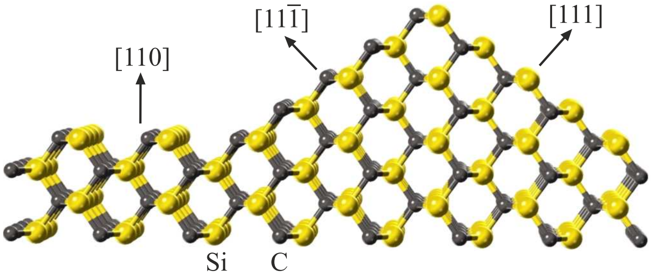

Figure 2. Structure of surfaces (111) and $(11\bar{1})$ SiC. The angle between the directions [111] and $[11\bar{1}]$ is 70.5°. The angle between directions [110] and [111], as well as between directions [110] and $[11\bar{1}]$, is 35.3°. Large balls of yellow-orange color conventionally represent silicon atoms; small dark atoms represent carbon atoms.

It follows from Figure 1, *b* and Figure 2 that the silicon surface after SiC growth on it using the MCSA [1–5] method is covered with faces (111) and $(11\bar{1})$ and the structure of these faces is different. The surface of face (111) ends with Si atoms, and carbon atoms come out onto the surface $(11\bar{1})$ face, i. e. after the synthesis of SiC, the so-called „silicon" and „carbon" faces are formed. As we showed earlier in Ref. [14], the growth of films of a number of compounds, in particular aluminum nitride films, is fundamentally different on these faces. Nitrogen atoms join silicon atoms on the „silicon" face (111) at the beginning of AlN growth and only then aluminum atoms join silicon atoms. Then they grow, alternating with each other. Aluminum atoms are first attached to carbon atoms on the „carbon" face $(11\bar{1})$, and then nitrogen atoms link to these atoms. As a result, the so-called semi-polar AlN layers are formed, consisting of peculiar AlN „domains" with opposite symmetry relative to each other in the arrangement of atoms. This explained our motivation for using this type of substrate for growing Ga_2O_3 films. It was assumed that gallium atoms would interact with silicon atoms on the silicon surface, and oxygen atoms would first be deposited on the carbon surface, thus it would be possible to establish the type of surface on which Ga_2O_3would grow better.

Thus, the aim of the study is to clarify the fundamental possibility of growth by the HVPE method of epitaxial films of alpha, beta and epsilon polytypes of Ga_2O_3. on a hybrid SiC/Si substrate with orientation (110) at substrate temperatures from 500 to 1050°C.

2. Synthesis methods

SiC/Si substrates with orientation (110) were grown by the method of coordinated substitution of atoms (MCSA) [1] in a mixture of carbon monoxide and silane gases ($CO + SiH_4$). The total pressure of the gas mixture ($CO + SiH_4$) was 80 Pa, the flow rate of the gas mixture was 4 sccm, the percentage of SiH_4 in the flow in the mixture was 25%. The growing was conducted for 20 min at a temperature of 1250°C. Silicon plates of *p*-type of conductivity and orientation (110) with a resistance of $50\,\Omega \cdot cm$ were the substrates for growth.

Ga_2O_3 layers were deposited using the HVPE method on the surface of hybrid SiC/Si substrates grown by the MCSA method on the surface of Si (110). Precipitation was conducted using the following chemical reaction [9]

$$4GaCl + 3O_2 = Ga_2O_3 + Cl_2. \qquad (1)$$

Gallium chloride was synthesized directly in the source region of the reactor by flowing gaseous hydrogen chloride (HCl, 99.999%) above metallic gallium (Ga, 99.9999%). The yield of the GaCl synthesis reaction was approximately 85%. The oxygen required for the gallium oxide formation reaction was supplied in a mixture with argon (20% oxygen, 80% argon). The synthesis of gallium oxide was conducted under conditions of excessive oxygen flow. The ratio of components of the VI/III groups was in the range of 2−8. The rate of deposition of Ga_2O_3 was determined by the HCl flow through the gallium source and depended on the deposition temperature, which varied in the range of 500−1050°C. The synthesis temperature was chosen in such a way that each of the grown phases grew in its stable state zone. We previously found in Ref. [10] that Ga_2O_3 is deposited only in the stable β-phase on a sapphire substrate at a temperature of 800−1080°C. Ga_2O_3 is deposited only in the metastable ε-phase at the synthesis temperature of 550−600°C [10], and Ga_2O_3 is deposited only in the metastable α-phase at the synthesis temperature of 500−520°C [10]. It was in the region of these temperature ranges that Ga_2O_3 films were grown on SiC/Si substrates with orientations (110). The rate of deposition of Ga_2O_3 started approximately from the values of $0.4-0.5\,\mu$m/min at 500°C with a total gas flow of $\sim 5000\,cm^3$/min and ended with values of $0.8-1.0\,\mu$m/min at 1080°C [9–11]. The deposition time was selected so that the film thickness was $0.5-1\,\mu$m. The process of growing Ga_2O_3 films is described in more detail in Refs. [9–11].

