



# Growth of silicon carbide by sublimation sandwich method in the atmosphere of inert gas

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Received 11 November 1998; accepted 27 July 1999

Communicated by A.A. Chernov

## Abstract

Silicon carbide growth by sublimation sandwich method in the atmosphere of an inert gas is studied both experimentally and theoretically. An analytical description of diffusion transport of gaseous reactive species, coupled with quasi-equilibrium heterogeneous reactions at the source-wafer and substrate surfaces is derived. The species transport inside the sandwich cell is shown to be essentially determined by conditions in the ambience. The growth rate is studied as a function of process parameters (substrate temperature, temperature difference between the source-wafer and the substrate, and others). The developed approach is extended to the transient from the diffusion to the collisionless regime of the species transport. The theoretical results are in good agreement with the experimental data obtained. © 2000 Published by Elsevier Science B.V. All rights reserved.

PACS: 64.70; 81.10; 51.20

Keywords: SiC; Sublimation growth; Sandwich system; Diffusion mass transport

## 1. Introduction

Growth of bulk SiC crystals to fabricate high-quality substrates of a large diameter is now one of the hot topics in present semiconductor technology [1,2]. At the moment, the modified Lely method (see, for example, Ref. [3]) is a widely used tech-

nique to grow SiC crystals. It is based on sublimation of the source (specially prepared material which contains the growth elements — silicon and carbon) and transport of the vaporized species in the gas phase to the substrate where SiC crystal growth occurs. To obtain high-quality SiC bulk crystals, precise control and adjusting vapor-phase composition (partial pressures of main gaseous species — Si, Si<sub>2</sub>C, and SiC<sub>2</sub>) is necessary over the whole growth system and during the long time of the growth process. Inefficient control of the

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vapor-phase content usually results in graphitization of the growing SiC crystal or a highly defective material is obtained [4].

The simplest variant of sublimation technique — so-called sublimation sandwich method [5,6] — allows avoiding some problems related to the control of the vapor-phase content. This is related to the possibility of independent adjustment of three important process parameters — the substrate temperature, the temperature difference between the substrate and the source-wafer, and the temperature of the external material source which provides the needed vapor-phase composition in the growth chamber (ambience).

Basic mechanisms of SiC growth in the sandwich system under vacuum conditions at relatively low temperatures (1600–2000°C) were studied in detail in Ref. [7]. Under these conditions, transport of the gaseous species from the source to the substrate is collisionless. At the same time, higher temperatures — 2000–2800°C — are also of practical importance. In this temperature range, it becomes possible to increase the doping level of SiC crystals and to obtain the material with lower concentration of native defects. Use of high temperatures requires introducing an additional vapor atmosphere with a controlled pressure into the growth chamber, that can change the transport mechanism from the collisionless to the diffusive one.

In this paper, growth of SiC crystals by sublimation sandwich method in a wide range of pressures covering both diffusive and collisionless mechanisms of the species transport is studied experimentally and theoretically. Dependencies of the growth rate versus basic process parameters are measured. A model of SiC growth in the sandwich system via diffusive transport of the gaseous species is developed. In particular, it is shown how the collisionless and the diffusive transport mechanisms can be accounted for in a unified approach.

Let us note that many publications on simulation of transport processes in sublimation systems have been appeared lately (see, for example, Refs. [8–10]). A detailed review of the growth models can be found in Ref. [11]. Most of the papers, however, use numerical approaches which give detailed patterns of the processes but often are not able to trace their physical mechanisms. The model presented in

this paper allows a simple analytical implementation which clearly accounts for the experimentally observed features of the process.

## 2. Experimental procedure

Growth of SiC epitaxial layers was carried out in the growth chamber shown schematically in Fig. 1. The chamber consists of a cylindrical graphite or tantalum container and an assembly of the growth cells located along the container axis (only one growth cell is shown in Fig. 1 for simplicity). Every growth cell (“sandwich”) included a substrate and a source-wafer both made of monocrystalline SiC. The growth process was carried out in the argon atmosphere and the pressure varied from  $10^{-5}$  up to 760 Torr. This allowed us to control the mechanism of the species transport from the source-wafer to the substrate, which was collisionless at a low pressure and diffusive at a higher one.

A controlled axial temperature distribution (nearly uniform in the radial direction) was adjusted inside the container by means of a resistive heater. It enabled to control independently the substrate temperature  $T^s$  and the temperature difference  $\Delta T^{ws} = T^w - T^s$  between the source-wafer

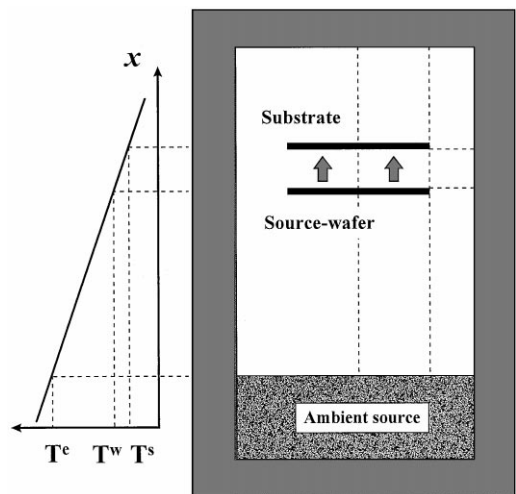


Fig. 1. Reactor design for growth of SiC crystals by sublimation sandwich method (dashed lines indicate boundaries of the subdomains used for calculation of the coefficients  $R^{ab}$  – see text).

and the substrate by proper choice of the growth cell position in the container [7] (hereafter the superscripts s, w, and e specify the substrate, the source-wafer, and the ambience, respectively). The substrate temperature was varied in our experiments from 1600 to 2400°C. The temperature difference  $\Delta T^{ws}$  was varied within the range of 1–3°C.

