Kinetic Monte Carlo Simulation of Defect-Mediated Organization in Quantum Dot Self-Assembly

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ABSTRACT

Finding useful mechanisms for controlling the spatial ordering of self-assembled quantum dots remain a challenge. We propose that growing spiral steps emerging from screw dislocations can interact with diffusing impurities to nucleate or form spatially-ordered, self-assembled quantum dot arrays. This hypothesis is suggested by the micrometer-scale growth hillocks on natural graphite crystals from Namibia. We have carried out Kinetic Monte Carlo simulations on an atomistic model of a (001) surface of a simple cubic crystal and to investigate this hypothesis. We studied the effects of interaction energies, diffusion lengths, temperature, and chemical potential on the growth rates, step flow, kink motion and impurity diffusion and segregation. Under appropriate conditions the impurity atoms clustered together at the corners of the growth spiral, suggesting that screw-dislocation-generated growth spirals may be employed as a template for controlling the spatial organization of quantum dots during self-assembly.

Keywords: quantum dots, self-assembly, spatial organization, kinetic Monte Carlo

1 INTRODUCTION

The interaction of impurities with a growth spiral has been suggested as a possible mechanism for the formation of unusual surface topographies observed on the (001) surfaces of natural graphite crystals from western Namibia.[1] Growth hillocks occur on these crystals that are localized along the steps and at the corners of the steps of the growth spirals (Figure 1). Although the scale of these features is quite large (on the order of tens of micrometers [1]), the proposed impurity-growth spiral mechanism could also be effective in controlling spatial organization in quantum dot (QD) self assembly [2,3] at the nanoscale using growth-spiral steps emanating from an isolated screw dislocation, or perhaps even an array of screw dislocations intersecting a surface.

Under appropriate conditions, to be explored further below, we propose the following scenario: Adatom impurities on the crystal surface diffuse toward and stick to a regular array of advancing growth steps emanating from one or more screw dislocations that terminate at a crystal surface. During growth of the host crystal, the steps advance by the motion of kinks on the steps, which drive impurities to move toward the step corners. Diffusion of impurities on the terraces could also favor higher impurity concentrations at the step corners. The increased impurity concentration at the corners of the steps favors the formation of impurity clusters. Once such clusters form they would both pin the advancement of the steps at the corners and eventually lead to hillock formation as subsequent growth would eventually bury the immobile impurity clusters. Evidence of a step-pinning mechanism, as noted in [1], is the presence of reentrant 120° and 60°

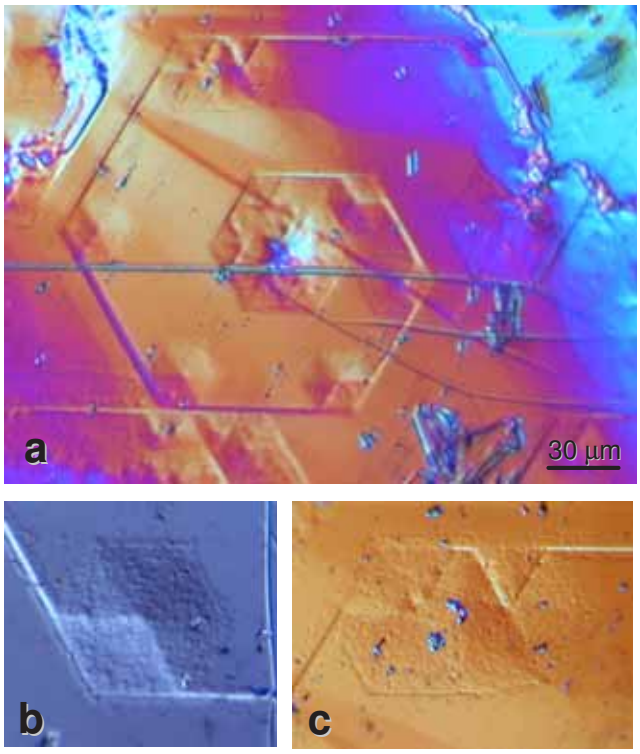

Figure 1. Nomarski differential interference microscope images of the surface of a naturally-occurring graphite crystal, etched from calcite, from western Namibia showing a growth-spiral step and regularly-arranged growth hillocks at the corners of the steps. (b) Higher magnification of a 30-µm-wide growth hillock at a step corner, and (c) a pair growth hillocks at a step corner and another along a step edge. Further details of the surface morphology are given in [1].

