

# Model of morphology evolution in the growth of polycrystalline $\beta$ -SiC films

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## Abstract

The growth of  $\beta$ -SiC films via chemical vapor deposition (CVD) has been under intensive investigation because this is viewed to be an enabling material for a variety of new semiconductor devices in areas where silicon cannot effectively compete. However, the difficulty in achieving single-crystal or highly textured surface morphology in films with low bulk defect density has limited the use of  $\beta$ -SiC films in electronic devices. Although several researchers have reported results relating the morphology of  $\beta$ -SiC films to deposition parameters, including substrate temperature and gas composition, detailed knowledge of the effects of deposition parameters on film morphology and crystallographic texture is still lacking. If these relationships between deposition parameters and film morphology can be quantified, then it may be possible to obtain optimal  $\beta$ -SiC film morphologies via CVD for specific applications such as high-power electronic devices.

The purpose of this study is to predict the dependence of the surface morphology of  $\beta$ -SiC films grown by CVD on substrate temperature and inlet atom ratio of Si:C, and to model the morphological evolution of the growing polycrystalline film. The Si:C ratio is determined by the composition of the reactant gases, propane ( $C_3H_8$ ) and silane ( $SiH_4$ ). A two-dimensional numerical model based on growth rate parameters has been developed to predict the evolution of the surface morphology. The model calculates the texture, surface roughness, and grain size of continuous polycrystalline  $\beta$ -SiC films resulting from growth competition between nucleated seed crystals of known orientation. Crystals with the fastest growth direction perpendicular to the substrate surface are allowed to overgrow all other crystal orientations. When a continuous polycrystalline film is formed, the facet orientations of crystals are represented on the surface. In the model, the growth parameter  $\alpha_{2D}$ , the ratio of the growth rates of the  $\{10\}$  and  $\{11\}$  faces, determines the crystal shapes and, thus, the facet orientations of crystals. The growth rate parameter  $\alpha_{2D}$  used in the model has been derived empirically from the textures of continuous  $\beta$ -SiC films reported in the literature. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Polycrystalline  $\beta$ -SiC; Modeling; Growth morphology

## 1. Introduction

One of the silicon carbide polytypes,  $\beta$ -SiC, is considered as an excellent candidate for use in high-power electronic devices. However, the difficulty in achieving single crystal films and uniform surface texture via chemical vapor deposition (CVD) has limited the possible application of  $\beta$ -SiC.

The surface morphology of a continuous polycrystalline  $\beta$ -SiC film is determined by the reactor operating conditions, including the substrate temperature and the

inlet gas composition. At the present time, the effects of these operating parameters on the resulting surface morphology are not fully understood. An understanding of the relationships between operating conditions and film morphology may lead to an optimal yield of films that are highly  $\langle 100 \rangle$ -textured, with  $\{100\}$  facets.

The van der Drift model [1,2] represents a growth mechanism of continuous polycrystalline films from randomly oriented nucleated seed crystals. This model calculates the crystallographic texture and the surface morphology of the continuous polycrystalline film resulting from growth competition between nucleated seed crystals. As the film thickness increases and a continuous film is formed, those crystals having their fastest growth direction perpendicular to the substrate

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surface will overgrow all other orientations and the orientation of the crystals are represented on the surface. The model is expressed by the growth-rate parameter,  $\alpha_{3D} = \sqrt{3}V_{100}/V_{111}$ , where  $V_{100}$  and  $V_{111}$  are the growth velocities of the  $\{100\}$  and  $\{111\}$  facets. The  $\alpha_{3D}$  value can be determined from the texture of a continuous polycrystalline film, assuming the absence of secondary nucleation and twinned crystals [2]. After the film growth rate  $V_{100}$  is determined, the growth rate  $V_{111}$  of  $\{111\}$  face can be calculated from the known values of  $\alpha_{3D}$  and  $V_{100}$ .

