Strain in heteroepitaxial growth

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(February 9, 2022)

We use atomistic simulations with an empirical potential (EAM) to study the elastic effects of heteroepitaxial islands on adatom diffusion. We measure the diffusion barrier on pure stressed substrate and near a misfit island, as well as the detachment barrier from islands of different size.

I. INTRODUCTION

Heteroepitaxy is the growth by deposition of one material on another. Since the two materials are different, stress can be generated, and it leads to a number of interesting and important phenomena. In this paper we consider various effects due to this strain by using the embedded atom method (EAM).

We consider the case where the adatoms are “larger” than the substrate atoms. Then if the adlayers are pseudomorphic (follow the periodic order of the substrate without dislocations), they have to be compressed. The size difference is not necessarily the only source of stress: the compressive stress of few monolayers of Ag on Pt(111) five times larger than expected from the size difference presumably due to charge transfer. Since the elastic energy of the stressed layer is proportional to its height, the excess elastic energy can, in the course of growth, overcome the barrier of creating a dislocation network for relaxation. Thus pseudomorphic growth cannot be stable for large thickness.

However dislocated growth is not the only possibility: the adatoms can form three-dimensional islands instead of normal layer-by-layer growth by merging of two-dimensional islands. The energetic reason for this is that three-dimensional islands can relax: the lattice constant in the majority of an island can be close to its bulk value, and only the bottom of the island is stressed significantly. In case of Volmer–Weber growth, the islands nucleate on the substrate, while in the Stranski–Krastanov case the first few layers grow epitaxially (wetting layers), and then islands form.

Three-dimensional islands are important for practical applications, as they are a good candidate for lateral electron confinement. Certain semiconductor systems (e.g., InAs on GaAs) develop pseudomorphic three-dimensional structure with a relatively narrow size distribution for the islands. Since this ordering takes place spontaneously during epitaxial growth the islands are called self-organized quantum dots. The uniformity of quantum dots and, in particular, the possible narrowing of the island size distribution due to strain, is an important technological issue, and considerable effort has gone into measuring and modeling this effect.

A simplified atomic level simulation of strained epitaxial systems has been done by Orr et al. using the dynamic Monte–Carlo method in one dimension. Surface particles were allowed to hop to neighboring sites. The hopping probability depended on both the bond and the local strain. The strain was found by local relaxation after each motion and global relaxation after fixed number of timesteps. The elastic lattice was modeled with harmonic forces between nearest and next-nearest neighbors. Qualitative effects that are observed in experiment are found in this treatment, e.g. the formation of three-dimensional islands whose size distribution depends on growth rate. However, the treatment is very schematic, and contains free parameters.

More realistic theories fall in two classes. Empirical approaches take as input certain presumed effects on growth in heteroepitaxy such as the tendency to detach from large two-dimensional islands due to the build-up of strain, the effects of strain on adatom diffusion, and the probability of conversion of a two-dimensional island to a three-dimensional one. However, these parameters are based on a combination of fitting and classical elastic theory with no way to estimate the size of various effects for a real material.

Schroeder and Wolf studied the effect of strain on surface diffusion for a Lennard-Jones lattice. This treatment can potentially estimate all the relevant effects. However, the Lennard-Jones potential is quite different from that found in the substances of interest. They observed that the activation barrier is a linear function of strain over a wide range: compressive strain enhances diffusion, while tensile strain hinders it. The strain changed mostly the energy of the saddle point, the stable sites were not much affected. The strain field of a coherent two-dimensional island is not uniform (the edges are more relaxed than the center), therefore this is reflected on the diffusion of adatoms on top of the island.