notches in the hillocks at the corners and step edges, respectively (Figure 1b and 1c). Under less than optimal conditions, immobile impurity clusters could form along the steps, particularly the longer steps, and pin them as well.

2 SIMULATION METHOD

Kinetic Monte Carlo (KMC) [4,5] simulations of an atomistic solid-on-solid (SOS) model of impurities interacting with host atoms on a (001) surface of a simple cubic crystal have been carried out. In our model, each surface site could be occupied by a single host or impurity atom. While the number of impurities was fixed, host atoms could adsorb to or evaporate from the surface. Both impurities and host atoms could diffuse to laterally nearest-neighbor sites (irrespective of height difference in our model), although impurities were forbidden to diffuse on top of other impurities. Following the model described in Ref. 6, Monte Carlo moves were generated based on the rates of adsorption (r_a), evaporation (r_{ei}), and diffusion from surface site i to a neighboring surface site j ($r_{i\to j}$), were calculated according to the following expressions:

$$r_a = \nu \exp\left(\frac{3\Phi_{11}}{k_B T}\right)\exp\left(\frac{\Delta\mu}{k_B T}\right) \quad (1)$$

$$r_{ei} = \nu \exp\left(\frac{\Delta E_i}{k_B T}\right) \quad (2)$$

$$r_{i\to j} = d_s \left(x_l / a\right)^2 r_{ei}, \; l = 1, 2, \quad (3)$$

where the surface-atom vibration frequency $\nu = 10^{12}$ s^{-1}, k_B is the Boltzmann constant, T is the temperature, and $\Delta\mu$ is the chemical potential driving force for host atoms. Evaporation and diffusion rates depend on an energy barrier $\Delta E_i = m\Phi_{11} + n\Phi_{22} + p\Phi_{12}$, where $m, n, p = \{0\ 1, 2, 3, 4, 5\}$ represent the number of bonds of a given type formed with the surface atom at site i, and Φ_{11}, Φ_{22} and Φ_{12} are the nearest-neighbor bond energies for host-host, impurity-impurity, and host-impurity interactions, respectively. In Eq. 3, a is the lattice spacing, and x_l is the mean diffusion distance for host (l = 1) and impurity atoms (l = 2), respectively. The diffusion factor $d_s = 1$ for most surface atoms, but for impurity atoms bonded to steps, $d_s = \exp(-\Phi_{12}/k_B T)$, as an enhancement of impurity diffusion along steps. An enhancement for diffusion for host atoms at steps was not similarly implemented in order to save computational time.

To begin, a spiral with relatively straight steps was grown on a 141×141-site surface having a single screw dislocation at the center of the simulation cell, with $\Phi_{11} = -0.0800$ eV, T = 100.0 K and $\Delta\mu$ = 5.0 k_BT. Boundary conditions were periodic at the top and bottom and reflective at the left and right of the simulation cell [7]. The surface was initially flat except for a straight unit-height step emanating from the dislocation and terminating at the reflective boundary at the right. Under the same conditions, a crystal without a dislocation had a negligible growth rate. Time was monitored in terms of Monte Carlo Sweeps (MCS), where 1 MCS is accomplished when the number of Monte Carlo moves equals the number of surface sites, as well as in real time (seconds) [4,5]. After 400 MCS (0.56 s) of initial growth, impurity atoms were randomly distributed on the surface, and the simulation continued at the same T and $\Delta\mu$ as before the impurities were added.

