

BRIEF NOTE

Estimation of supersaturation at steps during chemical vapor deposition of 4H-SiC (000 $\bar{1}$) from reported growth rate and cross-sectional profile of spiral hillock

To cite this article: Kazuhiro Mochizuki and Tomoyoshi Mishima 2022 *Jpn. J. Appl. Phys.* **61** 118002

View the [article online](#) for updates and enhancements.

You may also like

- [Efficient stimulated slowing and cooling of the magnesium fluoride molecular beam](#)
Dapeng Dai, Yong Xia, Yinfei Fang et al.
- [Fish-inspired robots: design, sensing, actuation, and autonomy—a review of research](#)
Aditi Raj and Atul Thakur
- [Magnetic field influence on the light yield from fiber-coupled BCF-60 plastic scintillators of relevance for output factor dosimetry in MR-linacs](#)
Claus E Andersen



Estimation of supersaturation at steps during chemical vapor deposition of 4H-SiC (000 $\bar{1}$) from reported growth rate and cross-sectional profile of spiral hillock

Kazuhiro Mochizuki*¹ and Tomoyoshi Mishima¹

Hosei University, Koganei, Tokyo 184-8584, Japan

*E-mail: kazuhiro.mochizuki.66@hosei.ac.jp

Received September 7, 2022; revised September 30, 2022; accepted October 10, 2022; published online October 31, 2022

Based on the Burton–Cabrera–Frank (BCF) and Cabrera–Levine theories, supersaturation at steps (σ_{step}) during chemical vapor deposition of 4H-SiC (000 $\bar{1}$) at 1570 °C under the condition of C/Si ratio of unity was estimated from the reported growth rate and cross-sectional profile of a spiral hillock, as a function of surface diffusion length of C₂H₂ molecules ($\lambda_{\text{C}_2\text{H}_2}$). The previously assumed zero σ_{step} in the BCF theory was found to be a possible source of error in the case $\lambda_{\text{C}_2\text{H}_2} > 0.63 \mu\text{m}$ because of the estimated ratio of σ_{step} to the surface supersaturation exceeding 0.1.
 © 2022 The Japan Society of Applied Physics

In spite of its polytypism, SiC has been used for highly efficient power devices.^{1–7} This owes to homoepitaxial growth on misoriented SiC substrates,^{8–11} in which polytype is controlled by step-flow growth. As predicted by Frank,¹² a growth step is also provided by a threading dislocation with a screw component. This was confirmed, for example, in the case of chemical vapor deposition (CVD) of 4H-SiC on on-axis 4H-SiC (000 $\bar{1}$) by Masumoto et al.; spiral growth occurred from threading screw dislocations.¹³ These step-flow growths have been analyzed based on the Burton–Cabrera–Frank (BCF) theory¹⁴ not only for SiC CVD^{15–17} but also for molecular beam epitaxy (MBE) of Si,^{18,19} GaAs,²⁰ InGaAsSb,²¹ and GaN.^{22,23} In these analyses, the supersaturation at steps (σ_{step}) had simply been assumed to be zero. Strictly speaking, this assumption should be unrealistic because of a finite growth rate R_g . Accuracy of σ_{step} estimation becomes high in the case of high surface supersaturation σ (i.e. large R_g); e.g. a R_g of $15 \mu\text{m h}^{-1}$ in the above-described case of CVD of 4H-SiC on an on-axis 4H-SiC (000 $\bar{1}$) at growth temperature T of 1570 °C.¹³ Accordingly, in this paper, we estimated σ_{step} during CVD of 4H-SiC (000 $\bar{1}$) from the reported cross-sectional profile of a spiral hillock.¹³

According to Cabrera and Levine,²⁴ σ is given, in the case $\sigma \ll 1$, as

$$\sigma = \frac{19 \gamma \nu}{n R T \lambda_o}, \quad (1)$$

where γ is the free energy of the side surface of a spiral step (i.e. 0.3 J m^{-2}),^{3,15} ν is the molar volume of the growing species (i.e. $2.07 \times 10^{-29} \times 6.02 \times 10^{23} \text{ m}^3$),¹⁵ n is the number of spirals or the number of Si–C bilayer step-height at the center, R is the ideal gas constant, and λ_o is the interstep distance of a growth spiral.²⁵ Since Masumoto et al. observed a two-bilayer high growth spiral (with λ_o of $0.45 \mu\text{m}$) on on-axis 4H-SiC (000 $\bar{1}$) by atomic-force microscopy (i.e. $n = 2$),¹³ σ was calculated from Eq. (1) to be 0.0051. When ζ is defined as $1 - (\sigma_{\text{step}}/\sigma)$, R_g is given as [Eq. (5.37) in Ref. 26]