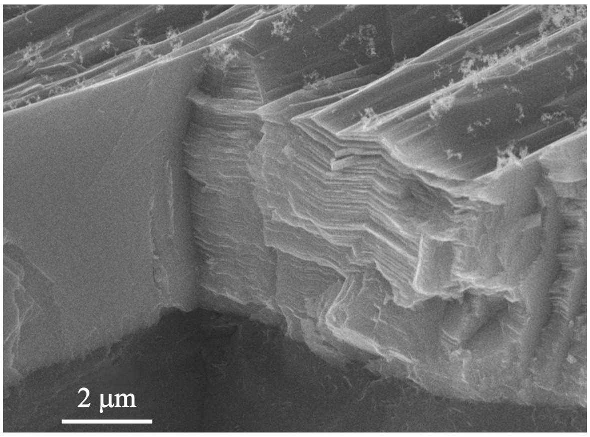

Figure 3. SEM image of the end chip of β-Ga_2O_3 film grown on hybrid SiC/Si (110) substrate at a temperature of 1050°C.

The grown samples of Ga_2O_3 films were studied using RS spectroscopy and high-resolution transmission electron microscopy (TEM). The chemical composition (distribution of chemical elements) was determined using an X-ray spectrometer (EDS), which is an attachment to a scanning electron microscope (SEM).

3. Experimental findings and their analysis

The results of the study showed the following. A continuous layer of Ga_2O_3 with a thickness of about $5\,\mu$m was grown at a temperature of 1050°C. The image of the end chip of this layer and the substrate obtained using a scanning electron microscope (SEM) is shown in Figure 3.

Figure 3 shows layered stacking of layers, indicating the formation of β-phase of Ga_2O_3. The RS spectrum acquired from this sample is shown in Figure 4. The presence of lines $A_g^{(3)}$ and $A_g^{(6)}$ in the spectrum clearly indicates the β-phase of Ga_2O_3.

Figure 5 shows images of various sections of the end chips of the interface in the sample of Ga_2O_3/SiC/Si (110) acquired using high-resolution transmission electron microscopy (TEM).

It follows from Figure 5, *a* and *b* that the morphological structure of the SiC layer at the boundary with Ga_2O_3 has the form of pyramidal „teeth", i.e. similar to those shown in Figure 2. The SiC layer is quite loose. This can be seen from comparing the contrast of SiC (dark areas) with the lower, more contrasting and lighter layer

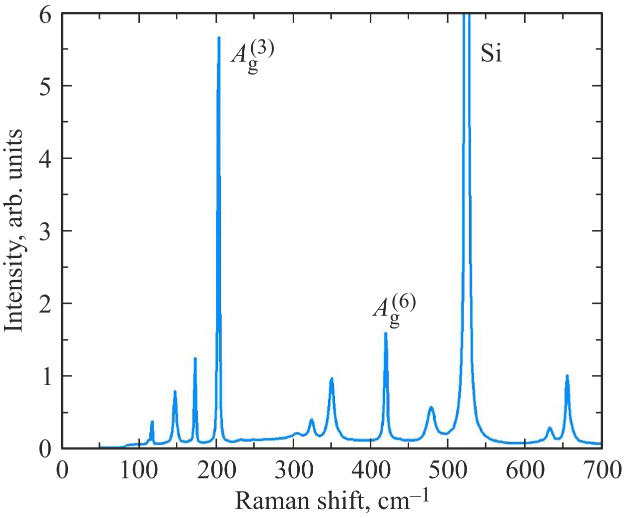

Figure 4. RS spectrum of Ga_2O_3 film grown on a hybrid SiC/Si (110) substrate at a temperature of 1050°C. The lines $A_g^{(3)}$ and $A_g^{(6)}$ indicate the formation of β-phases of Ga_2O_3.

of the Si substrate. A light structureless layer is visible in the area shown in Figure 5, *d* at the very end of the SiC layer (on the surface of the „teeth"). Crystalline planes (Moire patterns) begin to appear in the lower part of the SiC layer, in the Si substrate layer, and in the Ga_2O_3 layer. These planes are not visible in the lighter, thinner layer because it is an amorphous structure. Figure 5, *c* shows the same section of the interface, but obtained from a more visual angle. Figure 5, *d* shows a smaller-scale image of the area of Ga_2O_3–SiC–Si (110). Two crystal blocks of Ga_2O_3 are clearly visible in this figure, originating on different faces of SiC, namely on the faces (111) and the faces $(11\bar{1})$ SiC (Figure 2). They grow like a crystalline druse in opposite directions to each other. The microdifraction pattern shown in Figure 5, *e* clearly indicates the formation of twins of β-polytype (phase) of Ga_2O_3. The structure of Ga_2O_3 is improved away from the interface of Ga_2O_3–SiC–Si (110), which is in full accordance with the principle of geometric selection of by A.V.Shubnikov, which is formulated as follows: „only by those crystals are predominantly developed whose direction of maximum growth rate is perpendicular to the substrate". Thus, microscopy and microdifraction data clearly show that a single-crystal epitaxial β-phase of Ga_2O_3 has formed in this region. However, it also follows from these data that the Ga_2O_3 layer grows not on silicon carbide, but on some very thin, about 1.5 nm amorphous layer.