The axial temperature distribution was measured using a W–Re thermocouple at temperatures below 1800°C and by an optical pyrometer at higher temperatures. The procedure of temperature measurement is described in more detail in Ref. [7].

To control the vapor-phase composition (partial pressures of the main reactive species), an external reactive ambience either of SiC–C or SiC–Si types was created inside the growth chamber. The former (SiC–C ambience) was adjusted by a powder of polycrystalline SiC placed in the hot zone of the container maintained at temperature  $T^e$  (see Fig. 1). To provide excess silicon in the vapor-phase (SiC–Si ambience), liquid silicon was additionally introduced into the hot zone of the container using a special graphite holder. The ambient source temperature  $T^e$  was controlled by varying its position along the axis.

Monocrystalline SiC wafers of 10 mm diameter, grown by the Lely method, with vicinal surfaces close to the (000 $\bar{1}$ )C or (0001)Si planes, were used both as the substrate and the source-wafer. The growth of 6H–SiC was carried out during 1–4 h. No evidence of graphitization or liquid silicon droplet generation both on the substrate and the source-wafer was observed in our experiments. The thickness of the grown homoepitaxial layer was measured to determine the growth rate. For this, the boundary between the substrate and the grown epilayer was distinguished using the difference in their luminescent properties.

No effect of substrate orientation on the growth rate and surface morphology was observed in the experiments while undoped SiC was growing on the vicinal planes. This fact confirmed that the growth of SiC layers was controlled by the species transport to the substrate and thus was not influenced by surface kinetics.

The growth rate versus basic process parameters — the substrate temperature  $T^s$  and the temperature difference between the source-wafer and the

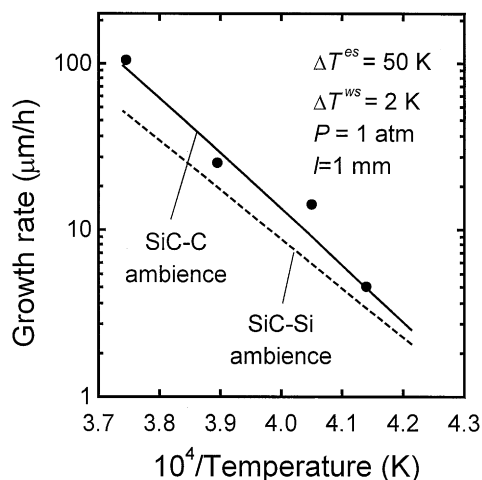


Fig. 2. Growth rate versus reciprocal substrate temperature for the SiC–C (—) and SiC–Si (---) systems. Points (•) indicate experimental data obtained in 6H–SiC growth in the SiC–C ambience.

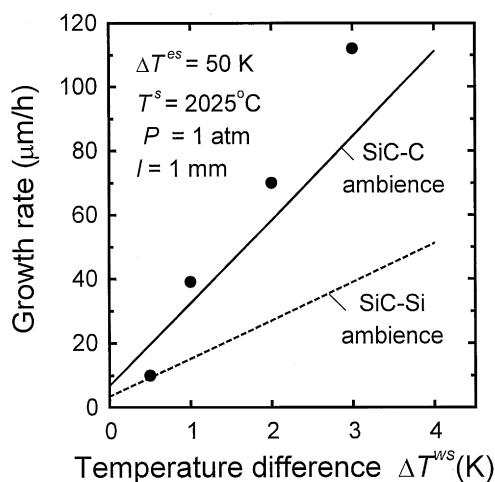


Fig. 3. Growth rate versus temperature difference between the source-wafer and the substrate for the SiC–C (—) and SiC–Si (---) systems. Points (•) indicate the experimental data obtained in 6H–SiC growth in the SiC–C ambience.

substrate  $\Delta T^{ws}$  — are measured under the SiC–C ambient conditions. The results of the measurements are summarized in Figs. 2 and 3 (here  $\Delta T^{ws} = 1^\circ\text{C}$  and  $T^s = 2300^\circ\text{C}$ , respectively, temperature difference between the ambient source and the

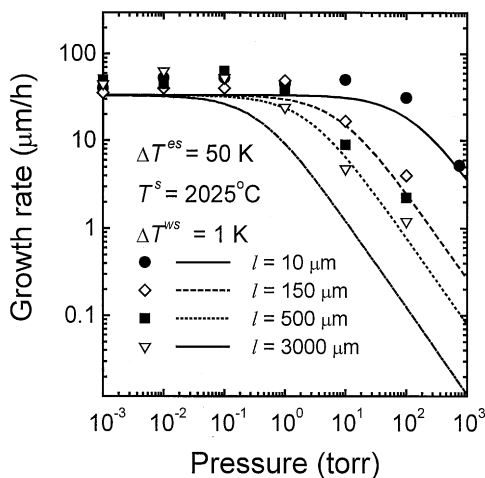


Fig. 4. Growth rate versus total pressure at different values of the clearance between the source-wafer and the substrate. Experimental points are obtained in 6H-SiC growth in the SiC-C ambience.

substrate is  $\Delta T^{es} = 50^\circ\text{C}$ , the clearance between the wafers is  $l = 0.5$  mm, and the total pressure in the system is  $P = 1$  atm). One can see that the growth rate exponentially decreases with the reciprocal of the temperature and linearly depends on the temperature difference. The growth rate almost vanishes as  $\Delta T^{ws} \rightarrow 0$ , this is an evidence of a small contribution of the species fluxes coming to the substrate from the ambience. This does not mean, however, that the growth process is not influenced by the ambience in this case. Actually, the ambient source controls the vapor-phase composition inside the sandwich cell, which in turn provides the main species fluxes between the wafers. This effect is exhibited, in particular, in the growth rate activation energy which appears to be equal to that of  $\text{SiC}_2$  partial pressure in the ambience (a detailed discussion of this feature is presented in the appendix).

