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Island growth in the presence of anisotropic diffusion with long atomic jumps

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ABSTRACT

Kinetic Monte Carlo (KMC) simulations have been conducted to study the influence of a recently predicted surface crowdion [1] on the nucleation and growth of islands during the the early stages of thin film epitaxy. Comparisons are made between island populations grown in the the presence of the same anisotropic macroscopic diffusion tensor but with differing microscopic diffusion mechanisms. In one instance only anisotropic nearest neighbour hopping is permitted, and in other simulations nearest neighbour hopping is isotropic but long atomic jumps are permitted in one direction. The densities of stable islands are compared with the predictions of a mean field set of rate equations. It is found that long atomic jumps reduce the efficiency with which monomers search the bare substrate and subsequently increase the density of stable islands. The long atomic jumps also change the concentration of monomers around growing islands, and alter island-island correlations.

INTRODUCTION

The work presented in this paper is motivated by the recent discovery of the surface crowdion on strained Cu(001) [1]. It is speculated that the surface crowdion may mediate highly anisotropic non-diffusive adatom transport during homoepitaxy; however, hitherto the crowdion has only been only predicted theoretically. This paper describes a theoretical and numerical investigation of the effects of the crowdion's hypothesised transport properties on two dimensional epitaxial island growth. The ultimate aim of this work is to guide experiments that can demonstrate the existence of the surface crowdion.

The surface crowdion is a self interstitial defect in which a surface adatom is subsumed into a single close packed atomic row in surface; the additional atom is accommodated by shunting the 5 or so atoms to either side of it along the close packed row. An image of the surface crowdion defect in Cu, calculated by Xiao *et al.* [1] using the embedded atom method, is shown in panel (a) of figure 1. The substrate is strained compressively normal to the elongated direction of the crowdion, and is in tension along it. The surface crowdion was discovered as an intermediate metastable state on a low energy pathway for exchange diffusion. In the traditional picture of exchange diffusion (for example Al on Al(001) [2]) the direction that the initial surface atom moves into the substrate determines which atom will be ejected to the surface, and which surface site it ends up in. This is not the case if the exchange process is interposed by a *metastable* crowdion state. Once formed the

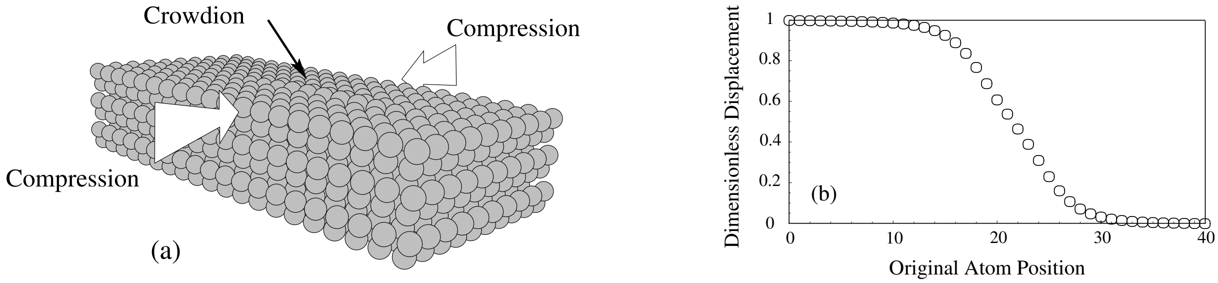

Figure 1: Panel (a) shows the structure of the surface crowdion in the (001) surface of strained Cu calculated using the embedded atom method [1]. Panel (b) shows the distribution of atomic displacements along the crowdion row.

crowdion, like a dislocation, can be considered as an entity in its self; defined by the distribution in atomic displacements along the close-packed row (figure 1 (b)) but distinct from the individual atoms that make it up. Again, like a dislocation, translating the crowdion one atomic spacing along the close packed row is achieved by a relatively minor shuffle in the displacement of the participating atoms. The energy barrier for such a translation of the crowdion is found to be tiny: less than 0.001 eV (below the accuracy of the embedded atom method used to calculate it). Moreover, the effective mass of the crowdion (estimated from the distribution of displacements in panel (b) of figure 1) is approximately 7% of that of an individual Cu atom.

