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Models for Impurity Incorporation during Vapor-Phase Epitaxy

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Abstract. Impurity incorporation during vapor-phase epitaxy on stepped surfaces was modeled by classifying rate-limiting processes into i) surface diffusion, ii) step kinetics, and iii) segregation. Examples were shown for i) desorption-limited Al incorporation during chemical vapor deposition (CVD) of (0001) SiC, ii) preferential desorption of C atoms from kinks during CVD of Al-doped (000-1) SiC, and iii) segregation-limited C incorporation during metalorganic vapor-phase epitaxy of (0001), (000-1), and (10-10) GaN.

Introduction

Impurity incorporation during vapor-phase epitaxy has been modeled via, for example, site competition [1,2] and surface vacancies [3,4]. The latter, however, cannot explain the variation in impurity doping around facets [5]. Moreover, in the cases of homoepitaxial growths of SiC and GaN, misoriented substrates are often used for polytype [6] and doping-uniformity [7] controls, respectively. Accordingly, we modeled impurity incorporation during step-flow growth by taking Al-doped SiC and C-doped GaN, as examples. We believe the models should be beneficial for determining allowable off-angle variations for desired doping-level uniformities in advanced devices. Although Al was chosen due to the availability of a thermodynamic model [8], N doping for SiC could be similarly treated under the assumption of the N segregation coefficient being unity [9].

Proposed Models

Impurity incorporation during vapor-phase epitaxy on stepped surfaces was modeled by classifying rate-limiting processes into i) surface diffusion [10], ii) step kinetics [11], and iii) segregation [12] (Table I).

i) **Desorption** limits impurity incorporation at step-edges when surface diffusion length λ is less than a half of the average inter-step distance, λ_o. This should be the case with incorporation of Al, whose λ was estimated to be less than 2 nm at 1550°C [10], into stepped 4H-SiC (0001). This is due to relatively large λ_o (eg., 7.2 nm for $\theta = 8°$) originating from four-bilayer-high steps [13]. Based on the Burton−Cabrera−Frank (BCF) theory [14], we derived the following equation for x in $Al_xSi_{1-x}C$ [10]:

$$F_{Al} / x = [\gamma P_{Si}^{e} / K (2 \pi m_{Al} k_B T_g)^{1/2}] + [F_{Si} - P_{Si}^{e} / (2 \pi m_{Si} k_B T_g)^{1/2}] [\lambda_o / 2\lambda_{Al} \tanh (\lambda_o / 2\lambda_{Al})], \quad (1)$$

where F_i, P_i^e, and m_i (i = Al, Si) are, respectively, the incident flux, equilibrium vapor pressure, and mass of i atom, K and γ are, repectively, the equilibrium constant and activity coefficient for AlC, T_g is growth temperature, and k_B is Boltzmann's constant. Eq. (1) explains why x was independent of the off-angle θ (ranging from 2° to 8°) when the C/Si ratio, r, was small (i.e., 1.8 [15]); due to large P_{Si}^e, the first term in the right-hand side, which corresponds to the Al desorption flux, became dominant (solid line in Fig. 1). Eq. (1) also explains why x increased with θ when r was large (i.e., 4–6 [16]); due to small $P_{\mathrm{Si}}^{\mathrm{e}}$, the second term in the right-hand side, which corresponds to the Al flux incorporated into the solid, became so large that x increased with the step density on the surface (dashed and dotted lines in Fig. 1).

Table I. Rate-limiting processes of impurity incorporation during vapor-phase epitaxy.

Classification of host-atom desorption from kinks	Surface-diffusion length of impurity atoms	
	Less than $\lambda_o/2$	Much larger than $\lambda_o/2$
Preferential desorption of host atoms from kinks	Surface diffusion	Step kinetics
Negligible desorption of host atoms from kinks		Segregation

