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The Early Stages of Quantum Dot Self-Assembly: A Kinetic Monte Carlo Simulation

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The influence of a periodic strain field in a silicon substrate on the nucleation of surface atomic clusters is studied using a Kinetic Monte Carlo (KMC) model for Ge quantum dot formation. The effect of strain on island diffusion is determined by calculating the binding energy of an island with the Modified Embedded Atom potential. KMC simulations have been carried out on the basis of diffusion pathways on reconstructed Si surfaces and effective island diffusion kinetics. It is found that island diffusion coupled with surface stress fields play a dominant role in precisely forming atomic clusters during the early stages of evolution under an extremely weak inhomogeneous stain field. The results explain experimental observations on the ordering of Ge self-assembled quantum dos along underlying buried interfacial dislocation arrays in a relaxed 800 Å $Si_{0.85}Ge_{0.15}$ buffer layer.

Keywords: Quantum Dot, Surface Strain Field, Island Diffusion, Kinetic Monte Carlo Simulation.

1. INTRODUCTION

With the continued shrinkage of device dimensions in Si VLSI, nanosize atomic clusters with quantum properties have become attractive for next-generation electronics. A pronounced way of forming semiconductor islands of several hundred angstroms in size is to use self-organization effects during hetero-epitaxial growth. However, one of the major challenges in massively fabricating self-organized quantum dots (SAQDs) is the uniformity in size and spatial distribution.

Recently it has been shown that self-assembled quantum dots on semiconductor substrates result from coupling atom and island diffusion with periodic surface stress fields. For example, Dobbs[7] developed rate equations to model the formation of coherent quantum dots in Stranski-Krastanov systems. Another way to study the mechanisms of quantum dot formation is through kinetic Monte Carlo methods (e.g., Barabasi,[1,2] Scholl,[21] and Meixner.[17,18] However, most of their work focused on the problem of the size distribution of quantum dots. Self-assembly is still not precise enough for electronic and photonic applications as a result of size and space non-uniformities. On the other hand, there exist some experimental observations indicating that self-organization of quantum dots is strongly influenced by buried misfit dislocation networks in semiconductor strained heterostructures.[12,28] They preferentially nucleate along buried dislocations, which has a significant spacing larger than the average surface diffusion length of single adatoms.[11] Thus, the way by which the substrate strain field controls the nucleation location of quantum dots becomes an interesting problem.

During physical adsorption, adatoms deposited on the substrate perform thermally activated hopping between possible lattice sites. A natural explanation is that due to changes in lattice distances by the elastic strain, the potential energy of surface atoms is changed, and adsorbed atoms would have a different diffusion energy barrier. Thus, the diffusion of single adatoms is not totally random, but will be directed by the strain field. Indeed, some investigations have shown that there is an effect of the elastic strain field on atomic diffusion. For example, Schroeder used a classical Lennard-Jones (LJ) pair potential model to calculate the energy profiles of FCC, BCC and Simple Cubic (SC) crystalline surfaces and found that the strain field changes the saddle point energy much more than the binding energies.[22] He also found that tensile strain increases the barrier and compressive strain decreases the barrier. The magnitude of these changes is about 0.15 eV per 1% strain. A more complicated case is considered by Hoshino[9] via *ab inito* calculations for the migration of Si adatoms on a strained Si(111) surface. The inhomogeneity of the Si surface induced by the adatom makes the two different activation energies (negative of the energy barrier) change, with a maximum of 0.05 eV per 1% strain. Based on first principles calculations, Shu summarized the change in the surface diffusion barrier by a strain field as a linear relationship:[25]

$$E_i = E_i^0 + A\Delta\sigma\epsilon^{\text{ext}} \quad (1)$$

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where A is the surface area per atom. σ denotes the intrinsic surface-stress tensor and ϵ^{ext} is the external strain field. The numerical values of $A\Delta\sigma$ also show that a compressive (or tensile) strain may either increase or decrease the diffusion barrier as seen by negative signs of $A\Delta\sigma_{yy}$.