The combination of tiny barrier for translation and small effective mass lead to the following hypothesis. As the crowdion is formed, if even a small fraction of the saddlepoint potential energy is retained as kinetic energy then the crowdion will be born with a finite velocity. Thus, once this crowdion is formed it skates unhindered along the close packed row until phonon scattering or interactions with other surface features cause the crowdion to decay and emit an atom from its centre back to the surface. Thus, for the case of self diffusion (where atoms are quantum mechanically identical) the formation and decay of a crowdion will result in the seemingly long jump of a surface adatom. As only one direction of crowdion is ever metastable, due to its dependence on the local stress state [1], the crowdion jumps will result in highly anisotropic diffusion with long jumps in one direction.

In searching for the evidence of crowdions it is not sufficient to simply detect anisotropic diffusion: the strain state of the substrate required to make crowdions metastable naturally breaks the four-fold symmetry of the substrate and renders nearest neighbour hopping anisotropic. The most conclusive experimental evidence for the participation of surface crowdions in self diffusion would be from isotopic tracer experiments; however, the work presented in this paper seeks evidence for crowdions in the patterns of two dimensional island growth as the resources[1] for conducting these experiments are more abundant. To this end a suite of kinetic Monte Carlo (KMC) simulations of island growth were performed. These simulations are described in the next section, and the results of them are discussed in the antepenultimate section.

[1]expertise, equipment, and inclination

KINETIC MONTE CARLO SIMULATIONS

The simulations of island growth performed in this investigation are similar in spirit to those performed by Bales and Chrzan [3]. The simulations are kept as simple as possible whilst retaining the essential features of interest for the investigation. These are: anisotropic nearest neighbour hopping, with jump rates in the x and y directions of R_x and R_y respectively; crowdion jumping with a rate R_c; deposition of atoms on the substrate, with a flux F; and finally isotropic relaxations at island edges. The hypothesized motion of crowdions is represented by a long jump of d_c atomic spacings in the x direction. These jumps are assumed to be instantaneous and sample the substrate, that is, they are cut short should they encounter any surface adatoms or islands along thier path.

Island growth was simulated with differing degrees of anisotropy in the diffusion tensor. The anisotropy was parameterised by $\lambda = \left(\frac{D_{xx}}{D_{yy}}\right)^{1/4}$, with D_{xx} and D_{yy} the principle components of the diffusion tensor. For simplicity of comparison simulations were conducted with the same macroscopic diffusion tensors for both: anisotropic nearest neighbour hopping with no crowdion jumping; and isotropic hopping but including crowdion jumps of d_c atomic spacings. The diffusion tensors for these two cases are are respectively

$$\boldsymbol{D} = \frac{a^2}{2} \times \left| \begin{array}{cc} R_x & 0 \\ 0 & R_y \end{array} \right|, \tag{1}$$

and

$$\boldsymbol{D} = \frac{a^2 R_h}{2} \times \left| \begin{array}{cc} 1 & 0 \\ 0 & 1 \end{array} \right| + \frac{a^2 R_c}{4} \times \left| \begin{array}{cc} 2d_c^2 & 0 \\ 0 & 1 \end{array} \right|, \tag{2}$$

with a the nearest neighbour atomic spacing, and R_h the isotropic nearest neighbour hopping rate.

RESULTS

Neither anisotropic diffusion nor crowdion diffusion do little to change the *shape* of the distribution of island sizes. However, comparable differences were observed in the densities of stable islands $\langle n_\chi \rangle$, the island-island correlations, and the exponent χ in the scaling relation of the density of stable islands given by $\langle n_\chi \rangle \sim \left(\frac{D}{F}\right)^{-\chi}$ [4]. These are now discussed in more detail.

<u>Island Densities</u>

Self-consistent mean-field rate equation calculations of stable island densities grown in the presence of anisotropic diffusion predict that $\langle n_\chi \rangle$ will be the same for all growth with the same $\frac{D_o}{F}$, where $D_o = \sqrt{D_{xx} D_{yy}}$ [5]. However, KMC simulations of growth with anisotropic nearest neighbour hopping show that $\langle n_\chi \rangle$ decreases with increasing λ but identical D_o and F. Conversely, for the case of isotropic hopping with crowdion jumping, island densities increase with the d_c for a given λ.

