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Synthesis and characterization of arrays of Si-whiskers with SiC-coated tips

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Arrays of Si-whiskers of two types (with the ordered „classical" and „triangular" structures) coated on the tips with a thin layer of cubic SiC polytype (3*C*-SiC) were obtained. The results of X-ray phase analysis, energy-dispersive spectroscopy and Raman spectroscopy indicate the formation of thin layers of the said SiC polytype on the Si-whisker tips, as well as the presence of free fullerenelike carbon. On the triangular-structure samples where a portion of incoming Si vapor is spent on growing the film by the vapor−crystal mechanism, more intense formation of silicon oxide (SiO_2) and polysilicic acids is observed, which is associated with a larger free area of the Si-substrate active surface.

Keywords: silicon carbide, whiskers, Raman spectroscopy.

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Silicon carbide (SiC) is a wide-bandgap semiconductor ($E_g \sim 2.4{-}3.2$ eV [1]) with the indirect-gap structure. It is known that there exist a large number of SiC crystal polytypes: cubic 3*C*-SiC [2,3], hexagonal 4*H*-SiC [4] and 6*H*-SiC [5]; due to their unique properties, each of them finds application in various fields, namely, in photodetectors [4], in the form of nano- and micro-crystalline powders for reinforcing light metals and alloys [6], in 3D-printing [7], in metal-oxide-semiconductor field-effect transistors (MOSFETs) [8,9] and field-emission devices [10,11].

3*C*-SiC may be used in MOSFETs operating in the voltage range of 600−1200V [8]. The 3*C*-SiC band gap (2.3 eV) is 0.9 eV narrower than that of 4*H*-SiC. Hence, in the 4*H*-SiC-based MOSFETs, the „near interface traps" which limit the charge carrier mobility in the channel are localized in the 3C-SiC conduction band and are not expected to affect the transport properties [9]. Crystallographic compatibility of 3*C*-SiC with silicon allows growing heteroepitaxial films and 3*C*-SiC structures on the Si-substrates [12–15].

However, obtaining epitaxial films and nanostructures on the Si-substrates or Si-whiskers has certain difficulties. First of all, some mismatch in the 3*C*-SiC and Si lattices ($\sim 20\%$ [1]) induces at the heterointerface a stress which is released due to formation of such crystallographic defects as stacking faults, dislocations, twins, inclusions, etc. [14,15]. In addition, the difference between the SiC and Si thermal expansion coefficients (from 8 to $\sim 23\%$ [13]) promotes arising of a high stress at the stage of cooling after SiC deposition on Si [16].

In this regard, of great interest is fabrication of thin epitaxial films and SiC nanostructures on the Si-substrates or Si-whiskers without using the SiC deposition techniques. This study was devoted just to developing a method for obtaining SiC coatings on Si-whiskers.

The study employed two types of (111) Si-substrates with Si-whisker arrays grown by the vapor−liquid−crystal method [17,18] along the $\langle 111 \rangle$ triple axis. The natural SiO_2 layer on the grown whiskers did not exceed 2 nm [19].

In the experiments, substrates with the „classical" regular arrays of Si-whiskers (Fig. 1, *a*, *c*) were used, as well as substrates with arrays of Si-whiskers in which a part of incoming Si vapor was spent on growing the film by the vapor−crystal mechanism, which resulted in formation of a regular „triangular" substrate structure with Si-whiskers (Fig. 1, *b*, *d*).

A thin layer of carbon was applied to the substrates of both types by the thermal evaporation method; after that, the samples were placed in vacuum thermal-annealing chamber „Ikar-M". Annealing was performed for 2 h at the temperature of 1100 °C in vacuum of $5 \cdot 10^{-5}$ Pa.

The annealed samples were examined by scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), X-ray diffraction analysis (XRD) and Raman spectroscopy. SEM and EDS studies were carried out using scanning electron microscope JCM 6000 Plus (Jeol, Japan) in the secondaryelectron mode with the accelerating voltage of 10 kV for SEM and 15 kV for EDS analysis. X-ray diffraction analysis was performed using powder X-ray diffractometer XṔert PRO MPD (Panalytical, Netherlands) in the Bragg-Brentano geometry using copper radiation (CuK_α, $\lambda = 0.154$ nm). The Raman spectroscopy investigation was performed using NTEGRA SPECTRA („NOVA SPB", Russia) with the laser wavelength of $\lambda = 532$ nm. The measurements were carried out along the laser beam directed perpendicular to the substrate surface.