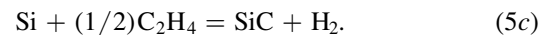
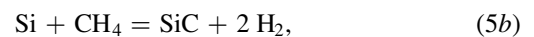
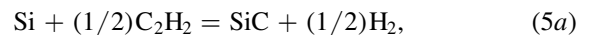
$$R_g = C \frac{\sigma^2}{\sigma_1} \tanh\left(\frac{\sigma_1}{\sigma}\right), \quad (2)$$

$$\sigma_1 = \frac{9.5 \gamma \nu}{n R T \lambda}, \quad (3)$$

$$C = 2 \zeta \Omega \frac{n_{\text{so}}}{\tau} \text{ (for a two-bilayer high growth spiral)}, \quad (4)$$

where λ , Ω , n_{so} , and τ are the surface diffusion length, molecular volume of growing species (i.e. $2.07 \times 10^{-29} \text{ m}^3$),¹⁵ equilibrium surface concentration, and mean residence time of growing species, respectively. Note that R_g is proportional to σ^2 in the case $\sigma \ll \sigma_1$, whereas R_g is proportional to σ in the case $\sigma \gg \sigma_1$.

With respect to SiC CVD in a SiH₄–C₃H₈–H₂ system, the following chemical reactions are known to be dominant^{15,27,28}



We used the equilibrium constants reported in Ref. 29 and calculated the equilibrium vapor pressures of Si, C₂H₂, CH₄, and C₂H₄, as listed in Table I. In Ref. 13 the C/Si ratio was relatively small (i.e. unity). Under such condition, R_g is known to increase with the increase of the C₃H₈ flow rate.¹⁵ The growth in Ref. 13 was thus considered to be limited by the supply of C-containing growing species, as is described in Ref. 13. Since C₂H₂ molecules have the largest equilibrium vapor pressure (Table I), λ in Eq. (3) can be represented by λ of C₂H₂ molecules ($\lambda_{\text{C}_2\text{H}_2}$). Here n_{so}/τ is given by the Knudsen's equation as

$$\frac{n_{\text{so}}}{\tau} = \frac{P_e}{\sqrt{2 \pi m k T}}, \quad (6)$$

where k is Boltzmann constant, and P_e and m are, respectively, the equilibrium vapor pressure and mass of C₂H₂ molecules.

To the authors' knowledge, there have been no reports on $\lambda_{\text{C}_2\text{H}_2}$ on 4H-SiC (000 $\bar{1}$). We therefore calculated $\sigma_{\text{step}}/\sigma$ as a function of $\lambda_{\text{C}_2\text{H}_2}$ (Fig. 1). When $\lambda_{\text{C}_2\text{H}_2} < 0.324 \mu\text{m}$, $\sigma_{\text{step}}/\sigma$ becomes negative; however, σ_{step} must be positive because of positive R_g (i.e. $15 \mu\text{m h}^{-1}$).¹³ $\lambda_{\text{C}_2\text{H}_2}$ should therefore be larger than $0.324 \mu\text{m}$, which is discussed later. The estimated $\sigma_{\text{step}}/\sigma$ exceeds 0.1 in the case $\lambda_{\text{C}_2\text{H}_2} > 0.63 \mu\text{m}$. The previously assumed zero σ_{step} in the BCF theory could thus be source of error, although experimental determination of $\lambda_{\text{C}_2\text{H}_2}$ is needed. In the case of a two-bilayer high (i.e. $h = 0.5 \text{ nm}$)¹³ growth spiral, the step velocity v_{step} is given as

$$v_{\text{step}} = R_g \lambda_o / h = 3.75 \times 10^{-7} (\text{m s}^{-1}). \quad (7)$$

Table I. Reported growth condition for CVD on on-axis 4H-SiC (000 $\bar{1}$),¹³ together with calculated parameters.

Growth temperature (°C)	1570
Growth pressure (kPa)	2.7
Growth rate ($\mu\text{m h}^{-1}$)	15
SiH ₄ flow rate (sccm)	30
C ₃ H ₈ flow rate (sccm)	10
H ₂ flow rate (slm)	20
Si equilibrium pressure (Pa)	1.1×10^{-5}
C ₂ H ₂ equilibrium pressure (Pa)	1.9
CH ₄ equilibrium pressure (Pa)	7.0×10^{-14}
C ₂ H ₄ equilibrium pressure (Pa)	1.7×10^{-4}
Supersaturation σ	0.0051

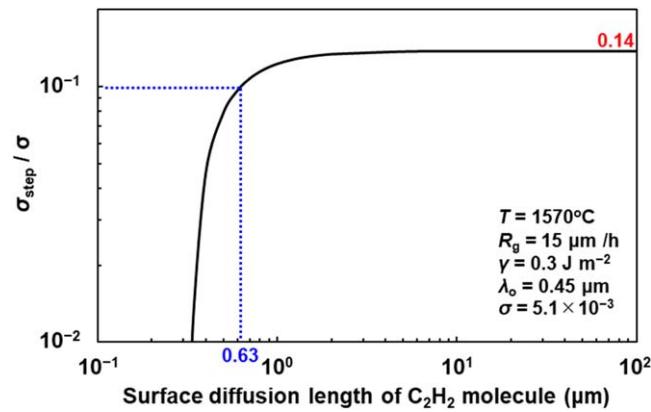


Fig. 1. (Color online) Calculated $\sigma_{\text{step}}/\sigma$ as a function of surface diffusion length of C₂H₂ molecules on 4H-SiC (000 $\bar{1}$).