During the past several years X-ray diffraction (XRD) has been used to determine the effects of operating parameters on polycrystalline  $\beta$ -SiC film orientation. Many investigators [3–12] have reported XRD data for the growth of  $\beta$ -SiC films on Si(100) substrates using atmospheric-pressure CVD (APCVD) and an  $\text{SiH}_4$ ,  $\text{C}_3\text{H}_8$ ,  $\text{H}_2$  inlet gas mixture. Using XRD, these investigators have examined the dependence of  $\beta$ -SiC morphology on substrate temperature and inlet Si:C atom ratio. Among these, Wu et al. [3] reported a series of XRD patterns of polycrystalline  $\beta$ -SiC films grown at substrate temperatures from 1263 to 1433 K and a fixed inlet Si:C ratio of 0.42. They found that, whereas the preferred orientation of continuous polycrystalline films was (111) at 1323 K with negligible degree of (100) orientation, its orientation changed to (100) by increasing the substrate temperature to 1433 K.

Since two preferred surface orientations,  $\{100\}$  and  $\{111\}$ , are usually observed in  $\beta$ -SiC APCVD growth on Si(100) substrates using a silane–propane–hydrogen inlet reactant gas mixture [3–12], the model can be simplified to the growth of two-dimensional crystals from the growth of three-dimensional crystals. In a two-dimensional model, the growth parameter is defined as  $\alpha_{2D} = \sqrt{2}V_{10}/V_{11}$ , where  $V_{10}$  and  $V_{11}$  are the growth velocities of the  $\{10\}$  and  $\{11\}$  facets. This approach is

restricted to the situation where SiC is deposited on Si(100) substrates; when SiC is grown on Si(111), the  $\{110\}$  and  $\{111\}$  orientations are typically observed.

Although it has been possible in the present study to correlate the growth parameter  $\alpha_{2D}$  with operating conditions using published experiments, it has proven difficult to extract consistent growth rate data from the same body of work. In an attempt to quantify the dependence of growth rate on deposition conditions, Allendorf and Kee [13] calculated SiC growth rate as a function of substrate temperature and Si:C inlet atom ratio through the use of a detailed gas-phase and surface chemical kinetic mechanisms. Allendorf and Kee [13] considered steady-state, rotating disk APCVD of SiC from an  $\text{SiH}_4$  and  $\text{C}_3\text{H}_8$  mixture in  $\text{H}_2$  carrier gas. Using the validated theoretical predictions of Allendorf and Kee [13], it has been possible to obtain realistic values for the growth rate of (100) $\beta$ -SiC, and these are used, along with the experimentally determined values of  $\alpha_{2D}$ , in a morphology evolution model to study the effect of operating conditions on film texture and roughness.

The purpose of the present work is to predict the dependence of the surface morphology of  $\beta$ -SiC films grown by CVD on substrate temperature and inlet atomic ratio of Si to C, and to model the morphological evolution of the growing polycrystalline film. In this study,  $\beta$ -SiC APCVD films grown on Si(100) substrate with an  $\text{SiH}_4$ – $\text{C}_3\text{H}_8$ – $\text{H}_2$  inlet gas mixture are considered. The growth rates of the films are calculated from a rigorous transport and kinetic model applied to a pedestal reactor, using gas-phase momentum, mass, and energy conservation equations containing detailed homogeneous and heterogeneous chemistry. The growth rate parameter  $\alpha_{2D}$  is determined empirically from the texture of continuous  $\beta$ -SiC films reported in the literature [3–12]. Finally, a two-dimensional numerical model based on the growth-rate parameter  $\alpha_{2D}$  and the film