In this paper we use more realistic potentials than Schroeder and Wolf, namely the EAM approximation. Unfortunately, this method is appropriate for metals, not semiconductors, which are the materials of most technological interest. However, these potentials are probably more reliable than the various phenomenological interactions which have been proposed for semiconductors and serve to give perspective on the effects which can be important in growth. Also, this is a computationally intensive approach, and can only treat one island at a time. Thus, we can only calculate parameters which can eventually be inputs into an empirical theory. To this end we investigate effect of strain on the diffusion barrier of adatoms, the detachment energy from a two-dimensional island, and the energy landscape for diffusion nearby.
II. SIMULATIONS

In our simulations we use a substrate of slab geometry, periodic in the lateral directions, with an open surface at the top bounded by a frozen lattice below. The atoms of the substrate and the adlayers or adatoms were allowed to relax according to the potential described below. We did not introduce dislocations in the substrate. The relaxation was achieved by using conjugate gradient methods.

It is necessary to have the elastic part of the substrate as deep as wide, because the elastic effects penetrate roughly isotropically. If the lattice was shallower then the deformation field would be cut off and we would lose long range effects. This restriction has severe consequences on the lattice sizes that are computationally tractable.

For an interatomic potential, we used the embedded atom method (EAM) which is believed to give a good representation of transition metals. The form of the potential is

\[ \phi^{ij}(\mathbf{R}) = F^{i}(\rho^{\text{host}}) + \frac{1}{2} \sum_{j \neq i} \rho^{i}(\mathbf{R}_{ij}) \]

The pair potential part, \( \phi^{ij}(\mathbf{R}) \) is attributed to electrostatic interactions, while the embedding function \( F^{i}(\rho^{\text{host}}) \) is interpreted as the interaction of the ion cores with the free electrons. The explicit form of the functions used in our simulation are given in Ref. 1.

This pseudopotential provides reasonable values for many bulk properties. Whether it is appropriate for surface simulations is not as clear for various reasons. Nevertheless, the EAM is more realistic approach than pair potentials such as Lenard-Jones, and computationally tractable for the necessary system sizes as opposed to first principle calculations. We selected the Ag/Ni system based on its large misfit (16% compression of the Ag adlayer) from the elements available with the EAM potential. This way we could achieve significant stress in the islands on a substrate of relatively small, computationally tractable size: \( 32^3 \) in the following calculations.

III. RESULTS

We measured the effect of strain on the diffusion barrier. The substrate lattice was compressed in the horizontal direction by a given factor, and was allowed to relax vertically. Then an adatom was placed on top, and the whole system was allowed to fully relax. Fig. 2 shows the energy of the system when a Ag adatom was placed on a stable (fcc), metastable (hcp) and bridge point of a stressed Ag(111) substrate. The diffusion barrier (the difference of the bridge and the stable/metastable energy) is also plotted.

Near zero stress the barrier was close to a linear function of the lattice constant, with increasing barrier for tensile strain. This is the expected behavior: under compressive strain the energy landscape becomes more uniform, while under tensile strain the adatom feels more the separate attracting potential of the surface atoms. For large tensile strain this trend breaks down: the surface becomes softer, bringing down bridge energies, resulting in a smaller diffusion barrier. However, this linearity was only over a rather restricted range of strains. Note that we do not reproduce the result of Ratsch et al. who used the LDA, and did find linearity of the diffusion barrier with strain, as suggested on phenomenological grounds by Dobbs et al. On the other hand, effective medium theory calculations agree with our results, up to a 10 meV systematic shift, see Fig. 1n.

When the lattice is unstrained, the fcc adsorption sites are slightly lower in energy than the hcp sites. However, in our calculations this trend reverses for large tensile strain. Note that the major effect here is not on the bridge energies, but on the energies of the stable sites, contrary to the effect found by Schroeder and Wolf.

We applied the same procedure to the Ag/Ni(111) heterodiffusion system, the barriers and energies are depicted on Fig. 2. While the behavior of the diffusion barrier is qualitatively the same as in the Ag self-diffusion case, the dependence of energies on strain is different. Around zero stress, the stable sites are unaffected, and the bridge energy changes. From this we can draw the conclusion that whether the energy of the stable sites or the bridge point changes under stress is system dependent, no general statements can be made.