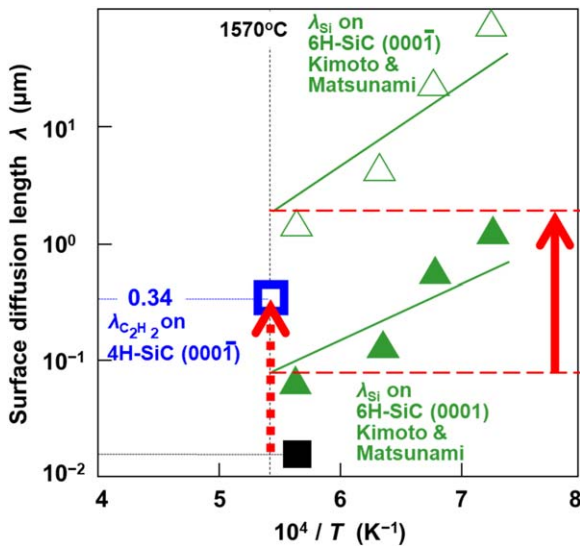


Fig. 2. (Color online) Temperature dependences of surface diffusion lengths of Si adatoms (λ_{Si}) and C₂H₂ molecules ($\lambda_{\text{C}_2\text{H}_2}$) on 6H-SiC (000 $\bar{1}$), 6H-SiC (000 $\bar{1}$), and 4H-SiC (000 $\bar{1}$) reported by Kimoto and Matsunami,¹⁵ Kimoto and Cooper,³ and Mochizuki.¹⁷ $\lambda_{\text{C}_2\text{H}_2}$ on 4H-SiC (000 $\bar{1}$) at 1570 °C is estimated under the assumption that the reported ratio of λ_{Si} on 6H-SiC (000 $\bar{1}$) to λ_{Si} on 6H-SiC (000 $\bar{1}$) at 1570 °C (solid arrow)¹⁵ is the same as the ratio of $\lambda_{\text{C}_2\text{H}_2}$ on 4H-SiC (000 $\bar{1}$) to $\lambda_{\text{C}_2\text{H}_2}$ on 4H-SiC (000 $\bar{1}$) (dotted arrows). $\lambda_{\text{C}_2\text{H}_2}$ on 4H-SiC (000 $\bar{1}$) at 1570 °C is assumed to be equal to $\lambda_{\text{C}_2\text{H}_2}$ on 4H-SiC (000 $\bar{1}$) at 1500 °C (open square).¹⁶

The kinetic coefficient K_{step} defined, in the case $\sigma \ll 1$, as

$$K_{\text{step}} = v_{\text{step}} / (R T \sigma_{\text{step}}), \quad (8)$$

was calculated to be larger than 1.8×10^{-10} in the case $\sigma_{\text{step}} < 0.14$ (Fig. 1).

Here the validity of $\lambda_{\text{C}_2\text{H}_2} > 0.324 \mu\text{m}$ is discussed. If we assume that $\lambda_{\text{C}_2\text{H}_2}$ on 4H-SiC (000 $\bar{1}$) at 1570 °C is equal to the mean value reported at 1500 °C [i.e. 15 nm; solid square in Fig. 1(a)]¹⁷ and that the ratio of λ_{Si} on 6H-SiC (000 $\bar{1}$) to λ_{Si} on 6H-SiC (000 $\bar{1}$) at 1570 °C [reported by Kimoto and Matsunami;¹⁵ solid arrow in Fig. 2] is the same as the ratio of $\lambda_{\text{C}_2\text{H}_2}$ on 4H-SiC (000 $\bar{1}$) to $\lambda_{\text{C}_2\text{H}_2}$ on 4H-SiC (000 $\bar{1}$) at 1570 °C [dotted arrows in Fig. 2], $\lambda_{\text{C}_2\text{H}_2}$ on 4H-SiC (000 $\bar{1}$) at 1570 °C becomes $0.34 \mu\text{m}$ [open square in Fig. 2]. It is therefore possible that $\lambda_{\text{C}_2\text{H}_2}$ is larger than $0.324 \mu\text{m}$.

