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Island-size selectivity during 2D Ag island coarsening on Ag(111)

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Abstract

We report on the early stages of submonolayer Ag island coarsening on the Ag(111) surface carried out using kinetic Monte Carlo simulations for several temperatures. Our simulations were performed using a very large database of processes identified by their local environment and whose activation barriers were calculated using the semi-empirical interaction potentials based on the embedded-atom method. We find that during the early stages, coarsening proceeds as a sequence of selected island sizes, creating peaks and valleys in the island-size distribution. This island-size selectivity is independent of initial conditions and results from the formation of kinetically stable islands for certain sizes as dictated by the relative energetics of edge atom detachment/attachment processes together with the large activation barrier for kink detachment. Our results indicate that by tuning the growth temperature it is possible to enhance the island-size selectivity

(Some figures in this article are in colour only in the electronic version)

The phenomenon of coarsening or ripening plays an important role in a wide variety of processes in many branches of the physical sciences. Particular attention has been paid to Ostwald ripening (OR) [1] which is a general feature at late stages of phase separation, driven by lowering of excess surface free energy associated with island edges. In OR, islands larger than a critical size grow at the expense of smaller ones. Scanning tunneling microscopy (STM) studies at room temperature have revealed that during the late stages, Ag/Ag(111) coarsening is dominated by OR [2, 3]. What has not been studied in depth so far is the initial stage of the coarsening process which may point to certain features that could be used to tune growth patterns of thin films.

In this paper, we present results of kinetic Monte Carlo (KMC) simulations of the initial stages of coarsening of two-dimensional Ag islands on Ag(111). These simulations made use of a very large database of processes which was obtained from previous self-learning KMC (SLKMC) [4–6] simulations of small and large Ag/Ag(111) island diffusion carried out at 300 and 500 K. All processes in this database move atoms from one fcc site to another. We examined the dependence of island-size distribution (ISD), as coarsening proceeds, on the choice of initial ISD and shape of the islands, and the surface temperature. Although most of the results shown here are for a Gaussian ISD, we have also carried out simulations starting with random, delta ISDs and random distribution of monomers.

In an SLKMC simulation, rather than using a fixed catalog of processes with given activation barriers, processes and their energetics are obtained on the fly and stored in the database, whenever a new configuration is detected. In an earlier study [7], we used this database to carry out long timescale (few hundred seconds) KMC simulations of Ag(111) island coarsening at room temperature. In determining activation energies we used interaction potentials based on the embedded-atom method (EAM) as developed by Foiles et al [8]. A simplification was introduced by assuming a ‘normal’ value for all diffusion prefactors, although we are aware that multi-atom processes may be characterized by high prefactors [9–11]. Rates are, however, not expected to be strongly affected in the explored low/moderate temperature regime. More details about database acquisition/types of processes frequented and recipes for speeding KMC simulations can be found in [7].
The initial configuration for these coarsening simulations was created by dividing the empty lattice into boxes and placing islands of different sizes randomly at the center of the box to prevent overlap of islands. The number of islands of a particular size depends on whether the starting ISD is a Gaussian or a delta function. To avoid finite-size effects we carried out simulations using a relatively large system size of $1024 \times 1024$ fcc lattice units with periodic boundary conditions, and in order to obtain good statistics we averaged our results over 10 runs.

Our starting ISD with a Gaussian distribution has a total of 742 islands with a peak of 100 islands at the average island size and a width of three. The total number of islands is kept constant (742) for all further simulations by keeping the peak island count and the width of the Gaussian distribution constant regardless of the average island size. We also take the total number of islands in the initial delta ISD to be 742, as in all others. For simplicity the initial shapes of islands are chosen arbitrarily and islands of the same size are assigned the same shape. For the results presented here, most of the island shapes are either compact or close to compact. In addition, we have carried out coarsening simulations with fractal island shapes and initial random ISD, and also initial random distribution of monomers.