One of our goals is to study the elastic effects of an island on the energy landscape observed by the diffusing adatoms. To pursue this we deposited a large hetero-island and an adatom on the substrate, and computed the energy of the system for different positions of the adatom, the configuration is shown on Fig. 2.

In Fig. 3 we plot the diffusion barriers of a Ag adatom on top of Ni(111) substrate, as a function of the distance from a Ag island of radius of 4 atoms. There are two different barriers: one seen by an adatom diffusing away from the island, and a different one for approaching it. The oscillation is due to the nature of the lattice: on top of an fcc(111) lattice an adatom can be in the fcc site (stable) or hcp site (metastable). The diffusion barrier is measured between the bridge point and the stable or metastable site.

According to the results, near the island it is easier to diffuse away from a stable site, and easier to diffuse inward from a metastable site. The island does not have a strong attractive or repulsive long-range effect on the adatom. However if the adatom is very close, it can only diffuse inwards: it is captured by the island.

The small island of the previous result was pseudomorphic with the substrate. For larger islands this is not the case. Fig. 4 shows the diffusion barriers near an island of radius of 7 atoms, which is already not pseudomorphic, as can be seen on Fig. 3. The distortion of the energy landscape is much larger in this case, and the attraction...
of the island can be felt at larger distances. The effect of the island is not only attraction (the outward barriers larger than the inward ones) but also enhancing diffusion near the island: the diffusion barriers in both directions are decreased. Probably this is due to the fact that the substrate near the compressed island is also compressed.

To check that how much of this effect is due to the presence of the compressed hetero-island, we repeated the previous calculation with homoepitaxial island: the large Ag island has been replaced with same size Ni island. The obtained barriers (Fig. 5) show even smaller effect than the case of the small hetero-island. On a considerable range the energy landscape is deformed: the outward and inward directions are not equivalent (as in a sawtooth potential) but there is no global attraction or repulsion.

We measured the detachment barrier from a strained island. Fig. 3 shows the binding energy as a function of island size, it is the same as the detachment barrier up to a sign. The trend is decreasing barrier for large enough islands in all cases, as expected. For large islands the detachment barrier of an extra atom at the middle of the hexagonal island’s edge (see Fig. 3a) is smaller than the detachment barrier of the corner atom, or the next atom after the corner. This is plausible, as the extra atom at the middle of the edge is less coordinated than the compared atoms.

It has to be noted that the binding energy of the island of radius of 5 is very different compared to the nearby sizes. The explanation is the following. The binding energy is defined as the energy of the island with an adjacent adatom, the zero point is when the adatom is infinitely far away. The island of this size is at the borderline of pseudomorphic and not pseudomorphic islands. When we measured the energy of the island in itself, the relaxation converged to a pseudomorphic state, see Fig. 3a. But when the adatom was added, this was enough perturbation that the system converged to a not pseudomorphic state (Fig. 3b). Thus the addition of the adatom triggered a much lower energy state, hence the large negative bonding energy. It is possible that the bare island also has a lower energy non-pseudomorphic state, but we did not do a detailed search.

We also tried to obtain an energy landscape on top of an island. This was quite difficult, because the island atoms are very soft, deform very much in the presence of an adatom on top, and there is no well defined stable, metastable and bridge site. Fig. 5b depicts a case when a the adatom is in a deformed four-fold hollow site.

IV. SUMMARY

In this paper we studied the elastic effects of heteroepitaxial islands on diffusion using atomistic simulations with EAM potential. Compressive strain enhances diffusion, small tensile strain hinders it, but large tensile strain also tends to enhance it. Whether the energy of the stable site changes or the bridge energy, depends on the system.

The energy landscape near a compressed island is deformed: the island attracts the adatom, and the diffusion is increased near the island. Even a homoepitaxial island deforms the energy landscape, but the change is much smaller, and only the symmetry of the potential is broken.

