

# Experimental Measurements and Modelling of Fundamental Attachment and Detachment Reactions on Barium Sulphate (001) Using Hydrothermal Scanning Probe Microscopy

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Using the Hydrothermal Atomic Force Microscope (HAFM)(Higgins et al., 1998), we have investigated the nanometer scale dynamics of barium sulphate growth. In the moderate supersaturation range, we have measured step growth kinetics on barium sulphate (001) as a function of step length, supersaturation, and temperature. In the discussion of our data, we consider the classical thermodynamic model introduced by Burton, Cabrera and Frank (1951), the kink-limited thermodynamic model of Voronkov (1973), and the kinetic models of Chernov (1998), Temkin (1969), and Zhang and Nancollas (1990). The assumption of equilibrium conditions at the elementary step edges is shown to be questionable when the energetics of kink formation gives rise to low equilibrium kink density. The resulting estimates of critical sizes are overestimated and thus, kink and step energetics becomes systematically overestimated. Approaching the data from the point-of-view of one-dimensional nucleation on the steps followed by constant growth at kinks gives kink formation energies that are reasonable and vary by little with errors in the kinetic modelling. Furthermore, the kinetic models provide estimates for the fundamental detachment rates at kink sites, thus giving experimental parameters for model simulations. Using a one-dimensional nucleation model, we report kink detachment coefficients for <120> monolayer steps of:  $v = 114 (\pm 14)$ ,  $187 (\pm 17)$ , and  $357 (\pm 43) \text{ s}^{-1}$ , at 90,

108, and 125 °C, respectively, giving an activation energy,  $E_a = 0.39 (\pm 0.05) \text{ eV}$ . The kink formation energy,  $\epsilon$ , was found to be  $0.16 (\pm 0.02) \text{ eV}$ . The lack of increase in experimental kink density with increase in temperature points to surface diffusion limitations in the experiments. Due to the kinetic limitations, whether from mass transport or attachment to kink sites, our results demonstrate that knowledge of the kink kinetics as a function of temperature is important prior to application of the classical thermodynamic model to kinetic data. The implications of these findings are of fundamental interest for studies of mineralization processes and help in our understanding of problems associated with macroscopic observations of crystal growth and dissolution and other heterogeneous reactions.

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