Table 1  
Simplified surface reaction mechanism<sup>a</sup>

Reaction	$A$	$\beta$	$E$
$\text{H} + \text{Si}(\text{S}) \rightarrow \text{Si}(\text{S}) - \text{H}$	$2.180 \times 10^{12}$	0.5	0.0
$\text{H} + \text{C}(\text{S}) \rightarrow \text{C}(\text{S}) - \text{H}$	$2.180 \times 10^{12}$	0.5	0.0
$2\text{Si}(\text{S}) - \text{H} \rightarrow 2\text{Si}(\text{S}) + \text{H}_2$	$7.230 \times 10^{24}$	0.0	61 000.0
$2\text{C}(\text{S}) - \text{H} \rightarrow 2\text{C}(\text{S}) + \text{H}_2$	$7.230 \times 10^{24}$	0.0	61 000.0
$\text{CH}_4 + \text{Si}(\text{S}) \rightarrow \text{C}(\text{S}) + \text{Si}(\text{B}) + 2\text{H}_2$	$4.197 \times 10^7$	0.5	0.0
$\text{C}_2\text{H}_4 + 2\text{Si}(\text{S}) \rightarrow 2\text{C}(\text{S}) + 2\text{H}_2 + 2\text{Si}(\text{B})$	$9.367 \times 10^{17}$	0.5	0.0
$\text{C}_2\text{H}_2 + 2\text{Si}(\text{S}) \rightarrow 2\text{C}(\text{S}) + 2\text{Si}(\text{B}) + \text{H}_2$	$1.216 \times 10^{19}$	0.5	0.0
$\text{SiH}_2 + \text{C}(\text{S}) \rightarrow \text{C}(\text{B}) + \text{SiH}_2(\text{S})$	$6.120 \times 10^{11}$	0.5	0.0
$\text{Si} + \text{C}(\text{S}) \rightarrow \text{C}(\text{B}) + \text{Si}(\text{S})$	$6.334 \times 10^{11}$	0.5	0.0
$2\text{CH}(\text{S}) \rightarrow 2\text{C}(\text{S}) + \text{H}_2$	$2.250 \times 10^{24}$	0.0	61 000.0
$2\text{SiH}(\text{S}) \rightarrow 2\text{Si}(\text{S}) + \text{H}_2$	$2.250 \times 10^{24}$	0.0	61 000.0
$\text{SiH}_2(\text{S}) \rightarrow \text{Si}(\text{S}) + \text{H}_2$	$2.912 \times 10^{14}$	0.0	9000.0

<sup>a</sup> Arrhenius parameters in form  $k_i = AT\beta \exp(-E/RT)$  in units ( $A$  in moles, cubic centimeters, and seconds;  $E$  in calories per mole). The surface radical sites and bulk species are represented by S and B.

