

Investigation of Mesoporous Silicon Carbonization Process

N. I. Kargin, G. K. Safaraliev, A. S. Gusev, A. O. Sultanov, N. V. Siglovaya, S. M. Ryndya, A. A. Timofeev

Abstract—In this paper, an experimental and theoretical study of the processes of mesoporous silicon carbonization during the formation of buffer layers for the subsequent epitaxy of 3C-SiC films and related wide-band-gap semiconductors is performed. Experimental samples were obtained by the method of chemical vapor deposition and investigated by scanning electron microscopy. Analytic expressions were obtained for the effective diffusion factor and carbon atoms diffusion length in a porous system. The proposed model takes into account the processes of Knudsen diffusion, coagulation and overgrowing of pores during the formation of a silicon carbide layer.

Keywords—Silicon carbide, porous silicon, carbonization, electrochemical etching, diffusion.

I. INTRODUCTION

THE silicon carbide (SiC) detains a particular place among wide-bandgap semiconductor materials used in electronic devices. For a number of factors, one of the major ways to realize the potential of SiC is the use of SiC/Si templates as a substrate material in the group-III nitrides technology [1]-[4].

The epitaxy of SiC layers of high crystallinity on silicon substrates is limited by a high level of mismatch in the lattice parameters ($\sim 19.72\%$) and temperature expansion coefficients ($\sim 8\%$), which predetermines the occurrence of high dislocation density ($10^5 - 10^6 \text{ cm}^{-2}$).

Different buffer layers can be used in order to reduce the defect density during the epitaxial growth of SiC on silicon. Contradictory requirements are imposed on such buffer layers. On the one hand, the buffer layer must have high crystalline quality, since the structure of the growing film is largely determined by the state of the surface of the substrate material, on the other hand, it must be sufficiently ductile to effectively relax the elastic stresses arising at the heterointerface [5].

The possibility of release of elastic stresses caused by the lattice parameters and the thermal expansion coefficients mismatches allows to consider porous silicon as an extremely attractive material for the formation of a buffer layer in the case of SiC on Si heteroepitaxy [1]. In that context, the study of the porous silicon carbonization process as the initial stage of the 3C-SiC growth from the gas phase is a relevant scientific and technical task. Therefore, the main purpose of

this paper is an analytic description of the carbonization process, taking into account our experimental and literary data. The overwhelming majority of works devoted to the carbonization of porous silicon are related to computer modeling, based on the separation of the growth process into the simplest single acts of atomic processes: surface diffusion, adsorption and desorption [6], [7]. At the same time, studies of the kinetics of diffusion processes during the carbonization of porous silicon have not been practically carried out.

II. EXPERIMENTAL

In progress of the work, the porous silicon layers of $2 \mu\text{m}$ thickness were obtained by electrochemical etching of three-inch Si (100) wafers in the system of $\text{HF}:\text{H}_2\text{O}:\text{CH}_3\text{CH}(\text{OH})\text{CH}_3$. Silicon plates were placed in an electrochemical cell on a ceramic table (anode) covered with a copper grid. The cathode was made in the form of a spiral of plumb wire. A galvanostatic anodizing regime was used to form a porous layer, in which the anode current density through the sample was maintained constant in time. In the previous work [8], we describe the structure of the porous layers and the kinetics of their formation.

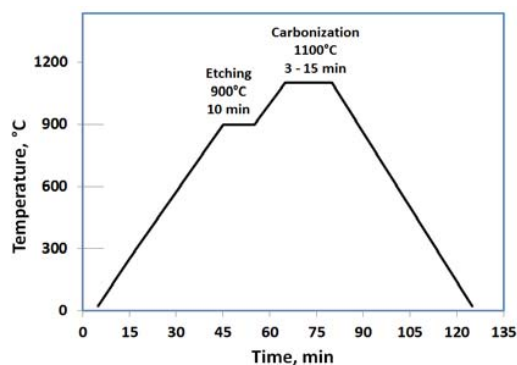


Fig. 1 Diagram of SiC/Si and SiC/por-Si structures formation process

The carbonization of the experimental samples was carried out in a shower type CVD reactor with cold walls in the $\text{H}_2 - \text{C}_2\text{H}_4$ gas system. The process consisted of two stages (Fig. 1). In the first stage, the substrate was heated in a hydrogen atmosphere. Temperature rise rate: $30-40 \text{ }^\circ\text{C/min}$. Then, ethylene (15 sccm) was added to the growth chamber at the stage of carbonization. Carbonization of the silicon surfaces was carried out at a substrate temperature of $1100 \text{ }^\circ\text{C}$ and at a process pressure of 5 torr. In this way, two series of experimental samples (on bulk and porous silicon) was obtained with the variation of the carbonization time

Nikolai I. Kargin is with the National Research Nuclear University MEPhI, Moscow, Russian Federation, (corresponding author, phone: 495 788-56 99; e-mail: NIKargin@mephi.ru).

