First-principles analysis of the activation energy of solute-additive bonds in the solvent of the SiC solution growth

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In the solution growth of SiC, controlling the degree of step-bunching is important because macrosteps convert threading dislocations to defects on the basal plane and it enables to grow the high-quality crystal [1]. The composition of solvent has a significant effect on step structure. The experiment by Komatsu et al. shows that Al and Sc suppress the formation of macrosteps, while Fe, Mn, and Nb promote it [2]. From the in-situ observation, in the SiC solution growth, the relationship between step velocity and step height disappeared when Al is added and step-bunching is suppressed [3]. This indicates that the rate-limiting process shifts from diffusion to interface kinetics. In this study, we investigated the stability of bonding between the growth unit (C atom) and additives (X) in the solvent to reveal the process of the SiC solution growth.

Using first-principles molecular dynamics, we calculated the activation free energies of bond formation E_f and dissociation E_d of the C-X bond in the solvent. The free energies have been obtained by the blue moon ensemble method. The modeled solvents are Si-40at%Cr-2at%X (X=Al, Sc, Fe, Nb, Mn). All models consist of 55 atoms, one of them is C, another one of them is X, and the remaining 53 atoms are solvent (Si and Cr). The Si-Cr based solvent is often used to improve C solubility and growth rate.

The stableness of the C-X bond in the solvent was investigated based on the relationship between the value of $k_\mathrm{B}T$ and the calculated bond dissociation energies E_d listed in Table 1. According to this, the bond between the additives which promote macrosteps (Fe, Nb, and Mn) and C is stable ($E_\mathrm{d} > k_\mathrm{B}T$), while the bond between the additives which suppress macrosteps (Al and Sc) and C is unstable ($E_\mathrm{d} < k_\mathrm{B}T$) in the solvent.

A recent study using the kinetic Monte Carlo method showed that when the impurity-solute bond energy on the kink is lower than about $k_\mathrm{B}T$, the step propagation is inhibited, however when it is higher than about 1.5 $k_\mathrm{B}T$, the step velocity is accelerated [4]. A change in step velocity implies a change in the rate of the kinetic process because supersaturation on the surface is fixed in that model. Based on these findings, when Al and Sc are added, step propagation is inhibited, that is the incorporation of the growth unit is inhibited. It is supposed that the rate-limiting process is shifted to the kinetic process and step bunching is suppressed. In contrast, when Fe, Nb, and Mn are added, step velocity i.e. the incorporating rate of the growth unit is accelerated because the bond energy is higher than $1.5\,k_\mathrm{B}T$, the rate-limiting process is shifted to the diffusion process and step-bunching is promoted.

Table 1.
Relationship between bonding energy and $k_\mathrm{B}T$.

additive	macrostep	bond energy
Al, Sc	suppress	$E_\mathrm{d} < k_\mathrm{B}T$
Fe, Nb, Mn	promote	$E_\mathrm{d} > k_\mathrm{B}T$

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