In the early stages of island growth nucleation of new islands depends on the ability of diffusing monomers to find each other. The efficiency with which diffusing monomers

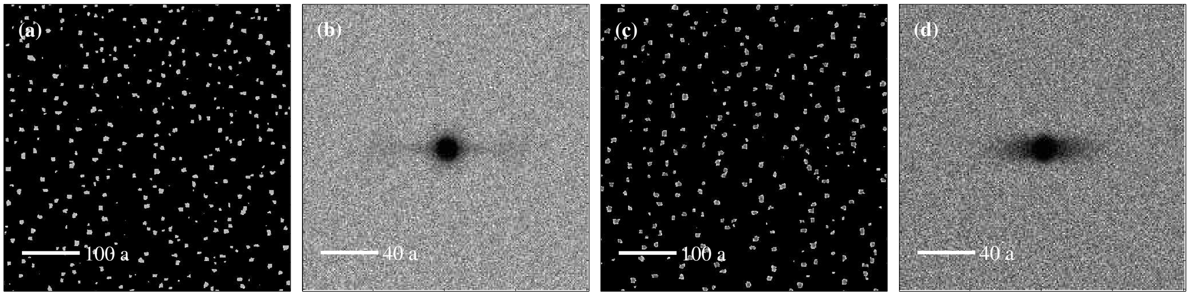

Figure 2: Images ((a) and (c)) of islands and corresponding island-island correlations plots ((b) and (d)—each averaged over 80 maps) with coverage 0.05 ML, grown with $\lambda = 2$ with the fast diffusion in the x direction. Plots (a) and (b) have isotropic hopping and a crowdion jump length $d_c = 50$ (which gives a ratio of $\frac{R_c}{R_h} = 6 \times 10^{-3}$), and (c) and (d) have anisotropic hopping with no crowdions.

search the surface can be characterised by the number of unique lattice sites N_u visited as a function of time [6]. A random walker will visit fewer N_u in N steps the more anisotropic its walk. However, by keeping D_o fixed the walker must make more steps in a given time, and actually visits a larger N_u than an isotropic walker would in the same time. Thus anisotropically hopping monomers can search for each other over a larger area and nucleation of islands is less dense. The same argument is used to explain the rise in $\langle n_\chi \rangle$ with d_c for crowdion mediated diffusion; the larger d_c the less efficiently the monomers search the substrate.

These results indicate that although the diffusion tensor gives information about the speed of mass transport it gives no information about site searching. Hence theories of island nucleation and growth based on the diffusion tensor alone, without consideration of the details of the transport mechanism, omit some physics essential to the proper solution to the problem.

Island-Island Correlations

Images of typical archipelagos of adatom islands, and their corresponding island-island correlation functions are shown in figure 2. The island-island correlations give a measure of the probability of finding an island at a given displacement from any other island. It can be seen that the elongation of the dark denuded regions in the direction of fast diffusion (x direction) is less pronounced for the crowdion diffusion than for anisotropic hopping. This arises because the mean concentration distribution of monomers around the islands in each case are different. This is illustrated most clearly in figure 3 which shows the distribution of monomers diffusing in one dimension to a sink. In the derivation of Fick's law the gradient in concentration is defined over the jump distance, and so clearly Fick's law will not hold within a distance ad_c of a sink. In fact, at the island edge the only terms that can still be included in Fick's law are the nearest neighbour jumps, and, as can be seen from the dotted line figure 3, the concentration profile near the island edge looks like that for only slow nearest neighbour hopping. In the opposite limit the profile tends to that for fast nearest neighbour hopping with the same diffusivity.

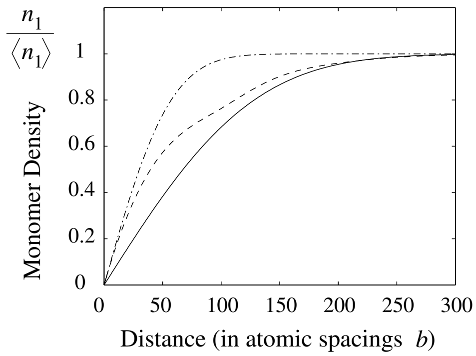

Figure 3: Concentration profiles near an island edge calculated numerically after 10^5 time units. The solid line is calculated for nearest neighbour hopping with $R_h = 1$, the dashed line is for hopping and crowdion diffusion with the same diffusion coefficient but with $R_h = 0.2$, $R_c = 8 \times 10^-5$, and jump length $d_c = 100$, and the dashed-dotted line is calculated for nearest neighbour hopping only with hopping rate $R_h = 0.2$.