We conducted chemical composition studies along the phase interface of Ga_2O_3–SiC–Si (110) to determine the chemical composition of this amorphous layer. The chemical composition (distribution of chemical elements) was determined using an X-ray spectrometer (EDS), which is an attachment to a scanning electron microscope (SEM). Figure 6 and the table show a typical example of the distribution of chemical elements along the area of interface of Ga_2O_3–SiC–Si (110) to a depth of 60 nm upward from the SiC layer, into the area of Ga_2O_3 film and 60 nm down from the SiC layer into the depth of the silicon substrate.

It follows from the data acquired that the entire area just above and just below the SiC layer is enriched with excess carbon. The silicon carbide layer itself is highly enriched in carbon. Here we have given only one of the parts of the interface. These areas are even more carbon-rich in some parts. For instance, the atomic weight percentage of carbon in the SiC layer reaches 87.5% in some parts of the interface. Naturally, the initial SiC layer obtained by the MCSA method was stoichiometric [1–5]. It was not only the SiC layer that was enriched in carbon. Both the silicon substrate and the Ga_2O_3 layer were enriched with carbon in addition to the SiC layer. This raises the question of how carbon was formed and what role it plays in the nucleation of Ga_2O_3 on the surface of SiC/Si (110)? The first part of the question is not difficult to answer. It is enough to turn to the reaction (1), during which chlorine is produced. The initial reagent GaCl reactions (1) are formed by passing HCl through molten metallic gallium (this is how the HVPE method works), i. e., Cl_2 is present in the reactor in addition to reagents and oxygen. As is known, chlorine, which is produced during the reaction (1), interacts with carbides of various substances, in particular with silicon carbide, at temperatures above 700–1000°C [15]. It was shown in this paper that ordered ensembles of nanopores of the order of 0.8–2 nm are produced in carbides under the impact of chlorine, and a significant restructuring of the carbide crystal lattice occurs, as well as a significant displacement of carbon atoms from their original position in the carbide matrix. This phenomenon was explained and a theory of this process was developed in [16]. According to this theory, the phenomenon of self-organization occurs during the chemical interaction of silicon carbide with chlorine that leads to the formation of an ordered structure of pores and carbon atoms in silicon carbide. The reaction of chlorine with silicon carbide has the following form in this case

$$2Cl_2 + SiC = SiCl_4 + C. \qquad (2)$$

This reaction proceeds at temperatures above 700°C was noted above. This reaction does not occur at temperatures below 700°C. The chemical analysis data shown in the table and TEM images (Figure 6) clearly indicate the formation of excess carbon on the surface of the SiC film, while the SiC layer became loose after deposition of Ga_2O_3, which can be determined based on the difference in contrast of the layer surface SiC, shown in Figure 6. These data clearly indicate that the SiC layer is enriched with carbon just before the nucleation of the film Ga_2O_3, as a result of the removal of silicon by reaction (2) and the formation of an excessive concentration of silicon vacancies in SiC. The film Ga_2O_3 is formed and grows further only after this. It follows from these data that the mechanism of the reaction of the formation of Ga_2O_3 is much more complicated than

