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Features of silicon carbide synthesis by cold implantation of carbon recoil atoms

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Received April 4, 2022
Revised May 31, 2022
Accepted May 31, 2022

The Auger electron spectroscopy method confirmed a high concentration of carbon atoms (~ 85 at.%) introduced into silicon by cold implantation of recoil atoms. Carbon atoms are concentrated in a thin (~ 5 nm) near−surface region of silicon. Annealing of such a structure did not reveal a noticeable diffusion of carbon, which prevents obtaining a layer of SiC with a thickness of more than a few nm. This problem was solved by using radiation-enhanced diffusion. This made it possible to control the distribution profiles of carbon atoms in a wide range. Annealing at 1150°C allowed obtaining layers of amorphous−crystalline SiC with a thickness of 50−150 nm. Higher annealing temperatures are required to obtain a single−crystal SiC film.

Keywords: cold implantation, radiation−enhanced diffusion, silicon carbide, recoil atom, thin films.

DOI: 10.21883/TPL.2022.07.54042.19212

Paper [1] has proposed a new method for synthesizing silicon carbide 3*C*-SiC, namely, cold implantation of carbon recoil atoms. Development of this method would create a clean, fast and low−cost technique for synthesizing 3*C*-SiC films on silicon substrates. This method allows obtaining high carbon atom concentrations in a thin near−surface layer of silicon (~ 10 nm). However, further investigations showed that annealing of such a structure at 1150°C changes the initial profile of carbon atoms only slightly, which means that thermal diffusion of carbon atoms in silicon is almost absolutely absent. This fact prevents obtaining a synthesized SiC layer thicker than a few nanometers. The absence of considerable carbon diffusion is possibly caused by formation of Si−C bonds even at an early stage of annealing at temperatures below 1150°C. This can result in a drastic decrease in the diffusion rate since the carbon diffusion coefficient in SiC is four orders of magnitude lower than in silicon [2]. To increase thickness of the synthesized SiC layer, we tried to raise the carbon atom diffusion rate by using such a phenomenon as radiation−enhanced diffusion (RED). RED is a flexible technique allowing a wide−range control of shape and depth of the implanted impurity distribution [3].

Cold implantation of the carbon recoil atoms was performed into the substrates made from *n*-Si (111) ($7.5\,\Omega \cdot$ cm). The samples were mounted in the ion implanter vacuum chamber on a holder able to be cooled with liquid nitrogen. To study the RED effect on the profile of carbon atoms, radiation defects (RD) were introduced into silicon. This was done by room−temperature implantation of Ar^+ ions (ion energy of 40 keV, fluence of $2 \cdot 10^{15}\,\mathrm{cm}^{-2}$). The maximum of the RD profile was at the depth of ~ 74 nm. After RD creation, the samples were cooled to the temperature of ~ 100 K; after that, acetylene (C_2H_2) was briefly let in so as to create on the silicon surface a solid−phase acetylene film. Then the samples were irradiated with Ar^+ ions with the energy of 40 keV and fluence of $5 \cdot 10^{14}\,\mathrm{cm}^{-2}$ to ensure implantation of recoil carbon atoms from the acetylene film. Parameters of the cold implantation were the same as in [1]. Upon the implantation, samples were isothermally annealed in vacuum ($P \sim 10^{-4}$ Pa) at 1150°C for 30 min and 3 h. The samples were characterized by such methods as secondary ion mass−spectrometry (SIMS), Auger−electron spectroscopy (AES), X−ray diffraction analysis, infrared (IR) spectroscopy and atomic force microscopy (AFM).

High concentration of carbon recoil atoms in the silicon near−surface region we have obtained in [1] was confirmed by AES. The AES results are presented in Fig. 1, *a*. The shape of the carbon atom AES profile agrees well with the SIMS data. Carbon atom concentration at the depth of ~ 3 nm is ~ 85 at.%. Fig. 1, *b* presents SIMS profiles of carbon atoms in arbitrary units after annealing in different modes. Profile *1* corresponds to the initial distribution of carbon recoil atoms after implantation. The absolute concentration value at the distribution maximum is $3 \cdot 10^{22}\,\mathrm{cm}^{-3}$ [1]. Profile *2* describes the carbon atom distribution after annealing the sample at 1150°C for 30 min. This profile differs from profile *1* only slightly. SIMS profiles *3* and *4* relate to samples with RD after annealing for 30 min and 3 h, respectively. One can see that RED has significantly decreased the concentration of carbon atoms and made uniform their distribution in layers ~ 50 nm thick (profile *3*) and 150 nm thick (profile *4*).