Unfortunately, although Shu showed that the effect of strain on diffusion (about 0.1 eV per 2% strain) is quantitatively significant, in practice the applied external field which exhibits a significant effect on self-organization is much weaker. For example, the strain field of buried interfacial dislocations can be estimated as $\nu b/h$, where ν is Poission's ratio, b is Burger's vector and h is the thickness of the substrate layer on the surface. In recent experiments on Ge self-assembled quantum dots on partially relaxed SiGe buffer layers,[11, 12] the thickness is about 80 nm and the length of the Burger's vector is about 0.2 nm. Thus, the strain magnitude is only on the order of 0.1%. Thus, the diffusion energy barrier for an unclustered single atom changes only by 0.01 eV or less. This value is obviously much smaller than strain-free diffusion barriers. In other words, atom clustering effects have to be considered. However, the simulation time for KMC by tracking single adatom hoppings will become unrealistically long. Therefore, modelling clustering effects is one of the motivations behind the current research.

In the present study, we focus on the mechanism of self-assembled quantum dot nucleation on a semiconductor surface in a heteroepitaxial system at the atomistic scale. An effective island diffusion model is proposed to represent the clustering effects during the nucleation as discussed in Section 2, where a simplified model for the migration energy of island diffusion inspired by Mattsson's work[15] is developed using the Modified Embedded Atom Method (MEAM).[3–5] In Section 3, we develop a KMC computer simulation on the basis of effective island kinetics. In order to arrive at reasonable comparison with experimental observations, we first calculate the periodic strain field generated by a buried interfacial misfit dislocation network. The simulation results show agreement with experimental data. The effects of the substrate temperature are also discussed, and the conclusions are finally drawn in Section 4.

2. ISLAND DIFFUSION

A possible reason that single atom diffusion is not able to explain quantum dot self-assembly that is observed experimentally is that the model for single atoms does not account for interactions between atoms. When adatoms jump close enough to one another, they will form clusters. As the size of a cluster becomes large, a new surface is formed. Thus, the effects of external elastic fields on clusters become much larger than a simple linear summation of its effects on individual atoms. This mechanism is consistent with continuum treatments (e.g., Ref. [27]). However, the explicit form of this nonlinear dependence has to be determined by an atomistic approach.

There are several mechanisms for the diffusion of an atom cluster, including random motion of periphery atoms, vacancy migration across the cluster, evaporation and condensation of atoms in the island, and dislocation motion in the island, all of which can induce a shift of the mass center of an island.[14] Since small-size quantum dots are defect-free, we will consider here the motion around the periphery and the evaporation/condensation processes. During the simulation of island diffusion, a simplification is made in which the reconstructed dimer structure of the surface is ignored. The validity of this assumption is supported by the existence of surface steps. It is known that the orientation of different surface steps are totally randomly distributed, and that the normal size of each step is much smaller than the average diffusion length of atom clusters. Thus the random distribution of surface steps dominates any local diffusion anisotropy due to dimer surface reconstruction. The thermodynamic investigations of Metiu[19] indicate that the equilibrium shape of an island is roughly square. We assume here that the island will rearrange all its atoms automatically, and new adatoms join on the periphery of a rectangular spiral. We include island diffusion in the formulation by treating the cluster as one entity. For simplicity, every motion of an island is assumed to be a jump of the island's mass center from one regular lattice site to a nearest neighbor. Hence, this motion should be looked as a final result of many periphery atoms' edge diffusion.

To consider the bias effect of an applied strain field on cluster diffusion, an approach similar to that proposed by Mattson et al.[15] is adopted. We consider the island to be fixed on the surface and calculate the binding energy as a function of island size. Here, we use the Modified Embedded Atom Method (MEAM) for a Si surface, where the parameters for the MEAM of Si and Ge are adopted from Refs. [5, 3] and the geometric factors in MEAM in Ref. [10] are also used.

The excess island binding energy is shown in Figure 1. The result indicates that a semiconductor island has a remarkably different behavior from a metal island. We fit the results for the island binding energy with a 3rd order polynomial function,

$$E_{bc}^{(i)}(N,\varepsilon) \approx (0.0174N^3 - 0.675N^2 + 29.55N - 72.56) \cdot[\varepsilon_x(x,z) + \varepsilon_z(x,z)] \quad (2)$$

where $E_{bc}^{(i)}$ is the change of binding energy of an island with size N. The superscript (i) means that the center of mass of the island is at the lattice site i with the position of (x, y). Following the same method of single atom diffusion, the activation energy barrier of an island on a strained surface can be written as:

$$E_a^{(i)} = E_{a0}^{(i)}(N) + E_{bc}^{(i)}(N, \varepsilon(\bar{x}, \bar{y})) - E_{bc}^{(i)}(N, \varepsilon(x, y)) \quad (3)$$