Gadzhimet K. Safaraliev, Alexander S. Gusev, Azret O. Sultanov, Natalia V. Siglovaya, Sergey M. Ryndya, and Alexey A. Timofeev are with the National Research Nuclear University «MEPhI», Moscow, Russian Federation, (e-mail: safaraliev@duma.gov.ru, ASGusev@mephi.ru, karabi86@mail.ru, nat.ncstu@rambler.ru, ryndya_sm@mail.ru, alexmail21@mail.ru).

parameter (from 3 to 15 minutes).

LYRA 3 (TESCAN) high-resolution scanning electron microscope (SEM) with a Schottky cathode was used to study the topography of the experimental samples. Values of the pores mean radii and thicknesses of carbonized layers were determined from the analysis of SEM images.

III. DISCUSSION

A layer of porous silicon is a single-crystal framework in which a pore system is formed as a result of electrochemical treatment (Figs. 2 (a) and (b)). Such pores when using silicon with a (100) crystal orientation can be reduced to an array of cylindrical channels directed perpendicular to the surface of the wafer (Figs. 2 (c) and (d)). In other words, porous silicon can be represented as extended volume elements oriented parallel to the direction of the gas flow [9], [10]. In this case an effective diffusion coefficient can be represented as:

$$A \cdot D_{\text{eff}} = \sum A_i \cdot D_i \quad (1)$$

where A is the surface area of the material, A_i is the cross-sectional area of the i -th volume element, D_i - the diffusion factor in the i -th element of the volume. Thus, the diffusion of carbon in porous silicon can proceed both through the pores and through the “solid” material. The effective diffusion factor in this case is described by:

$$D_{\text{eff}} = a D_{\text{por}} + (1-a) \cdot D_c \quad (2)$$

where a is the area ratio of the open pores on the planar surface of the sample; D_{por} - the diffusion factor in the pores, $D_c = (2.9 \pm 0.5) \times 10^{-18} \text{ m}^2/\text{s}$ - the diffusion factor of carbon atoms in SiC. Analysis of the experimental data (Fig. 3) leads to a linear time dependence of the a parameter:

$$a = a_0 - \alpha t \quad (3)$$

where $a_0 = 0.045$ is the area ratio of the open pores on the surface at $t = 0$, $\alpha = 0.0000427 \text{ s}^{-1}$.

The criterion determining the mechanism of diffusion in the pores is the Knudsen number:

$$K_n = \frac{\lambda}{d} \quad (4)$$

where λ is the mean free path of the molecule, m; d is the pore diameter, m.

In the case under consideration $d \approx 13 \text{ nm}$ and $K_n \approx 2.15 \times 10^5 \gg 1$. Therefore the diffusion in the pores occurs according to the Knudsen mechanism [11], [12]:

$$D_{\text{Kn}} = \frac{2}{3} \overline{r_p} \sqrt{\frac{8RT}{\pi M}} = \overline{V} \overline{r_p}(t) \quad (5)$$

where D_{Kn} is the Knudsen diffusion factor; $\overline{r_p}$ - arithmetic mean radius of pores; R - universal gas constant; T -

temperature of the process (K); M - molar mass of the substance. The parameter V (nm/s) is the average speed of carbon atoms in the cylindrical pores.