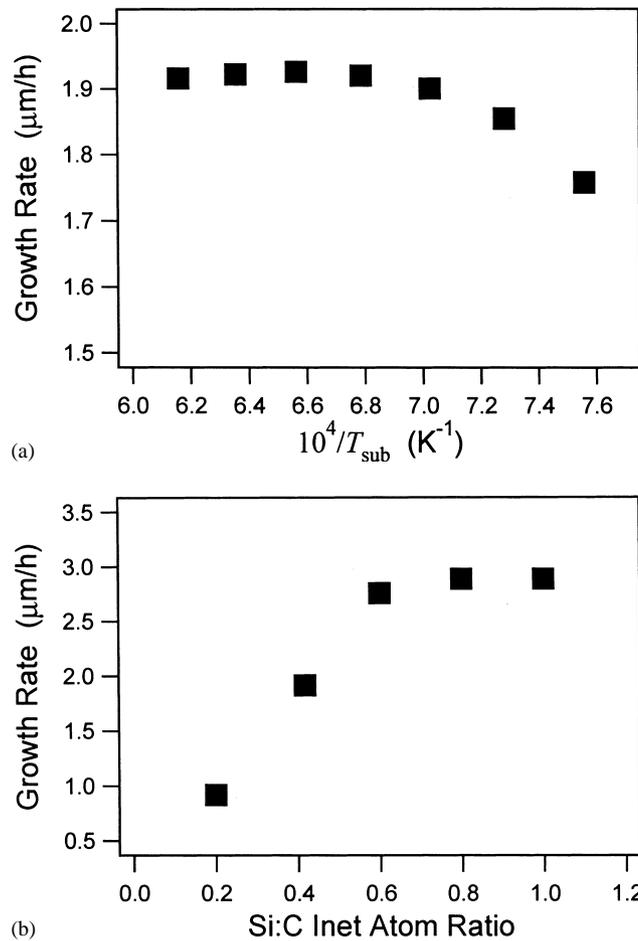


Fig. 1. Growth rate of  $\beta$ -SiC film as a function of (a) the substrate temperature and (b) the inlet Si:C atom ratio, for the operating conditions:  $T_{\text{inlet}} = 300 \text{ K}$ ;  $P = 760 \text{ Torr}$ ;  $U_{\text{inlet}} = 2.49 \text{ cm/s}$ ;  $L = 3 \text{ cm}$ ; and inlet mole fractions  $X_{\text{H}_2} = 0.9964$ ;  $X_{\text{SiH}_4} = 2 \times 10^{-4}$ ;  $X_{\text{C}_3\text{H}_8} = 1.6 \times 10^{-4}$ .

growth rate is used to simulate the evolution of the surface morphology.

## 2. Model description

A numerical model is applied to calculate growth rates of  $\beta$ -SiC films in stagnation flow (pedestal) reactors. Calculations are also performed to determine the effects of operating conditions, such as substrate temperatures and Si:C inlet atom ratio, on the growth rate. A computer program [14] is used to compute gas-phase composition, temperature and velocity profiles, and deposition rates. The Fortran chemical kinetic codes called Chemkin-III [15] and Surface Chemkin [16] are used for the analysis of gas-phase and surface chemical kinetics. The gas-phase reaction and surface reaction mechanisms used in the calculations are simplified from those reported by Allendorf and Kee [13]. The gas-phase multicomponent transport properties are calculated by using a computer package [17].

The evolution of surface morphology of two-dimensional polycrystalline  $\beta$ -SiC films is simulated by a two-dimensional numerical model, which is based on prescribed values of the growth rate parameter  $\alpha_{2D}$  and the film growth rate  $V_{10}$  obtained from the pedestal reactor calculations. Initially, randomly oriented seed crystals are placed at random locations on the substrate, and each face of each crystal is propagated over a finite time step using the prescribed  $\alpha_{2D}$  and  $V_{10}$ .

## 3. Results and discussion

As stated above, the values of  $\alpha_{2D}$  used in this study are based on published XRD data taken from  $\beta$ -SiC films grown on Si(100) using  $\text{SiH}_4$ ,  $\text{C}_3\text{H}_8$ , and  $\text{H}_2$ . Those data were taken at substrate temperatures ranging from 1323 to 1673 K, and inlet Si:C atom ratios between 0.2 and 0.83. The experimental results indicate that the SiC films have (100)-preferred orientations at substrate temperatures above approximately 1423 K and for inlet Si:C