The detachment barrier from a compressed island decreases with larger island size. The diffusion barriers on top of an island are hard to measure, because the island is soft and distorted near an adatom, there is no well defined diffusion path. This is probably due to the fact that we chose to work with a system that dislocates easily.

Our general conclusion from this detailed microscopic study is, in some sense, negative. Empirical theories depend on making general statements about the effects of strain which can be modeled with a few parameters. Our study shows that while the qualitative ideas behind these theories are correct – a large two-dimensional island is destabilized by strain, for example – the form of the effect is quite complicated. Also, the representation of the diffusion barriers as linear in the strain is true only over a limited range in our calculations, and in the EMT

The complexity of our results may be due to the small sizes of the two-dimensional islands that we were able to deal with, and to the fact that our metallic systems dislocate. Still, we think that these results should serve as a warning against a naive application of continuum elasticity theory in this area. We should note that in Refs. 14 unreasonable assumptions about the size of elastic effects were found to be necessary: Elastic couplings would have to be much larger than any effect that we calculate here in order to give significant narrowing. In our opinion the physical reason for the narrow size distribution of quantum dots is still obscure.

We are grateful to Brad Orr for useful discussions. This work is supported by DOE grant DEFG-02-95ER-45546.

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FIG. 1. Diffusion barrier of Ag adatom on stressed Ag(111) substrate. a) Comparison of the diffusion barrier obtained by density-functional theory (circles, from Ref. [14]), effective medium theory (squares, from Ref. [15]) and our calculations with EAM potential (triangles). The barrier is plotted against the ratio of the stressed and the equilibrium lattice constant. b) The effect of strain on the bridge energy and the adsorption site energy of the same system (using EAM potential). Note that around zero stress, the bridge energy is relatively constant, while the stable/metastable energy is changing. (Energy is in eV on all figures.)

FIG. 2. Diffusion barrier of Ag adatom on stressed Ni(111) substrate. a) diffusion barrier and b) bridge and fcc adsorption site energies as function of the ratio of the stressed and equilibrium lattice constant. This case the fcc site energy is constant near equilibrium, and the bridge energy is changing.

FIG. 3. The configuration to measure the effect of an island on the energy landscape. White circles denote substrate atoms, black ones are the hetero atoms. The hexagonal island is of radius 7 on this figure, the black atoms on the top right corner are part of the island because of the periodic boundary conditions. The adatom is moved in the direction of the arrow.
FIG. 4. Diffusion barrier of Ag on Ni(111) near a small Ag island (radius is 4 atoms). The island is pseudomorphic. The bottom figure is magnification of the top figure around the equilibrium barriers.

FIG. 5. Diffusion barrier of Ag on Ni(111) near a large Ag island (radius is 7 atoms). The island is not pseudomorphic. The scale of the plots is the same as on the previous figure.

FIG. 6. Diffusion barrier of Ag on Ni(111) near a large Ni island (radius is 7 atoms). Same scale as previous figure.

FIG. 7. Bonding energy of an atom to strained Ag islands as a function of island radius. The three curves represent different positions of the bonding atom: an extra atom on the middle of the edge of a hexagonal island (triangles), the corner atom of the island (full circles), and the neighbor of a corner atom where the corner atom already absent (empty circles). The case of radius=5 is explained in the text.
FIG. 8. Relaxed island of radius 5 without and with an adjacent adatom. The “pseudomorphic atoms” are grey. (An atom is considered pseudomorphic if it is closer to the stable site extrapolated from the lattice than to other stable or metastable sites.) a) Without adatom: The majority of the island is pseudomorphic, only the edges are pushed out. Note the deformed edges. b) With adatom: The perturbation of the adatom was enough that only the nearby part of the island is pseudomorphic. The other parts are also relaxed, with smooth dislocation network connecting the relaxed parts.

FIG. 9. Unusual deformations like this four-fold hollow site occur on top of an island.