

BRIEF NOTE

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## Analysis of surface diffusion of carbon- and nitrogen-containing molecules during homoepitaxial growth of 4H-SiC (0001) under silicon-rich conditions

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Reported experimental results on homoepitaxial 4H-SiC grown by chemical vapor deposition on 1°- and 4°-off (0001) surfaces under silicon-rich conditions in a SiH<sub>4</sub>-C<sub>3</sub>H<sub>8</sub>-N<sub>2</sub>-H<sub>2</sub> system are quantitatively analyzed according to surface diffusion theory dealing with step dynamics. The surface-diffusion lengths of carbon- and nitrogen-containing molecules are, respectively, estimated to be  $\lambda_C = 25$  nm and  $\lambda_N \geq \lambda_C$  at 1773 K. This magnitude relationship agrees with the reported assumption made for the variation in nitrogen concentration on (000 $\bar{1}$ ) facets of 4H-SiC grown by physical vapor transport. © 2020 The Japan Society of Applied Physics

Toward the realization of an advanced energy-saving society, SiC has been used for highly efficient power devices despite its polytypism.<sup>1,2)</sup> This is due to homoepitaxial growth on misoriented (0001) substrates (with an off angle  $\theta$  being 1° or larger),<sup>3-6)</sup> in which polytype control is achieved by step-flow growth during chemical vapor deposition (CVD). Even in the case  $\theta = 1^\circ$ , good surface morphology was achieved in a conventional SiH<sub>4</sub>-C<sub>3</sub>H<sub>8</sub>-N<sub>2</sub>-H<sub>2</sub> system when growth temperature was 1773 K, growth pressure was 80 Torr, and the atomic ratio of carbon and silicon in supplied gasses ( $C/Si$ ) was less than unity (i.e. silicon-rich conditions).<sup>6)</sup>

With respect to step flow growth, the Burton-Cabrera-Frank (BCF) theory dealing with step dynamics<sup>7)</sup> has been applied for molecular beam epitaxy (MBE) to discuss the surface diffusion of silicon adatoms,<sup>8,9)</sup> gallium adatoms,<sup>10)</sup> and As<sub>*j*</sub> and Sb<sub>*j*</sub> (*j* = 1, 2, 4) molecules,<sup>11)</sup> for CVD to discuss the surface diffusion of silicon adatoms,<sup>12-16)</sup> silicon or carbon clusters,<sup>17)</sup> C<sub>2</sub>H<sub>2</sub> molecules,<sup>18)</sup> and aluminum-containing molecules;<sup>19)</sup> for physical vapor transport (PVT) to discuss the surface diffusion of carbon adatoms<sup>20)</sup> and nitrogen adatoms.<sup>21)</sup> In contrast, Ferro and Chaussende<sup>22)</sup> contested the validity of these applications of the BCF theory by pointing out the reported  $\theta$ -independent aluminum concentration (i.e.  $k$  in the diluted solid solution Al<sub>*k*</sub>Si<sub>1-*k*</sub>C) in CVD-grown 4H-SiC.<sup>23)</sup> In Ref. 23, however,  $C/Si$  was small (i.e. 1.8),<sup>24)</sup> which results in  $k$  being mainly limited by the desorption flux of aluminum-containing molecules.<sup>19)</sup> When  $C/Si$  is large (i.e. 4-6), on the other hand,  $k$  is mainly limited by the surface-diffusing flux of aluminum-containing molecules,<sup>19)</sup> agreeing with the reported  $\theta$ -dependent aluminum concentration in CVD-grown 4H-SiC.<sup>25)</sup> While aluminum (a p-type dopant in 4H-SiC) substitute silicon sublattice, nitrogen (an n-type dopant in 4H-SiC) substitute carbon sublattice.<sup>26)</sup> Judging from the so-called “site competition” proposed by Larkin et al.,<sup>27)</sup> we consider the above-described situation is reversed in the case of nitrogen-doped 4H-SiC; namely, the surface-diffusing flux of nitrogen-containing molecules dominates when  $C/Si$  is small.