To capture features dominating the early stages of coarsening we carried out simulations for 3.0 s. Figures 1(a) and (b) show ISDs after 3 s of coarsening for initial average island sizes of 15 and 16 atoms for Gaussian initial ISDs, while figures 1(c) and (d) display ISDs after 10.0 ms and 1.0 s of coarsening for initial average island size of 10 atoms when the initial ISD is a delta function. As is evident, during coarsening there is a dramatic change in the ISD from a smooth Gaussian or delta distribution to a non-smooth distribution with peaks and valleys at specific island sizes. From figure 1 it can be seen that island sizes whose populations are either a peak or a valley in the ISD remain so as the coarsening proceeds. Furthermore the behavior of ISD with peaks and valleys is independent of the initial configuration and the initial average island size. Table 1 summarizes island sizes up to 35 atoms according to whether they constitute a peak, a valley or neither in the ISD after 1.0 s of coarsening. For some island sizes (19, 27 and 30 atoms) the ISD has neither a peak nor a valley (table 1). Islands containing either 23 or 24 atoms, may constitute a peak, but for the most part, the 23 atom one is a peak, while the 24 atom one is neither a peak nor a valley. Note that at much later times all islands will follow OR, resulting in one large island; the total energy of the system will decrease as more bonds are formed until it saturates when one large island is formed.

We note from figure 1 that the characteristics of coarsening are independent of whether the initial ISD is Gaussian or a delta function. We also observed the same behavior when coarsening simulations were started with an initial configuration created
Figure 2. Decay of the number of islands with time for several island sizes at $T = 300$ K. At $t = 0$ the number of islands is 100. The inset shows the same at very early stages.

by depositing atoms at very low temperature (135 K). At this temperature islands are fractal and ISD is random. Thus, in what follows we concentrate our discussion on the results only for the Gaussian distribution. Figure 2 shows the decay in the number density of islands with 11–14 atoms with time. It is clear that 11 atom and 13 atom (valleys) islands decay exponentially in the very first few microseconds of coarsening. The densities of islands with 12 and 14 atoms (peaks) increase for the first few microseconds before starting to decay at a much slower rate. The same pattern emerges for all island sizes constituting peaks or valleys. A similar decay of island densities is also observed when the initial ISD is a delta function.

Peaks and valleys in the ISD during coarsening and differences in the rate of decay of densities of corresponding island sizes show that coarsening occurs through a sequence of selected island sizes, which form kinetically stable islands. In addition, ISD exhibits the same characteristic behavior even when the shapes of islands are altered in the initial configuration: all islands with kinetically stable (or low-energy) or fractal or other irregular shape lead to the same results for ISD [12]. This shows that island-size selectivity is independent of parameters of initial configuration including shapes of the islands, and hence the broader implications of our results.

From experimental [2, 13] and theoretical studies [7] it is known that for 2D Ag/Ag(111) coarsening is due to evaporation–condensation mediated by monomer diffusion between islands. For further investigation into island-size selectivity, we examined the energetics of detachment processes on the basis of island size. We find that for all island sizes larger than eight atoms, the most frequent detachment process is an atom detaching from a step edge to create a monomer. For island sizes smaller than eight atoms, the energy barrier for concerted diffusion is quite small (0.1–0.3 eV) compared to the single atom detachment process, causing these islands to diffuse and coalesce with others. In addition, we find that the number of events of edge atom detachment for island sizes whose populations are valleys in the ISD is higher than for island sizes whose populations are peaks. Figure 3 shows the most frequent detachment processes (of edge atoms) for islands along with their corresponding activation barriers. Because the detachment barrier for an atom with at least three nearest neighbor atoms is greater than 0.7 eV, they rarely detach to create monomers at room temperature. These arguments based on system energetics confirm findings in our KMC simulations that islands whose populations are valleys in the ISD usually have an edge atom in their shapes. From figure 3 it can also be seen that the difference between an edge diffusion barrier and an edge atom detachment barrier is quite small, especially on a B-type step edge, making detachment of an edge atom relatively easy and hence a frequent process. Any island with an edge atom either loses this atom through detachment (leaving a smaller island of selected size) or attracts (less frequently) a nearby monomer (creating a bigger island of selected size), the overall result being the creation of island sizes whose populations show up either as peaks or valleys in the ISD. Consequently, island sizes whose populations are peaks in the ISD do not have edge atoms: all atoms have at least three nearest neighbors, making them kinetically stable islands; a result again confirmed by our KMC simulations. Consider, for example, the non-selected island set of sizes 11, 13, 15 and 17 atoms whose densities are zero in figure 1, and the other of sizes 20, 22, 25, 28, 31 and 34 atoms whose densities are small but non-zero. The former set rarely forms kinetically stable shapes, while the latter does, albeit less frequently than the ones that show up as peaks in the ISD.