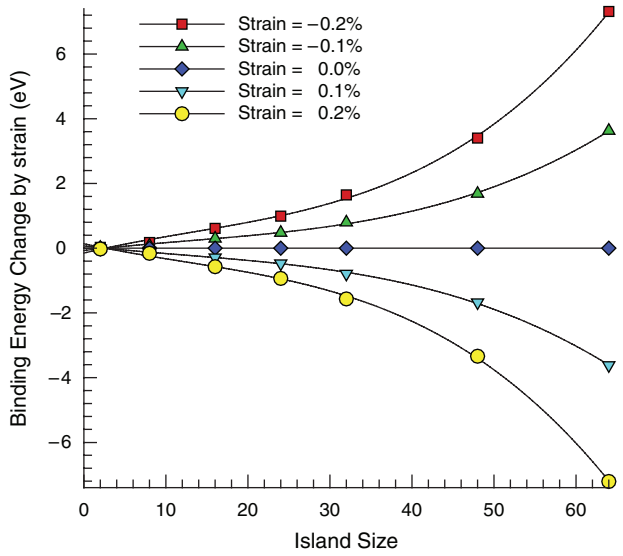

Fig. 1. Binding energy change of an island as a function of size.

where $E_{a0}^{(i)}$ is the activation energy of the island without a strain field. The dependence of the activation energy on the island size and temperature has been determined by Mills et al.[20] It is found that the activation energy changes very little for different island sizes (from $N = 250$ to 2000). Thus, we assume here that the semiconductor surface has a constant value: $E_{a0}^{(i)} \approx 0.79$ eV.

The "random cluster scaling theory" (RCST) gives the island diffusion coefficient as:[24]

$$D^{(i)} \sim N^{-3/2} e^{-} E_a^{(i)}/k_B T \tag{4}$$

where $D^{(i)}$ is the diffusion coefficient of island diffusion. If we assume that islands perform uncorrelated random walk, then

$$D^{(i)} \propto \langle \nu_h \rangle \langle \delta d_{c.m.}^2 \rangle \tag{5}$$

where $\langle \nu_h \rangle$ is the jump rate for island diffusion; $\langle \delta d_{c.m.}^2 \rangle$ is the mean-square displacement of the island mass center per jump event. Since in our accelerated model, every jump distance is assumed to be fixed no matter what size the island is, this means:

$$\langle \delta d_{c.m.}^2 \rangle = \text{const.} \tag{6}$$

Obviously, we have:

$$\langle \nu_h \rangle = \nu_0 N^{-3/2} e^{-E_a^{(i)}/k_B T} \tag{7}$$

We choose the rate constant as: $\nu_0 = 10^{13}$ s^{-1}. The evaporation process in an island can be simulated by chemical kinetics analysis, as discussed in details by Shao et al.[23] and Mattsson et al.[16] Based on the fact that the evaporation is a first-order rate process, we adopt the following relation:

$$p(t)\mathrm{d}t = k_e \mathrm{d}t \exp[-k_e t] \tag{8}$$

Here $p(t)\mathrm{d}t$ is the probability that an island with size N will emit one atom between t and $t + \mathrm{d}t$. k_e is the evaporation rate constant and is dependent on the size N and temperature T, and is of the form:[16, 23]

$$k_e = A \exp[-E_e/k_B T] N^{1/2} \exp[B/N^{1/2}] \tag{9}$$

where A, B and E_e are constants. For $T < 650$ K, $A = 0.063$, $B = 4.07$; for 650 K $< T <$ 950 K, $A = 0.051$, $B = 4.87$; and for $T > 950$ K, $A = 0.086$, $B = 4.55$.[23]

