MECHANISM OF FORMATION OF SELF-ASSEMBLED NANOSTRUCTURES IN HETEROEPITAXY

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Abstract

We briefly review the recent results on formation of self-assembled nanostructures during heteroepitaxy of immiscible metals. The methods of microscopic modelling of multicomponent growth are described. Results of simulation of self-assembled structures with alternating strips using both lattice and off-lattice atomistic models are presented.

1. INTRODUCTION

The controlled growth of multicomponent films is important field of epitaxy offering many possibilities of preparation of novel artificial nanostructured materials. Recently a growing number of experimental observations have been reported on the formation of nanoscale regular patterns in metal heteroepitaxy for both semiconductor as well as metal substrates. In the case semiconductors substrates the surface reconstruction is often used, for example, the surface Si(111)-7x7 with large unit cells of reconstruction is used as a template for preparation of nanocluster metal arrays [1]. In metallic system spontaneous self-organization is utilized. An example is the observation of "droplet" and "stripe" structures in Cu-Pb films on Cu(111) [2,3].

Interesting class of structures prepared by self-organization form periodic compositionally modulated lateral superlattice structures. These "self-assembled lateral multilayers" (SALM) have been prepared by co-deposition of two immiscible metal on an anisotropic surface. Two metallic systems with the interesting magnetic properties have been found: Co-Ag and Fe-Ag films grown on Mo(110) [4,5]. SALM structure was observed also for growth of $CoSi_2$ on the Si(100) surface [6]. It was observed already before these studies that growth of two immiscible metal on isotropic surface, Co-Ag on Ru(0001) [7], can lead to a pattern with alternating stripes. However, instability of growth was reported in this case which was supposed to be generic for multi-component growth.

It is know from the thermodynamical considerations that the composition-modulation wavelength reflects a competition between chemical interactions, favoring phase separation, and elastic interactions (arising from mismatch in atomic sizes), favoring alloying [8]. However, it is not understood so far what is the real microscopic mechanism of formation of multi-component structures and what is the role of kinetics. It is also not well explored how features of nanostructures depend on control and material parameters. The latter is the crucial knowledge for preparation of such nanostructures.

In this contribution, we will describe how numerical simulations of growth [9] can be employed for solving these problems and what are difficulties and today's limitations. In particular, we

shall underline that off-lattice simulations need to be used for the correct description of systems with strain. Then we shall show that by using simplified simulations it is possible to obtain information on dependences of morphology on control and material parameters.

2. METHODS OF STUDY

In this section we describe methods of study of stripe structures used in the literature and discuss possible methods of simulation of these structures.

2.1. Models with continuous description of elastic interactions

A continuum elasticity model of SALM formation has been developed by Marchenko [10] and Vanderbilt [11]. This model predicts that the lowest energy state domain patterns are periodic stripe and ordered droplet phases [12]. This is in qualitative agreement with the experiments. However, the physical applicability of the continuum theory for formation of SALM structures in metal alloys is uncertain due to rather small length scales observed in experiments (order of 2 nm cf. [4,7]). Therefore, models combining continuum elasticity theory with discrete spin model were proposed [13,14] revealing a failure of continuum description. Parameters of these hybrid models could be calculated by standard *ab intio* electronic-structure calculation for specific materials but the models are static and do not allow to study kinetic effects.

2.2. Lattice simulations – kinetic Monte Carlo (KMC)

Kinetic Monte Carlo is now the standard tool for study of crystal growth [9] which can be in principle used for also the study of formation of stripe structures. Usually the discrete position of atoms are supposed (lattice simulation) in KMC. Then it is possible to perform simulations on realistic time scales. Crucial point is to identify relevant microscopic processes and to know what are rates for them. This information can be obtained by application of molecular dynamics simulation (cf. bellow). There is no problem to consider multi-component systems with different binding energies at the cost of increase of the number of parameters. However, due to fixed atomic position it is not straightforward to implement effect of elastic interactions.

We use growth model in 2+1 dimension with two species (A and B) deposited on a planar substrate with a step and the size M x N. Particles are randomly deposited with fluxes F_A and F_B. Particles interact with nearest-neighbors through attractive two particle interaction with binding energies E^{AA}, E^{BB}, E^{AB}. Diffusion of adatoms on the surface is described by thermally activated hopping to nearest-neighbor sites with Arrhenius rate given by an activation energy. Activation energies for different hops depend on combinations of the binding energies which in turn depends on the configuration at initial and final position. Since we are interested only in submonolayer regime we disregard second layer nucleation.