3 RESULTS

Diffusion parameters and bond energies were varied in order to study their effects on the surface topography. Using $x_l/a = 1.0$ for host atoms, $x_l/a = 0.01$ for impurities, $\Phi_{22} = -0.0810$ eV, and $\Phi_{12} = -0.0425$ eV, the following dynamics were observed. After only 1 MCS, the impurities had already diffused to form small clusters, which were mostly dimmers, as shown in Figure 2a. These small clusters eventually disappeared as individual impurities diffused to larger clusters and to the spiral growth steps [Figure 2b]. Eventually, the impurities formed

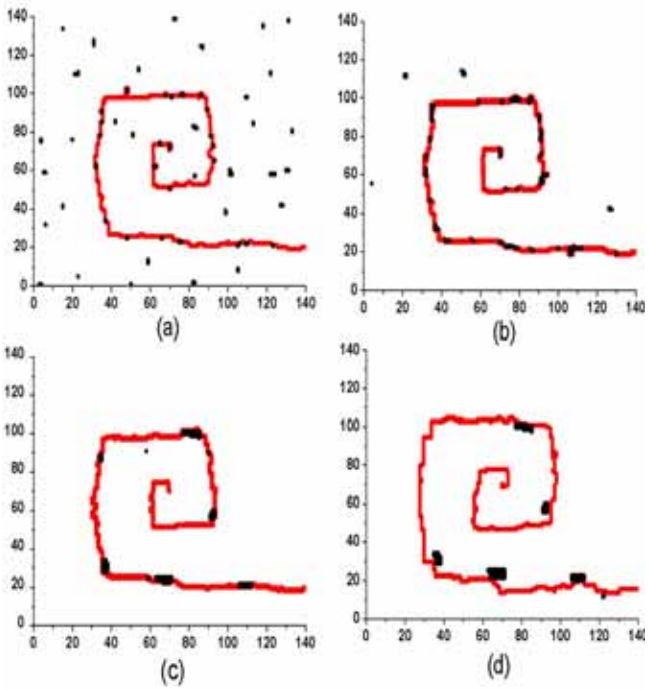

Figure 2. Comparison of surface morphologies (a) 1 MCS (2.8×10^{-8} s) (b) 10 MCS (9.4×10^{-6} s) (c) 150 MCS (1.3×10^{-2} s), and (d) 350 MCS (6.8×10^{-2} s) after the addition of 100 impurities to a 141×141-site surface with a growth spiral at T = 100.0 K. The continuous red curves represents the spiral growth steps (drawn from an interpolated contour computed from surface-height differences) emanating from a central screw dislocation. Black markers indicate the positions of the impurities.

