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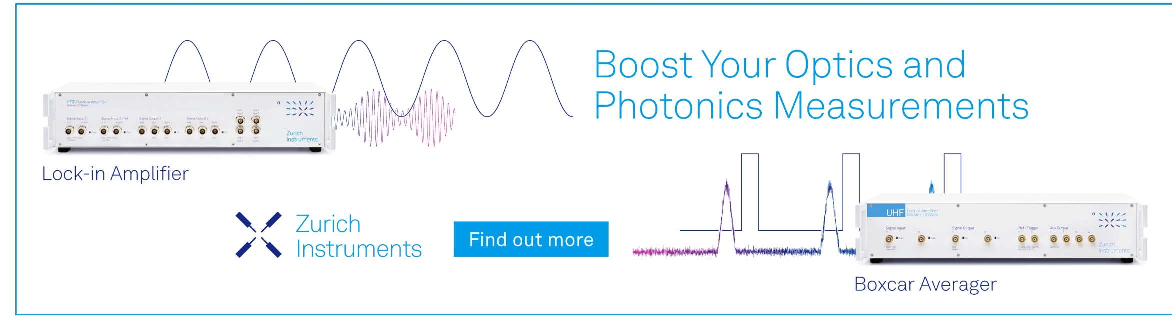

Theoretical consideration of step-flow and two-dimensional nucleation modes in homoepitaxial growth of 4*H*-SiC on (0001) vicinal surfaces under silicon-rich condition

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Reported experimental results on homoepitaxial growth of 4*H*-SiC on (0001) Si-face vicinal surfaces under silicon-rich conditions in a $SiH_4-C_3H_8-H_2$ system are quantitatively analyzed according to the surface-diffusion theory dealing with step dynamics. The surface-diffusion length of C_2H_2 molecules, which are the main carbon-containing chemical species reacting with silicon adatoms on the surface, is determined to be 12–36 nm at 1500 °C. According to the two-dimensional nucleation theory using these values, the maximum growth rate for step-flow growth is estimated as a function of the off-angle of 4*H*-SiC substrates. © *2008 American Institute of Physics*. [DOI: 10.1063/1.3043433]

Despite its polytypism, silicon carbide (SiC) has shown significant promise for high-power device applications.[1] This is due to homoepitaxial growth on off-oriented (0001) substrates (with an off angle θ larger than 1.5°),[2–4] in which polytype control is achieved by step-flow growth. On the other hand, to eliminate the basal plane dislocation issue that has hampered the reliability of bipolar[5] and metal-oxide-semiconductor power devices,[6] there has been growing interest in the growth of 4*H*-SiC on nominal[7] and vicinal[8,9] (0001) surfaces. Although an uncommon gas (methyltrichlorosilane) was supplied in Ref. 7, a conventional $SiH_4-C_3H_8-H_2$ growth system for vapor-phase epitaxy (VPE) of SiC also achieved good surface morphology on 4*H*-SiC (0001) vicinal surfaces when the C/Si ratio (r is the atomic ratio of carbon and silicon in supplied gases) is less than unity: $r=0.5-0.75$ for $\theta=1°$, growth temperature $T_g=1500$ °C, growth pressure, $P_g=80$ Torr,[8] and $r=0.6$ for $\theta=0.79°$, $T_g=1600$ °C, and $P_g=250$ mbar.[9]

Homoepitaxial growth on vicinal (0001) surfaces was achieved by Powell *et al.*[10] in 1991 for 6*H*-SiC with θ as small as 0.1°. Their polytype control was attributed to the presence of surface disturbances (e.g., dislocations), not to the surface step density.[10] In recent studies on homoepitaxial growth of 4*H*-SiC, however, the step bunching was observed when $r=1$ for $\theta=1°$ (Ref. 8) and $r=0.6$ for $\theta=0.42°$,[9] which means the epitaxial growths in Refs. 8 and 9 were carried out in the step-flow mode.[11] During step-flow growth under silicon-rich conditions, almost all of the step edges are assumed to be occupied by silicon [Fig. 1(a)], and they can accept no more silicon atoms until another carbon atom enters the step edges, as discussed by Nishinaga and Suzuki[12] with regards to molecular beam epitaxy (MBE) of GaAs under gallium-rich conditions.