In conclusion, we estimated $\sigma_{\text{step}}/\sigma$ to be as large as 0.14 in the reported case of SiC CVD on 4H-SiC (000 $\bar{1}$). By experimentally determining surface diffusion length and taking $\sigma_{\text{step}}/\sigma$ into account, we can improve the accuracy of BCF analysis of SiC and other semiconductors.

ORCID iDs Kazuhiro Mochizuki <https://orcid.org/0000-0002-8687-2568> Tomoyoshi Mishima <https://orcid.org/0000-0002-1332-1351>

- 1) T. Kimoto, M. Kaneko, K. Tachiki, K. Ito, R. Ishikawa, X. Chi, D. Stefanakis, T. Kobayashi, and H. Tanaka, IEEE Int. Electron Devices Meeting, 2021, p. 761.
- 2) X. Wang, H. Wen, and Y. Zhu, Asia Conf. Power and Electrical Eng., 2021.
- 3) T. Kimoto and J. A. Cooper, *Fundamentals of Silicon Carbide Technology: Growth, Characterization, Devices and Applications* (Wiley, New York), (Singapore, 2014).
- 4) K. Mochizuki, *Vertical GaN and SiC Power Devices* (Artech House, Boston, MA, 2018).
- 5) J. Lutz, H. Schlagenotto, U. Schuermann, and R. D. Doncker, *Semiconductor Power Devices* (Springer, Berlin, 2011).
- 6) B. J. Baliga, *Silicon Carbide Power Devices* (World Scientific, Singapore, 2005).
- 7) A. Nakazaki, J. Maruyama, T. Kayumi, H. Hamachi, J. Moritani, and S. Hine, Proc. Int. Symp. Power Semiconductor Devices and ICs, 2000, p. 370.
- 8) N. Kuroda, K. Shibahara, W. S. Yoo, S. Nishino, and H. Matsunami, Extended Abstracts of the 19th Conf. on Solid State Devices and Materials, 1987, p. 227.
- 9) H. S. Kong, J. T. Glass, and R. F. Davis, *J. Appl. Phys.* **64**, 2672 (1988).
- 10) J. A. Powell, D. J. Larkin, L. G. Matus, W. J. Choyke, J. L. Bradshaw, L. Henderson, M. Yoganathan, J. Yang, and P. Pirouz, *Appl. Phys. Lett.* **56**, 1442 (1990).
- 11) H. Saitoh and T. Kimoto, *Mater. Sci. Forum* **483–485**, 89 (2005).
- 12) F. C. Frank, Discuss. Faraday Soc. **5**, 67 (1949).
- 13) K. Masumoto, K. Kojima, and H. Okumura, *J. Cryst. Growth* **475**, 251 (2017).
- 14) W. K. Burton, N. Cabrera, and F. C. Frank, Philos. Trans. R. Soc. A **243**, 299 (1951).
- 15) T. Kimoto and H. Matsunami, *J. Appl. Phys.* **78**, 3132 (1995).
- 16) S. Nakamura, T. Kimoto, and H. Matsunami, *J. Cryst. Growth* **270**, 455 (2004).
- 17) K. Mochizuki, *Appl. Phys. Lett.* **93**, 222108 (2008).
- 18) H. C. Abbink, R. M. Broudy, and G. P. McCarthy, *J. Appl. Phys.* **39**, 4673 (1968).
- 19) E. Kasper, *Appl. Phys. A* **28**, 129 (1982).
- 20) T. Nishinaga and K.-I. Cho, *Jpn. J. Appl. Phys.* **27**, L12 (1988).
- 21) K. Mochizuki and T. Nishinaga, *Jpn. J. Appl. Phys.* **27**, 1585 (1988).
- 22) T. Akasaka and H. Yamamoto, *Jpn. J. Appl. Phys.* **53**, 100201 (2014).
- 23) K. Mochizuki, N. Kaneda, K. Hayashi, H. Ohta, F. Horikiri, and T. Mishima, *Jpn. J. Appl. Phys.* **60**, 128003 (2021).

- 24) N. Cabrera and M. M. Levine, *Phil. Mag.* **1**, 450 (1956).
- 25) T. Nishinaga, *Jpn. J. Appl. Phys.* **54**, 050101 (2015).
- 26) T. Nishinaga, *Kessho Seicho (Crystal Growth)* (Asakura, Tokyo, 2014), p. 89.
- 27) C. D. Stinespring and J. C. Wormhoudt, *J. Cryst. Growth* **87**, 481 (1988).
- 28) M. D. Allendorf and R. J. Kee, *J. Electrochem. Soc.* **138**, 841 (1991).
- 29) T. Kimoto, Step-Controlled Epitaxial Growth of α -SiC and Device Applications (dissertation) Kyoto Univ (1996).