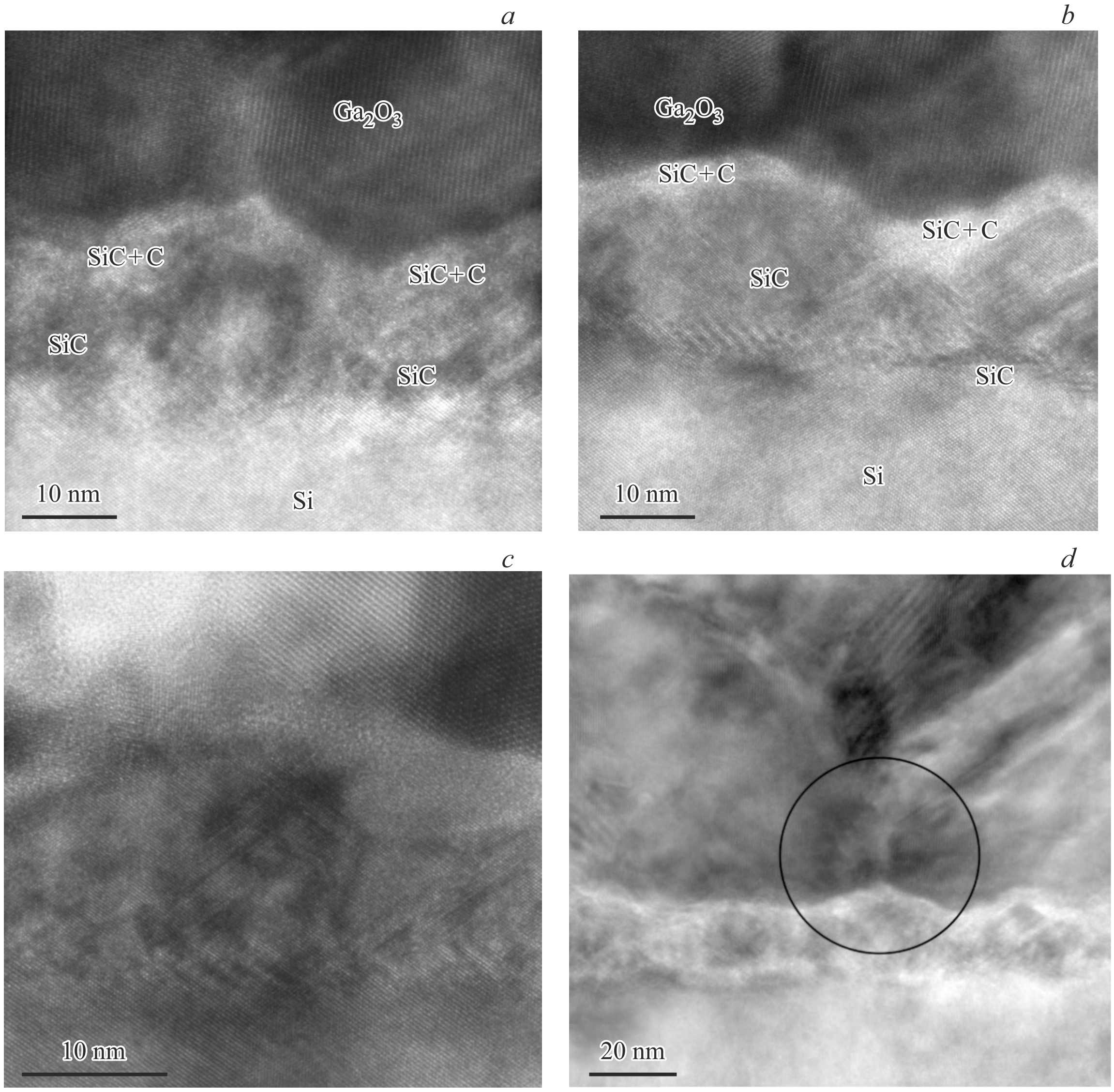

Figure 5. TEM images of the microdifraction pattern from various sections of the interface in the sample of Ga_2O_3/SiC/Si (110). *a* and *b* — interface of Ga_2O_3−SiC−Si (110), taken from its various sections; *c* — interface of Ga_2O_3−SiC; *d* — general view of the interface of Ga_2O_3−SiC−Si (110) at a lower magnification than in Figure *a* and *b*, the area of formation of twins of β-phases of Ga_2O_3 is marked by a circle; *e* — picture of microdifraction from the selected area electron diffraction (SAED) of Ga_2O_3−SiC−Si (110) where the twinning of β-phase of Ga_2O_3 takes place, this area is marked by a circle in Figure 5, *d*, indicating the reflexes from the twins of β-phases of Ga_2O_3 along the axis (100); the reflexes of the main matrix β-Ga_2O_3 and twin reflexes; *f* — TEM image from the area β-phases Ga_2O_3 away from the SiC boundary−Si (110); *g* — the microdifraction pattern acquired from the area of β-phase of Ga_2O_3, the TEM image of which shown in Figure 5,*f*.

it is assumed if we take into account only the reaction (1). The data obtained indicate that both the substrate and the SiC layer itself participate in the formation of crystalline Ga_2O_3. It is quite obvious that the reaction (1) is a total reaction involving a number of intermediate steps. The reaction (1) determines only the initial and final states. The chemical analysis data (see table) show that oxygen penetrates not only into the SiC layer, but also into the silicon substrate. Gallium does not penetrate the SiC layer and, moreover, does not penetrate the silicon substrate. It is contained only in Ga_2O_3 layer. It is well known that gallium does not form compounds such as gallium carbide with carbon (we do not mean organometallic compounds here). An article [17] was published earlier, the authors of which tried to initiate an interaction reaction between molten gallium and a hydrocarbon medium using ultrasound. Even the title of this article looked somewhat defiant: „The interaction between molten gallium and the hydrocarbon medium induced by ultrasonic energy — can gallium carbide be formed?“. It was found in this study that gallium carbide cannot be obtained in a stable form. Only very small, short-lived gallium clusters are formed