Ferro and Chaussende proposed a model on nitrogen incorporation at the 4H-SiC {0001} terraces rather than step-edges.<sup>22)</sup> In their model, nitrogen incorporation is assumed to be driven by the formation of carbon vacancies, due to H<sub>2</sub> etching, at the surface or near the surface. This model, however, cannot explain the variation in nitrogen doping on (000 $\bar{1}$ ) facets of 4H-SiC grown by PVT at 2573-2673 K.<sup>21)</sup> In contrast, Yokomoto et al. successfully explained the nitrogen-doping variation by the BCF theory with an assumption that surface-diffusion length of nitrogen adatoms is longer than that of carbon adatoms.<sup>21)</sup>

Since this assumption has yet to be verified, the present study deals with CVD, instead of PVT, of 4H-SiC to discuss the surface diffusion of carbon- and nitrogen-containing molecules.

Among the experimental studies on the effect of  $\theta$  on nitrogen incorporation into 4H-SiC,<sup>6,25,28)</sup> CVD growth under silicon-rich conditions was carried out by Saito and Kimoto<sup>6)</sup> only. We therefore used the results of their experiments<sup>6)</sup> whose growth conditions are described above. During step-flow growth under such silicon-rich conditions, almost all the step edges are considered to be occupied by silicon,<sup>18)</sup> and they can accept no more silicon atoms until another carbon atom enters the step edges, as discussed in the case of GaAs MBE under gallium-rich conditions.<sup>29)</sup> This was experimentally confirmed by the growth rate  $R$  under silicon-rich conditions being limited by the supply of carbon.<sup>6)</sup> Figure 1 shows our surface model, where Si-C bilayer steps with height  $h$  are separated by equal distance  $\lambda_0$ . SiC homoepitaxial growth on off-oriented (0001) substrates is known to result in macroscopic step bunching; in the case of 4H-SiC, four-bilayer height is dominant, i.e.  $h = 1.01$  nm.<sup>30)</sup> The step edges are assumed to act as a perfect sink for the diffusing carbon- and nitrogen-containing molecules on the surface.

Since the net fluxes of carbon- and nitrogen-containing molecules onto the surface are equal to the diffusion fluxes toward the step edges, the continuity equations are<sup>7)</sup>

$$-D_C d^2 n_C(y) / dy^2 = F_C - n_C(y) / \tau_C, \quad (1a)$$

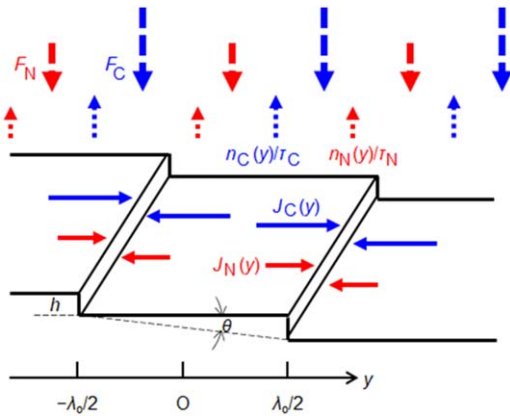
$$-D_N d^2 n_N(y) / dy^2 = F_N - n_N(y) / \tau_N, \quad (1b)$$

where  $D_i$  and  $n_i$  ( $i = C, N$ ) are the surface diffusivity and the surface density of  $i$ -containing molecules, respectively,  $F_i$  ( $i = C, N$ ) is the flux of  $i$ -containing molecules arriving at the surface, and  $\tau_i$  ( $i = C, N$ ) is the mean residence time of  $i$ -containing molecules on the surface. Under the boundary condition where  $n_i(\pm\lambda_0/2)$  takes its equilibrium value  $n_{i0}$  ( $i = C, N$ ),<sup>10)</sup> the solutions of Eqs. (1a) and (1b) are, respectively, given by

$$n_C(y) = F_C \tau_C + (n_{C0} - F_C \tau_C) [\cosh(y/\lambda_C) / \cosh(\lambda_0/2\lambda_C)], \quad (2a)$$

$$n_N(y) = F_N \tau_N + (n_{N0} - F_N \tau_N) [\cosh(y/\lambda_N) / \cosh(\lambda_0/2\lambda_N)], \quad (2b)$$

where  $\lambda_i \equiv (D_i \tau_i)^{1/2}$  ( $i = C, N$ ) is the surface-diffusion length of  $i$ -containing molecules. The flows of  $i$ -containing