According to the simulation of surface mass fluxes in $SiH_4-C_3H_8-H_2$ growth system,[13,14] the surface reaction of silicon adatoms with C_2H_2,

$$Si+(1/2)C_2H_2 \leftrightarrow SiC+(1/2)H_2 \quad (1)$$

is most active among the surface reactions involved, including other carbon-containing species such as C_2H_4, CH_4, CH_3, Si_2C, and CH_2. Based on the reaction in Eq. (1), Kimoto and Matsunami analyzed using the Burton–Cabrera–Frank[15] (BCF) theory, the surface diffusion of silicon adatoms under carbon-rich conditions. However, they have not discussed the case under silicon-rich conditions.[16]

The BCF theory dealing with step dynamics[15] has been applied for MBE in order to discuss the surface diffusion of silicon adatoms,[17,18] gallium adatoms,[19] and As_i and Sb_i molecules ($i=1$, 2, and 4).[20] Based mainly on the last approach by Mochizuki and Nishinaga,[20] the present study deals with surface diffusion of C_2H_2 molecules during VPE growth on 4*H*-SiC (0001) Si-face vicinal surfaces under silicon-rich conditions.

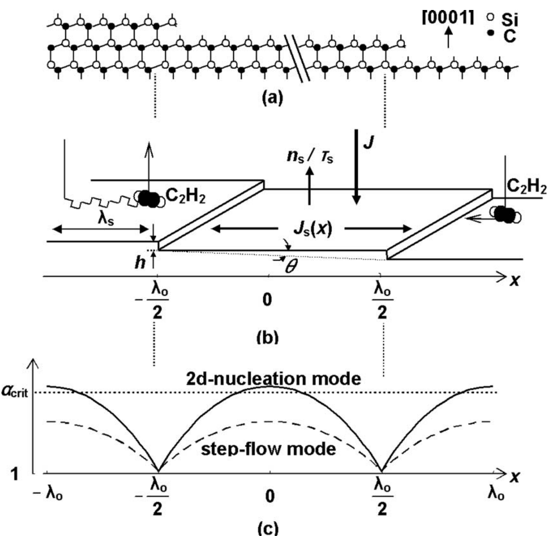

FIG. 1. Schematic of growing silicon-rich 4*H*-SiC (0001) Si-face vicinal surface showing (a) atomic arrangement (hydrogen-passivation effect ignored) and (b) surface diffusion of C_2H_2 molecules, and (c) distributions of supersaturation ratio for step-flow (broken curve) and two-dimensional nucleation modes (solid curve).

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Figure 1(b) schematically illustrates the surface model, where Si–C bilayer steps with height h are separated by equal distance λ_o. It is known that SiC homoepitaxial growth on off-oriented (0001) substrates results in microscopic step bunching, which is peculiar to SiC polytypes.[11] In the case of 4*H*-SiC, two- and four-bilayer heights are dominant,[11] i.e., $h=0.504$ or 1.01 nm. The steps are assumed to act as a uniform sink for the diffusing silicon adatoms and C_2H_2 molecules on the surface. As reported by Saito and Kimoto,[8] growth rate R is limited by the supply of carbon under silicon-rich conditions. This fact allows the assumption that the surface diffusion of C_2H_2 molecules is a rate-limiting process.

Two modes are known to exist in the epitaxial growth of 4*H*-SiC. The first is step-flow growth mode, where nucleation on terraces does not occur. Since the net flux of C_2H_2 molecules onto the surface is equal to the diffusion flux toward steps, the continuity equation is[15]

$$-D_s d^2 n_s(x)/dx^2 = J - n_s(x)/\tau_s, \tag{2}$$

where D_s and $n_s(x)$ are the surface diffusivity and the surface density of C_2H_2 molecules, respectively, and J is the flux of C_2H_2 molecules arriving at the surface. Under the boundary condition where $n_s(x)$ takes its equilibrium value n_{so} at the step edges,[19] the solution of Eq. (2) is given by

$$n_s(x) = J\tau_s + (n_{so} - J\tau_s)[\cosh(x/\lambda_s)/\cosh(\lambda_o/2\lambda_s)], \tag{3}$$

where τ_s and $\lambda_s[\equiv(D_s\tau_s)^{1/2}]$ are the mean residence time and the surface diffusion length of C_2H_2 molecules, respectively. The flow of C_2H_2 molecules in the x direction $J_s(x)$ is obtained as

$$\begin{aligned} J_s(x) &= -D_s dn_s(x)/dx \\ &= \lambda_s(J - n_{so}/\tau_s)\sinh(x/\lambda_s)/\cosh(\lambda_o/2\lambda_s). \end{aligned} \tag{4}$$