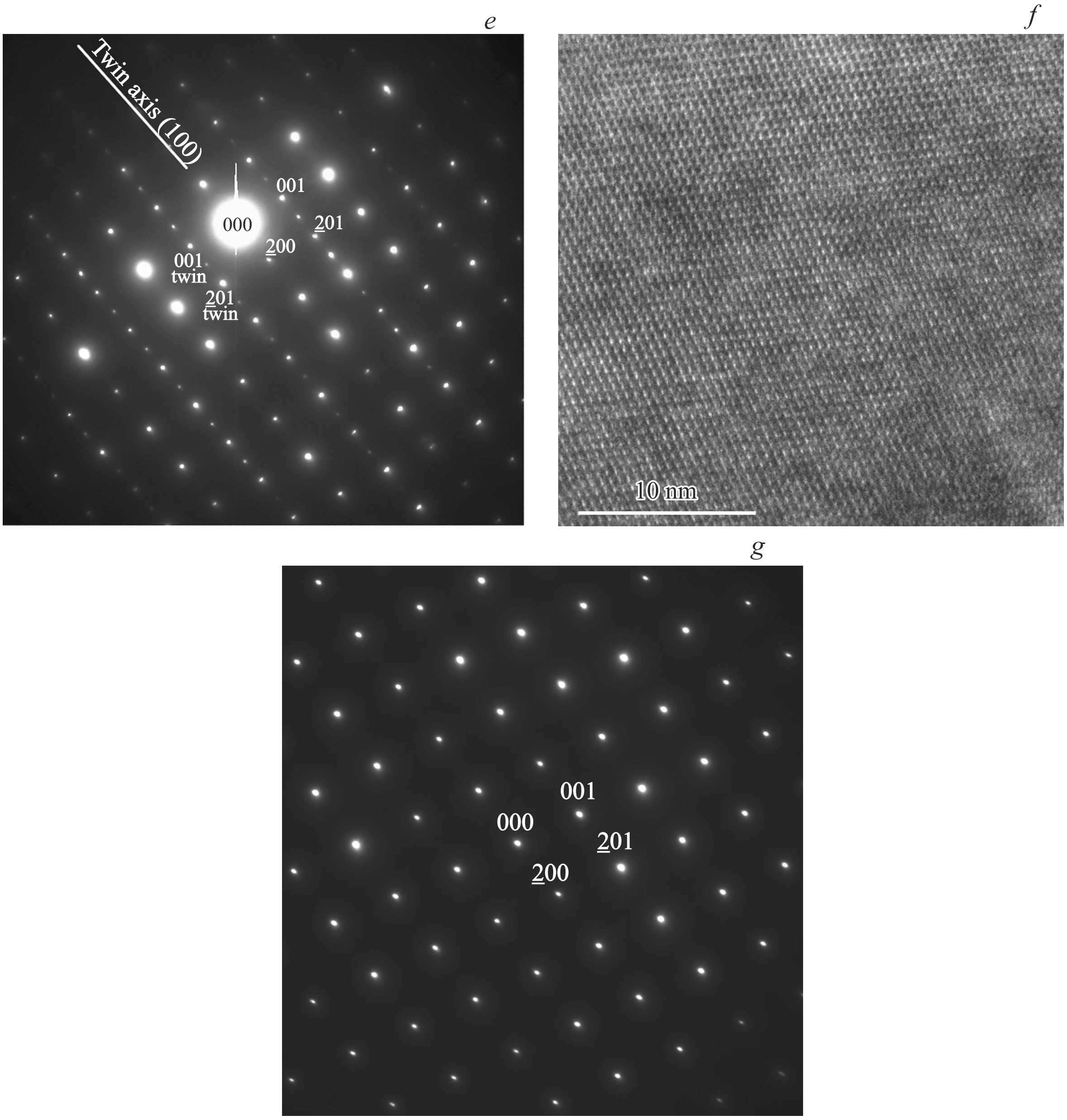

Figure 5 (*continued*).

under the impact of cavitation which are surrounded in the first coordination sphere by oxygen atoms and only then by carbon atoms. Actually, it's not gallium carbide! Our data also showed that gallium does not interact with carbon, even at a higher temperature than the temperature at which the interaction of gallium with a hydrocarbon medium was studied [17].

Thus, we found that the growth of the Ga_2O_3 layer begins with the formation of a carbon-rich SiC layer. Then oxygen atoms penetrate into it, and only then gallium atoms begin to attach to these oxygen atoms. Only then does the formation of the layer of β-phases of Ga_2O_3 begins. It can be said that the layer of Ga_2O_3 obtained as a result of the reaction (1) „spontaneously" prepares a surface for growth.

Chemical composition from the points of interface of Ga_2O_3–SiC–Si (110), marked in Figure 6

№ Spectrum	Percentage chemical elements in at.%					
	C	O	Si	Ga	Cu	Total %
Spectrum 1	42.72	24.88	2.78	20.60	9.01	100.00
Spectrum 2	66.12	4.31	20.08	0	9.49	100.00
Spectrum 3	61.31	1.74	27.64	0	9.31	100.00

The film of Ga_2O_3 of epitaxial quality cannot grow if the SiC layer is not enriched with carbon. A layer of Ga_2O_3 phase in a crystalline state cannot be formed on such a surface, neither from the gallium face nor from the oxygen face Ga_2O_3. As a result, a thin nucleus layer of Ga_2O_3 phase is not formed which is the necessary building base for further film growth. A thin layer of SiC enriched in carbon and, obviously, saturated with silicon vacancies is such a base, into which oxygen penetrates and is well adsorbed on the surface. The further growth of crystalline Ga_2O_3 begins with the formation of this layer. A conclusion follows from these results. The reaction of carbonization of SiC (2) does not occur at temperatures below 700°C, therefore Ga_2O_3 phases will not grow, especially the metastable phases of Ga_2O_3 will not grow, which include α- and ε-phases of Ga_2O_3.