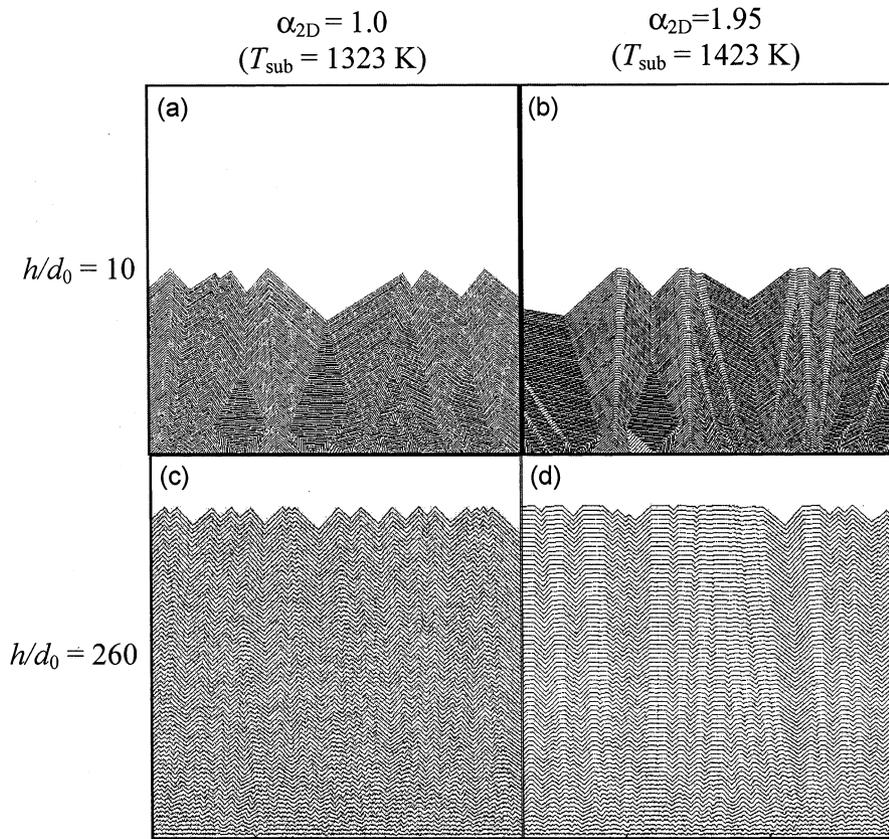


Fig. 2. Film morphology predicted by two-dimensional numerical model. The average distance between nucleated seed crystals is represented as  $d_0$ . (a) and (b) The relatively thin film (thickness:  $10d_0$ ) morphologies for two different growth parameter values: (a)  $\alpha_{2D}=1.0$  and (b)  $\alpha_{2D}=1.95$ . (c) and (d) The relatively thick film (thickness:  $260d_0$ ) morphologies for two different growth parameter values: (c)  $\alpha_{2D}=1.0$  and (d)  $\alpha_{2D}=1.95$ .

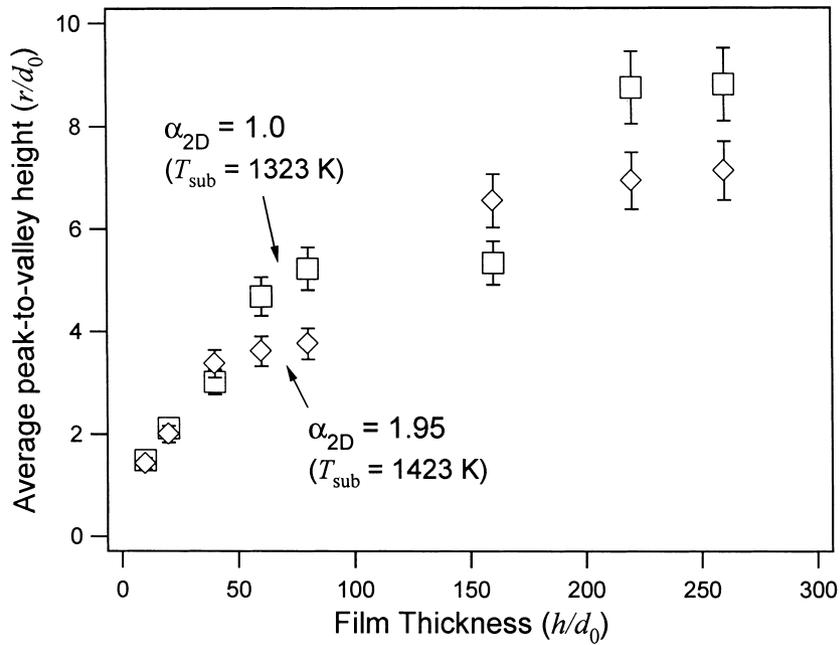


Fig. 3. Surface roughness prediction for different film thickness and  $\alpha_{2D}$  values.