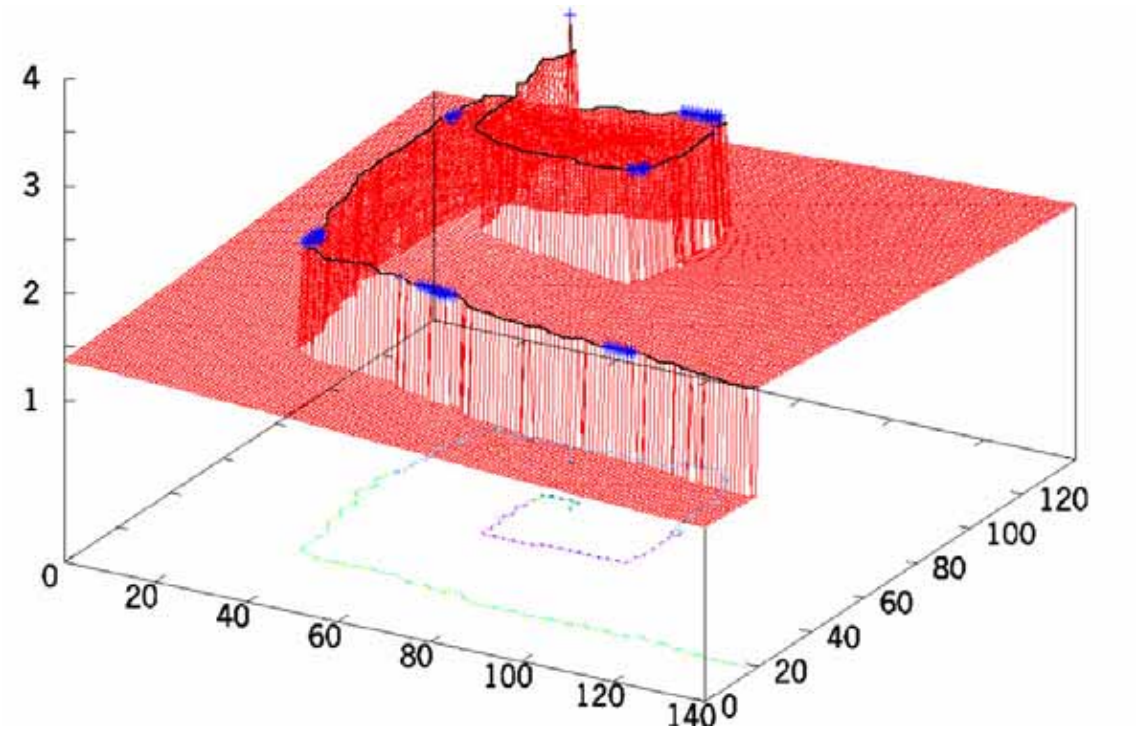

Figure 3. Three-dimensional view of a surface at 150 MCS (1.3×10^{-2} s) [compare Figure 2c] after the addition of 100 impurities to a 141×141-site surface with a growth spiral at T = 100.0 K. The blue markers indicate the positions of impurities.

a small number of clusters (QDs) as shown in Figures 2c, 2d and 3, just before they were laterally buried by the continual addition of host atoms to the growing spiral. Before becoming laterally buried, the QDs were typically located along steps or near the corners of the spiral.

The effects of the impurities on the overall growth rate of a surface with a growth spiral from a single dislocation are illustrated in Figure 4. Initially (region I in Figure 4) the impurities diffused on the terraces to form small clusters or attached to host atoms at the growth-spiral steps. The overall growth rate was relatively slow [1.1 monolayers per second (ML/s)] in this region due to impurity "poisoning" of the steps and kinks.[8] As time progressed the impurities formed larger clusters, and some migrated to the step corners. As impurities clustered and eventually became laterally buried by host atoms, kink sites once again became available for growth, and the growth rate increased to approximately 1.7 ML/s (region II in Figure 4). Finally, once all of the impurities were buried the growth rate increased to its maximum rate of 2.6 ML/s (region III in Figure 4).

The surface dynamics was found to be very sensitive to the choice of parameters in Eqs. 1-3. The temperature and chemical potential values were selected to yield a growth spiral with several turns and well-defined corners on a surface of reasonable size for the simulation. The bond energies were constrained to satisfy $(\Phi_{11}+\Phi_{22})/2 - \Phi_{12} < 0$, in order to favor the phase separation of impurities from the host crystal, yet Φ_{12} was maintained sufficiently negative to keep the impurities interacting with the steps. Making Φ_{22} too much stronger resulted in the impurities forming large clusters on the terraces that could become immobile even before reaching the growth steps. Making Φ_{12} too much weaker resulted in increased impurity diffusion and a decreased tendency for the creation of impurity clusters. On the other hand, making Φ_{12} too much stronger caused the impurities to become laterally buried too easily by the advancing growth steps. While it was straightforward to

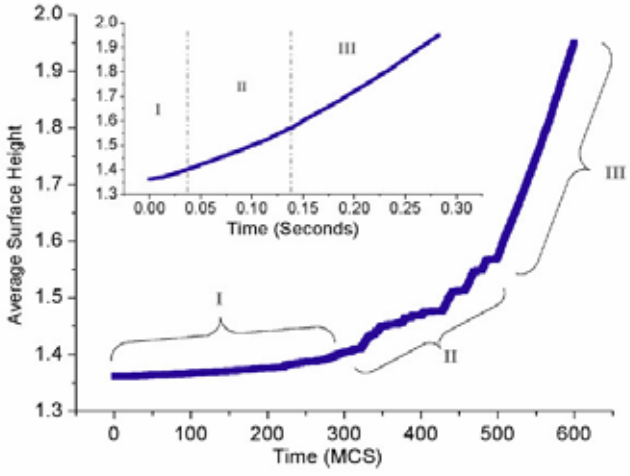

Figure 4. Average surface height (in monolayers) as a function of time under the same conditions as in Figure 2. The dynamics in region I were dominated by impurity diffusion on the terraces and at the steps. In region II impurities formed clusters and got partially buried laterally by host atoms, while in region III all impurities were laterally buried.

