Numerical study on crystal growth hysteresis in spiral growth

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Step dynamics is one of the fundamental physical processes of crystal growth. There are numerous steps with atomistic-scale heights on the crystal surface. A growth unit such as an atom or molecule that lands on the surface usually migrates laterally until it reaches the steps –or until it desorbs into the mother phase. The growth unit that reaches a step becomes incorporated into the crystal, leading to advancement of the step. Every passage of the step increases the height of the surface by a monolayer (layer-by-layer growth). Therefore, the understanding of what determines the generation of steps and the rate of the advancement is essential to elucidate the crystal growth mechanism. In this study, we focus attention on the growth hysteresis, which is one of the impurity-induced phenomena on the step dynamics.

Let us consider the crystal growth from aqueous solution. When the solution includes impurities, the crystal growth rate when the supersaturation is increased is different from that when it is decreased. The growth hysteresis has been observed in some experimental setups with different combinations of crystal and impurity, suggesting the existence of some universal impurity effect. Therefore, the elucidation of the growth hysteresis mechanism leads to deepen our knowledge of impurity effects on crystal growth. It has been considered that the hysteresis results from the interaction between the impurities adsorbed on the crystal surface and advancing steps. As the supersaturation is decreased, the step velocity is decreased, leading to the increase in ad-impurities, then it retards the step advancement further. This positive feedback causes the catastrophic change in the step velocity. Once the step motion stops, the surface will be polluted by ad-impurities until the impurity desorption and adsorption reach equilibrium. Therefore, it is difficult for the step to restart again even if the supersaturation is increased again; namely, it is hysteresis. The interdependence between the step velocity and the number of ad-impurities was formulated based on a mean field approximation, elucidating the existence of multi-solutions of the step velocity at a certain supersaturation region [1]. In addition, the numerical simulations reproduced the hysteresis of the step velocity in the realistic situation on which the mean field approximation is inapplicable [2]. In this study, we investigate the hysteresis of the growth rate normal to the crystal surface.

We adopt a numerical scheme that combines a phase-field (PF) method and a Monte Carlo (MC) method [2]. In this scheme, the step dynamics is solved by the PF method and the random impurity adsorption-desorption kinetics is modeled by the MC method. We introduce a screw dislocation on the crystal surface as a step source. We start the calculation from an impurity-free surface and repeat down-and-up cycles of supersaturation. When the supersaturation is decreased, the normal growth rate drops at a certain supersaturation. When the supersaturation is increased, the normal growth rate increases rapidly to that in the impurity-free case. The catastrophic changes appear in every cycle. The supersaturation at which the normal growth rate drops is different from that when it is increased; namely, the hysteresis is reproduced. The hysteresis appears in the supersaturation range as predicted by the mean field theory.

To summarize, we prove that the hysteresis of the normal growth rate is caused by the same mechanism with that of the step velocity. The supersaturation range at which the hysteresis appears can be derived from physical quantities relating to the step advancement and impurity adsorption-desorption kinetics, so we might be able to evaluate these quantities by comparison with experiments.

Reference: [1] H. Miura and K. Tsukamoto, 2013, Cryst. Growth Des. 13, 3588-3595. [2] H. Miura, 2016, Cryst. Growth Des. 16, 2033-2039.

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