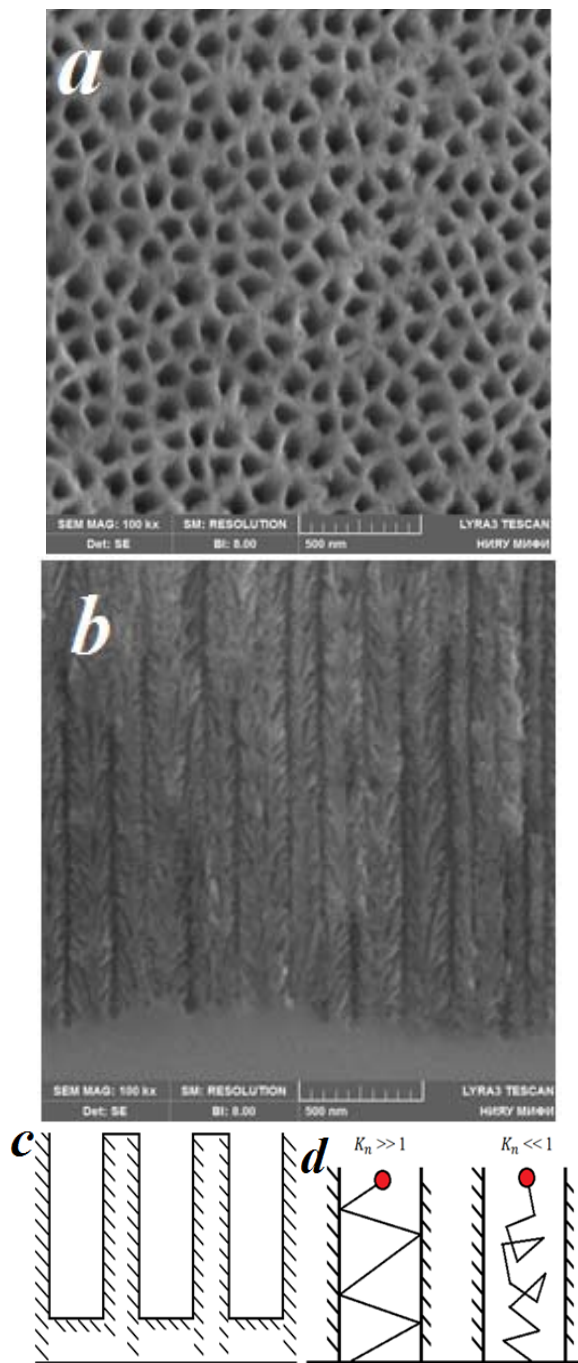


Fig. 2 (a) SEM image of surface of a por-Si layer. (b) SEM image of the cross-section of a por-Si layer. (c) Schematic representation of the porous structure with an ideal cylindrical pore shape. (d) Mechanisms of diffusion in micropores: molecular diffusion mechanism ($K_n \ll 1$); Knudsen diffusion ($K_n \gg 1$)

Under the Knudsen diffusion the carbon atoms reaching the

pore walls are adsorbed on them for a while and after desorption move in an arbitrary direction. The delay time on the walls of the pores reduces the diffusion flux density.

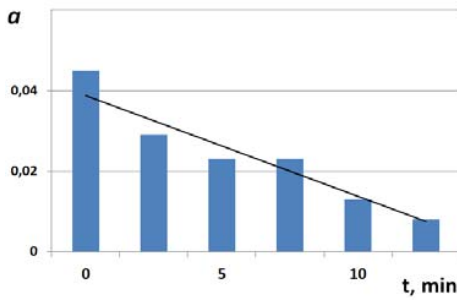


Fig. 3 Time dependence of the area ratio of the open pores a

Equation (5) describes the diffusion through the smooth-faced pores with cylindrical shaped walls. It is necessary to consider that the transport of particles in the pores is complicated by the tortuosity of the channels, their mutual crossing and bifurcation, the variable cross-section. An empirical permeability coefficient Π is introduced for considering the complex pore morphology.

$$D_{por} = \Pi D_{Kn} \quad (6)$$

In addition, in the process of carbonization, porous system is simultaneously affected by factors such as coagulation and pore overgrowth [13]. The experimental time-dependence of the arithmetic mean radius of the pores can be fitted by an expression of the following form:

$$\bar{r}_p(t) = -\omega t^2 + \nu t + r_0, \quad (7)$$

where $\omega = 0,00029855 \text{ nm}^2/\text{s}^2$ (the factor of pores overgrowth) and $\nu = 0.31 \text{ nm/s}$ (the factor of coagulation). The parameter $r_0 = 6.5 \text{ nm}$ is the arithmetic mean pore radius at $t = 0$.

Taking into account (3)-(7), the effective diffusion factor is:

$$D_{eff} = D_{eff0} + [a_0 R_{II} \nu - a (R_{II} r_0 - D_c)] t - R_{II} (a_0 \omega + \alpha \nu) t^2 + \alpha R_{II} \omega t^3, \quad (8)$$

where $R_{II} = \Pi V$ - average speed of carbon atoms in pores with complex morphology; $D_{eff0} = a_0 R_{II} r_0 + (1 - a_0) D_c$ is the effective diffusion coefficient of carbon atoms at time $t = 0$ overgrowth and coagulation of pores.

