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Shape changes of two-dimensional atomic islands and vacancy clusters diffusing on epitaxial (111) interfaces under the impact of an external force

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Abstract

Surface nanostructures migrate as a consequence of atomic diffusion. Under the effect of a force, arising for instance from an electric current or a thermal gradient (electromigration or thermomigration phenomena), the atomic diffusion is preferential in specific directions and affects the nanostructures making them move and change shape. In this work, based on Kinetic Monte Carlo simulations, we show the impact of an external force on the shapes of 2D atomic islands and vacancy clusters located on homoepitaxial (111) surfaces. At different temperatures, we identify critical values of the strength of the external force applied to the edge atoms, that lead to a series of transitions of the morphology of both islands and vacancy clusters from hexagonal to triangular-like shape. The shape variation is strongly dependent on the external force direction and on the step edge anisotropy.

Keywords: A1. Diffusion, A1. Interfaces, A1. Nanostructures, A1. Surfaces

1. Introduction

Diffusion at surfaces plays a key role in crystal growth. Regardless of the huge amount of experimental and simulation studies concerning crystal surfaces, a number of questions related to the elementary atomic diffusion mechanisms at surfaces remain still to be answered. For instance, an open issue is how surface diffusion can be modified by external forces applied in specific directions. The collective diffusion of atoms biased by an external force may change the surface morphology [1–4] or the properties of an entire nanostructure, like its shape, as shown analytically [5–7] and suggested by simulations [8, 9]. Examples of forces can be those induced by a thermal gradient or an electric field, leading to thermomigration and electromigration respectively. Electromigration has been studied since the sixties because an electric current through a circuit, if not carefully controlled, can lead to the formation of hillocks, voids and eventually to the disruption of the circuit [10]. Thermomigration causes the motion of voids in KCl [11] and UO_2 (used as fuel in nuclear reactors) [12] and has been recently used to induce the motion of nanostructures on carbon nanotubes [13]. In this work we describe different scenarios of biased surface diffusion, with particular attention to the shape changes of 2D nanostructures moving under the effect of an external force. We have developed a Kinetic Monte Carlo (KMC) model for (111) surfaces to explain the motion of clusters (2D one-atom thick holes and islands) in different physical conditions (temperature, force field, surface anisotropies).

2. Kinetic Monte Carlo model

The KMC method allows to simulate the dynamic evolution of systems from state to state and is therefore suitable to predict the shape of 2D clusters and voids moving under the effect of a force [14]. We have implemented the method using a standard lattice model where an atom jumping from one edge of the box re-enters on the opposite edge. The crystal surface is represented by a lattice of positions that can be either occupied (by atoms) or empty. The lattice is hexagonal, to simulate a (111) surface. The surface evolves with an exchange between an occupied and an empty position, representing a jump of an atom to a neighbor position. Figure 1 shows some examples of atom motion and some of their possible trajectories.

Atoms cannot jump on top of other atoms, therefore adatom diffusion is outside islands and inside 2D holes. This corresponds to considering that atoms diffusing on

top of islands or of the terrace outside the holes cannot be incorporated at steps, i.e. we consider a very high Ehrlich-Schwoebel barrier. This is for instance appropriate for the Si(111) surface, where the E-S Barrier is very large as experimentally ([15]) and theoretically ([16]) found (0.6 eV).

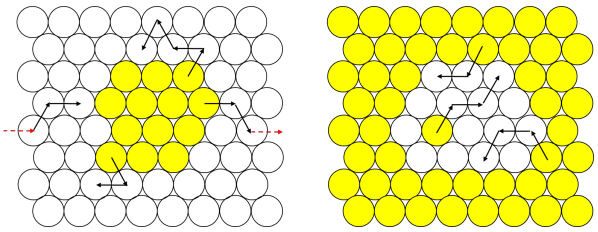

Figure 1: (111) surface pattern. Yellow circles represent occupied positions (top layer), while white circles are empty positions. The figure on the left represents a 2D one-atom-thick island, while that on the right shows a 2D vacancy island with an adatom in the middle. Some possible trajectories of atoms are shown with arrows. The red arrows give an idea of the boundary conditions for a jump at the edges of the simulation box.