3. KMC SIMULATION RESULTS

The current computer simulations follow the standard kinetic Monte Carlo method[13] based on the effective island diffusion model developed above, and are performed on a 350×350 nm^2 surface area. Two infinitely long straight dislocations are assumed to be buried 80 nm underneath the surface at $x = 250$ nm and $z = 250$ nm, respectively. Since the 80 nm buffer layer is thick and the distances between parallel dislocations is large, the strain field generated by interfacial dislocation networks is known to be extremely weak. Thus, it is reasonable to treat both the interface and the top surface of the substrate as flat. This simplifies the strain field calculation to a simple formula by using the complex variable representation method:[26]

$$\varepsilon_{xx} = \frac{2}{\pi} \frac{(c_{11} - c_{12})}{(c_{11} + c_{12})} \frac{(b_x x + b_z h) x h}{(x^2 + h^2)^2} \tag{10}$$

The elastic stiffness coefficients are set as $c_{11} = 15.79 \times 10^{11}$ erg/cm^3, $c_{12} = 6 \times 10^{11}$ erg/cm^3 and $c_{44} = 7.65 \times 10^{11}$ erg/cm^3 for Si.[8] The edge component of the Burger's vector of an interfacial dislocation in a partially relaxed SiGe buffer layer is estimated directly from the equivalent lattice constants as $b_x \approx -1.93$ Å and $b_z \approx -2.73$ Å, in which the negative sign means that the extra half plane is extended into the substrate.

We notice from Figure 2 that the position of the maximum compressive strain is at the intersection of the extension of the extra half plane and the surface. It can be shown that if the extra half plane is in the upper buffer layer, the maximum compressive region will be at the intersection

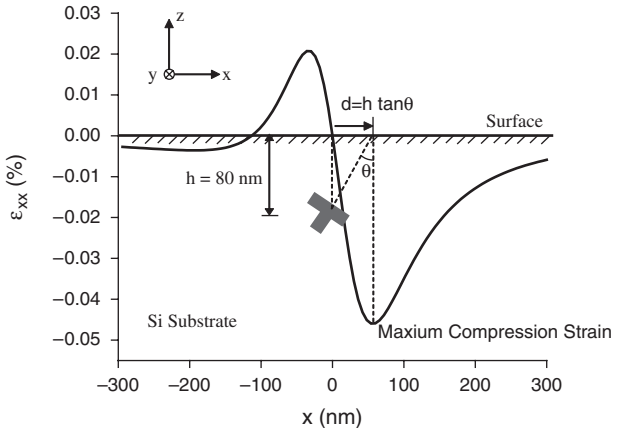

Fig. 2. Surface tangential strain, ϵ_{xx} of an interfacial dislocation buried at 80 nm underneath the Si surface.

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of the slip plane and the surface. It is also found that the strain field decays to zero in the range of 1 μm. In the experiments of Kim et al.[11, 12] the distance between dislocations is about 9 μm. Thus, it is reasonable to use the single dislocation solution (Eq. 10) as the periodic network solution if the length scale of the simulated surface is on the order 1 μm.

With the periodic strain field solved above, we consider that both single adatom and effective island diffusion occur on the surface during a deposition. Specifically, we assume that the hopping of an island effectively follows the same pathways of a single atom as calculated in Ref. 25. Figure 3 shows the evolution of the diffusion process for 500 atoms on the top of the surface at a temperature of 650 °C. The background contours represent the strain field imposed by the interfacial dislocation network. The white dots denote atoms. The clusters of adatoms which contain more than 6 atoms are shown by block arrows pointing to the nearest spot.

It is clear that by introducing island diffusion, Ge atom clusters tend to migrate toward the maximum compression area on the Si surface, even though the external strain field variation is very small. Because of thermal emission, a population of single atoms coexists with islands, as can be seen in Figure 3. The results are in good agreement with the experimental observations for the initial stages of SAQD nucleation, where the coverage of Ge dots is very low ($c_0 = 4.0$ Å).[12]

In Figure 4, we simulate 500 atoms deposited on the surface with the calculated external fields. It is found that during the first 10 μsec, the majority of single atoms diffuse and then cluster to small islands. The island density increases to a maximum value. After the initial 10 μsec, large islands begin to form due to effective island diffusion. The island density decreases by coalescence until it becomes a minimum value, in which equilibrium is obtained between the emission of atoms from the island and the clustering of islands.