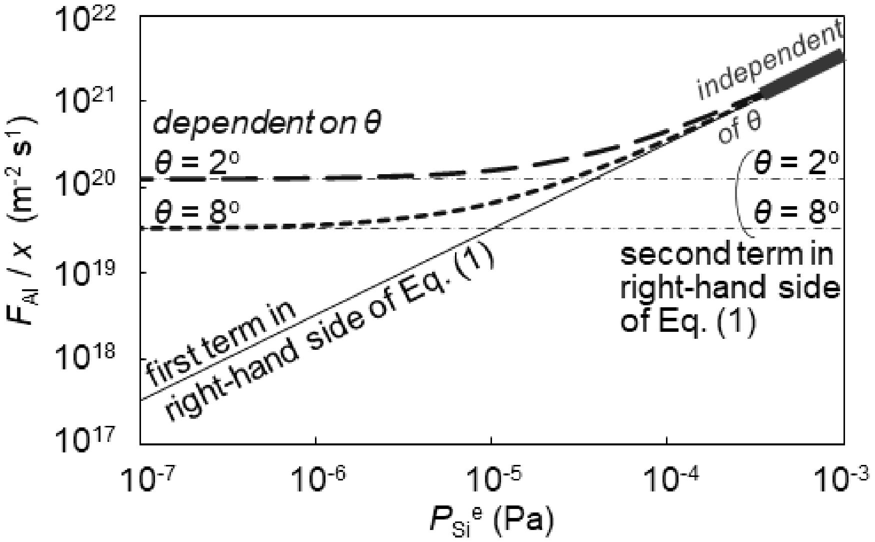

Fig. 1. F_{Al}/x, calculated as first term (solid line) and second term (dashed and dotted lines) in right-hand side of Eq. (1), as a function of equilibrium vapor pressure of Si, with assumptions of T_{g} of 1550°C, growth rate of 1.3 µm/h, and λ_{Al} of 2.0 nm.

ii) Preferential desorption of host atoms from kinks limits impurity incorporation at kinks even when $\lambda >> \lambda_o/2$. This should be the case with incorporation of Al into 4H-SiC (000-1) that has one-bilayer-high steps [13]. We assume that a C atom making two bonds with a Si atom stays at kinks, while that a C atom making one bond with a Si atom easily desorbs from kinks [Fig. 2(a)].

Since r is typically small (eg., $r \leq 6$ [16]), some surface-diffusing Al atoms that arrive at kinks keep waiting (for an average time τ_{C}) until C atoms make one bond with Si atoms at kinks [Fig. 2(b)] before they are incorporated into the solid [Fig. 2(c)]. Based on the reported experimental results [16], surface Al concentration n_{Al} (normalized by the mean residence time τ_{Al}) was calculated (Fig. 3). n_{Al} in the vicinity of step-edges (i.e., local minima in Fig. 3) on (000-1) is much larger than that on (0001), indicating longer τ_{C} on (000-1).

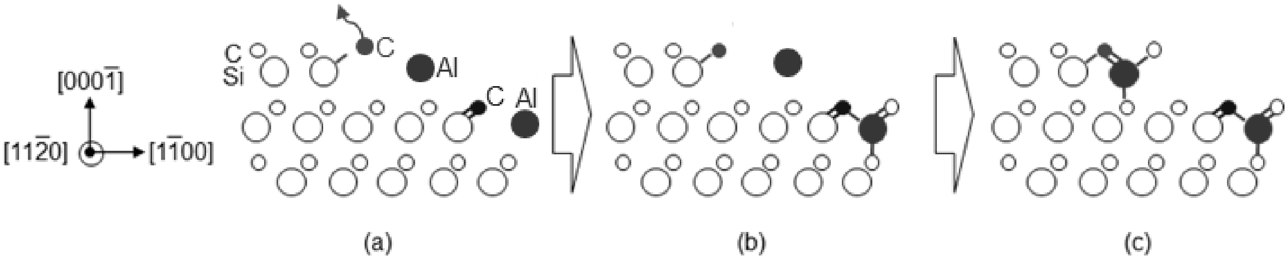

Fig. 2. Schematic illustrations of (a) preferential desorption of a C atom having one bond with a Si atom, (b) adsorption of a C atom to a dangling bond of a Si atom and bonding of an Al atom to two C atoms, and (c) bonding of another Al atom to three C atoms at kinks on 4H-SiC (000-1).