**Fig. 1.** (Color online) Schematic illustration of the stepped surface.  $y$ -axis is taken perpendicular to the step edge and its origin at the middle point between steps.  $\lambda_C$ : mean step distance;  $F_C$ : incident flux of carbon-containing molecules;  $F_N$ : incident flux of nitrogen-containing molecules;  $n_C$ : surface concentration of carbon-containing molecules;  $n_N$ : surface concentration of nitrogen-containing molecules;  $\tau_C$ : mean residence time of carbon-containing molecules;  $\tau_N$ : mean residence time of nitrogen-containing molecules;  $J_C$  and  $J_N$ : surface diffusion fluxes of carbon- and nitrogen-containing molecules.

molecules in the  $y$  direction [ $J_i(y)$  in Fig. 1] are obtained as

$$J_C(y) = \lambda_C(F_C - n_{C0}/\tau_C) \sinh(y/\lambda_C) / \cosh(\lambda_C/2\lambda_C), \quad (3a)$$

$$J_N(y) = \lambda_N(F_N - n_{N0}/\tau_N) \sinh(y/\lambda_N) / \cosh(\lambda_C/2\lambda_N). \quad (3b)$$

The step velocity is calculated by considering carbon-containing molecules diffusing from both the left and right

sides of the step edges.  $R$  is given by the product of the step velocity and  $h/\lambda_C$  as follows:

$$R = (2h\lambda_C/n_C\lambda_C)(F_C - n_{C0}/\tau_C) \tanh(\lambda_C/2\lambda_C), \quad (4)$$

where  $n_C$  is the density of sites of adsorbed carbon-containing molecules on the surface. If  $n_C$  is assumed to be equal to the density of silicon adatom sites on the surface ( $1.21 \times 10^{15} \text{ cm}^{-2}$ ),<sup>13,18</sup>  $F_C - n_{C0}/\tau_C$  can be calculated from Eq. (4).

Based on the same experimental results,<sup>6</sup> one of the present authors estimated  $\lambda_C$  to be 24–36 nm at 1773 K for  $\theta = 1^\circ - 45^\circ$ . Here we re-examine  $\lambda_C$  by limiting the experimentally obtained  $R(\theta \text{ (deg)}, C/Si)$  in Ref. 6 to the cases of  $\theta = 1^\circ$  and  $4^\circ$ ; namely,  $R(1, 0.5) = 1.93 \mu\text{m h}^{-1}$ ,  $R(1, 0.6) = 2.11 \mu\text{m h}^{-1}$ ,  $R(1, 0.75) = 2.91 \mu\text{m h}^{-1}$ ,  $R(4, 0.5) = 2.53 \mu\text{m h}^{-1}$ ,  $R(4, 0.6) = 3.19 \mu\text{m h}^{-1}$ , and  $R(4, 0.75) = 3.88 \mu\text{m h}^{-1}$ . By assuming  $\lambda_C$  is equal to 20, 25, or 30 nm, we calculated  $F_C - n_{C0}/\tau_C$  from Eq. (4) as a function of  $C/Si$ , as shown in Fig. 2. In each figure, the line shows the least-squares fit to the experimental results. Since  $C/Si$  was experimentally varied under a fixed flow rate of  $\text{SiH}_4$ ,<sup>6</sup> it is reasonable that  $F_C$  is a linear function of  $C/Si$ . The absolute values of the intercept with the vertical axes in Figs. 2(a)–2(c) give an equilibrium desorption flux of carbon-containing molecules  $n_{C0}/\tau_C$ . Due to the best fit to the experimental results [Fig. 2(b)],  $\lambda_C$  is determined to be 25 nm.