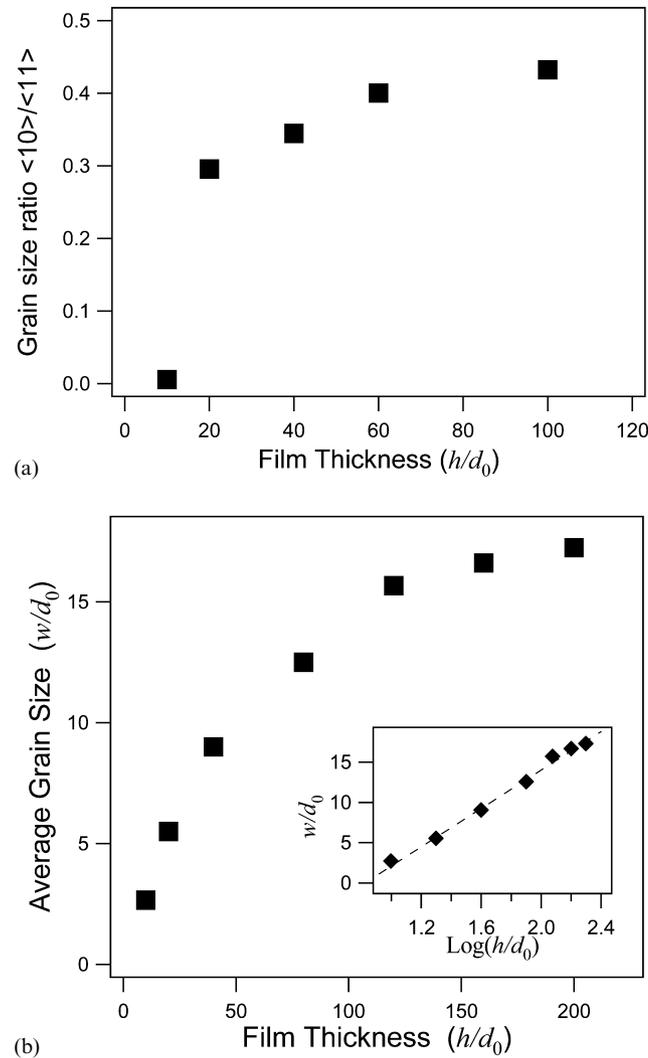


Fig. 4. Evolutions of (a) the relative sizes of the  $\langle 10 \rangle$ - and  $\langle 11 \rangle$ -orientated grains and (b) the average grain sizes with the film thickness for  $\alpha_{2D} = 1.95$ .

ratios between 0.3 and 0.83. In those studies, as long as the inlet Si:C ratio was below unity, the resulting film orientation was relatively insensitive to that parameter when the substrate temperature was above 1423 K. These observations are consistent with thermodynamic calculations of the Si–C system, which predict that optimum values of Si:C in the gas phase will be slightly less than unity for single-phase growth of SiC [18,19].

### 3.1. Simulations of film growth rate

Although the surface reaction mechanism of  $\beta$ -SiC growth proposed by Allendorf and Kee [13] is somewhat complex, the mechanism can be simplified if the goal is solely to determine the growth rate. Numerical calculations have been performed to obtain a simplified surface reaction mechanism for  $\beta$ -SiC growth. The reaction rate

of each elementary surface reaction has been evaluated to identify the predominant surface reactions from the detailed surface reaction mechanism. It is found that, among carbon-containing species, heterogeneous reactions involving  $\text{CH}_4$ ,  $\text{C}_2\text{H}_2$ , and  $\text{C}_2\text{H}_4$  are the most important, and among the Si-containing gas species, the heterogeneous reactions involving  $\text{SiH}_2$  and Si are the most significant. The simplified surface reaction mechanism is listed in Table 1.

The growth rates have been calculated at the different substrate temperatures that are to be used in the two-dimensional morphology evolution model. In the model the substrate temperature is varied between 1323 and 1623 K. The upper limit of substrate temperature 1623 K is chosen to avoid the melting point of the Si substrate, which is 1683 K [13]. Other operating conditions are chosen to match the experimental data of Wu et al. [3].

The Si:C inlet atomic ratio is fixed at 0.42, a standard value. The inlet mole fractions of SiH<sub>4</sub> and C<sub>3</sub>H<sub>8</sub> are set to  $2.0 \times 10^{-4}$  and  $1.6 \times 10^{-4}$  respectively. The inlet mole fraction ratio of H<sub>2</sub>:(SiH<sub>4</sub>+C<sub>3</sub>H<sub>8</sub>) is 2778.

