Physics of the Solid State, 2023, Vol. 65, No. 1

03,11

Change of the elastic strain in SiC films growing on Si substrates by the method of consistent atomic substitution

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Received September 23, 2022
Revised September 23, 2022
Accepted September 24, 2022

Sequential stages of synthesis of SiC epitaxial films on *n*- and *p*-type Si(111) substrates in a mixture of carbon monoxide and silane are studied by X-ray diffraction (XRD) and Raman scattering methods. It was found that the elastic strain in SiC films grown on *n*-type Si(111) is absent in contrast to SiC films grown on *p*-type Si(111), where the deformations are formed and completely relaxed by the 40 min of synthesis. A dramatic change in the SiC film structure is observed on the third minute of the growth, which is associated with the formation and growth of pores in the SiC layer. Differences in the lattice constants of SiC films grown on *p*- and *n*-type Si substrates are determined and verified via analysis of the change in the curvature of SiC/Si wafers.

Keywords: Silicon carbide on silicon, elastic strain, nanostructures, microstructure evolution.

DOI: 10.21883/PSS.2023.01.54976.480

1. Introduction

In the work [1], the evolution of the crystal structure and surface morphology of SiC films synthesized on the Si surface by the method of coordinated substitution of atoms was investigated by the X-ray diffraction (XRD) and the method of total external reflection of X-rays (TERXR). A detailed description of the method of coordinated substitution of atoms can be found in the reviews of [2,3]. The essence of the method is that the substitution of Si atoms in silicon for C atoms is carried out using the reaction (1):

$$2\mathrm{Si}(crystal) + \mathrm{CO}(gas) = \mathrm{SiC}(crystal) + \mathrm{SiO}\uparrow(gas). \tag{1}$$

This reaction, as shown in [2,3], proceeds in two stages. At the first stage, an ordered ensemble of elastically interacting carbon-vacancy defects is formed, called dilation dipoles in [2]. Dilation dipoles are oriented along the direction $\langle 111\rangle$ Si. At the first stage, an intermediate state is formed in silicon (an analogue of the activated complex in chemical reactions) „silicon vacancy–carbon atom–silicon matrix“ ($\mathrm{C}-V_{\mathrm{Si}}$). Carbon atoms at this stage are located in the interstitial positions of the silicon matrix. It can be said that a metastable superlattice is formed near the silicon surface. In a cubic symmetry crystal, these two dilation centers (a carbon atom and a silicon vacancy) elastically interact with each other. If dilation dipoles are located perpendicular to the plane (111) of silicon, then they are attracted to each other [2,3]. At the same time, almost all the dilated elastic energy that arose due to the introduction of a carbon atom and the formation of a vacancy relaxes [2,3]. We note that it is the elastic interaction between pairs of point dilation defects C and V_{Si} that determines the kinetics of the reaction (1). At the second stage of the reaction, carbon atoms are displaced into silicon vacancies. As a result, the sublattice formed by dilation dipoles and part of the silicon lattice pass into silicon carbide, and the vacant vacancies merge into pores formed under the silicon carbide layer. The transition of carbon atoms to the place of silicon vacancies is carried out due to the coordinated offset of atoms, i.e. the breaking of old bonds between atoms and the formation of new bonds occur simultaneously and in concert. This, in fact, ensures the high crystalline perfection of the silicon carbide film.

The transformation of the intermediate structure into SiC is accompanied by the formation of voids, since the volume of the Si cell is two times larger than the volume of the SiC cell. The length of all links is reduced by 20%, namely from 2.35 to 1.88 nm. The offset proceeds in layers, i.e. several layers of precarbide silicon are simultaneously transformed into SiC with the film shifting perpendicular to the substrate surface. As a result, the SiC film is formed sufficiently uniform in thickness and without noticeable voids. All voids end up in silicon under the film SiC [2,3]. It is interesting to note that the distance between the atoms C lying along the plane (111), projected onto the plane $(11\bar{2})$, in SiC is 3.08 Å. Thus, the distance between the planes of five cells in SiC $\sim$ 15.4 Å up to the first decimal place coincides with the distance between the planes of four cells SiC $\sim$ 15.4 Å. This means that when an intermediate substance is converted into silicon carbide, not all bonds are broken, but only those that do not match the bonds in Si [2]. At the same time, an empty space is formed under the place where the bonds were broken, namely under the Si layer. It is for this reason that elastic deformations in the SiC [2,3] layer are almost completely absent. However, since the process of transformation of Si into SiC takes place over time, deformations may occur at different stages of transformation and the morphology of the SiC surface may change. In addition, as shown in [2], since the upper layer of the Si substrate plane undergoes shrinkage when converted to SiC, shrinkage pores may form on the surface. The latter affect the distribution of elastic deformations in the SiC film during growth. For „healing" shrinkage pores in [2], it was proposed to add silane (SiH) to the reaction zone to the CO gas$_4$). In addition, the morphology and stresses in SiC are influenced by temperature, reactor pressure, conductivity and orientation of the Si [4] substrate.