The influence of temperature on atom and island diffusion is shown in Figures 5 and 6. In Figure 5, we define a total vector distance as

$$R_{\text{tot}} = \left| \sum_{i=1}^{n} \mathbf{R}_i \right| / n$$

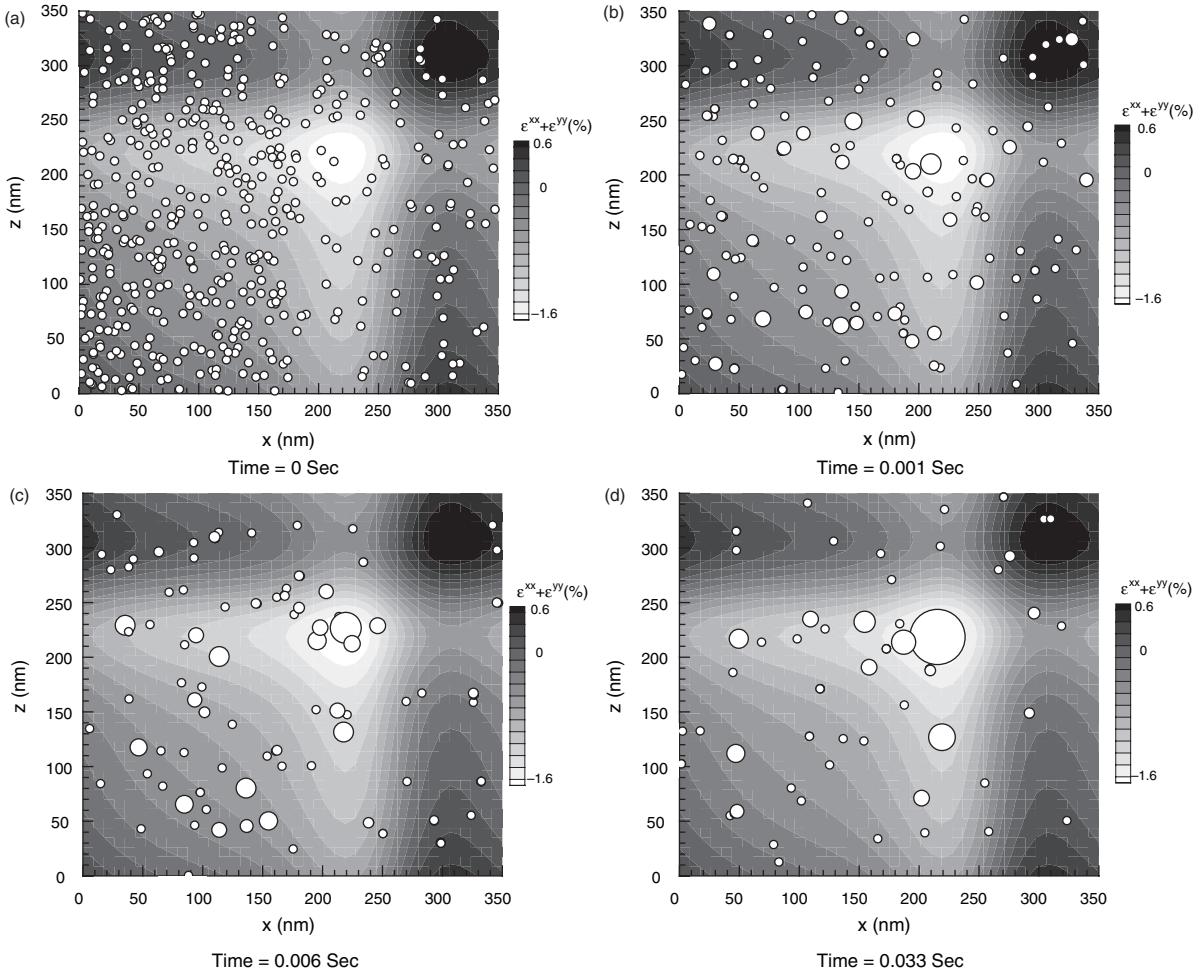

Fig. 3. KMC simulation for 500 Ge atoms on (001) Si surface at 650 °C. The small white dots denote single atoms. The larger (scale to island sizes) white dots denote atomic clusters.