find parameters favoring diffusion of impurities to the steps, it was difficult to find parameters favoring their forming clusters at the steps, and particularly difficult to form clusters near the corners. Enhancing the impurity diffusion along the steps was found to be important, in that for simulations without the step diffusion enhancement factor d_s, (but under otherwise identical conditions), impurities formed smaller clusters along the growth spiral steps and showed less tendency to form clusters at the step corners. Increasing the number of impurities increased the number of clusters on the steps and decreased the growth rate.

4 DISCUSSION

Studies of the variation of the above parameters and detailed observations of the morphological evolution as a function of time suggests that there are at least three possible mechanisms favoring the spatially-organized self-assembly of quantum dots in our simulations, which are illustrated in Figure 5: (i) Effective "pushing" of impurities along steps toward corners by the advancement of kinks as the host crystal grows by the addition of host atoms at kink sites [moves *i* in Figure 5]. Bond energies can be tuned to favor host atoms over impurities to bond at the kink sites, but additional studies will be required to establish the appropriate parameter ranges. (ii) Net "downhill" diffusion of impurities due to effective energy barriers to impurity migration to move "up" a kink as compared to moving "down" a kink toward a corner.[9] For example, as shown in moves *ii* in Figure 5, an impurity moving uphill must break two lateral bonds to neighboring host atoms, while an impurity atom moving downhill need only temporarily break one bond. Further neighbor interactions, Schwoebel-like barriers for atoms moving along steps near kinks, and explicit activation energies could further enhance this effect. (iii) Impurity adatoms on terraces would tend to diffuse toward corners more than to steps due to the "lightning rod effect" since corners have larger effective areas on the terraces from which to draw diffusing impurities [move *iii* in Figure 5].

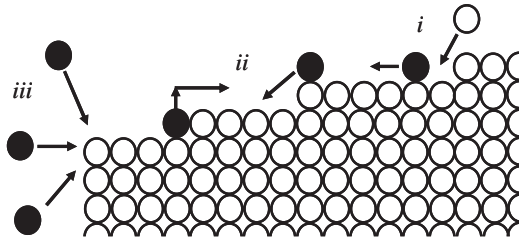

Figure 5. Diagram viewed looking down at the topmost layer on the surface showing the three atomistic-level moves for mechanisms of self-assembly of quantum dots at spiral step corners. Open circles represent host atoms and filled circles represent impurities. A step corner is located at the left in both diagrams. (a) Mechanism *i* shows impurities driven to the corners by kink motion during host growth. (b) In mechanism *ii,* uphill diffusion is slower than downhill diffusion. Mechanism *iii* favors impurity segregation at the corners since corners have larger effective areas on the terraces from which to draw diffusing impurities.

Our results suggest that the proposed mechanism of controlling the spatial organization of self-assembled quantum dots by using the interaction of impurities with regularly-spaced steps of dislocation-induced growth spirals is feasible, but careful tuning of growth conditions and interaction strengths may be necessary. Additional simulations are needed to more completely explore the surface-morphology dependence on the model's parameters. Simulations using larger system sizes are needed to statistically quantify and hopefully learn how to control the arrangement, size, uniformity, and shapes of the resulting QDs.[10] More detailed models taking into account more specific activation barriers, impurity-induced strain effects, and dimmer mobility also can be developed toward this end.

We are grateful to John Rakovan and Steve Hackney for helpful discussions. This work was supported in part by the National Science Foundation (Grant No. SES 0304439).

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