We attempted to confirm this conclusion by growing Ga_2O_3 film on the surface of SiC/Si (110) at a temperature of 550°C Ga_2O_3. ε-phase of Ga_2O_3 should be stable at this temperature according to data from Refs. [10,11]. The first results confirmed our conclusion that it is impossible to grow on a clean SiC/Si (110) surface without buffer layers and various additives.

No Ga_2O_3 layer formed on the surface of SiC/Si (110) as seen on the images (Figure 7). Only individual crystals of Ga_2O_3 resembling snowflakes are present on the substrate. They have nothing to do with the surface of the substrate. It is quite obvious that these crystals formed near the surface of the substrate in the vapor phase and then settled on it. A cluster of intergrown crystals of Ga_2O_3 is particularly clearly visible in Figure 7, *b*. Such clusters nucleate in the vapor phase owing to the homogeneous nucleation mechanism [18]. The barrier of nucleation of Ga_2O_3 is high, so very few nuclei are formed, since the substrate is not involved in the nucleation process. Ga_2O_3 layers grow only when a carbon-enriched SiC layer is formed. The oxygen involved in the reaction (1) interacts with this layer. This leads to a significant change of the adsorption and wetting properties of the substrate. In addition, the elastic constants of the substrate surface also significantly change. As a result, the elastic energy, which is usually produced during the growth of films on foreign substrates, significantly changes. Thus, the formation of a carbon-enriched SiC layer with oxygen atoms embedded in it is a kind of seed or „pre-nucleus“ for this system. The growth of Ga_2O_3 film becomes possible only after the formation of this „pre-nucleus“. It should be noted that the chlorine released during the reaction (1) plays the role of a catalyst that initiates the growth of crystalline phases of Ga_2O_3.

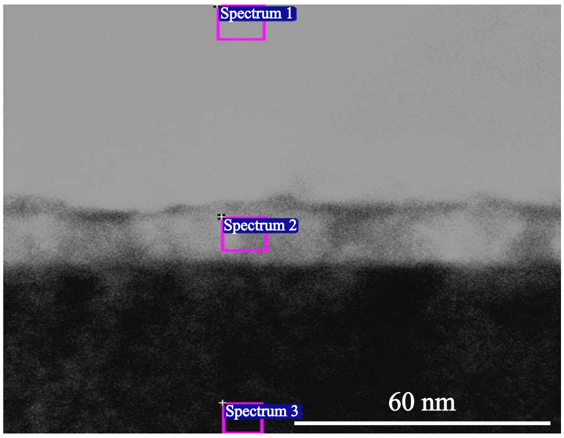

Figure 6. SEM image of sections of the interface of layers of $Ga_2O_3-SiC-Si$ (110), at the points from which the chemical composition was determined.

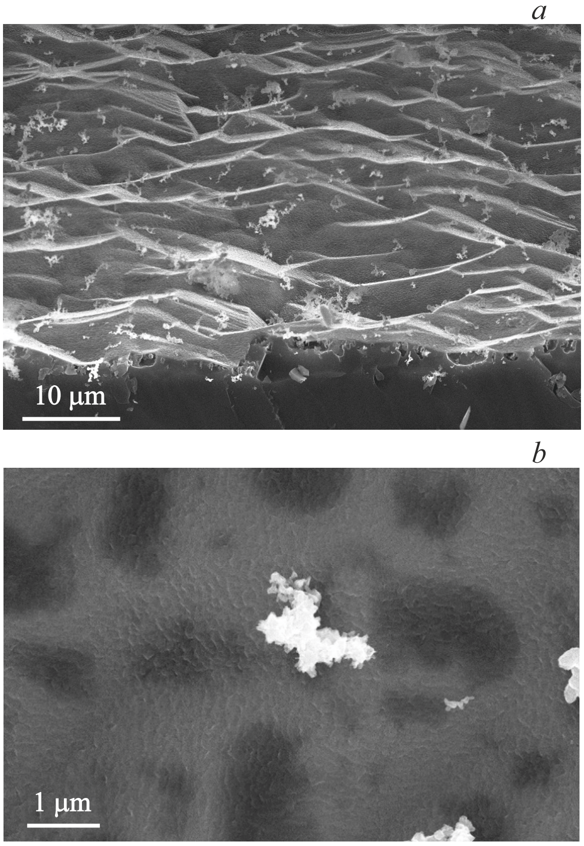

Figure 7. SEM image of the surface of SiC/Si (110) substrate on which attempts were made to deposit a layer of Ga_2O_3 film at a temperature of 550°C. *a* — end section of surface of SiC/Si (110) with individual crystals of Ga_2O_3, resembling snowflakes; *b* — view of the SiC/Si (110) surface from above.

