Multiscale Modelling of Self-Organized Mono-layer Surface Atomic Clusters

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ABSTRACT

We present here a novel multiscale modelling approach to investigate the conditions for atomic cluster self-organization on atomically flat substrates during epitaxial deposition processes. A phase field model is developed for the free energy of the system, which includes short-range as well as long-range elastic interactions between deposited atoms and atom clusters. The effects of externally applied periodic strain fields through the substrate are also investigated. At very low atomic coverage, a Kinetic Monte Carlo method is used to determine the nucleation conditions for atomic clusters forming on surfaces with periodic strain fields.

Keywords: multiscale modelling, atomic clusters, kinetic Monte Carlo, adatom interactions, self-organization

1 Introduction

Self organization of surface atomic clusters, which is an important aspect of future photonic and electronic devices, is driven by natural instabilities in reaction-diffusion kinetics, and by periodic external force fields. Examples are periodic fields generated by an interfacial dislocation array[1] or by a surface laser field[2]. In the present approach, we present a statistical mechanics model to describe the dynamics of deposited adatoms clustering and the formation of spontaneously ordered structures. The model builds on Suo's approach [3], and is an extension of Walgraef's model [4]. Specifically, we include the effects of external elastic fields and long-range interactions between adatom clusters. In addition to the continuum approach, we investigate the mechanism of clustering at the atomic scale using the Kinetic Monte Carlo method. Comparison and connections between these two methods are discussed in the last section.

2 Phase Field Modelling

2.1 Theoretical Model

We divide a macroscopic surface area into a set of mesoscopic cells and write the partition function $Z^{(i)}$ using the number of substrate sites ($N_S^{(i)}$) and the number of adsorbates within the cell ($N_A^{(i)}$) in each i^{th} mesoscopic cell. By applying the mean field approximation and Sterling's formula, we obtain the total free energy of a system in a form similar to reference [4]. In the present case, the interaction between individual adatoms and the substrate is ignored and the atomic cluster is considered as the parts of the substrate surface to store the elastic energy generated by the external strain field. Thus the energy per i^{th} atom (W_S^i) is approximated as: $W_S^i = \tau \cdot \varepsilon^{(ext)} a^2$, where $\varepsilon_{ext} = \varepsilon - \varepsilon^{(0)}$ is the external strain field applied in the substrate and a is the lattice constant [5]. The dynamic equation for surface atoms based on the conservation of the adsorption (α) and desorption rates (β) and atomic mass current ($\vec{J}$) can be written as:

$$\begin{aligned}\partial_t c &= \frac{1}{\alpha+\beta}(c_0 - c) \\ &\quad + \vec{\nabla}\cdot\left\{\frac{D}{k_B T}\vec{\nabla}\left[\varepsilon^{ext}\tau + k_B T \ln\left(\frac{c}{1-c}\right)\right.\right. \\ &\quad \left.\left. -\varepsilon_0 c - \xi_0^2 \nabla^2 c\right]\right\} \qquad (1)\end{aligned}$$

where $\epsilon_0 = -\sum_j \epsilon_{ij}$ and $\xi_0^2 = \gamma\epsilon a^2$, in which γ is the lattice coordination number, ϵ is the pair interaction energy, a is the lattice constant and positive sign of energy is for attractive interactions.

2.2 Numerical Solution

A Fourier-spectral method is adopted to numerically solve equation (1) with periodic boundary conditions [6]. The 1^{st} order ordinary differential equation (ODE) in Fourier space is solved by the DVODE package with fixed-leading-coefficient implementation [7]. Figure (1) shows a numerical solution for the case of Si layers deposited on a periodically strained surface subjected to a 1-D sinusoidal strain field over the substrate ($\varepsilon_{\max} = 0.05$), in which we choose $a_{Si} = 5.4\,\mathring{A}$, $\tau \approx 0.02\,\mathrm{s}$, $\epsilon_0 \approx 0.22\,\mathrm{eV}$, at temperature $T = 400\,\mathrm{K}$ and the mean coverage of 0.2. Figure (2) shows the same situation but in a 2-D case. In Figure (3), we calculated a surface quantum dot pattern on the 80 nm SiGe buffer

layer with two perpendicular interface dislocations underneath. The uniform coverage is 0.15. The alignments of Ge dots and the existence of corresponding denuded zones are consistent with the experiments of Kim *et al.* [1] which validate the present approach.