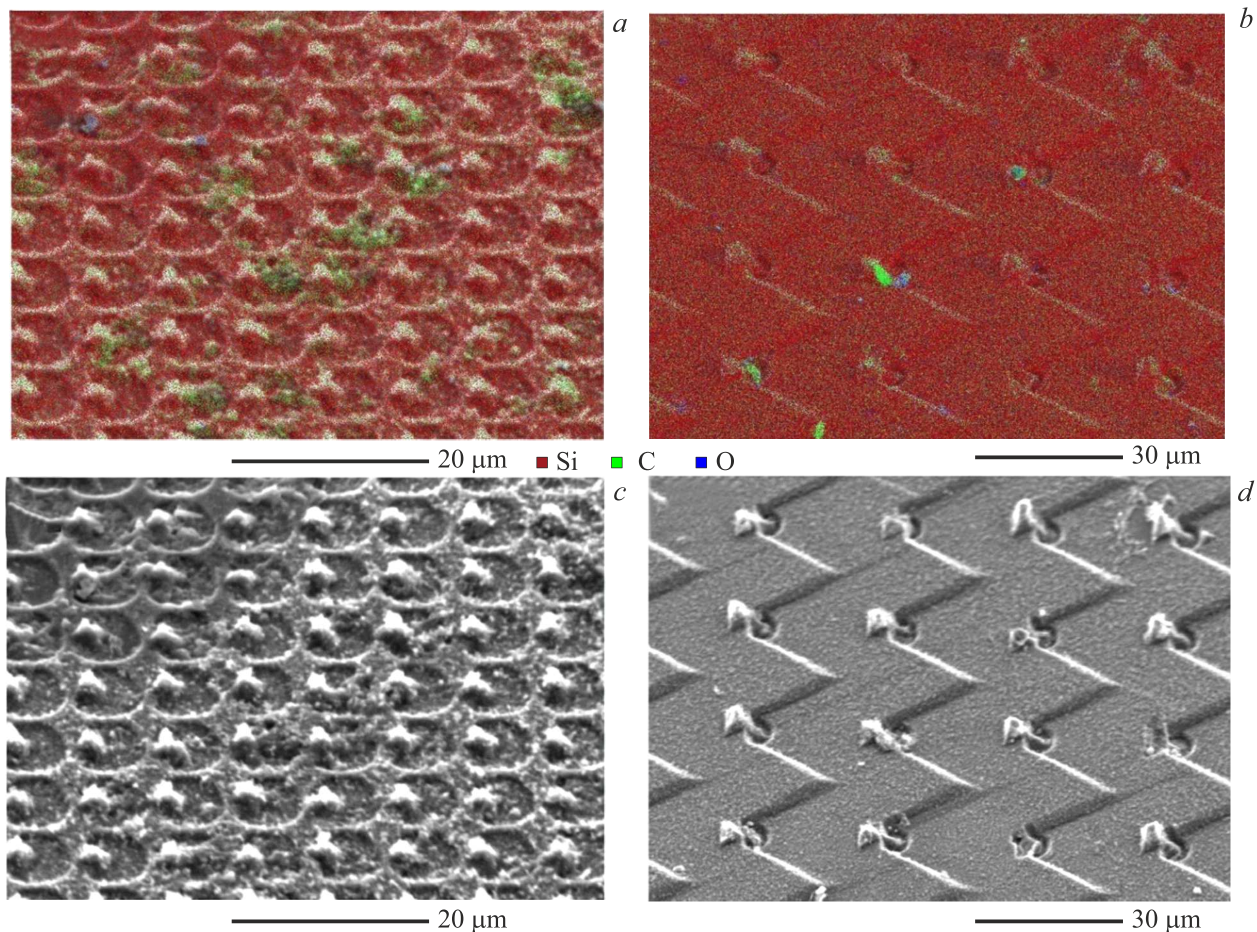

Figure 1. Arrays of Siwhiskers with tips coated with thin SiC layers: element distribution map (*a*) and SEM image (*c*) of a sample with the regular classical structure; element distribution map (*b*) and SEM image (*d*) of a sample with the regular triangular structure. The colored figure is given in the electronic version of the article.

At the end of the stages of carbon deposition and vacuum annealing, the studied samples appeared to be arrays of Si-whiskers coated on the tips with thin SiC layers. The results of constructing the element distribution map (Fig. 1) demonstrate localization of carbon aggregates on the Si-whisker tips, which evidences either creation of a thin carbon film on the Si-whiskers or formation of SiC. Therewith, no oxygen aggregates were detected on the whisker tips; however, minor aggregates of O were observed on the triangular-structure substrate surface. In addition, a relatively uniform carbon layer was observed on the Si substrate itself.

Results of the XRD analysis (Fig. 2, *a*) demonstrate the presence of both the reflections related to the β-phase of 3*C*-SiC and a reflection of the fullerene-like carbon phase C_{60}. For the triangular-structure sample, SiO_2 peaks are also observed, which is confirmed by the mapping results (Fig. 1, *b*). Possibly, this is associated with partial oxidation of the substrate surface. In addition, a peak at $2\theta \approx 36.3^\circ$ is observed, which may be related to the peak of polysilicic acid phases.

The Raman spectroscopy data (Fig. 2, *b*) confirm the SEM and XRD results. For instance, there are observed Si peaks at 304 and 522 cm^{-1}, 3*C*-SiC peaks at 774 and 944 cm^{-1} corresponding to the absorption bands of TO and LO modes of Si−C vibrations at point Γ of cubic silicon carbide polytype β-SiC (3*C*-SiC), and a peak at 980 cm^{-1}. The Raman peak at 980 cm^{-1} is associated with surface group Si−OH [20] whose total content per unit mass depends on the specific surface area of the sample. This complies with the Raman spectroscopy data where this peak is more intense in the triangular-structure sample having a larger active surface area of the Si- substrate. Low intensity of the TO absorption band peak is associated with the survey geometry relative to the Si-whiskers having SiC layers on the tips. This confirms the SiC localization on the Si-whisker tips.