Shown in Fig. 4 is the SiC growth rate versus total pressure in the container (here  $T^s = 1850^\circ\text{C}$ ,  $\Delta T^{ws} = 1^\circ\text{C}$ , and  $\Delta T^{es} = 10^\circ\text{C}$ ). It is seen that in a high-pressure range the growth rate decreases with the pressure while in a low-pressure one it saturates at the level of 30–50  $\mu\text{m/h}$ . The transient point between the two regimes depends on the clearance between the substrate and the source-wafer. This indicates that the observed behavior of

the growth rate is related to change of the species transport mechanism from the diffusion to the collisionless.

### 3. Model of species transport in the sandwich system

#### 3.1. General consideration

Following Ref. [7], we assume the vapor to consist of three dominating reactive species, namely Si,  $\text{Si}_2\text{C}$ , and  $\text{SiC}_2$ , which are transported in a carrier inert gas (normally Ar) via diffusion. Our study is restricted to a “diluted” system where the carrier gas prevails in concentration over the reactive species. For such a system, forced convection induced by the boundary Stephan flow as well as multicomponent diffusion effects are negligible. Estimate of the Grashoff number for our sandwich system shows that natural convection is also insignificant so that the gas mixture as a whole is nearly immovable. Under these conditions, the reactive species fluxes are totally determined by their binary diffusion in the dominating neutral gas and described by the Fickian law:  $\mathbf{J}_i = -(D_i/RT)\nabla P_i$  ( $i = \text{Si}, \text{Si}_2\text{C}, \text{SiC}_2$ ), where  $\mathbf{J}_i$  is the  $i$ th species molar flux,  $D_i$  is the binary diffusion coefficient,  $\mu_i$  is the molar mass,  $P_i$  is the partial pressure,  $R$  is the universal gas constant, and  $T$  is the local temperature.

Under steady-state conditions and in the absence of homogeneous gas-phase reactions, the species fluxes satisfy the continuity equations  $\nabla \cdot \mathbf{J}_i = 0$ . Using the Fickian law, neglecting weak dependence of the complex  $D_i/T$  on temperature and referring it to the average temperature  $\bar{T} = (T^w + T^s)/2$  we reduce the continuity equations to the Laplace ones

$$\nabla^2 P_i = 0. \quad (1)$$

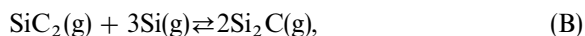
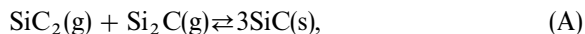
Boundary conditions for these equations depend essentially on the type of a surface where they are set. We consider the following three cases:

(a) *Chemically inert surface.* At such a surface no heterogeneous reaction occurs so that all the species fluxes are equal to zero:

$$\mathbf{n} \cdot \nabla P_i = 0, \quad (2)$$

where  $\mathbf{n}$  is the unit vector normal to the surface. Experimental studies show these conditions to be valid with a good accuracy for tantalum container walls.

(b) *Silicon carbide surface.* This type of surface can be associated either with the substrate or with the source-wafer. Two independent heterogeneous reactions are assumed to occur at the SiC surfaces:



where symbols “g” and “s” specify gas and solid phases, respectively. Assuming the growth to occur under mass transport limited conditions, we can use the mass action law equations for both the reactions in terms of the species boundary partial pressures:

$$P_{\text{Si}_2\text{C}} P_{\text{SiC}_2} = K_1(T), \quad (3)$$

$$P_{\text{Si}}^3 P_{\text{SiC}_2} = K_2(T) P_{\text{Si}_2\text{C}}^2. \quad (4)$$

In the latter equations,  $K_1(T)$  and  $K_2(T)$  are the temperature-dependent equilibrium constants calculated on the standard thermodynamic properties of the species involved (see, for example, Ref. [12]).

The boundary conditions (3) and (4) correspond to the two-phase heterogeneous equilibrium “SiC-solid–Si/C-vapor”. In this case, the system has one thermodynamic degree of freedom and therefore the vapor-phase composition cannot be determined uniquely. The deficient equation is given by the condition of stoichiometric incorporation of silicon and carbon atoms into an SiC crystal. Expressing the elementary silicon and carbon molar fluxes in terms of the species fluxes as  $\mathbf{G}_{\text{Si}} = \mathbf{J}_{\text{Si}} + 2\mathbf{J}_{\text{Si}_2\text{C}} + \mathbf{J}_{\text{SiC}_2}$ ,  $\mathbf{G}_{\text{C}} = \mathbf{J}_{\text{Si}_2\text{C}} + 2\mathbf{J}_{\text{SiC}_2}$ , and using the Fickian law, stoichiometric relationship is reduced to

$$\mathbf{n} \cdot (D_{\text{Si}} \nabla P_{\text{Si}} + D_{\text{Si}_2\text{C}} \nabla P_{\text{Si}_2\text{C}} - D_{\text{SiC}_2} \nabla P_{\text{SiC}_2}) = 0. \quad (5)$$

Thus, Eqs. (3)–(5) give the closed set of boundary conditions for the SiC surfaces.