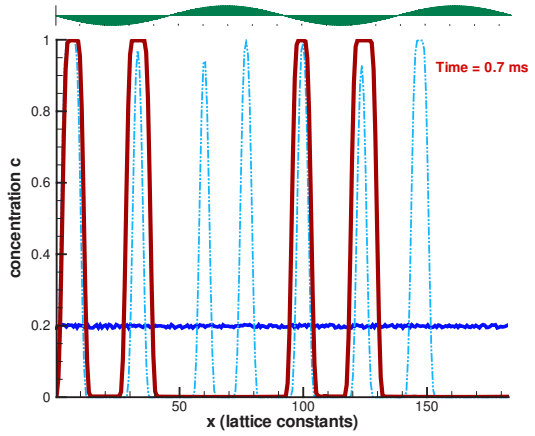

Figure 1: Numerical solution for the dynamic model with a 4-period sinusoidal external field. The initial conditions are small perturbations around the mean concentration. Concentration profiles are shown for the case with (red solid lines) and without (blue dashed lines) a periodic external field.

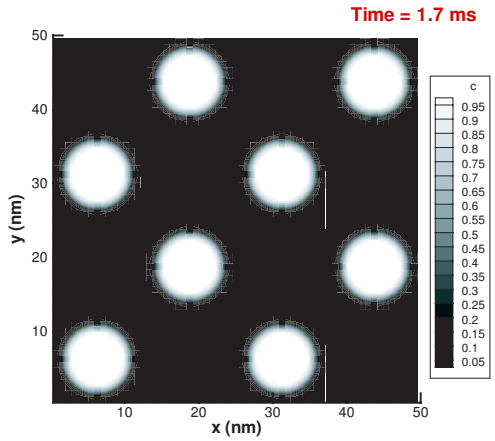

Figure 2: 2-D numerical solution for the same conditions as Fig.(1).

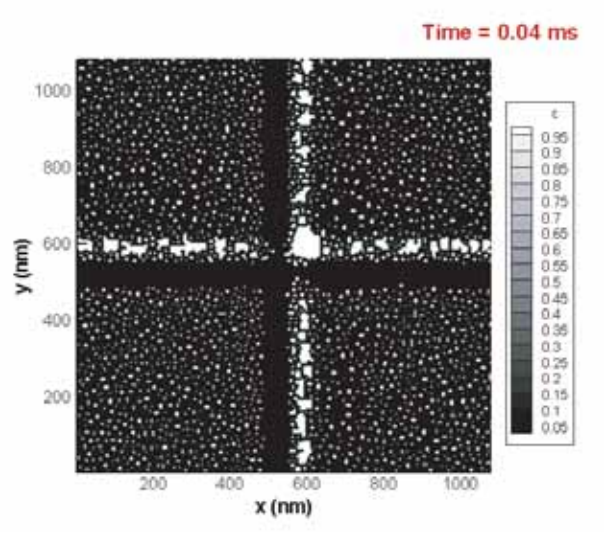

Figure 3: Numerical results for the model with two perpendicular interfacial dislocations underneath a 80 nm SiGe buffer layer. A grid of 128×128 is used.