4. Conclusions

Thus, the following was found as a result of the analysis of the processes of growth of Ga_2O_3 layers on SiC/Si (110) hybrid substrate:

– reactions (1) of SiC/Si (110) substrate if used for growth of Ga_2O_3 films may be suitable only for growth of β-phases of Ga_2O_3; the substrate temperature should be on the order of 1000°C or higher in this case;

– SiC/Si (110) substrate is a very suitable substrate for the growth of epitaxial layers of β-phases of Ga_2O_3;

– Ga_2O_3 phases are not formed on SiC/Si (110) substrates at temperatures below 700°C;

– the growth of Ga_2O_3 on SiC/Si (110) substrates takes place only if a SiC layer enriched in carbon and saturated with silicon vacancies forms on the substrate; Ga_2O_3 films do not grow in the absence of the surfaces of this layer;

– growth of Ga_2O_3 film on the carbon-rich surface of SiC/Si (110) begins with the introduction of oxygen atoms into it, which are then joined by gallium atoms and the growth of Ga_2O_3 layer begins;

– carbon-enriched SiC/Si (110) surface with interstitial oxygen atoms is a kind of „pre-nucleus“ phase for growth of Ga_2O_3 films;

– chlorine released during the reaction (1) plays the role of a catalyst that initiates the growth of crystalline phases of Ga_2O_3.

A number of conclusions and forecasts can be made based on the obtained results:

– Ga_2O_3 films either will not precipitate or will grow in the polycrystalline phase without the formation of a carbon-rich layer on the surface of any SiC crystals;

– the surface of SiC crystals and SiC/Si (110) heterostructures should be pre-enriched with a very thin layer of carbon (1–3 nm) for the growth of Ga_2O_3 layers on them, which, for example, can be done using the reaction (2); in this case, it will be possible to obtain not only β-phase of Ga_2O_3, growing at high temperature, but the metastable α- and ε-phases of Ga_2O_3 formed at lower temperatures;

– obviously, Ga_2O_3 films will grow well on the surface of a graphene layer, one of the ways to obtain which is the synthesis of graphene on the surface of SiC single crystals;

– Ga_2O_3 can be grown using hexagonal SiC crystals with a deviation from the base orientation (0001) and 3*C*-SiC/Si heterostructure, grown on Si with a deviation from the basic orientation (111), for example on 4°, i. e. Ga_2O_3 films can be grown on so-called vicinal surfaces; these surfaces are more easily enriched in carbon and, as shown in Ref. [19], ordered ensembles of carbon nanostructures are formed on Si (111) surfaces during the synthesis of SiC, which can serve as centers for nucleation of Ga_2O_3 films.

The fact that β-, α- and ε-phases of Ga_2O_3 were synthesized on the vicinal surfaces of SiC/Si (111) heterostructures in Ref. [11] we now associate with the formation of carbon nanostructures [19] on the steps of these surfaces. Silicon substrates of orientation (111) with a deviation 4° from the base direction towards [110] were used in this article [11], for the growth of cubic silicon carbide, and the temperature of synthesis of SiC was 1300°C. Such a high synthesis temperature stimulates the formation of carbon nanostructures on the SiC/Si viscinal surfaces. We did not yet realize all the subtleties of the growth of Ga_2O_3 layers on the SiC/Si surface when planning the work in Ref. [11]. When starting the study in Ref. [11], we decided to grow layers of Ga_2O_3 on the SiC/Si vicinal surface, based on the well-known fact that the formation of new phase nuclei is easier on stepped surfaces. It was only when conducting the studies described in this report that the whole picture of the process of growth of Ga_2O_3 films on SiC/Si substrates became clear and it became clear that the epitaxial growth of Ga_2O_3 is associated with SiC carbon enrichment. The temperature of synthesis of the SiC layer on Si in this work was 50°C lower than the temperature of synthesis of the SiC layer on Si, which was then used to grow Ga_2O_3 films in Ref. [11]. At the same time, the orientation of the surface face of Si was different. Carbon nanostructures were not formed on its surface for this reason, and Ga_2O_3 layers were not formed at the temperature of 550°C for this reason.

Funding

S.A. Kukushkin, E.V. Osipova and E.V. Ubyvovk performed their part of the work under the state assignment of FSUE Institute for Problems in Mechanical Engineering of the Russian Academy of Sciences № FFNF-2021-0001 of the Ministry of Science and Higher Education of the Russian Federation. A.V. Osipov performed his part of the work with the support of the Ministry of Science and Higher Education of the Russian Federation under the state assignment of St. Petersburg State University No. 95440344.