(c) *Surface with co-existing condensed phases.* As it was discussed above, SiC growth by sublimation sandwich method is normally carried out in a vapor ambience (with respect to the sandwich cell) where the reactive gaseous species are generated by a special material source. The source usually represents an SiC powder partly graphitized during

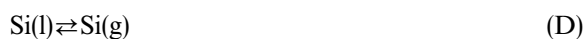
the growth. In this case, two condensed phases, namely SiC and graphite, co-exist with each other, both being in equilibrium with the vapor phase. As a result, vapor-phase composition at the ambient source surface is determined by the three-phase heterogeneous equilibrium “SiC-solid–C-solid–Si/C-vapor”, and the additional heterogeneous reaction



is to be taken into account. The mass action law equation for this reaction is given as

$$P_{\text{Si}} = K_4(T) P_{\text{SiC}_2}. \quad (6)$$

If liquid silicon is introduced into the ambience, the three-phase equilibrium “SiC-solid–Si-liquid–Si/C-vapor” is assumed to be established at the source surface. Correspondingly, reaction (C) should be substituted by the reaction



and the mass action law equation (6) is to be substituted by the relationship

$$P_{\text{Si}} = P_{\text{Si}}^0(T). \quad (7)$$

Here  $P_{\text{Si}}^0(T)$  is the saturated vapor pressure of silicon over its liquid phase.

Both the three-phase equilibria have zero thermodynamic degree of freedom, the species partial pressures being derived as the solution of Eqs. (3), (4) and (6) or (7) for the SiC–C and SiC–Si systems, respectively. Anyway, the resulting boundary conditions at the source surface in the ambience are set as

$$P_i = P_i^e(T). \quad (8)$$

Eq. (1) together with the boundary conditions (2), (3)–(5) and (8) give a closed set of the boundary-value problem describing the diffusive species transport in the container. Below we develop a simple approach allowing analytical solution of this problem.

### 3.2. Mass exchange between the sandwich cell and the ambience

Assume that the only surface that contains co-existing condensed phases in the system is that

of the ambient source. Below we show that in this case the elementary silicon and carbon molar fluxes are equal to each other over the whole growth chamber (stoichiometric correlation of the species fluxes) and, as a result, the vapor composition at the wafers is controlled by the ambience.

Following the method used above for derivation of the boundary conditions (5), the difference between the silicon and carbon fluxes can be expressed as  $\mathbf{G}_{\text{Si}} - \mathbf{G}_{\text{C}} = -(1/RT)\nabla\Omega$ , where  $\Omega = D_{\text{Si}}P_{\text{Si}} + D_{\text{Si}_2\text{C}}P_{\text{Si}_2\text{C}} - D_{\text{SiC}_2}P_{\text{SiC}_2}$ . Let us show that the complex  $\Omega$  has a constant value over the whole domain occupied by the gas. Multiply each of Eq. (1) by the corresponding diffusion coefficient and make up their linear combination similar to that used in the boundary condition (5). Since the diffusion coefficients weakly depend on temperature, we derive

$$\nabla^2\Omega = 0. \quad (9)$$

Then, using relationships (2) and (5), boundary conditions for the complex  $\Omega$  at the chemically inert and the SiC surfaces are reduced to

$$\mathbf{n} \cdot \nabla\Omega = 0. \quad (10)$$

Similarly, boundary conditions at the source surface in the ambience are derived from Eq. (8)

$$\begin{aligned} \Omega &= \Omega^e(T), \\ \Omega^e &= D_{\text{Si}}P_{\text{Si}}^e + D_{\text{Si}_2\text{C}}P_{\text{Si}_2\text{C}}^e - D_{\text{SiC}_2}P_{\text{SiC}_2}^e. \end{aligned} \quad (11)$$

Eq. (9) with the boundary conditions (10) and (11) has the unique solution  $\Omega = \Omega^e = \text{const}$ . Thus, the value of  $\Omega$  “generated” by the ambient source, is translated over the whole container, providing equality of the elementary silicon and carbon fluxes.

The obtained feature enables to find the species partial pressures at the source-wafer and the substrate. Indeed, application of the solution (11) to the substrate surface results in the relationship

$$D_{\text{Si}}P_{\text{Si}}^s + D_{\text{Si}_2\text{C}}P_{\text{Si}_2\text{C}}^s - D_{\text{SiC}_2}P_{\text{SiC}_2}^s = \Omega^e. \quad (12)$$

Combining this formula with the equilibrium conditions (3) and (4), we derive the partial pressure  $P_{\text{Si}_2\text{C}}^s$  as the root of the quadratic equation

$$(D_{\text{Si}}K_3^s + D_{\text{Si}_2\text{C}})(P_{\text{Si}_2\text{C}}^s)^2 - \Omega^e P_{\text{SiC}_2}^s - K_1^s D_{\text{SiC}_2} = 0, \quad (13)$$

where  $K_3^s = (K_2^s/K_1^s)^{1/3}$ . The other partial pressures  $P_{\text{Si}}^s$  and  $P_{\text{SiC}_2}^s$  are found using Eqs. (3) and (4). The species partial pressures at the source-wafer are derived in the same way.

The obtained solution shows that the gas-phase compositions at the substrate and at the source-wafer appear to be independent of each other as well as the container design. They are entirely determined by their temperatures and by the ambient conditions.