The binding energy of each surface atom is written: $E_{bin} = E_b \cdot nn$, where nn is the number of nearest neighbors of the considered surface atom. Only the surface layer is considered, while the underlying atomic layers are fully occupied. Thus, nn is variable between 3 (isolated adatoms with 3 nearest neighbors in the underlying layer) and 9 (atoms surrounded by 6 in-plane nearest neighbors and 3 atoms in the underlying layer). In the following, energy values are expressed as multiples of E_b, in the simulations we have used $E_b = 1$. Because of the hexagonal lattice, surface nanostructures like holes or islands have initial hexagonal shapes (when no forces are applied).

The jump probability of an atom depends on its binding energy and on the external force acting on it. The jump rates are proportional to:

$$\exp(-\frac{E_{bin} + E_{cg}}{k_B T})$$

k_B is the Boltzmann constant and T is the temperature. E_{cg}, the energy change due to the external force, can be positive or negative depending on the force direction and on the jump arrival site [17]. It reads: $E_{cg} = |F| \cdot a \cdot cos(\frac{\pi}{3} \cdot b - \delta)$, where a is a lattice parameter, equal to 1 in all directions; $|F|$ is the force acting on a jump of unit length; b is an integer between 1 and 6 defining the arrival site, in anticlockwise order; δ is the angle between the force and the x axis. Notice that E_{cg} does not depend on the position of the moving atom, but depends only on the jump direction.

Atomic jumps are selected according to a standard rejection-free Monte Carlo algorithm, where a time step is equal to the inverse of the sum of all jump rates [14]. This simple model is general and not specific to a particular system. It allows fast calculations and illustrates qualitatively different scenarios of nanostructure shape changes at surfaces.

3. KMC simulations

Without external force, atomic jumps are due to random thermal diffusion. Atoms diffuse on the terrace outside the islands and inside the holes respectively. We have simulated the displacement and the shape evolution of 2D holes and islands, with or without the effect of an external force.

3.1. Cluster diffusion-radius

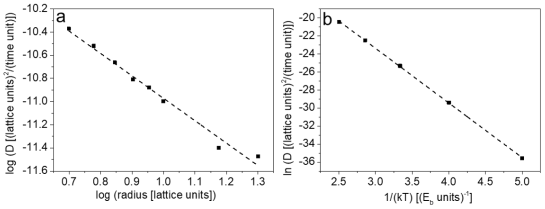

Figure 2: a: log-log plot of the diffusion coefficient of islands (without force) as a function of the radius at $k_B T = 0.3 E_b$. b: diffusion coefficient of an island with radius=10 lattice units (without force) as a function of temperature.

In order to validate the model, we have calculated the cluster diffusion coefficient as a function of its radius. In the present model, atoms detach from the edges of the nanostructure, then displace by diffusion on the terrace (outside for islands or inside for holes) and re-attach to an edge of the nanostructure. Without external forces, this diffusive motion of atoms leads to a brownian diffusion of the clusters. As shown in [18, 19], the diffusion coefficient of a cluster, proportional to its average square displacement per unit time, depends on the cluster radius as $R^{-\alpha}$. α is a coefficient that depends on the main mechanism of atomic transport; it is equal to 1, 2 or 3 for, respectively, atomic evaporation-condensation, diffusion on terraces or diffusion at the cluster periphery. Figure 2a shows the average square displacement per unit time of islands with different radius. Every point corresponds to the average squared displacement of a cluster over 100 simulations. Because of the atomic diffusion on terraces, a linear fit through the points of figure 2a gives, as expected, α=2. The simulations are

performed only for large clusters, therefore the diffusion coefficient does not depend on the occurrence of perfect sizes (i.e. closed shell clusters where the number of atoms is such that they can be packed in a shape with kink-free flat edges), as instead observed by Lai et al. and Heinonen et al. on (100) lattices for small clusters. For smaller clusters and lower temperatures, the occurrence of perfect sizes could give different results.

3.2. Cluster diffusion energy

The diffusion energy of a cluster in our simulations can be calculated by measuring the diffusion coefficient as a function of temperature. At high temperature clusters diffuse faster than at low temperature. Figure 2b shows the logarithm of the average square displacement of a hexagonal island as a function of $1/(kT)$. The slope of the linear fit gives the activation energy of the cluster diffusion process. It corresponds to the kink energy in our lattice model (6 E_b). The importance of the kink energy in the cluster diffusion has already been underlined in [19].