The predicted growth rate of  $\beta$ -SiC as a function of substrate temperature and inlet Si:C ratio is shown in Fig. 1. At lower temperatures, the strong dependence of  $\beta$ -SiC growth rate on temperature indicates that the growth rate is surface reaction rate limited, yielding an overall activation energy of approximately 4.5 kcal/mol. The dominant rate-limiting mechanism changes from the surface reaction rate to the mass transfer rate as the substrate temperature increases. This growth rate dependence on the substrate temperature is in reasonable agreement with the results of Wu et al. [3]. As can be seen in Fig. 1b, the system is mass transfer limited in the silicon precursor species when the inlet Si:C ratio falls below 0.6.

### 3.2. Simulations for surface morphology

From experimental data [3], it is concluded that the increase of the growth rate parameter  $\alpha_{2D}$  from 1 to 1.95 is due mainly to an increase in the substrate temperature from 1323 to 1423 K. The effect of Si:C inlet atom ratio on the  $\alpha_{2D}$  is not considered here because the experiments [3–12] indicate that, for inlet Si:C atom ratios ranging from 0.3 to 0.83,  $\beta$ -SiC films have (100) film texture for substrate temperatures above 1423 K.

The two-dimensional numerical model has been used to calculate the surface morphology of polycrystalline  $\beta$ -SiC films based on the growth rate parameter  $\alpha_{2D}$  and the growth rate of (10) $\beta$ -SiC. Fig. 2 shows the surface morphologies and the film textures of continuous polycrystalline  $\beta$ -SiC films for two different  $\alpha_{2D}$  values: 1.0 and 1.95. The film thickness in Fig. 2 is normalized with respect to the average distance  $d_0$  between initial nucleated seed crystals. When  $\alpha_{2D}$  is unity at a substrate temperature of 1323 K, as shown in Fig. 2a and c, the facets on the thin film (thickness  $10d_0$ ) surface in Fig. 2a are randomly orientated because each of the nucleated seed crystals is placed on the substrate surface with random orientation. However, the film texture has a mainly  $\langle 11 \rangle$  direction and this texture leads to mainly  $\{11\}$  facets on the surface of the thicker film (thickness  $260d_0$ ) shown in Fig. 2c. When  $\alpha_{2D}=1.95$  at a substrate temperature of 1423 K, as shown in Fig. 2b and d, a small fraction of  $\{10\}$  facets is observed in the thin film shown in Fig. 2b. The formation of  $\{10\}$  facets continues to occur as the film grows, eventually reaching the morphology seen in Fig. 2d. Fig. 3 shows the dependence of the surface roughness, measured as the average peak-to-valley height, on the film thickness and value of  $\alpha_{2D}$ . The surface roughness significantly increases with increas-

ing film thickness for both  $\alpha_{2D}$  values. However, when  $\alpha_{2D}$  is 1.95, the surface morphology of the film is smoother than that for  $\alpha_{2D}=1.0$ . This result suggests that the  $\{10\}$  facets result in an increasingly smoother surface morphology. The evolution of the relative sizes of the  $\langle 10 \rangle$ - and  $\langle 11 \rangle$ -orientated grains and average grain sizes are shown in Fig. 4. When  $\alpha_{2D}=1.95$ , the average grain size increases with increasing film thickness as expected, and the grain size ratio  $\langle 10 \rangle / \langle 11 \rangle$  also increases with film thickness because the preferred  $\langle 10 \rangle$  orientation of the crystallite continues to evolve for this value of  $\alpha_{2D}$ . As can be seen in Fig. 4b, the evolution of grain size follows the expected square-root scaling with film thickness.

## 4. Summary

In this work calculations have been performed to determine the growth rate of (100) $\beta$ -SiC and the evolution of film morphology. The dependence of growth rate and morphology on substrate temperature and inlet reactant composition have been examined. A two-dimensional morphology evolution model has been used to calculate the texture, surface roughness, and grain size of continuous polycrystalline  $\beta$ -SiC films. The results indicate that the surface morphology and the film texture of  $\beta$ -SiC are strongly affected by the substrate temperature. The results also determine the operating conditions optimizing the smoothness of surface morphology of  $\beta$ -SiC.

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