However, this is not the case for the species fluxes. Using the superposition technique for solution of the Laplace equations (1) (see, for example, Ref. [13]), we derive the approximate expression for the  $i$ th species average molar flux coming onto the substrate

$$J_i^s = \frac{P_i^w - P_i^s}{R_i^{ws}} + \frac{P_i^e - P_i^s}{R_i^{es}}. \quad (14)$$

Here the coefficients  $R_i^{ws}$  and  $R_i^{es}$  may be treated as the  $i$ th species diffusion resistances between the source-wafer and the substrate and between the ambient source and the substrate, respectively. Thus, the species fluxes arriving at the substrate contain contributions from the source-wafer and from the ambience.

The diffusion resistances are estimated approximately using the following analytical technique. The whole domain containing the gas phase is decomposed into several subdomains bordered in Fig. 1 by the dashed lines. Then, the original Laplace equations (1) written in the cylindrical coordinates are reduced by substitution of all the radial derivatives by corresponding finite differences (these differences describe average mass exchange between the subdomains through their lateral boundaries). As a result, the Laplace equations are transformed into a set of ordinary differential equations allowing an analytical solution. Finally, the

procedure results in the following relationships for the diffusion resistances:

$$\begin{aligned}
 R^{\text{es}} &= (R\bar{T}/D_i)(2R_0 + l/2), \\
 R^{\text{ws}} &= (R\bar{T}/D_i)[l + (l/2)^2/R_0], \\
 R_0 &= \frac{R_s^4}{2R_c^2} \sqrt{\frac{R_s}{R_c(R_c^2 - R_s^2)}} \\
 &\times \tanh\left(2H \sqrt{\frac{R_s}{R_c(R_c^2 - R_s^2)}}\right) \\
 &+ \frac{R_s^2 H}{R_c^2} + \frac{l}{2} \frac{R_s^2}{R_c^2 - R_s^2} + \frac{R_s R_c}{4l}. \quad (15)
 \end{aligned}$$

Here  $R_c$  is the container radius,  $R_s$  is the wafer radius,  $H$  is the distance between the container bottom and the source-wafer, and  $l$  is the clearance between the source-wafer and the substrate.

Since the clearance  $l$  is normally small as compared to all other dimensions of the container, then  $R_i^{\text{es}} \sim (R\bar{T}/D_i)2R_0$ ,  $R_i^{\text{ws}} = (R\bar{T}/D_i)l$ , and  $R_0 \sim R_s R_c/4l$ . These estimates show that the species fluxes coming onto the substrate are mainly determined by the small diffusion resistances of the clearance  $R_i^{\text{ws}}$ . Neglecting the small species fluxes coming onto the substrate from the ambient source, we obtain the estimate

$$J_i^s \sim \frac{D_i}{R\bar{T}} \frac{P_i^w - P_i^s}{l}. \quad (16)$$

The latter formula looks like there is no influence of the ambience on the transport processes inside the sandwich cell. However, this is not the case since this influence proceeds indirectly through the boundary species partial pressures  $P_i^s$  and  $P_i^w$  (see Eq. (13)).

When the species fluxes are found from Eq. (14), the crystal growth rate is calculated using the relationship

$$V_g = (J_{\text{Si}}^s \mu_{\text{Si}} + J_{\text{Si}_2\text{C}}^s \mu_{\text{Si}_2\text{C}} + J_{\text{SiC}_2}^s \mu_{\text{SiC}_2})/\rho_{\text{SiC}}, \quad (17)$$

where  $\mu_i$  is the  $i$ th species molar mass and  $\rho_{\text{SiC}}$  is the crystalline silicon carbide density.

### 3.3. Transition from the diffusive to the collisionless mechanism of the species transport

The developed model of sublimation growth under the diffusion transport conditions has much in common with the model proposed earlier for the collisionless transport mechanism (see Ref. [7]). According to Ref. [7], partial pressure of  $\text{Si}_2\text{C}$  at the substrate is determined in the latter case by the quadratic equation

$$\begin{aligned}
 &(\beta_{\text{Si}}^s K_3^s + \beta_{\text{Si}_2\text{C}}^s)(P_{\text{Si}_2\text{C}}^s)^2 - \theta(\beta_{\text{Si}}^e P_{\text{Si}}^e + \beta_{\text{Si}_2\text{C}}^e P_{\text{Si}_2\text{C}}^e) \\
 &- \beta_{\text{SiC}_2}^e P_{\text{SiC}_2}^e)P_{\text{Si}_2\text{C}}^s - K_1^s \beta_{\text{SiC}_2}^s = 0, \quad (18)
 \end{aligned}$$

where  $\beta_i^z = (2\pi m_i k T^z)^{-1/2}$  is the Hertz–Knudsen factor ( $z = w, s$ ),  $m_i$  is the  $i$ th species molecular mass,  $k$  is the Boltzman constant,  $\theta$  is a dimensionless geometrical factor which is close to unity as the clearance  $l$  is much less than the wafer diameter. In the case of diffusion transport as well partial pressures of the rest of the species are derived from Eqs. (3) and (4).