Scaling Exponent

Evans and Bartelt [6] have shown that the scaling exponent for point islands grown with infinitely isotropic diffusion (*i.e.*, no mobility on one direction) is $\frac{1}{4}$; however, Linderoth *et al.* [7] have shown this exponent rises quickly towards the isotropic value of $\frac{1}{3}$ with even the smallest relaxation of this constraint. This observation is born out by this work where even mobilities in the fast direction 16 times quicker than those in the slow direction yields $\chi = 0.34 \pm 0.05$.

Crowdion diffusion is observed to slightly raise the scaling exponent from $\chi = 0.33 \pm 0.05$ for isotropic diffusion to $\chi = 0.36 \pm 0.08$ for diffusion with $\lambda = 2$ and $d_c = 50$. It is believed that this is due to the trajectory of an adatom diffusing with crowdion jumps *looking* qualitatively different to that of an itinerant adatom moving by nearest neighbour hops alone *when viewed at the right scale*. Panel (a) of figure 4 shows the perambulation of a random walker who makes occasional jumps of 10 lattice spacings in the x direction. This looks qualitatively different from the path in panel (b) which is traced in the same amount of time by a monomer with the same diffusion tensor as in (a) but who occasionally makes jumps of 100 lattice spacings. This trajectory *looks* more like a Lévy walk[2]; however it must be stressed that the walk in panel (b) is *not* a Lévy walk; follow the trajectory for a longer time, as shown in panel (c), and the path resembles that in panel(a).

Amar *et al.* [8] have simulated island growth in the presence of *true* isotropic Lévy diffusion. These researchers found that broadening the tails of the jump-length probability distribution raised χ from 0.33 for a Gaussian walk to 0.38. It is proposed here for the case of crowdion diffusion that the island spacing naturally selects a scale at which it views the random walk, and thus if the island density is sufficiently large then crowdion diffusion to islands may *feel* as if monomers exhibit Lévy diffusion.

SUMMARY

It has been demonstrated in this work that the nucleation and growth of two dimensional islands is sensitive to the peripatetic modes of the diffusing monomers. It has been shown that diffusion with long anisotropic jumps, such as that hypothesized for surface crowdion mediated diffusion, alters the ensemble concentration distribution around growing islands and impacts island-island correlations. The work described above demonstrates that there are comparable differences in island growth patterns for different

[2] In a Lévy random walk the probability distribution of jump lengths has no finite second moment.

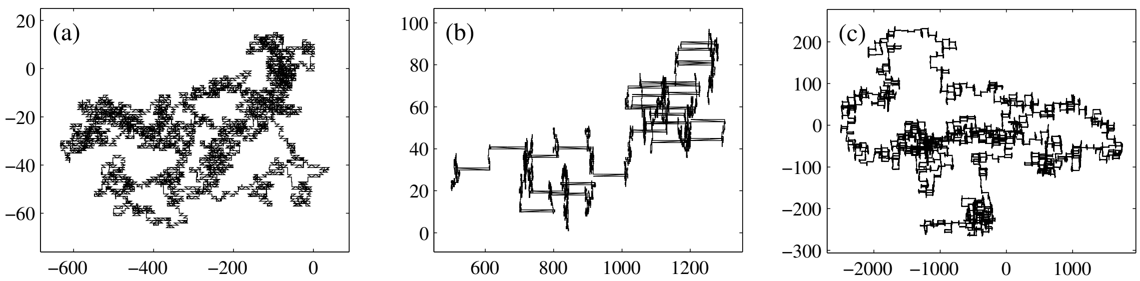

Figure 4: Panels (a), (b), and (c) show trajectories of diffusing adatoms moving by crowdion jumping and simple hopping. In all cases the diffusion tensors are identical with $\sqrt{D_{xx}D_{yy}} = 1/2$ (atomic units squared per time unit) and $\lambda = 2\sqrt{2}$ and nearest neighbour hopping is isotropic. In panel (a) d_c, is 10 atomic spacings, whilst in (b) and (c) it is 100. The trajectories in (a) and (b) are 4,000 time units long, whilst (c) is 80,000.

modes of diffusion; however, there is no feature to these patterns that allows insight to the diffusion modes with out comparison. Thus there is no irrefutable signature that indicates the participation of crowdion in a real island growth experiment. So, we must look to isotopic tracer experiments after all.

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