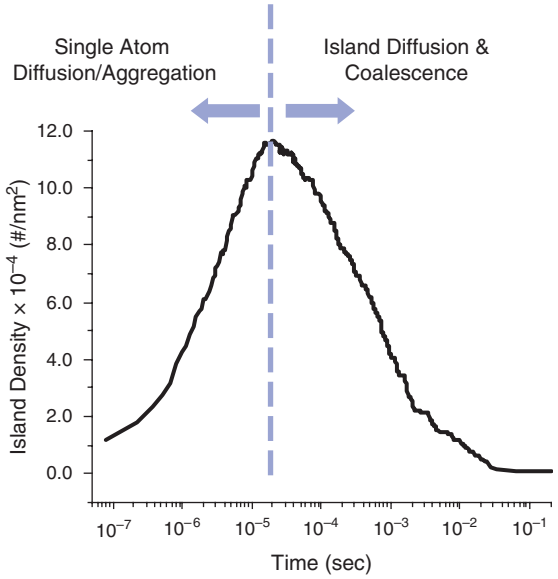

Fig. 4. Dependence of the island density on time indicates the effect of single atom diffusion and that of island migration.

where $\mathbf{R}_i$ denotes the position vector of the ith atom and n is the total number of atoms on the surface square. If the maximum compressive position is defined as R_0, which is the expected equilibrium spot, Figure 5 shows the ratio of the total vector distance to the equilibrium spot as a function of time at three different substrate temperatures. It is concluded that equilibrium takes place very quickly at higher temperatures. The figure also reveals that atom emission from islands provides only a fluctuation effect, and has no remarkable influence on the diffusion process. Thus, ignoring the evaporation effect is a reasonable approximation similar to the conclusions of Bogicevic et al.[6] However it should be noticed that the current simulation cannot explain why there exists different growth modes of thin films. In other words, it means that when the temperature becomes high enough and the island size become large, the effective island diffusion kinetics based on the consideration of binding energy changes is not complete.

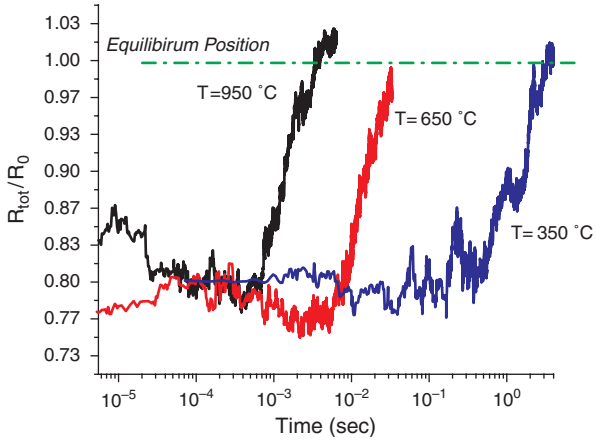

Fig. 5. Comparison of the total vector distance as a function of time at three different temperatures.

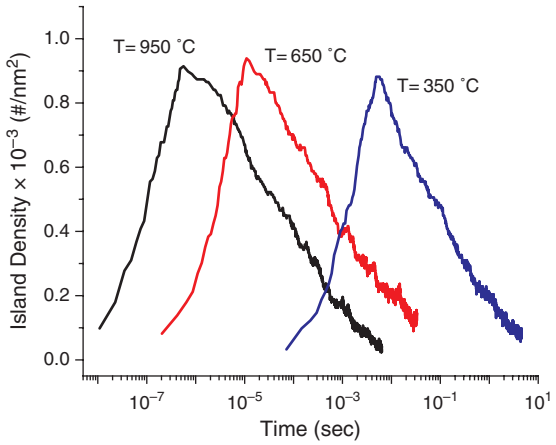

Fig. 6. Comparison of Ge island density at three different temperatures.

4. CONCLUSIONS

We presented here a study of the mechanism of the self-assembled quantum dot nucleation at the maximum compressive sites during the first stage of the deposition on a partially relaxed semiconductor buffer layer. By considering the binding energy changes due to the strain and using the Modified Embedded Atom Method, we obtained a cubic relationship of semiconductor material islands. The clustering effect during the nucleation process is then described by an effective island kinetic model. The KMC simulation result confirms the experimental observations that a surface periodic stress field provides drift motion for single atoms and clusters. However, in the case of a very weak strain bias, the single atom diffusion mechanism is not adequate to indicate self assembly, while cluster diffusion leads to the spatial ordering.

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