3.3. Temperature-shape dependence

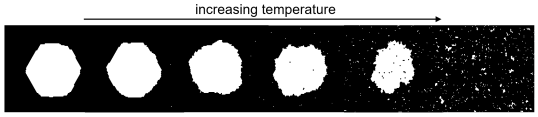

Figure 3: Shape of a 2D island (white) on a (111) surface. Every image is a snapshot of a simulation of the shape of the island at a fixed temperature, taken after a long simulation time. At low temperature the island is hexagonal, at higher temperature the corners become rounder, then the edges become rough and the island presents many vacancies. At very high temperatures the island disintegrates. From left to right k_BT=0.1, 0.2, 0.4, 0.5, 0.7, 0.9 E_b.

At low temperature the nanostructures are well faceted and present only few kinks. Increasing the temperature, the corners become rounder, the number of kinks increases, the facet length decreases and hexagonal shapes become more and more circular. The appearance of a roughening transition (between the 2nd and the 3rd image in figure 3) is a further validation of the model. Increasing more the temperature, single vacancies appear inside the nanostructure (black dots in figure 3), and the island at first assumes rapidly-changing non-regular shapes with very rough edges, and then disintegrates.

3.4. Shape changes

In the simulations we have applied a force towards the [1-10] or the [11-2] direction on a (111) surface. The force is implemented by adding a bias to the atom jump energy. This bias is negative for jumps in the force direction (and therefore facilitates these jumps), while it is positive for jumps in the opposite direction (that thus are disfavored). Thus atoms diffuse preferentially in the force direction. As a result, atoms are removed from an island edge (the back edge), move along the surface, goes out from one side of the simulation box and, because of the boundary conditions, they re-appear on the other side of the box. Then they diffuse in the force direction and reach the other side of the island (the advancing edge). Therefore islands move opposite to the force. Also 2D holes move opposite to the force, but the advancing edge in this case is the one where atoms are removed, and the back edge is the one where atoms accumulate.

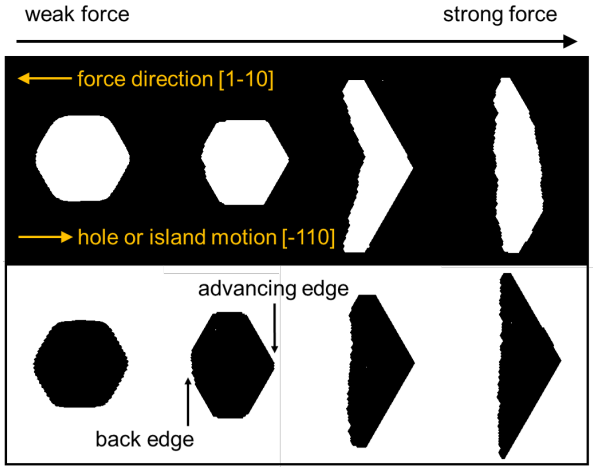

Figure 4: Shapes of a 2D island (white, first line) and a 2D hole (black, second line) on a (111) surface under a force that adds a bias to diffusion. The force is towards the left of the image. The force acting on the shapes on the right is higher than that acting on the shapes on the left. From left to right E_{cg}=0.0001, 0.001, 0.01, 0.1 E_b. $k_BT = 0.1E_b$.

Figure 4 shows the steady-state shapes of hexagonal structures for different values $|F|$ of a force in the [1-10] direction. For low $|F|$, the nanostructure keeps the unperturbed, hexagonal shape. At higher $|F|$, 2D holes and islands elongate perpendicularly to the force. When the force is in the [1-10] direction, the advancing edge of both islands and holes becomes more faceted, the edge length increases, the advancing corner sharpen and the nanostructure back side rounds. Increasing more $|F|$, the back side of the holes becomes flat, while that of the islands becomes at first concave, then flat. For very high $|F|$ values, also the advancing side of the islands flattens.

In islands, the atoms at the corner between two facets

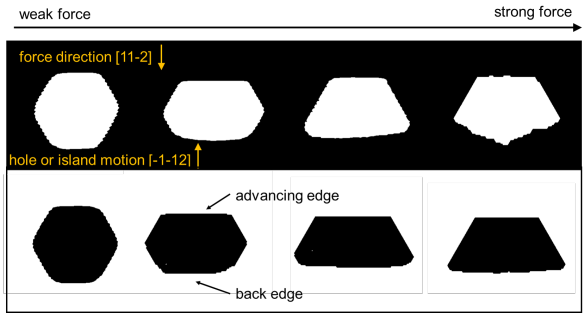

Figure 5: Shapes of a 2D island (first line) and a 2D hole (second line) on a (111) surface under a force that adds a bias to diffusion. The force is towards the bottom of the image. The force acting on the shapes implies an energy change from left to right E_{cg}=0.0001, 0.001, 0.01, 0.1 E_b.