The simulation presented here were performed for the simple choice $E^{AA} = E^{BB} = E^0$. Co-deposition with fluxes $F_A = F_B = 0.005$ ML/s at different temperatures T, different interactions E^{AB} and different system sizes. Deposition is stopped when the coverage is 0.5 ML, i.e. half of the system is filled. Further details of the model and the simulation will be described elsewhere.

2.3. Off-lattice simulations – molecular dynamics

Molecular dynamics (MD) is the natural tool for investigation of time dependent effects, however, it cannot by employed for the study of heteroepitaxy due to very short simulated times in comparison with experimental times. MD is used for investigation of equilibrium properties and calculation of rates of kinetic processes whose are then utilized in kinetic Monte Carlo simulation. The key ingredient of MD is the interaction potential. If one aims to reproduce experiment for a specific material then the *ab initio* calculation should be used even if *ab initio*

calculations are very computer demanding. However, if one is interested the generic behavior (e.g. how pattern formation depends on material parameters) then application of *ab initio* calculations turns to be practically non-treatable problem. For the latter purpose model or semi-empirical potentials are typically used.

In the study strip formation, we need to consider two different metals A and B which are also different from the substrate S. There is the difficulty with the choice of the potential. The reliable potentials for multi-component materials exist only for a few combinations of metals. In this situation, one can utilize the simplest possibility: the Lennard-Jones potential and the simple averaging scheme for calculation of potential parameter between different particle types. Lennard-Jones potential has two parameters: depth of the potential E and the equilibrium particle distance σ. In the minimal model we have parameters: E_S, E_A, E_B and $\sigma_S=1$, $\sigma_A=1-\varepsilon$, $\sigma_B=1+\varepsilon$ for three species S, A, B, interspecies energies E_{XY} given by geometrical average and interspecies distances σ_{XY} by algebraic average. To unsure comparability with the above lattice method simulations are also performed for simple cubic geometry this is done by using a convenient form of the potential [15].

2.4. Off-lattice simulations – kinetic Monte Carlo

In order to study in the same time the influence a competition between chemical and elastic interactions and effects of growth a combination of KMC and MD is needed. We adapt an off-lattice KMC method developed in [16].

3. RESULTS OF SIMULATIONS

Here we present the illustrative results of both lattice and off-lattice simulations.

3.1. Lattice KMC simulations

We have found that already lattice KMC simulation containing only binding interaction with proper energies can lead to the formation of stripe morphology. It is observed in the regime when interaction between particles of the different type is weaker than between those of the same type: $E^{AB} < E^0$ see Fig. 1. This is in agreement with hypotheses in [7]. The Figure 1 also shows that the strip width increases with decreasing binding energy between A and B particles.

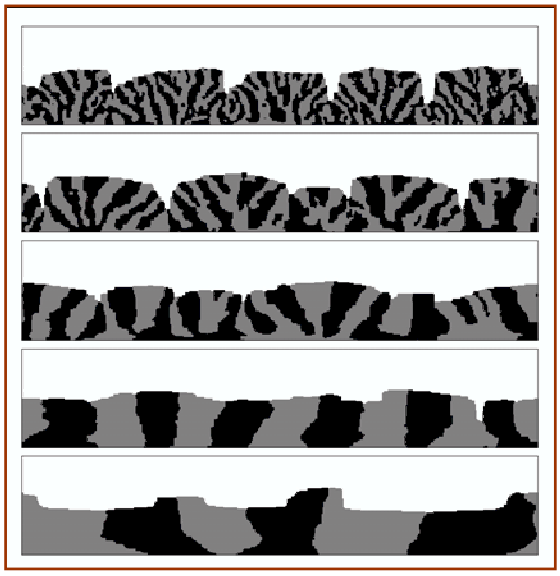

Fig.1. Strip morphology obtained by lattice KMC simulations for E^{AB}/E^0 = 0.6, 0.55, 0.47, 0.39, 0.31 (from top to bottom). System sizes are 512 x 100.