iii) Segregation limits impurity incorporation even when $\lambda >> \lambda_o/2$ and desorption of host atoms from kinks is negligible. This should be the case with incorporation of C into GaN that is typically grown with the N/Ga ratio exceeding 1000 [17−19]; namely, soon after a N atom making one bond with a Ga atom desorbs from kinks, another N atom makes one bond with the Ga atom. When the length of time before the C concentration at the step-edge site reaches its equilibrium value, τ_{step}, is much smaller than the meantime until a C atom incorporated at kinks moves through the step-edge site to the surface site, τ, the C concentration in the solid can be expressed as [20]

$$N = N_{\mathrm{surf}} + (N_{\mathrm{step}} - N_{\mathrm{surf}}) \exp\left(-D / V_{\mathrm{step}}\, a\right), \quad (2)$$

where N_{surf} and N_{step} are, respectively, the equilibrium C concentrations at the surface site and at the step-edge site, D is the diffusion coefficient in the solid, V_{step} is the average step velocity, and a is the lattice constant. As shown in Fig. 4, the results for (0001) [17], (000-1) [18], and (10-10) [19] growths are well reproduced with D of 2×10^{-13} $\mathrm{cm^2/s}$ that agrees with the experimentally determined value [21].

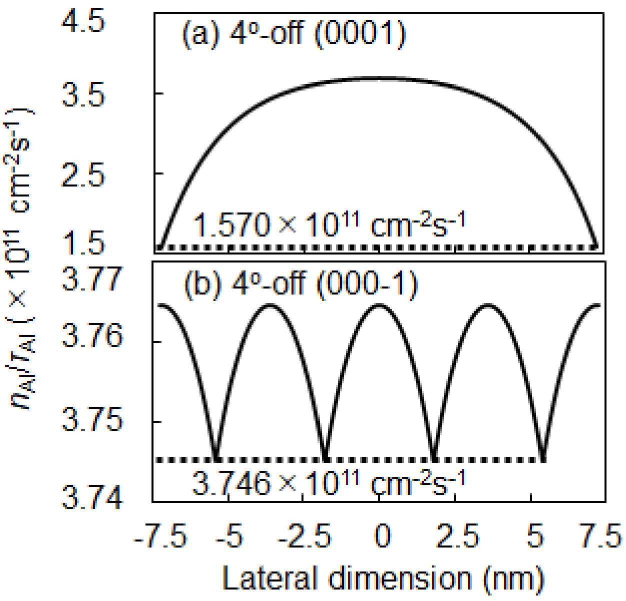

Fig. 3. Distribution of $n_{\mathrm{Al}}/\tau_{\mathrm{Al}}$ calculated with assumptions of T_g of 1550°C, growth rate of 1.3 µm/h, r of 6, and λ_{Al} of 2.0 nm.

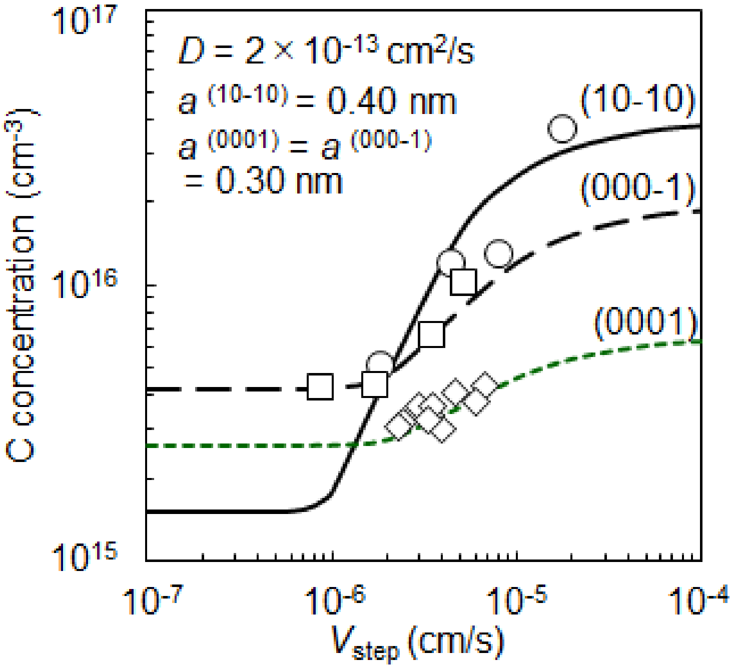

Fig. 4. Step-velocity dependences of carbon concentrations fitted to the reported results [17−19].

Summary

Impurity incorporation during step-flow growth was modeled and exemplified by SiC: Al and GaN: C cases. We believe the proposed models should contribute to determining allowable off-angle variations for desired doping-level uniformities in advanced SiC and GaN devices.

Acknowledgments

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