In the work [1], the problem of detecting the evolution of elastic deformations occurring in the SiC film during growth in the absence of SiH_4 was solved, i.e. the growth of films was carried out only in the CO atmosphere. As a result, the XRD and TERXR methods revealed that at 10 min of SiC growth, the sign of deformations changes from tensile to compressive, as well as a number of other growth features.

The purpose of this work — to continue the research started in [1] and to follow the evolution of elastic deformations in the SiC film grown by the method of substitution of atoms in a mixture of gases CO and SiH_4.

2. Sample preparation method and elastic deformation measurement methods

SiC samples were grown on the surface of the face (111) Si *p*- and *n*- of the conductivity type at the following synthesis times: 1, 3, 5, 20 and 40 min. The synthesis temperature of all samples is 1270°C. The pressure of the gas mixture CO and SiH_4, during the growth process, was maintained at the level of $P_{\mathrm{CO+SiH_4}} = 360\,\mathrm{Pa}$. The CO stream was equal to $Q(\mathrm{CO}) = 12\,\mathrm{cm^3/min}$, and the stream is SiH_4 — $Q(\mathrm{SiH_4}) = 4\,\mathrm{cm^3/min}$. Before the growth of SiC, Si plates underwent special treatment in order to remove silicon oxide and passivation with hydrogen according to the method [5].

The following techniques and instruments were used to study elastic deformations: X-ray diffractograms were taken using a Bruker Advance D8 X-ray diffractometer; Raman spectra — using a confocal Raman microscope Witec Alpha 300R; the analysis of changes in the curvature of the plates was carried out using an elastic stress meter Toho FLX-2320.

Parameters of reflexes (111) 3C-SiC(111) on XRD spectra

Time	SiC(111)/*n*-Si(111)		SiC(111)/*p*-Si(111)	
	2θ, deg	FWHM, arcmin	2θ, deg	FWHM, arcmin
1 min	35.857	16.10	35.893	15.96
3 min	35.891	18.88	35.903	18.98
5 min	35.869	19.65	35.863	19.01
40 min	35.854	16.19	35.857	15.5

3. Experimental results and analysis of elastic deformations

As follows from the XRD data (Figs. 1 and 2), the reflex (111) from the SiC layer, which was synthesized during 1 min, is the most intense and has a small broadening, and the reflex (220) is practically absent. This is observed for a SiC film grown both on a *p*-Si type substrate and on a *n*-Si type substrate. However, this reflex is shifted to the right for SiC films grown on a *p*-Si type substrate, compared to SiC films grown on a *n*-Si type substrate (see table). The table value of the reflex (111) for SiC corresponds to the value $2\theta = 35.641$. Comparing the tabular value of the angle 2θ with the data 2θ from the table, it can be shown that in the case of a film SiC/*p*-Si(111) synthesized during 1 min, elastic deformations in this structure have the order $\varepsilon_{111} \sim -0.6\%$, and a similar value for the film SiC/*n*-Si(111) — $\varepsilon_{111} \sim -0.5\%$. Thus, both in the SiC/*p*-Si(111) film and in the SiC/*n*-Si(111) film, compressive stresses are formed at the beginning of the process. However, the SiC/*p*-Si(111) film is elastically more stressed than the SiC/*n*-Si(111) film, which confirms the conclusions made earlier in [4]. The analysis showed that the broadening and elastic deformations increase by 20% at stage 3−5 min of synthesis and decrease to 40 min. The SiC films grown during 1 min and 40 min had the most perfect crystal structure. It should be noted that without the addition of SiH_4 to the reaction zone, the SiC film in the first 10 min of growth is stretched [1], and not compressed, as in this case. At the same time, the residual elastic deformation is less in SiC/*n*-Si structures.

In Fig. 3, *a* and *b*, Raman scattering spectra of light from SiC/*p*-Si(111) and SiC/*n*-Si(111) structures synthesized during 40 min. The spectra show that the SiC film is a cubic polytype 3C-SiC. The difference between the spectra for the part of the SiC film „hanging" over the shrinkage pore and the part of the film in contact with the solid surface of Si was found. In the pore region, the intensity of Si peaks decreases, and SiC peaks increases, which is explained by multiple internal reflections in the [6] pore. The position of the SiC peak ($796.5\,\mathrm{cm^{-1}}$) also differs for the pore area and the film's contact with the substrate.