3 Atomistic Modelling

3.1 Island Diffusion Kinetics

Our investigation shows that atomic island diffusion is mostly affected by the elastic field, causing spontaneous self-organization. In order to consider the strain effect on biased cluster diffusion, a simple model similar to the one proposed by Mattson et al. [8] is adopted. We consider an island fixed on the surface and calculate the binding energy for different island sizes. Here different from the metal-on-metal epitaxy in Mattson's work, the Modified Embedded Atom Methods (MEAM) for a Si surface is used[9]. By fitting the MEAM potential, we obtain the change on binding energy ($E_{bc}^{(i)}$) of a static island with size N and strain fields $\varepsilon_x(x,z)$, $\varepsilon_z(x,z)$ in a 3rd order polynomial function:

$$E_{bc}^{(i)}(N,\varepsilon) \approx \left(0.02N^3 - 0.68N^2 + 29.55N - 72.56\right) \cdot \left[\varepsilon_x(x,z) + \varepsilon_z(x,z)\right] \quad (2)$$

where the energy is in the unit of eV. The energy barrier of an island on a strained surface can be written as:

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

where $E_{a0}^{(i)}$ is the activation energy of the island without a strain field[10]. Here, we assume that the semiconductor surface has a fixed value: $E_{b0}^{(i)} \approx 0.79\,\text{eV}$.

To obtain the probability of island diffusion "events", an opposite thinking as Shöll did in his paper is applied.

First, From "random cluster scaling theory"(RCST), the following relationship is used for the diffusion coefficient of island diffusion $D^{(i)}$[11]:

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

If the random walk is uncorrelated, we can also have:

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

where $\langle \nu_h \rangle$ is the jump rate for island diffusion; $\left\langle \delta d^2_{c.m.} \right\rangle$ is the mean-square displacement of the island mass center per events. In our model, every jump distance is assumed to be fixed that:

$$\left\langle \delta d^2_{c.m.} \right\rangle = \text{const.} \tag{6}$$

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: $\nu_0 = 10^{13}\,\text{sec}^{-1}$. The evaporation process in an island is simulated by the chemical kinetics analysis see [12], [13]. Based on the fact that the evaporation is a first-order rate process, we adopt the following relation as the following:

$$p\,(t)\,dt = k_e dt \exp\left[-k_e t\right] \tag{8}$$

Here, $p(t)dt$ is the probability that an island with size N will emit one atom at a time between t and $t + dt$. k_e is the evaporation rate constant and is dependent on the size N and temperature T with the form of:

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

where A, B and E_e are constants and set to be: when $T < 650\,\text{K}$, $A = 0.063$, $B = 4.07$; when $650\,\text{K} < T < 950\,\text{K}$, $A = 0.051$, $B = 4.87$; when $T > 950\,\text{K}$, $A = 0.086$, $B = 4.55$.

3.2 KMC Simulation Results

Our simulation follows a standard Kinetic Monte Carlo method on $350 \times 350\,\text{nm}^2$ surface area. Two infinitely long straight dislocation lines are buried 80nm underneath the surface at $x = 250\,\text{nm}$ and $z = 250\,\text{nm}$, respectively. Figure 4 shows the diffusion process of 500 atoms on the top of the surface at a temperature of 650°C. The background contours are the strain field imposed by the interfacial dislocation network. The white dot denote the atoms. The clusters of adatoms which contain more than 6 atoms are declared by the block arrows pointing to the nearest spot.

It is clear that by introducing island diffusion, the Ge atom clusters tend to migrate toward the maximum compression area on the Si/SiGe/Ge surface, even though the external strain field is weak at the surface. It is consistent with the expectation made in the above subsection. Due to the emission effect, there always exists single atoms at the same time.