The step velocity is calculated by considering C_2H_2 molecules diffusing from both the left and right sides of the steps. Since two carbon atoms are provided by one C_2H_2 molecule at the step edges,[20] R is given by the product of the step velocity and tan θ (i.e., h/λ_o) as follows:[16]

$$R = (4h\lambda_s/n_o\lambda_o)(J - n_{so}/\tau_s)\tanh(\lambda_o/2\lambda_s), \tag{5}$$

where n_o is the density of sites of adsorbed C_2H_2 molecules on the surface. When $\lambda_s \gg \lambda_o/2$, R becomes independent of λ_o [i.e., $(2h/n_o)(J-n_{so}/\tau_s)$]. Since, according to Ref. 8 R depends little on θ when $\theta=4°-45°$ but decreases when $\theta=1°$, λ_s is estimated to be comparable to or less than $h/(2 \tan 1°)$ [$h/(2 \tan 1°)=14.4$ nm for $h=0.504$ nm and 28.9 nm for $h=1.01$ nm]. If n_o is assumed to be equal to the density of silicon adatom sites on the surface (1.21×10^{15} cm^{-3}), $J-n_{so}/\tau_s$ can be calculated from Eq. (5). As is clear from Fig. 2, when $\lambda_s=12-18$ nm in the case of $h=0.504$ nm and $\lambda_s=24-36$ nm in the case of $h=1.01$ nm, the least-squares fit of $J-n_{so}/\tau_s$ for $\theta=1°$ fits among those for $\theta=4°-45°$. This λ_s range agrees with the above estimated value (i.e., 14.4 and 28.9 nm).

The absolute values of the intercept with the vertical axes in Figs. 2(a) and 2(b) give an equilibrium desorption flux of C_2H_2 molecules (n_{so}/τ_s) of $(0.5-1.2)\times10^{14}$ cm^{-2} s^{-1}. This corresponds to the equilibrium vapor pressure of C_2H_2 molecules (P_o) of $(0.4-1.0)\times10^{-4}$ Pa, which is obtained from Knudsen's equation,[20]

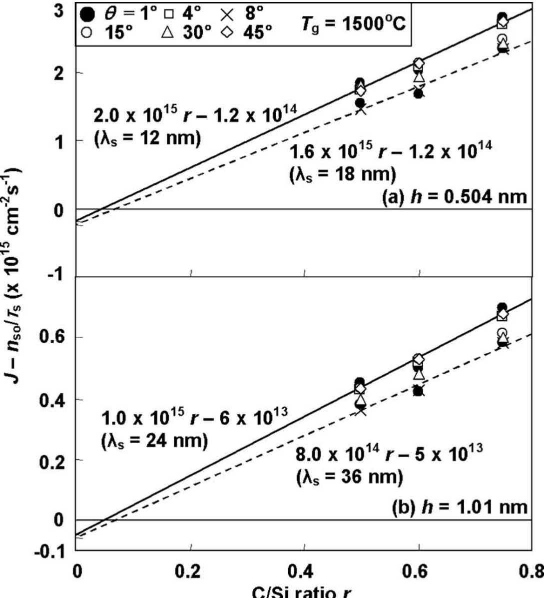

FIG. 2. Dependences of $J-n_{so}/\tau_s$ on C/Si ratio calculated from Eq. (5) for a surface diffusion length of 12–36 nm. Data denoted by symbols are taken from Saito and Kimoto's experiments (see Ref. 8), where 4*H*-SiC was grown on 4*H*-SiC (0001) substrates with an off-angle of 1°–45° in a SiH_4 (1.5–2.0 sccm)-C_3H_8–H_2 (8.0 slm)-Ar (0.8 slm) system (sccm denotes standard cubic centimeters per minute and slm denotes standard liters per minute) at a growth pressure of 80 Torr and a growth temperature of 1500 °C. Solid lines and corresponding equations show the least-squares fit to the results for an off-angle of 1°.

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$$n_{so}/\tau_s = P_o/(2\pi m k_B T_g)^{1/2}, \tag{6}$$

where m is the mass of a C_2H_2 molecule and k_B is Boltzmann's constant. In regard to MBE growth, since molecules can arrive at the growing surface without any barrier and their beam equivalent flux can be measured,[20] n_{so}/τ_s can be obtained from Eq. (6). In regard to VPE growth, however, P_o is difficult to determine because of many related parameters.[21] The procedure described above is thus effective for estimating n_{so}/τ_s for VPE.