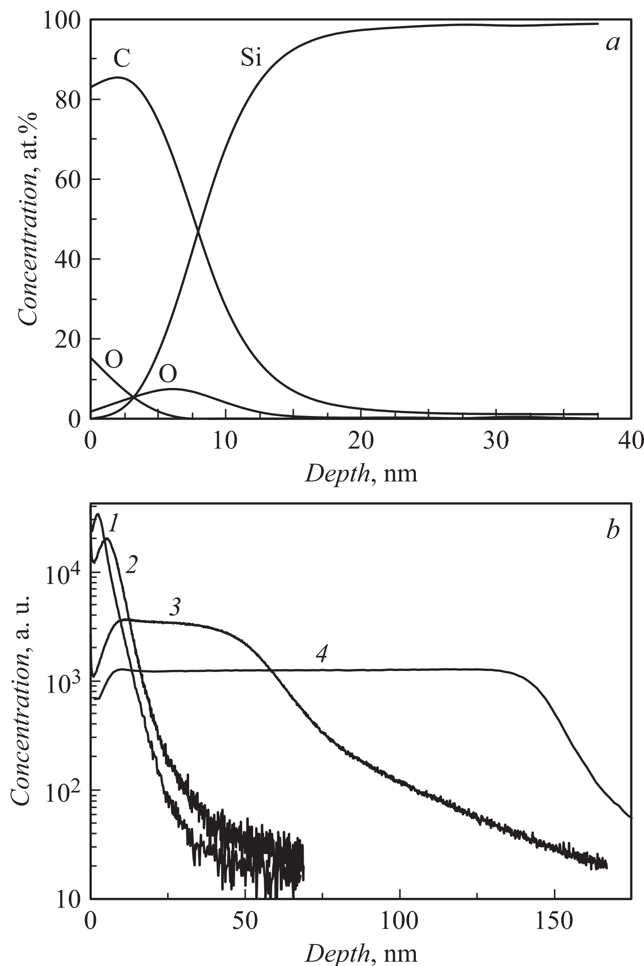

Figure 1. AES profiles (a) and SIMS profiles of carbon atoms in Si (b). *1* — after implantation, *2* — annealing for 30 min, *3* — annealing for 30 min with RD, *4* — annealing for 3 h with RD.

The effect of RED–induced „extension" of the carbon atom profile on the efficiency of the Si–C bonds formation manifests itself in the IR absorption spectra for three annealing modes (Fig. 2, a). Spectrum *1* corresponds to annealing for 30 min, while spectra *2* and *3* correspond to the cases when RD are introduced into the samples with subsequent annealing for 30 min and 3 h, respectively. It is clearly seen that the 30–min annealing leads to appearance of the absorption peak at $\sim 800\,\text{cm}^{-1}$ which is typical of tetrahedral Si–C bonds in crystalline SiC (spectrum *1*). Radiation–enhanced diffusion provides a sharp increase in amplitude and area of the $800\,\text{cm}^{-1}$ peak. The 800–cm^{-1} peak area is known to be proportional to the number of various optically active Si–C bonds [4]. The ratio of areas shows that RED increases the number of Si–C bonds by 3.6 times for spectrum *2* and by about 10 times for spectrum *3*. The ratio between the amorphous and crystalline phases in the synthesized SiC layer may be derived from the mathematical decomposition of spectrum *3* (Fig. 2, b). A narrow peak at $799.3\,\text{cm}^{-1}$ corresponds to tetrahedral bonds in the SiC crystalline phase, while the remaining components correspond to different types of Si–C bonds in the amorphous phase [4]. In the case of spectrum *3*, the crystalline phase fraction is 17%. That for spectrum *2* is 32%, which is evidently associated with a higher carbon atom concentration taking place in this case.

The crystal structure of the SiC film was studied by X–ray diffraction. There were revealed two reflection diffraction peaks characteristic of crystallographic planes SiC(111) and SiC(222) of cubic silicon carbide 3C-SiC. Estimation of the coherent scattering area gave the 3C-SiC crystallite size of ~ 7.5 nm.

Figs. 3, a, b present AFM images of the surface of the sample with RD (annealing for 3 h) in the scanning area of $1 \times 1\,\mu$m. There is observed a high density of grains shaped as trihedral pyramids and uniformly distributed over the entire plane. The grainsćrystallographic orientation coincides with the (111) orientation of the silicon substrate. The mean–square roughness measured at different points of the substrate is ~ 10 nm.