The interface between stripes is rather rough. So, this mechanism does not lead to a stable nicely ordered pattern. Notice that at the same time the profile of the grown step is very rough as well. In fact, we have found that roughness of step increases very rapidly with the time indicating a large value of growth exponent β. It is known from the studies of kinetic roughening (see e.g. [17]) that the roughness can strongly depend on detailed growth rules. To explore this fact we used two different variants of the code: i) code without corner rounding (the original code for which the above results were obtained) and ii) modified code with corner rounding implemented by allowing diffusion jumps to next nearest neighbors. We can see in Fig. 2 that the simulations with the modified code produce more regular strip structures. The boundaries between stripes as well as the roughness of the step are much more smooth.

The Figure 2 also shows that there is an increase of mean strip width with the temperature. Quantitative dependence is shown in Fig. 3.

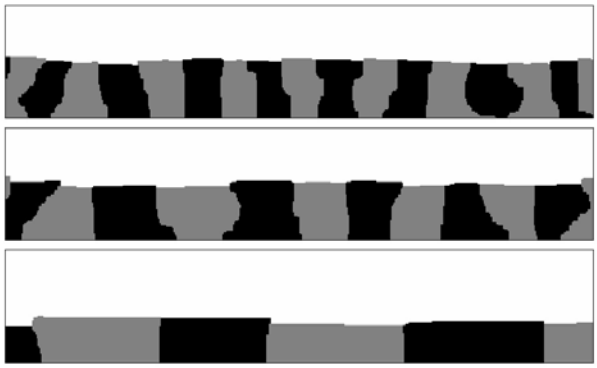

Fig 2. Strip morphologies obtained by lattice KMC simulation with modified code allowing corner rounding for temperatures T=400 K, 450 K, 500 K (top to bottom) and for $E^{AB}/E^{0} = 0.31$. For each temperature a section of size 512 x 100 of the 1024 x 100 system is shown.

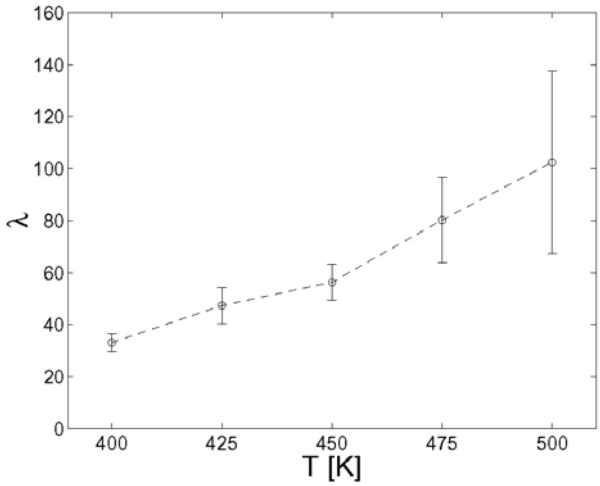

Fig. 3. Temperature dependence of mean stripe width λ measured in the same type of simulations as in Fig. 2. Results were obtained by averaging over five independent runs for the 1024 x 100 system.

3.2. Equilibrium MD simulations: competition of elastic and chemical interactions

In order to test the influence of misfit strain and binding energy we performed equilibrium MD simulation for full coverage on the surface and given ratio of A and B particles. Figure 4 shows typical configurations for the same number of A and B particles, different values of misfit ε and binding energy E_{AB}. We can see that the competition of both effects leads to regular alternating A and B stripes. Quantitative dependences of width of A and B stripe on mismatch and concentration of both components are presented in Fig. 5. We can see that for the same concentration of both components $\eta_A = \eta_B$ (left panel) width of strips of both types is approximately the same, whereas for different concentrations the situation is completely different. The bigger B particles form the thinner stripes at high B concentration than smaller A particles at high A concentration.