are easily removed, because they have few neighbors and can move in the force direction. Atoms removed from the back edge arrive at the front edge and leave kinks at the back edge from where atoms can easily be removed. Atoms arriving at the front edge, complete atomic rows of the front facets if they meet a kink. If the facet is perfect, without kinks, they become adatoms at steps and move along the inclined facets of the front edge, but slower than on the bare terrace. If they meet another step adatom, they can nucleate a new atomic row and the front facet advances. Otherwise, when they arrive at the end of the facet, they increase the length of that facet. As a result, the nanostructure elongates perpendicularly to the force.

Islands tend to keep the convex shape to maximize the bonds between atoms.

However, for high forces, when atoms of the back edge can be removed easily, a concave back can be observed. This is due to (i) a strong adatom flux coming from the front edge to the sides of the back edge (upper and lower part in the third image of the upper row in figure 4), and (ii) the cluster tendency to form facets where the atoms have four in-plane neighbors. Atoms removed from the sides of the back edge are replaced by those incoming from the front edge. This is not the case for atoms of the central part of the back edge and thus when a notch forms, other atoms can be removed and the back edge tends to form facets parallel to those of the front edge.

Further increasing the force, the atoms are very fast removed from the back and attach to the front. Therefore when the force is in the [1-10] direction, many atoms arrive on the inclined facets at the advancing edge, but the shape displaces before the reorganization of the facets that thus almost disappear. This mechanism is similar to the kinetic roughening phenomenon obtained in growing surfaces (for instance as a result of a high deposition rate in molecular beam epitaxy experiments [20]).

Similar arguments can be used to explain the shape of 2D holes. However in this case atoms at the corner between two facets have five in-plane neighbors and are thus difficult to remove. If no kinks are available, atoms at the hole advancing edge are removed from flat facets and leave kinks. These kinks allow to unzip the atomic rows of the front edge facets, that thus move opposite to the force. The back edge is flattened by the accumulation of the diffusing atoms. Because of mass conservation (the hole area must remain the same), as the angle between the front facets is fixed, if a flat edge at the back is formed, the shape must elongate perpendicularly to the force, up to a maximum length of 2.45 times the starting hexagon height, because of geometrical reasons.

When the force is applied in the [11-2] direction, increasing the force strength, the bottom lateral facets of the hexagon in figure 5 are reduced and for very high force values they disappear, leaving a half hexagon. Islands under strong forces develop a tail at the back edge that is not faceted. This tail is due to atoms removed more easily from the lateral corners (to jump towards the bottom in figure 5) than from flat portions of the back edge. When the force is high, the cohesion and stability of the back facet is reduced and atoms are easily removed, thus the back facet disappears.

We have also identified similar diffusion and shape behaviors for vacancy clusters (holes) on fcc(111) interface by atomistic simulations based on continuous space canonical Monte Carlo model. Applying an external force on the periphery atoms of the vacancy hole, we have observed a hexagonal to triangle shape transition similar to that obtained in KMC simulation. These results will be extensively discussed elsewhere.

4. Considerations on adatom attachment and detachment

Our model is valid in the limit of an infinite Ehrlich-Schwoebel barrier. When this energetic barrier is small, adatom attachment and detachment to/from a step, from/to both upper and lower terraces may affect adatom currents. Such effects have been considered to analytically describe cluster diffusion and edge fluctuations by Khare and Einstein [19], and then to study the displacement of clusters under electromigration by Pierre-Louis and Einstein [17]. They discussed that the electromigration force could produce different bias for

attachment and detachment and might thus affect the cluster behavior. They showed (i) that this bias decreases when the island size increases and (ii) that this bias is a second order effect for large enough Ehrlich-Schwoebel barrier. Likely, simulating the displacement of very small clusters would need to take into account this attachment-detachment bias.

5. Summary

We have developed a KMC model to simulate the evolution of nanostructures like 2D islands and voids on surfaces with hexagonal symmetry. Because of atomic surface diffusion, the nanostructures diffuse and, under an external force, move and assume a shape different from the equilibrium one. This shape depends on the force direction, on the strength of the force, and on the temperature. The facets of the advancing front are generally stabilized, while those of the back are destabilized.

Acknowledgments

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