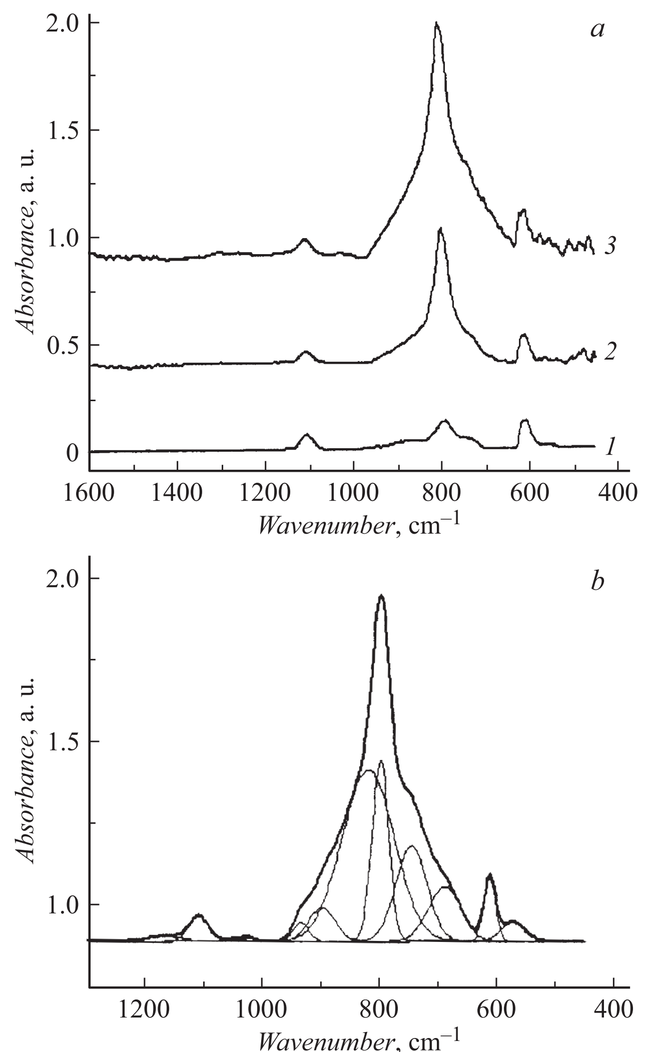

Figure 2. a — IR absorption spectra: *1* — annealing for 30 min, *2* — annealing for 30 min with RD, *3* — annealing for 3 h with RD; b — mathematical decomposition of the spectrum *3*.

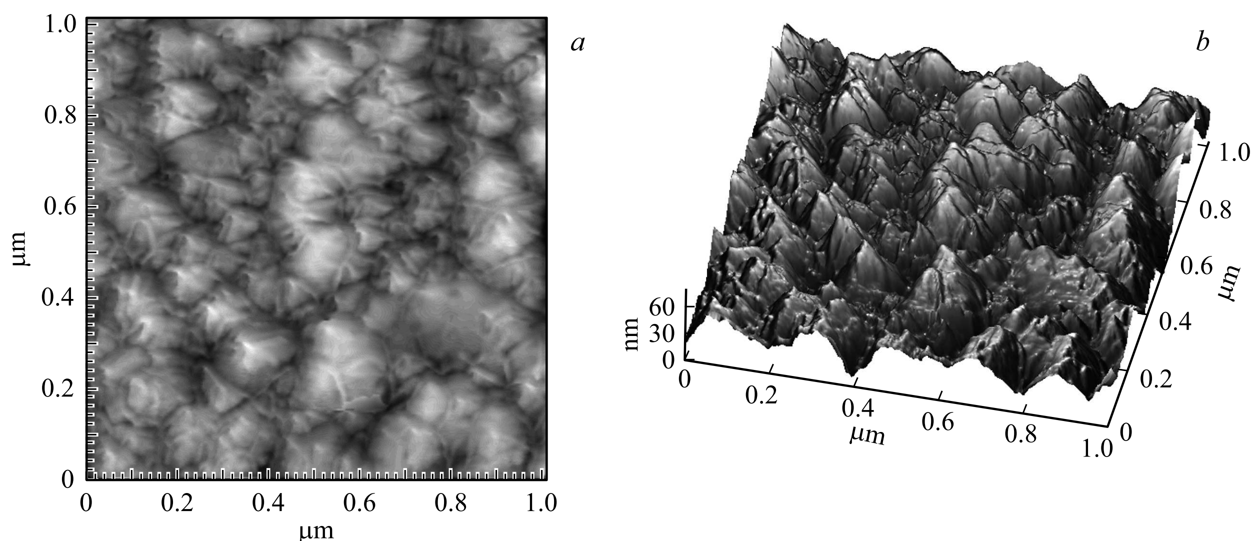

Figure 3. *a* — in−plane AFM image of the sample surface; *b* — 3D AFM image of the same area.

Thus, the studies accomplished allowed establishment of the main features of the method of cold implantation of recoil carbon atoms which should be taken into account in synthesizing SiC films by this method. The method enables obtaining high concentrations of carbon atoms (85 at.%) in the thin (~ 5 nm) near−surface region of silicon. No considerable thermal diffusion is observed during annealing of such structures. Using RED, it became possible to efficiently control the profile shape and depth distribution of carbon atoms. RED also essentially increases the number of Si−C bonds. Annealing of RD−containing structures at 1150°C resulted in formation of an amorphous−crystalline SiC layer with the thickness of several tens nanometers and crystallite size of 3*C*-SiC ~ 7.5 nm. To improve the crystallinity, annealing temperature should be higher than 1150°C.

Acknowledgements

The authors are grateful to S.P. Kirilenko for performing the AES analysis.

Financial support

The study was performed under the ITPM RAS State Assignment № 075-007706-22-00.

Conflict of interests

The authors declare that they have no conflict of interests.

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