We have also carried out simulations in which barriers for the most frequent detachment processes were increased, thereby increasing the difference between edge diffusion and detachment barriers. We find that with the increasing difference, the onset of island selectivity shifted to later times. This shows that the difference in energy barriers between edge atom detachment and edge diffusion processes controls the onset of island-size selectivity. Accordingly, we conclude that island-size selection is primarily due to adatom detachment and attachment processes at island boundaries owing to the relative ease with which atoms can detach in comparison with the relative difficulty for the detachment of atoms with at least three neighbors. Figure 4 is a snapshot of the morphology of the Ag(111) surface after coarsening at room temperature when the initial average island size was 19 atoms with Gaussian initial ISD. This snapshot corresponds to a $128 \times 128$ portion of a $1024 \times 1024$ system. Note the survival of compact 18 atom, 19 atom and 21 atoms islands. Accordingly, we conclude that island-size selection is primarily due to adatom detachment and attachment processes at island boundaries owing to the relative ease with which edge atoms can detach in comparison with the relative difficulty for the detachment of atoms with at least three nearest neighbors. Elsewhere we show that these factors also restrict the shapes of island that may form during coarsening [12]. Certain non-selected island sizes (valleys in ISD), which may otherwise form a kinetically stable shape do.
Figure 3. Activation barriers (in eV) for the most frequent detachment and edge diffusion processes.

Figure 4. Island morphology during room-temperature coarsening for initial average island size of 19 atoms with a Gaussian initial ISD. Pictures correspond to a 128 × 128 portion of a 1024 × 1024 system.

not persist in the simulations since their formation by adatom attachment or detachment is not found to be followed by shape rearrangement due to a high kink detachment barrier.

Figure 5 shows the variation of the ratio of number of attachment to detachment events at 300 K after 3.0 s of coarsening with initial average island size for initial Gaussian and delta ISDs. Figure 5 also shows the ratio for an average island size of \( N = 16^* \) when the coarsening is started with a Gaussian initial ISD in which all islands have shapes that are either low-energy [14] or kinetically stable. It can be seen that peaks and valleys are exactly at the same island size as in the ISDs. This shows that densities of selected island sizes decay because of attachment events while non-selected island sizes decay because of detachment of edge atoms. Interestingly, they all collapse to a single curve, indicating that this ratio is independent of all parameters for initial ISD and also of the shapes of the islands in the initial configuration. From this we conclude that island-size selectivity is the behavior of the early stages of Ag/Ag(111) coarsening and is independent of the initial configuration used to start the coarsening.

Figure 5. Ratio of number of attachment to detachment events at 300 K after 3 s of coarsening for a Gaussian initial ISD (\( N = 14, 16, 17 \)), delta initial ISD (\( N = 16 \)) and Gaussian initial ISD with islands either having kinetically stable or low-energy shapes (\( N = 16^* \)).

We also investigated how island-size selectivity depends on temperature after 3.0 s of coarsening. Figure 6 shows ISDs for an initial average island size of 16 atoms in the temperature range 200–310 K when the initial ISD is a Gaussian. It is easy to see that while the island-size selectivity is independent of temperature, the strength of selectivity is temperature dependent and is particularly strong in the range 250 and 270 K. This can be seen in figure 6 for 250 K for which the population of island sizes which correspond to peaks in the ISD increases beyond their magnitude in the initial configuration, at the expense of those which constitute valleys in the ISD. As the system coarsens further, the selectivity will
eventually decay and will look similar to ISDs after coarsening for shorter time scales at higher temperatures. At temperatures below 240 K coarsening occurs at a slower rate such that the island-size selectivity does not emerge during the initial 3.0 s of coarsening. Above 270 K coarsening happens at a faster rate and even though island density decays rapidly, island-size selectivity is still detected. In the temperature range 250–270 K, coarsening occurs at an optimal rate enabling island-size selectivity to be observed during the data taking. We also find that the smaller the average island size in the initial configuration, the more quickly the ISD changes to peaks and valleys.

In summary, we find that during the early stages, 2D Ag/Ag(111) island coarsening proceeds as a sequence of selected island sizes, whose densities decay at rates slower than that of the others because of the formation of kinetically stable island shapes. The densities of non-selected sizes (valleys) decay at a faster pace due to frequent adatom attachment/detachment processes. We also find that this behavior is independent of all parameters of the initial configuration showing that it is a characteristic of the early stages of Ag island coarsening on Ag(111). Finally, we find that the strength of island-size selectivity depends on temperature and is strongest between 250–270 K, though the peaks and valleys in the ISD are independent of temperature. It is thus possible to tune the growth temperature so as to take advantage of the enhanced island-size selectivity. We await experimental findings to validate our predictions.

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