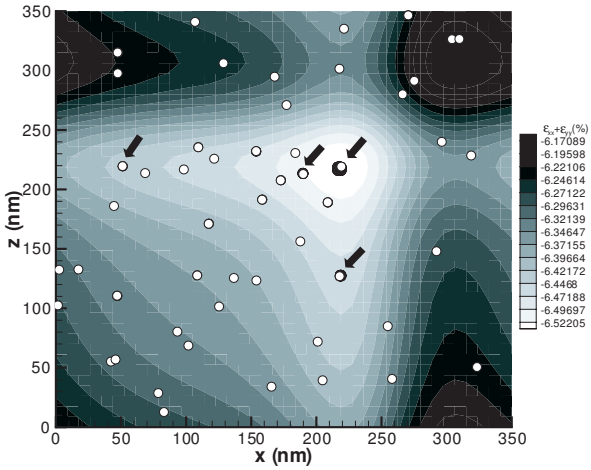

Figure 4: KMC simulation for 500 atoms on surface at 650°C after 0.033 sec

Figure 5 compares the average mean square displacement between an atom diffusion only model and atom-cluster diffusion model. The atom-cluster coupling diffusion model shows a higher mobility and diffusion length and much lower island density. This indicates the self organization effects during the diffusion are taking place. This can also explain why experimentally quantum dots nucleate at places which have a larger distance than the average diffusion length of single atoms [14], [1]. It has been seen that the key role in the simulation is the island diffusion process. Our MEAM calculation shows that in semiconductor system, the self-organization effect tends to be stronger than in metallic systems.

We also compared the diffusion processes at three different temperatures. The results are shown in Figure 6, 7. It can be concluded that higher the temperature can equilibrate the atoms much quicker. Also it reveals that the atom emission process from islands just provides a fluctuation effect and has no remarkable influence on the whole process, which means ignoring the evaporation effect is a reasonable approximation as Bogicevic *et al.* did[15].

4 Conclusions

With the multiscale modeling of self-organized surface atomic clusters presented above, we conclude that a weak external period strain field have a significant effect on self-organized surface adatom clusters, especially in the low coverage case. The clusters are formed in the compressive stress region. With the comparison of

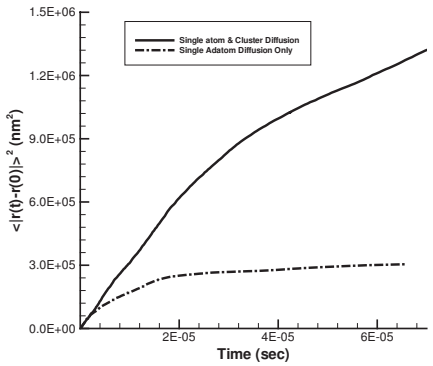

Figure 5: The comparison of average mean square displacement of atom-diffusion-only model and atom/cluster-diffusion model

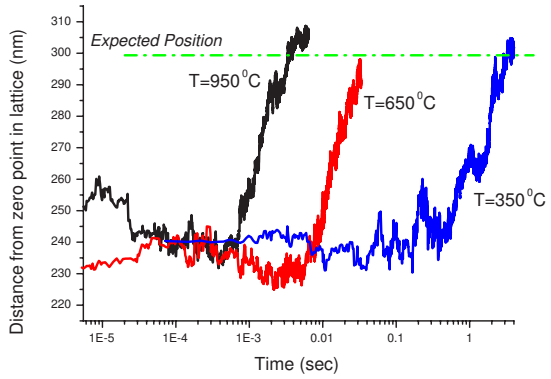

Figure 6: Comparison of distance from the zero point in each cell at three different temperatures

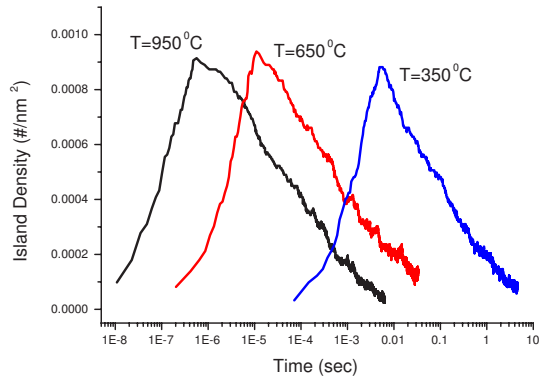

Figure 7: The comparison of Ge island density at three different temperatures

the experimental data, it confirms that the macroscopic elastic theory is valid in evaluating the interaction energy between microscopic adatoms and substrates. We also find that island diffusion plays a dominant role in the early stage of the quantum dot nucleation.

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