It is important that due to specific structure of Eq. (18) its solution depends only on the ratios  $\beta_i^s/\beta_{\text{Si}}^s = (m_{\text{Si}}/m_i)^{1/2}$  and  $\beta_i^e/\beta_{\text{Si}}^e = (m_{\text{Si}} T^s/m_i T^e)^{1/2}$ . Similarly, solution of Eq. (13) depends only on the ratios  $D_i/D_{\text{Si}}$ . With the estimate  $D_i \sim (k\bar{T})^{3/2}/P\sigma_{i,\text{Ar}}^2 m_{i,\text{Ar}}^{1/2}$  (here  $\sigma_{i,\text{Ar}}$  is the collision cross section of  $i$ th species molecules and Ar atoms,  $m_{i,\text{Ar}} = 2m_i m_{\text{Ar}}/(m_i + m_{\text{Ar}})$  is their reduced mass), we obtain  $D_i/D_{\text{Si}} \sim (m_{\text{Si},\text{Ar}}/m_{i,\text{Ar}})^{1/2}(\sigma_{\text{Si},\text{Ar}}/\sigma_{i,\text{Ar}})^2$ . Since  $T^s$  and  $T^e$  are both close to  $\bar{T}$ , and since  $m_i$  and  $\sigma_i$  of different molecules are the same in order of magnitude, both the ratios  $\beta_i^e/\beta_{\text{Si}}^e$  and  $D_i/D_{\text{Si}}$  appear to be close to  $\beta_i^s/\beta_{\text{Si}}^s$ . Thus, in the case of small clearance  $l$  (weak mass exchange between the ambience and the sandwich cell, i.e.  $\theta \sim 1$ ), the vapor composition at the wafers is weakly sensitive to change of the transport mechanism from the collisionless to the diffusion.

Relationship (17) for the growth rate is valid regardless of the transport mechanism, however, the reactive species fluxes under free-molecular conditions are calculated using the expressions obtained in Ref. [7]

$$J_i^s = [\theta \beta_i^w P_i^w - \beta_i^s P_i^s + \theta(1 - \theta) \beta_i^e P_i^e]/N_A. \quad (19)$$

Accepting here  $\theta \sim 1$  and taking into account that  $T^s \sim T^w \sim \bar{T}$ , Eq. (19) can be rewritten as  $J_i^s \sim (1/\mu_i R \bar{T})^{1/2} (P_i^w - P_i^s)$ . Then, the above mentioned estimates for the diffusion coefficients are expressed in terms of the  $i$ th species molecular free path  $\lambda_i$  as  $D_i \sim (R \bar{T}/\mu_i)^{1/2} \lambda_i$ . Combining the latter formulae, we obtain the estimate for the species fluxes coming onto the substrate

$$J_i^s \sim \frac{D_i}{R \bar{T}} \frac{P_i^w - P_i^s}{\lambda_i}. \quad (20)$$

Comparing the latter expression with Eq. (16), one can conclude that the average molecular free path  $\lambda_i$  represents a characteristic length determining the mass transport resistance  $R_i^{ws}$  under collisionless conditions. In this case, however, the characteristic length is not constant but depends on the total pressure as  $P^{-1}$ . Since the diffusion coefficients depend on the pressure in the same way, the species fluxes as well as the growth rate remain constant as the pressure changes. Under the diffusion transport conditions, the characteristic length  $l$  is constant and the growth rate decreases as  $P^{-1}$ .

Similarity of Eqs. (20) and (16) allows to describe the transient from the collisionless to the diffusion regime of transport within a unified approach. Indeed, in the diffusion regime the complex  $R \bar{T} \lambda_i / D_i$  can be treated as a “free-molecular” resistance of the Knudsen layers at the wafers, while  $R \bar{T} l / D_i$  — as a diffusion resistance of the gas layer between them. “Series connection” of these resistances results in the expression  $(R \bar{T} D_i)(\lambda_i + l)$  for the total mass-transport resistance between the wafers (factor 2 before  $\lambda$  is omitted similar to other factors in the above mentioned estimates). At high pressure  $\lambda_i \ll l$ , and the Knudsen layers contribution to the total resistance (diffusion regime), is negligible. However, as the pressure falls down, this contribution increases, and when  $\lambda_i \gg l$ , it becomes dominating. Thus, using the sum of  $\lambda_i$  and  $l$  instead of each length gives the needed unified description of the process.

#### 4. Results and comparison to experimental data

Let us compare the theoretical predictions with the experimental data obtained while growing

6H-SiC crystal in the sandwich system. In all the below calculations, the vapor composition in the ambience was found using Eqs. (3), (4) and (6) or (7) for the SiC–C or SiC–Si systems, respectively. At the substrate, it was calculated using Eqs. (3), (4) and (13), and at the source-wafer — in the same way but with the temperature  $T^w$  instead of  $T^s$ . The species fluxes coming onto the substrate were calculated based on the formulae (14) and (15), though use of the approximate Eqs. (16) gave very close results. The latter relationships were used for calculation of the transient transport regime, the clearance  $l$  being substituted by the constrain  $l + \lambda_i$ .

In Fig. 5 the reactive species partial pressures at the substrate versus its reciprocal temperature (solid lines) calculated for two types of the ambient sources: (a) SiC–C and (b) SiC–Si (the input data for calculations correspond to the experimental conditions of Figs. 2 and 3 — see Section 2) are shown. To compare, the dashed lines in Fig. 5 indicate the partial pressures related to the respective three-phase equilibria at the temperature  $T^s$ . Calculations show that as the substrate temperature  $T^s$  approaches the ambient one  $T^e$ , the dashed and the solid lines merge. Thus, the vapor composition at the substrate is determined both by its temperature and by the ambient conditions (temperature and type of the three-phase equilibrium). These results clearly show that the ambient source influences the growth through control of the vapor composition at the wafers.