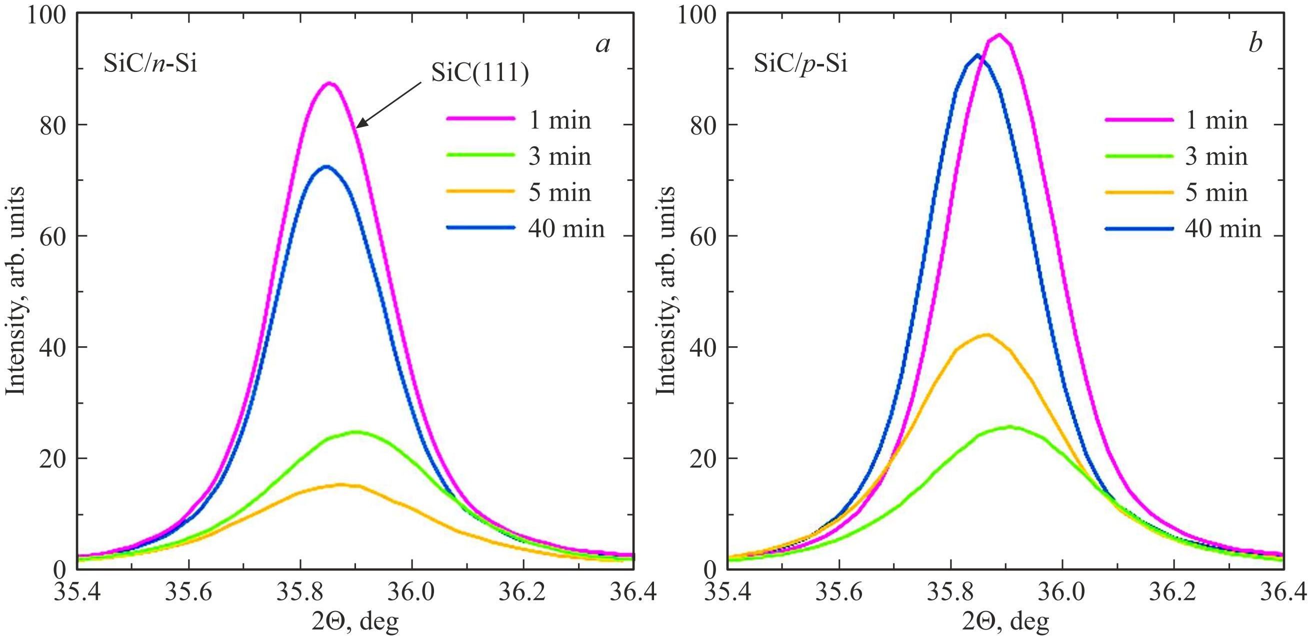

Figure 1. SiC(111)peaks on XRD spectra of substrates *a* — SiC/*n*-Si, *b* —SiC/*p*-Si.