Acknowledgments

The study was conducted using the equipment of the unique scientific facility „Physics, Chemistry and Mechanics of Crystals and Thin Films“ of Institute for Problems in Mechanical Engineering of the Russian Academy of Sciences, Federal State Unitary Enterprise (St. Petersburg). TEM studies were conducted using the equipment of the „Nanotechnologies“ International Research Center of the St. Petersburg State University.

Conflict of interest

The authors declare that they have no conflict of interest.

References

[1] S.A. Kukushkin, A.V. Osipov. J. Phys. D: Appl. Phys. **47**, 313001 (2014). DOI: 10.1088/0022-3727/47/31/313001

[2] S.A. Kukushkin, A.V. Osipov, N.A. Feoktistov. FTT **56**, *8*, 1457 (2014). (in Russian). DOI: 10.1134/S1063783414080137

[3] S.A. Kukushkin, A.V. Osipov. Inorg. Mater. **57**, *13*, 1319 (2021). DOI: 10.1134/S0020168521130021

[4] S.A. Kukushkin, A.V. Osipov. Russ. J. Gen. Chem. **92**, *4*, 584 (2022). DOI: 10.1134/S1070363222040028

[5] S.A. Kukushkin, A.V. Osipov. Kondensirovannye sredy i mezhfaznye granitsy, **24**, *4*, 407 (2022). (in Russian). DOI: 10.17308/kcmf.2022.24/10549

[6] N.S. Jamwal, A. Kiani. Nanomaterials **12**, 2061 (2022). URL: https://doi.org/10.3390/nano12122061

[7] S.J. Pearton, J. Yang, P.H. Cary, F. Ren, J. Kim, M.J. Tadjer, M.A. Mastro. Appl. Phys. Rev. **5**, *1*, 011301 (2018). URL: https://doi.org/10.1063/1.5006941

[8] S.I. Stepanov, V.I. Nikolaev, V.E. Bougrov, A.E. Romanov. Rev. Adv. Mater. Sci. **44**, 63 (2016).
URL: https://www.elibrary.ru/item.asp?id=26987785

[9] S.A. Kukushkin, V.I. Nikolaev, A.V. Osipov, E.V. Osipova, A.I. Pechnikov, N.A. Feoktistov. Epitaxial Gallium Oxide on a SiC/Si Substrate. Physics of the Solid State **58**, *9*, 1876 (2016). DOI: 10.1134/S1063783416090201

[10] A.V. Osipov, Sh.Sh. Sharofidinov, A.V. Kremleva, A.M. Smirnov, E.V. Osipova, A.V. Kandakov, S.A. Kukushkin. Kondensirovannye sredy i mezhfaznye granitsy, **25**, *4*, 557 (2023). (in Russian).
URL: http://doi.org/10.17308/kcmf.2023.25/11479

[11] A.V. Osipov, Sh.Sh. Sharofidinov, E.V. Osipova, A.V. Kandakov, A.Y. Ivanov, S.A. Kukushin. Coatings. **1**, 1802 (2022).
URL: http://doi.org/10.3390/coatings12121802

[12] A.V. Osipov, A.S. Grashchenko, S.A. Kukushkin, V.I. Nikolaev, E.V. Osipova, A.I. Pechnikov, I.P. Soshnikov. Contin. Mech. Thermodyn. **30**, 1 (2018).
URL: https://doi.org/10.1007/s00161-018-0662-6

[13] A.S. Grashchenko, S.A. Kukushkin, V.I. Nikolaev, A.V. Osipov, E.V. Osipova, I.P. Soshnikov. Physics of the Solid State **60**, *5*, 852 (2018). DOI: 10.1134/S1063783418050104

[14] A.A. Koryakin, S.A. Kukushkin, A.V. Osipov, Sh.Sh. Sharofidinov, M.P. Shcheglov. Materials. **15**, 6202 (2022). DOI: 10.3390/ma15186202

[15] R.N. Kutt, E.A. Smorgonskaya, S.K. Gordeev, A.V. Grechinskaya, A.M. Danishevsky. FTT **41**, *8*, 1484 (1999). (in Russian).

[16] S.K. Gordeev, S.A. Kukushkin, A.V. Osipov, Yu.V. Pavlov. FTT **42**, *12*, 2245 (2000). (in Russian).

[17] V.B. Kumar, M. Monte, O. Mathon, S. Pascarelli, Z. Porat, A. Gedanken. J. Am. Ceram. Soc. **100**, *7*, 3305 (2017).
DOI: 10.1111/jace.14869

[18] S.A. Kukushkin, A.V. Osipov. UFN **168**, *10*, 1083 (1998). (in Russian).
DOI: https://doi.org/10.3367/UFNr.0168.199810b.1083

[19] G.V. Benemanskaya, P.A. Dementyev, S.A. Kukushkin, A.V. Osipov, S.N. Timoshnev. Pis'ma v ZhTF **45**, *5*, 17 (2019). (in Russian). DOI: 10.21883/PJTF.2019.05.47390.17621

Translated by A.Akhtyamov