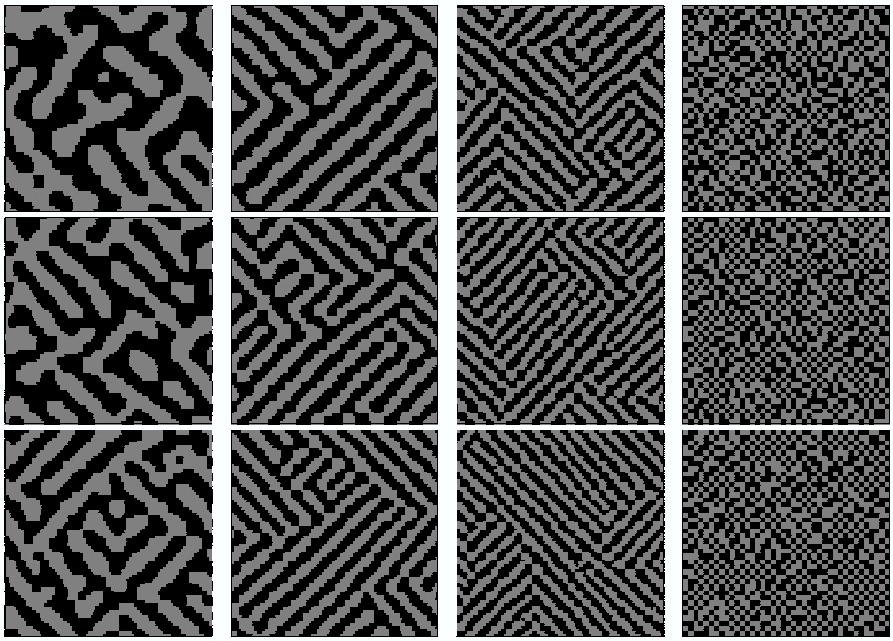

Fig. 4. Examples of equilibrated surface configurations obtained by off-lattice simulations with $E_{AB} = 0.6E_A$, $E_{AB} = 0.8E_A$, $E_{AB} = 0.9E_A$, $E_{AB} = 1.0E_A$ (from the left to the right) and ε=4.5% , ε=5.0%, ε=5.5% (top to bottom). The bigger B particles are shown in light gray. Panels for $E_{AB} = 1.0E_A$ show 40 x 40 sections the remaining panels show 80 x 80 sections.

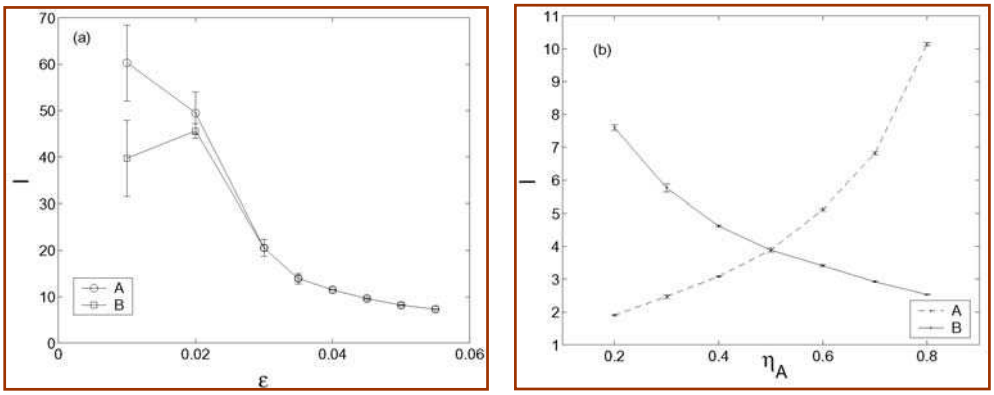

Fig. 5. Left panel: strip width for the same particle concentration and $E_{AB} = 0.6E_A$ as a function of misfit. Right panel: strip width for $E_{AB} = 0.9E_A$ and ε=5% as a function of A particle concentration η_A.

3.3. Off-lattice KMC simulation

Preliminary tests of off-lattice simulations verified that study of morphologies with this method is possible although rather computer time demanding. Fig. 6 shows an example obtained by extensive simulation. It illustrates that large dendritic instabilities can develop during growth in agreement with experiment [7].

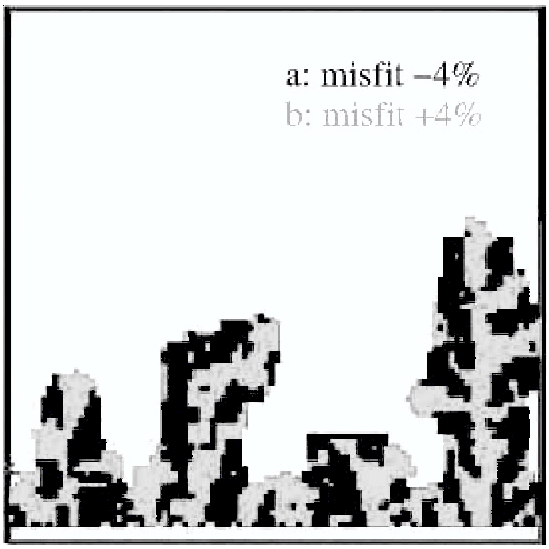

Fig. 6. Example of configuration obtained by off-lattice simulation.

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