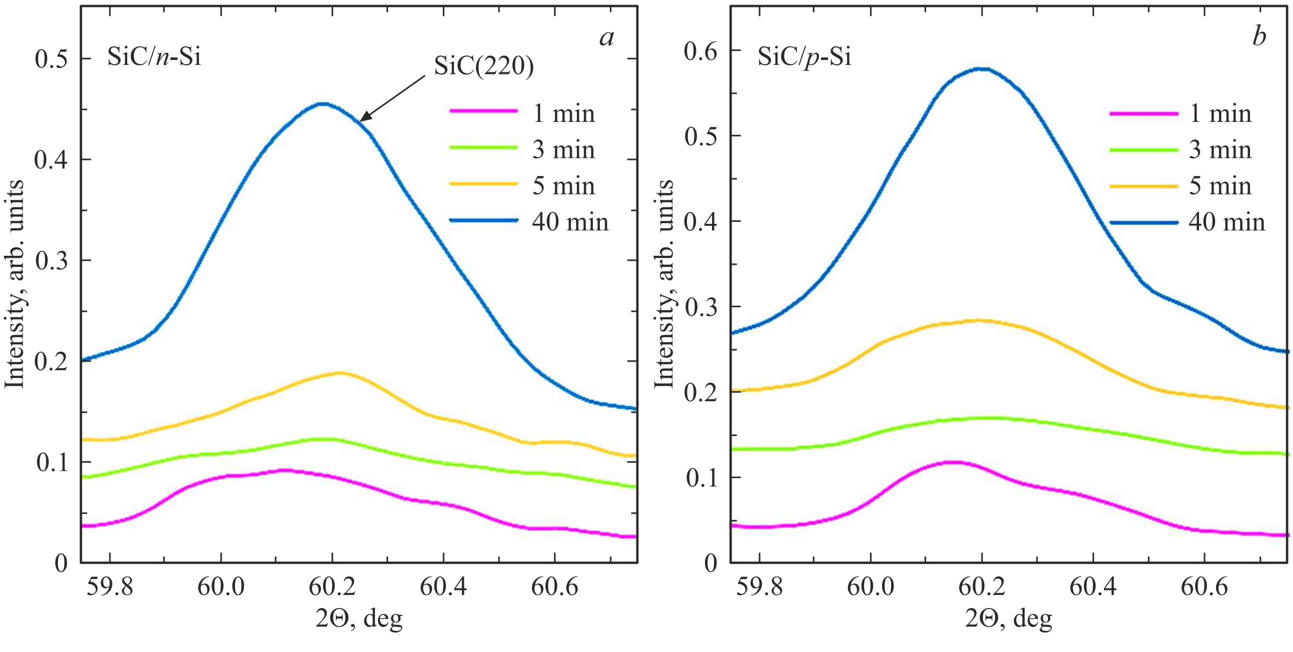

Figure 2. SiC(220)peaks on XRD spectra of substrates *a* — SiC/*n*-Si, *b* —SiC/*p*-Si.

The analysis of elastic deformations in the SiC film, carried out in accordance with the model [7], showed that the SiC/*p*-Si film is stretched in the pore region by 0.1%. From the Raman spectra, it was also found that the effective deformation in SiC/*n*-Si structures is 30% less than in SiC/*p*-Si.

The difference in elastic deformations of the SiC film on *n*- and *p*-substrates of the conductivity type also leads to a difference in the radii of curvature of the SiC/Si plates. The three-dimensional profile of the SiC/*p*-Si plate before and after growth is shown in Fig. 4. The hybrid structure of SiC/*p*-Si is concave relative to the original Si substrate, while the change in the radius of curvature is ~ 100 meters. The value of elastic deformation according to the Stony formula is -0.1% [8], which corresponds to the relative difference of the SiC constant lattices on *p*- and *n*-substrates of the type we obtained from XRD measurements. There is no change in the curvature of the plates SiC/*n*-Si(111) during

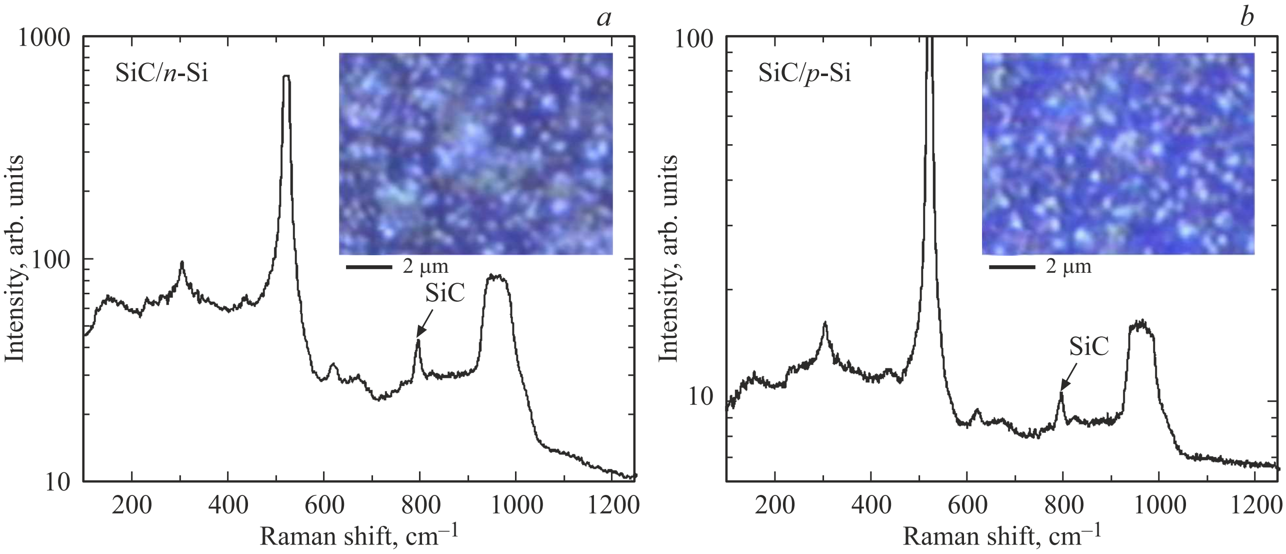

Figure 3. The Raman spectra of structures in the pore region after 40 min growth and micrographs of samples *a* — SiC/*p*-Si(111) and *b* — SiC/*n*-Si(111). Light spots correspond to the pores.