By assuming a highly diluted solid solution of  $\text{SiC}_{1-x}\text{N}_x$  ( $x \ll 1$ ),<sup>31</sup> we consider  $J_N(\lambda_C/2)$  being equal to  $x J_C(\lambda_C/2)$ . Therefore, the following equation is obtained from Eqs. (3a) and (3b):

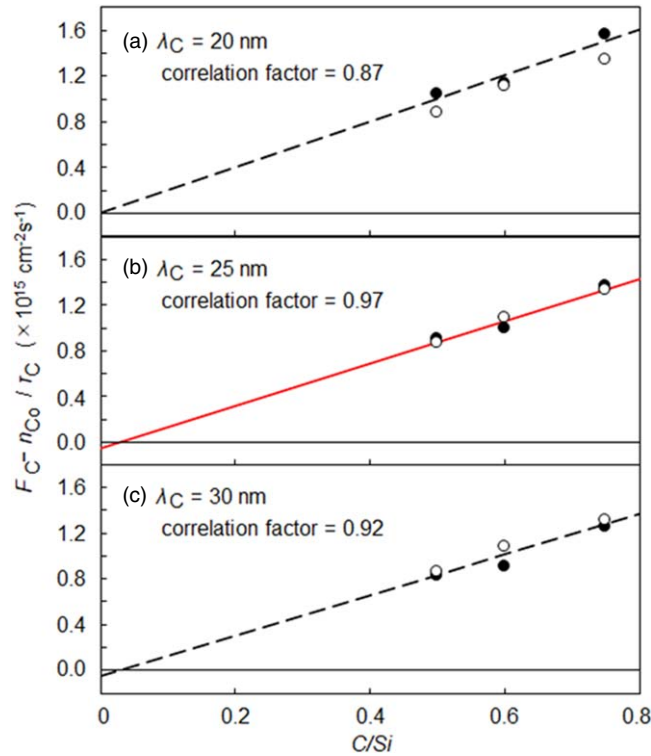
$$F_N - n_{N0}/\tau_N = x(\lambda_C/\lambda_N)(F_C - n_{C0}/\tau_C) [\tanh(\lambda_C/2\lambda_C) / \tanh(\lambda_C/2\lambda_N)]. \quad (5)$$

Since the volume of the Si–C pair is  $2.07 \times 10^{-23} \text{ cm}^3$ ,<sup>18</sup> the experimentally obtained  $x(\theta \text{ (deg)}, C/Si)$  in Ref. 6 is calculated as follows:  $x(1, 0.5) = 3.8 \times 10^{-4}$ ,  $x(1, 0.75) = 4.9 \times 10^{-4}$ ,  $x(1, 1) = 2.9 \times 10^{-4}$ ,  $x(4, 0.5) = 5.0 \times 10^{-4}$ ,  $x(4, 0.75) = 6.5 \times 10^{-4}$ , and  $x(4, 1) = 3.0 \times 10^{-4}$ . From Fig. 2(b),  $F_C - n_{C0}/\tau_C$  is obtained as  $8.4 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$  at  $C/Si = 0.5$ ,  $1.3 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$  at  $C/Si = 0.75$ , and  $1.7 \times 10^{15} \text{ cm}^{-2} \text{ s}^{-1}$  at  $C/Si = 1$ . Putting these values into Eq. (5) leads to  $F_N - n_{N0}/\tau_N$  as functions of  $\lambda_N$  and  $C/Si$ . To clarify the magnitude relationship between  $\lambda_N$  and  $\lambda_C$ , we assume  $\lambda_N$  as  $\lambda_C/2$  [=12.5 nm, Fig. 3(a)],  $\lambda_C$  [=25 nm, Fig. 3(b)], and  $2\lambda_C$  [=50 nm, Fig. 3(c)]. Since the experiments were carried out under a fixed flow rate of  $\text{N}_2$ ,<sup>6</sup>  $F_N - n_{N0}/\tau_N$  is independent of  $\theta$  and  $C/Si$  as long as  $F_N \gg n_{N0}/\tau_N$  is satisfied. This is nearly realized when  $\lambda_N$  is equal to or longer than  $\lambda_C$  at 1773 K [Figs. 3(b) and 3(c)]. When  $\lambda_N$  is shorter than  $\lambda_C$ , on the other hand, the calculated  $F_N - n_{N0}/\tau_N$  for  $\theta$  of  $1^\circ$  disagrees with the calculated  $F_N - n_{N0}/\tau_N$  for  $\theta$  of  $4^\circ$  [Fig. 3(a)]. Based on these results, we concluded that  $\lambda_N \geq \lambda_C$  at 1773 K.