Dependencies type $D_{eff}(t)$ and $d_c^2(t)$ is shown in Figs. 5 (a) and (b), respectively. The increase in the diffusion factor during the first stage of carbonization is evidently due to the predominance of the pore coagulation process (an increase in the mean pore radius enhances the contribution of Knudsen diffusion to the overall mass transfer process). When passing through the maximum point, the overgrowth factor of the pores formed by the SiC layer begins to predominate. The domain of the function $D_{eff}(t)$ is the time interval $[0; a_0/\alpha]$ (Fig. 5 (a)). Upon exiting the specified interval, the Deal-Grove model starts to operate [14].

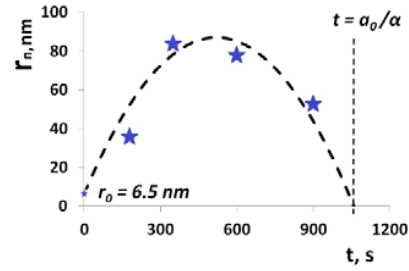


Fig. 4 The experimental dependence of the arithmetic mean radius of the pores on the process time

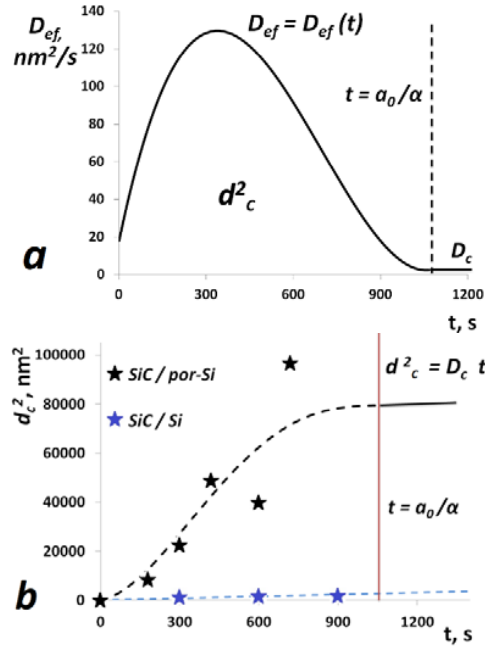


Fig. 5 (a) Dependence $D_{eff}(t)$ considering the pore coagulation processes; (b) Dependence $d_c^2(t)$ considering the pore coagulation processes

Integration of (7) with respect to time gives an expression for the square of the diffusion length of carbon atoms (carbonized layer thickness) - d_c^2 :

$$d_c^2 = D_{eff0} t + \frac{1}{2} [a_0 R_{II} \nu - a (R_{II} r_0 - D_c)] t^2 - \frac{1}{3} R_{II} (a_0 \omega + \alpha \nu) t^3 + \frac{1}{4} \alpha R_{II} \omega t^4 \quad (9)$$

IV. CONCLUSION

An approach in describing the carbonization kinetics of porous silicon samples, taking into account the processes of Knudsen diffusion, as well as the coagulation and overgrowth of pores during the growth of the SiC layer, was proposed. An analytical expression was obtained for the effective diffusion factor in the 3C-SiC/por-Si system.

The interaction of coagulation factors and pores overgrowth during the process of carbonization of porous silicon and their effect on the diffusion of carbon atoms in a porous system are

established.

It is shown that the proposed model of porous silicon carbonization satisfactorily describes the processes under consideration and can be used to solve a wide class of analogous problems.

This work was carried out using the equipment of MEPhI Shared-Use Equipment Center «Heterostructural microwave electronics and wide band gap semiconductor physics».

Education. In 2007 was conferred a title of Honoured Science Worker of the Russian Federation. He is an assistant of a State Duma Deputy, member of the Expert Council on integration problems of education, science and industry of the State Duma Committee on Education.

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Nikolay Kargin graduated from the Ogarev Mordovia State University (Physics Faculty) in 1979.

1984 – completed PhD in physical mathematics in the Saint Petersburg State University 1990 – became Associate Professor 1998 – received Doctor of Engineering Science 1999 – became Professor.

He has risen from a Senior Assistant to Professor at high school. Work places: Ogarev Mordovia State University (1984-1986), North Caucasian Federal University (1986-2007). At MEPhI: Rector Councilor, the Head of the Perspective research department (2008-2010), the Head of Perspective research development department as a Vice-rector (2010-2013), since 2013 up to the present time is an Acting Vice-rector for Innovative development, the Head of Perspective research development department.

Academic career: His research is broadly concerned with physics and technology of wide-gap semiconductors. He has published more than 200 works (including 3 monographs, 230 scientific works and 15 academic works).

Awards: In 1998 became an Honorary Worker of Russian Higher