Let us consider dependencies of the growth rate on process parameters. Shown in Fig. 2 is the growth rate versus reciprocal substrate temperature calculated for the same growth conditions (solid lines correspond to the SiC–C system and dashed lines to the SiC–Si system). Experimental values of the growth rate correspond to 6H-SiC crystals and the SiC–C ambience, they are marked by circles. It is seen that theoretical predictions agree well with the experimental data. In both the considered cases, the growth rate activation energy is close to that of the ambient partial pressure of the species limiting the crystal growth. For the SiC–C and SiC–Si systems, these species are SiC<sub>2</sub> and Si<sub>2</sub>C, respectively. This feature is discussed in detail in the Appendix using the linearized solution of the mass-transport problem.



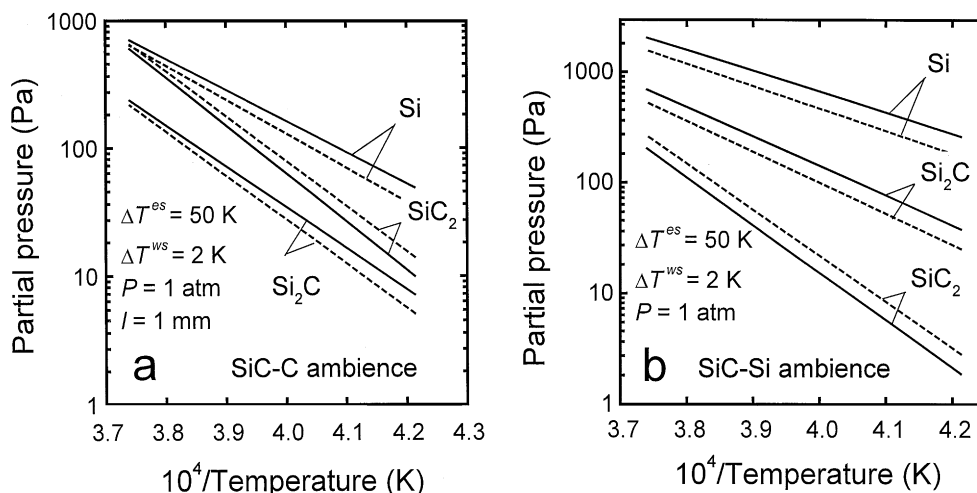


Fig. 5. The reactive species partial pressures at the substrate (—) and under the conditions of three-phase equilibria (---) of SiC–C (a) and SiC–Si (b) types versus the reciprocal substrate temperature.

The growth rate versus temperature difference between the source-wafer and the substrate is plotted in Fig. 3. As in the previous case, theoretical predictions are in good agreement with the experimental data obtained for the SiC–C system. Note that at zero temperature difference  $\Delta T^{\text{ws}}$ , the calculated growth rate is small but does not vanish completely. This effect is obviously related to small species fluxes between the sandwich cell and the ambience due to the temperature difference  $\Delta T^{\text{es}}$  (the ambience serves as a weak external material source in this case).

The growth rate depending on the total pressure (varied in a wide range covering both the collisionless and the diffusion mechanisms of transport) is shown in Fig. 4 (the input data for calculations correspond to the experimental conditions — see Section 2). Different lines in the figure correspond to different values of the clearance  $l$ , points mark the experimental values given in Ref. [6].

It is seen that for a given value of the clearance, growth rate exhibits a plateau at low pressures (collisionless transport) and decreases approximately as  $P^{-1}$  at higher pressures (diffusive transport). Transient point between these two regimes shifts towards the low-pressure area as the clearance  $l$  increases. The characteristic transient pressure  $P_t$  can be estimated from the equality  $\lambda_t \sim l$ .

Then,  $P_t \sim k\bar{T}/l\sigma_t^2$ , where  $\sigma_t$  is the collision cross section of carrier gas atoms and molecule of the species limiting the growth ( $\text{SiC}_2$  for SiC–C and  $\text{Si}_2\text{C}$  for SiC–Si systems).

Comparing the calculated results with the data of Ref. [6], one should keep in mind that variation of the clearance  $l$  results in a simultaneous change of the temperature difference between the substrate and the source-wafer  $\Delta T^{\text{ws}}$ . At high clearances, this difference is not controlled accurately and may deviate from the value used in the calculations. This can account for some discrepancy between the calculations and the experimental data, which is seen in Fig. 4.

## 5. Summary

In conclusion, SiC sublimation growth in a sandwich system in the atmosphere of an inert gas is studied both experimentally and theoretically. The growth rate versus basic process parameters — the substrate temperature, the temperature difference between the source-wafer and the substrate, and the total pressure in the growth chamber — is measured. The latter dependence allows one to distinguish two growth regimes at low and high pressures corresponding to the collisionless and the

diffusion mechanisms of the species transport. The transition from one transport mechanism to the other occurs at some value of the pressure which is dependent on the clearance between the wafers.

An analytical model of the species diffusive transport coupled with quasi-equilibrium heterogeneous reactions at the substrate and the source-wafer surfaces is developed. The model allows prediction of vapor composition (partial pressures of main reactive gaseous components) and the crystal growth rate.

Using the model, it is shown that the vapor composition in the sandwich cell depends only on the substrate and the ambient temperatures, and is not influenced noticeably by the growth chamber design and total pressure in the system.

In contrast, the crystal growth rate in the diffusion transport regime depends both on the growth chamber configuration (mainly on the clearance between the wafers) and on the total pressure. Transition between the diffusive and the collisionless transport mechanisms can be described within a unified approach using the idea of mass-transport resistances of the Knudsen and the gas layers. This transition occurs as the free-molecular resistances of the Knudsen layers become comparable to the diffusion resistance of the gas layer.