Next, the second growth mode, i.e., two-dimensional nucleation on terraces, is considered. Supersaturation ratios α_C and α_{Si} are defined as $n_s(x)/n_{so}$ for C_2H_2 molecules and similarly for silicon adatoms, respectively. As mentioned above, under silicon-rich conditions, the equilibrium vapor pressure of silicon adatoms must be similar to the incoming pressure of silicon, i.e., α_{Si} nearly equals unity.[19] Since α_C reaches a maximum at the center of a terrace, i.e., $x=0$ [Fig. 1(c)], the maximum supersaturation ratio for SiC is obtained from Eq. (3) as

$$\begin{aligned} \alpha_{max} &\equiv \alpha_{Si}\alpha_C(x=0) \approx 1 + (\lambda_o n_o R/4h\lambda_s) \\ &\times(\tau_s/n_{so})\tanh(\lambda_o/4\lambda_s). \end{aligned} \tag{7}$$

Nucleation on terraces becomes dominant when α_{max} exceeds α_{crit} [solid curve in Fig. 1(c)]. For a disk-shaped nucleation per second on a 10×10 nm^2 area, α_{crit} is given by[19]

$$\alpha_{crit} = \exp\{\pi h_1 \Omega \sigma^2/[(65 - \ln 10^{12})k_B^2 T_g^2]\}, \tag{8}$$

where h_1 is the one Si–C bilayer height (0.252 nm), Ω is the volume of the Si–C pair (2.07×10^{-23} cm^3), and σ is the surface free energy, which is assumed to be 2.22 J/m^2, as Kimoto and Matsunami[16] speculated from the calculation for 3*C*-SiC (111) by Pearson *et al.*[22] From Eqs. (7) and (8), the

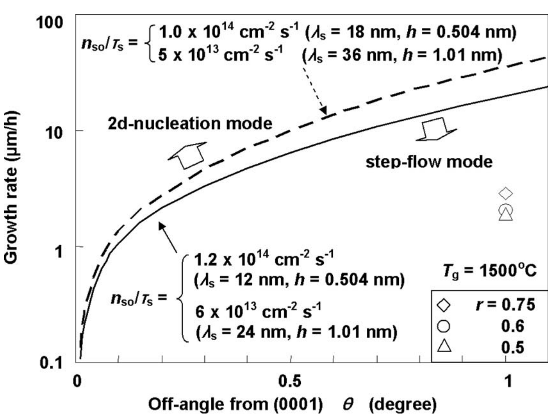

FIG. 3. Off-angle dependences of critical growth rate for a mode transition between step-flow (bottom-right region) and two-dimensional nucleation (top-left region) calculated with three sets of two parameters, namely, equilibrium desorption flux and surface diffusion length of C_2H_2 molecules, obtained from Fig. 2. Data denoted by symbols are taken from the experiment of Saito and Kimoto (see Ref. 8).

off-angle dependence of the critical growth rate (R_c) for mode transition between step-flow and two-dimensional nucleation is calculated at T_g=1500 °C. As is clear from Fig. 3, the range of R_C, originating from the variation in determining λ_s (Fig. 2), does not depend on h (h=0.504 or 1.01 nm). It is also confirmed that the three experimental data for step-flow growth in Ref. 8 are in the bottom-right region under the curves calculated using the n_{so}/τ_s and λ_s values obtained from Fig. 2.

As expected from Eq. (7), R_c increases with increasing n_{so}/τ_s. According to Eqs. (1) and (6), the increase in n_{so}/τ_s, i.e., the increase in P_o, is achieved by the reduction in the SiH_4 flow rate. However, to maintain r at less than unity (silicon-rich conditions), the C_3H_8 flow rate has to be limited, resulting in lower R_c. The calculated curves in Fig. 3 are thus considered to be close to the practical limit at T_g =1500 °C. To carry out a similar calculation at different T_g, e.g., 1600 °C,[9] the dependence of R on r has to be experimentally determined because of the difficulty in estimating P_o described above.

In summary, according to the surface diffusion and two-dimensional nucleation theories, a surface diffusion length of C_2H_2 molecules on 4H-SiC (0001) was derived as 12–36 nm at 1500 °C in a SiH_4–C_3H_8–H_2 system, and the maximum growth rate for step-flow growth was estimated as a function of the off-angle of 4H-SiC substrates.

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