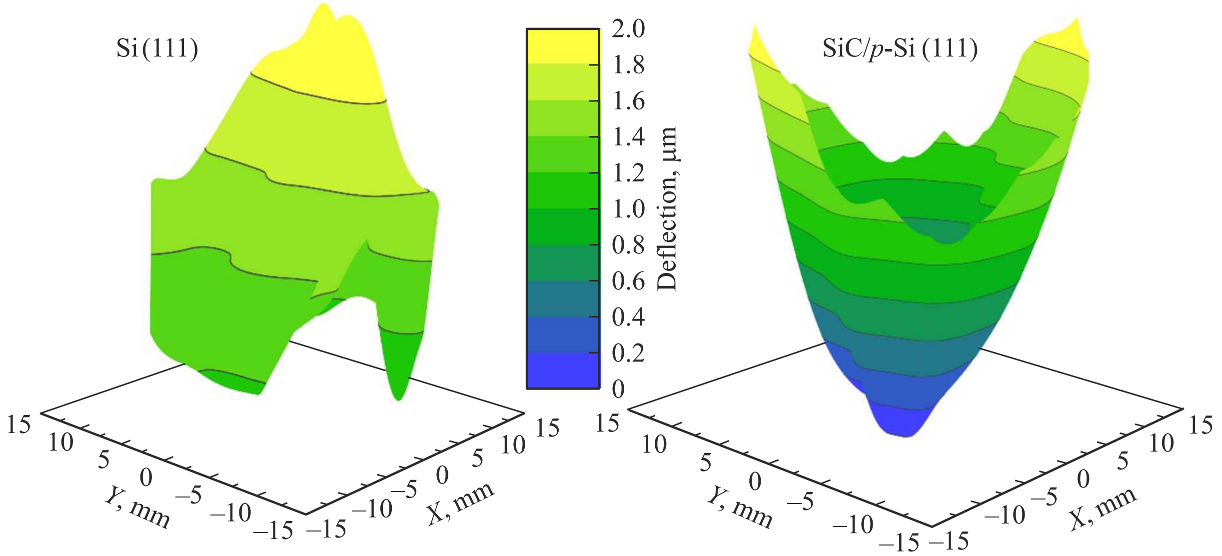

Figure 4. 3D profile of the substrate *p*-Si(111) and the concave plate SiC/*p*-Si(111) after 20 min of growth.

the growth process. Thus, the conclusion about smaller residual deformations in SiC/*n*-Si(111) structures relative to SiC/*p*-Si(111) is confirmed.

Conclusion

It was found that during the synthesis of SiC films on Si(111) by the method of coordinated substitution of atoms in a mixture of gases CO and SiH_4, the formation of a SiC film begins at 1 min of synthesis and ends by 40 min. It is shown that the elastic deformations formed in the films increase at the beginning of synthesis, and then, by 40 min of synthesis, they completely relax. The process of deformation development in SiC layers proceeds in different ways on substrates of Si*n*- and *p*-types of conductivity. The deformations of SiC/*n*-Si films turned out to be less than SiC/*p*-Si. This result was confirmed by analyzing the curvature of the SiC/Si plates. The method of Raman scattering of light showed the heterogeneity of the distribution of elastic stresses of the film over the pore and the film lying on the solid surface of the substrate.

Acknowledgments

The research was carried out 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).

Funding

Yu.A. Eremeev, S.A. Kukushkin, M.G. Vorobyev and A.V. Osipov performed their part of the work in the scope of the State assignment of FSUE IPMash RAS No. FFNF-2021-0001 of the Ministry of Science and Higher Education of the Russian Federation. A.S. Grashchenko performed his part of the work with the support of the Ministry of Science and Higher Education of the Russian Federation in the scope of the State assignment under the contract of St. Petersburg State University No. 75746688. A.V. Semencha performed his part of the work in the scope of the State assignment for conducting fundamental research 0784-2020-0022.

Conflict of interest

The authors declare that they have no conflict of interest.

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