The growth rate activation energy corresponds to that of the ambient partial pressure of the species limiting the crystal growth. This species is  $\text{SiC}_2$  or  $\text{Si}_2\text{C}$  for the ambience of SiC–C or SiC–Si types, respectively.

The results predicted using the model are in good agreement with the experimental data obtained while growing 6H–SiC in the sandwich system in the Ar atmosphere.

## Appendix A. Effective activation energy of SiC crystal growth rate

To estimate the slope of the growth rate as a function of the reciprocal substrate temperature we linearize solution of the problem using the small parameter  $\varepsilon = \Delta T^{\text{ws}}/\bar{T}$ . Then, the boundary conditions (3)–(5) are reduced to an array of linear equations in differences of the species partial pressures

between the source-wafer and the substrate

$$\begin{aligned}\Delta P_{\text{Si}}/P_{\text{Si}}^e &= \Delta P_{\text{Si}_2\text{C}}/P_{\text{Si}_2\text{C}}^e + \Delta K_3/K_3^e, \\ \Delta P_{\text{Si}_2\text{C}}/P_{\text{Si}_2\text{C}}^e + \Delta P_{\text{SiC}_2}/P_{\text{SiC}_2}^e &= \Delta K_1/K_1^e,\end{aligned}\quad (\text{A.1})$$

$$D_{\text{Si}}\Delta P_{\text{Si}} + D_{\text{Si}_2\text{C}}\Delta P_{\text{Si}_2\text{C}} - D_{\text{SiC}_2}\Delta P_{\text{SiC}_2} = 0.$$

Here  $\Delta P_i = P_i^w - P_i^s$ ,  $\Delta K_i = K_i^w - K_i^s$ ,  $i = \text{Si}, \text{Si}_2\text{C}, \text{SiC}_2$ ,  $K_i^e$  is the equilibrium constant referred to the ambient temperature  $T^e$  (due to smallness of the parameter  $\varepsilon$  all the non-perturbed unknowns with the superscripts e, w, and s are accepted equal).

Combining the linearized solution (A.1) with Eqs. (16) and (17), we derive the following expression for the growth rate:

$$V_g = \frac{1}{\rho_{\text{SiC}} R \bar{T}} \frac{\sum_{i \neq j} A_{ij} D_i D_j P_i^e P_j^e}{\prod_i D_i P_i^e}, \quad (\text{A.2})$$

where  $A_{\text{Si}, \text{Si}_2\text{C}} = (\mu_{\text{Si}} - \mu_{\text{Si}_2\text{C}})\delta K_3$ ,  $A_{\text{Si}_2\text{C}, \text{SiC}_2} = (\mu_{\text{Si}_2\text{C}} + \mu_{\text{SiC}_2})\delta K_1$ ,  $A_{\text{SiC}_2, \text{Si}} = (\mu_{\text{SiC}_2} + \mu_{\text{Si}})(\delta K_1 + \delta K_3)$ ,  $\delta K_i = \Delta K_i/K_i^e$ . Using the latter expression, we can clearly account for the main physical features of the growth process.

It is seen from Fig. 5a that in the sandwich system with the SiC–C ambience the species partial pressures satisfy the inequality  $P_{\text{Si}_2\text{C}}^e \ll P_{\text{SiC}_2}^e \ll P_{\text{Si}}^e$  in the whole temperature range of practical importance. Then, Eq. (A.2) can be reduced to

$$V_g \sim \frac{(\mu_{\text{SiC}_2} + \mu_{\text{Si}})D_{\text{SiC}_2}P_{\text{SiC}_2}^e}{\rho_{\text{SiC}} R \bar{T} l} (\delta K_1 + \delta K_3). \quad (\text{A.3})$$

Since  $\delta K_1$  and  $\delta K_3$  are weakly dependent on temperature ( $\delta K_i = \Delta K_i/K_i \sim G_i \Delta T^{\text{ws}}/RT^2$ , where  $G_i$  is the Gibbs free energy associated with the respective heterogeneous reaction), the slope of the growth rate dependence on the reciprocal temperature is entirely determined by that of  $\text{SiC}_2$  partial pressure.

Similarly, in the case of SiC–Si ambience, one can show that the growth rate slope is nearly equal to that of  $\text{Si}_2\text{C}$  partial pressure. Indeed, in this case  $P_{\text{SiC}_2}^e \ll P_{\text{Si}_2\text{C}}^e \ll P_{\text{Si}}^e$  (see Fig. 5b), and consequently

$$V_g \sim \frac{(\mu_{\text{Si}} - \mu_{\text{Si}_2\text{C}})D_{\text{Si}_2\text{C}}P_{\text{Si}_2\text{C}}^e}{\rho_{\text{SiC}} R \bar{T} l} \delta K_3. \quad (\text{A.4})$$

Thus,  $\text{SiC}_2$  and  $\text{Si}_2\text{C}$  represent the gaseous species limiting the crystal growth rate in the sandwich

system for SiC–C and SiC–Si types of the ambience, respectively (in both the cases Si is in excess in the vapor-phase).

It is interesting that the silicon-vapor flux is directed from the substrate to the source in the case of SiC–Si system. This can be seen from the mass balance equation (5) where SiC<sub>2</sub> flux is omitted:  $J_{\text{Si}}^{\text{s}}/\mu_{\text{Si}} \sim -J_{\text{Si}_2\text{C}}^{\text{s}}/\mu_{\text{Si}_2\text{C}}$ . This effect is related to the fact that Si<sub>2</sub>C (the limiting species) transfers two atoms of silicon per every atom of carbon. Since the growth of SiC is stoichiometric, the excess of silicon should be released via Si flux outgoing from the substrate.

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