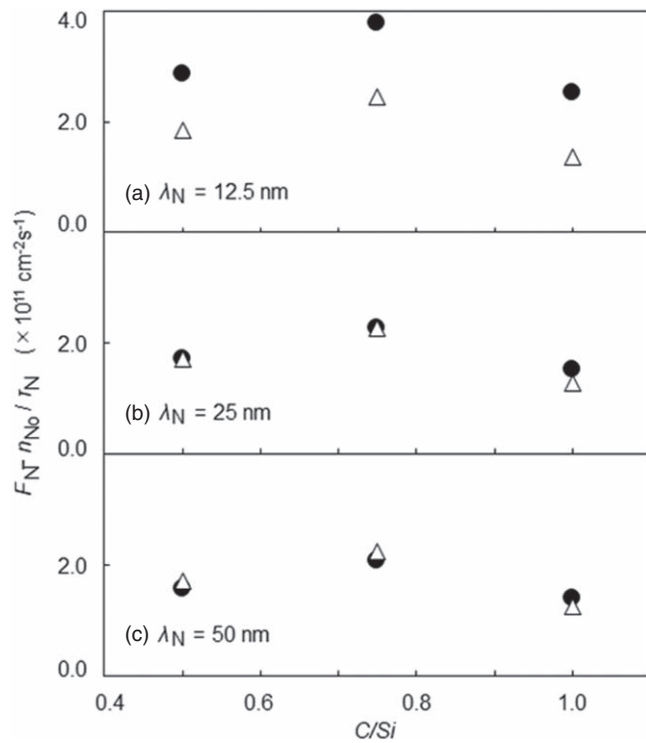
$\lambda_i$  ( $i = C, N$ ) is generally expressed as

$$\lambda_i = a \exp[(E_i^{\text{des}} - E_i^{\text{diff}}) / 2k_B T_g], \quad (6)$$

where  $a$  is the interatomic distance [i.e. 0.3 nm in the case of 4H-SiC (0001)],  $T_g$  is growth temperature, and  $E_i^{\text{des}}$  and  $E_i^{\text{diff}}$  are, respectively, the desorption energy and the activation energy of surface diffusion of  $i$ -containing molecules. Putting  $\lambda_C = 25 \text{ nm}$ ,  $\lambda_N \geq 25 \text{ nm}$ , and  $T_g = 1773 \text{ K}$  into Eq. (6)



**Fig. 2.** (Color online) Dependences of  $F_C - n_{C0}/\tau_C$  on  $C/Si$  calculated from Eq. (4) with assumptions of  $\lambda_C$  being equal to (a) 20, (b) 25, and (c) 30 nm. Lines show least-squares fit to experimental results (solid symbols:  $\theta = 1^\circ$ ; open symbols:  $\theta = 4^\circ$ ) at 1773 K.<sup>6</sup>



**Fig. 3.** Dependences of  $F_N - n_{No}/\tau_N$  on  $C/Si$  calculated from Eq. (5) with assumptions of  $\lambda_N$  being equal to (a) 12.5, (b) 25, and (c) 50 nm. Solid ( $\theta = 1^\circ$ ) and open ( $\theta = 4^\circ$ ) symbols denote the experimental results at 1773 K.<sup>6)</sup>

results in  $E_C^{des} - E_C^{diff} = 1.31$  eV and  $E_N^{des} - E_N^{diff} \geq 1.31$  eV. Under the assumption that these  $E_i^{des} - E_i^{diff}$  values are the same in the case of PVT-grown 4H-SiC (000 $\bar{1}$ ), the relation  $\lambda_N \geq \lambda_C$  (=90–112 nm) still holds at 2573–2673 K, which agrees with the reported assumption of  $\lambda_N > \lambda_C$  made for the observed nitrogen-doping variation on (000 $\bar{1}$ ) facets of PVT-grown 4H-SiC.<sup>21)</sup>

In conclusion, the estimated relations  $\lambda_C = 25$  nm and  $\lambda_N \geq \lambda_C$  at 1773 K in the case of CVD was found to agree with the reported assumption made in the case of PVT.

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