In addition, peaks are observed at 1364 and 1602 cm^{-1}; they are related to the graphite microcrystal vibration mode A_{1g} and stretching vibration E_{2G} in the graphite lattice plane. The *D* peak at 1364 cm^{-1} is associated with carbon atoms at the edge of the graphene layer of polycrystalline carbon materials consisting of many small microcrystals of

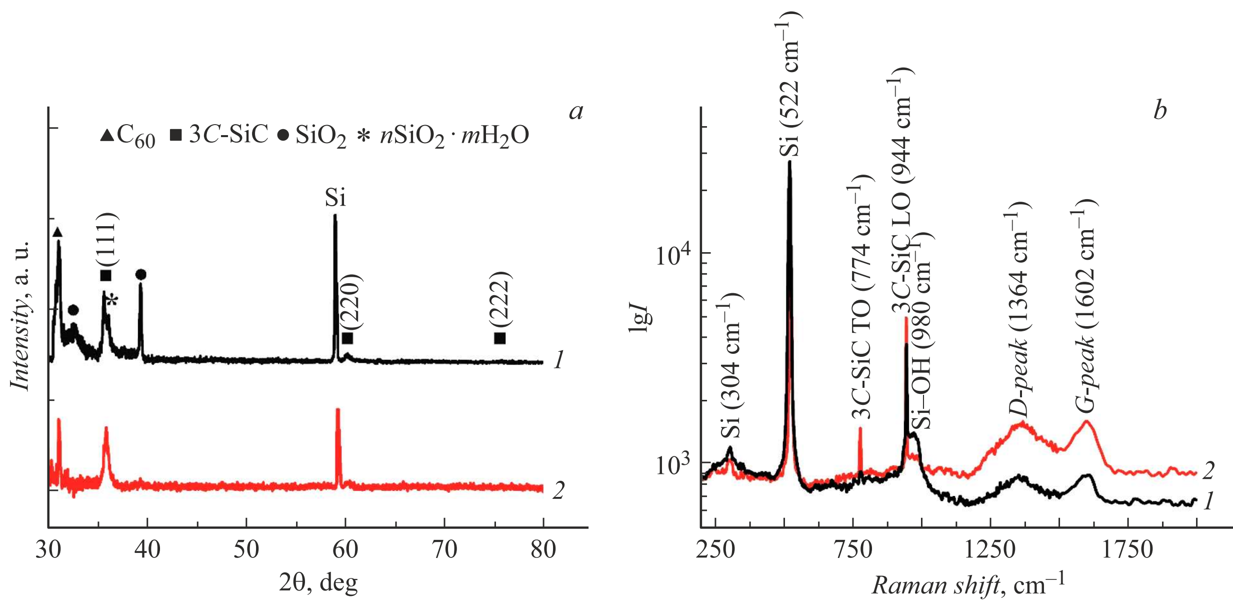

Figure 2. X-ray diffraction patterns (*a*) and Raman spectra (*b*) of the studied samples of arrays of Si-whiskers coated on the tips with SiC. *1* — sample with the triangular regular structure, *2* — sample with the classical regular structure.

graphite or amorphous diamond-like carbon. The peak at $1602\,\text{cm}^{-1}$ corresponds to graphite layers on the whisker surfaces arising during hightemperature vacuum annealing ($> 1000\,^{\circ}$C). The presence of those peaks confirms the presence of free carbon that has not reacted with the Si-whiskers, which is observed both in the mapping results (Fig. 1) and X-ray diffraction patterns (Fig. 2, *a*). The ratio of peaks D and G intensities (I_D/I_G) is a measure of the free carbon structure disorder: the higher its value, the higher the degree of free carbon disorder [21]. In our case, this ratio is higher in the classical-structure sample ($I_D/I_G = 1.05$).

Thus, there were obtained arrays of Si-whiskers of two types grown by the vapor−liquid−crystal method and coated on the tips with thin SiC layers. It is shown that the proposed method of applying a thin carbon layer with subsequent thermal annealing provides formation of thin layers of the 3*C*-SiC polytype on the Si-whisker tips. In the triangular-structure samples where a portion of incoming Si vapor is spent on growing the film by the vapor−crystal mechanism, more intense formation of silicon oxide SiO_2 and phase with the Si−OH bond is observed; this is associated with a larger free area of the Si-substrate active surface. Therewith, free carbon is present in the samples under study. In this regard, in future works we suppose to ensure completeness of the SiC layer growth reaction by optimizing such technological parameters as the applied carbon layer thickness and annealing temperature/time. The obtained results allow us to speak about applicability of this method for creating bilayer Si/SiC structures promising in view of using them as elements of MOSFETs and field emission devices.

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Conflict of interests

The authors declare that they have no conflict of interests.

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