10 Evolution of Two-Dimensional Nanoclusters on Surfaces

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1 POST-GROWTH KINETICS OF 2D NANOCLUSTERS

Many scientists are forging ahead with nanotechnology nowadays. Very often, one needs to assess the stability of nanostructures. This involves some detailed knowledge on how the boundaries and interfaces propagate. While this has long been a central problem in classical fluid dynamics and metallurgy, its extent of validity in nanoscale needs careful examination.

This paper focuses on the evolution of two-dimensional nanoclusters with shapes far from equilibrium. Before tackling this phenomenon quantitatively, we first describe the post-growth cluster kinetics in submonolayer homoepitaxy, including cluster diffusion and aggregation via diffusion.

1.1 Diffusion, Diffusion Mediated Coarsening, and Reshaping

Conventional wisdom presumes negligible cluster diffusivity. Though some theoretical studies point out such possibility (Voter, 1986), it is nevertheless quite a surprise when it was reported (Wen, 1994) that Ag clusters on Ag(100) with sizes over several hundred atoms can possess significant mobility (~10^{-17} cm^2/s for 100-atom islands). It was later found conclusively that such mobility is a direct consequence of equilibrium boundary fluctuations caused by atoms diffusing along cluster boundary (Pai, 1997). By carefully measuring cluster diffusivity of Cu/Cu(100) and Ag/Ag(100), Pai *et al.* obtained the peripheral mass mobility coefficient, σ_{PD}. As one will see in **1.2**, this kinetic parameter and the step line tension are already sufficient to describe the reshaping process of complicated worm-like nanoclusters.

At higher temperatures, evaporation and condensation of atoms at cluster boundary start to occur. However, the dominant contribution to cluster diffusivity remains to be peripheral diffusion for both Ag(100) and Cu(100) surfaces. While this is not the case for an open surface like Ag(110) (Morgenstern, 2001), we shall limit our discussion to the peripheral diffusion case.

Realizing clusters by themselves can diffuse, a new route for cluster coarsening can be envisioned. Contrary to the conventional Ostwald ripening in which the clusters exchange mass through the surrounding, cluster diffusion can

lead to coarsening simply by "colliding" with each other. Time-sequenced STM study (Pai, 1997) indeed shows direct evidence of such behaviour.

Clearly, upon cluster "collision", the aggregated cluster (now becomes one) has a shape far from equilibrium. This is often of dumbbell shape for adatom clusters, or extended worm-like vacancy clusters if the deposited layer starts to percolate (at ~0.6 monolayer). In all cases, their shapes shall relax accordingly to minimize the free energy. The relaxation kinetics depends on the mechanism of mass transport. In our case, the dominant mass transport is along cluster periphery. This is analogous to surface diffusion in the 3-D case (Mullins, 1957) but is different from viscous flow in hydrodynamics.

2 EVOLUTION OF NANOCLUSTER TOWARD EQUILIBRIUM SHAPE

2.1 Continuum Model Approach

The reshaping process observed with STM appears smooth and fluid-like for clusters as small as couple tens nanometer in length, suggesting a coarse-grained continuum approach is appropriate. From the cluster diffusion study, the dominant mass transport is shown to be along the boundary. In this case, the edge mass flow is governed by the local chemical potential gradient along periphery and the step edge mobility σ_{PD}. Noting that the local chemical potential is proportional to step line tension $\tilde{\beta}$ and local curvature κ, one derives the step normal velocity υ_n from local mass conservation law and obtains

$$v_n = -(k_B T)^{-1} \Omega^2 \sigma_{PD} \tilde{\beta} \nabla_\tau^2 \kappa(s) \qquad (1.1)$$

where Ω is the unit atomic area. In our formalism, σ_{PD} has the dimension of $Å s^{-1}$ and $\tilde{\beta}$ has the dimension of $eVÅ^{-1}$. The cluster boundary has been represented parametrically as $\mathbf{r}(s)=(x(s), y(s))$ and ∇_τ is the derivative along $\mathbf{r}(s)$.

This continuum model is purely geometry driven and is applicable to both adatom and vacancy clusters. Furthermore, without taking into account thermal fluctuations, its applicability is independent of cluster sizes for identical type of mass transport. For self-similar clusters, the characteristic reshaping time t_c will scale with the characteristic length λ as $t_c \sim \lambda^4$. This is supported by measurements on Ag(111) (Rosenfeld, 1998).

Modelling of reshaping is applied to extended worm-like clusters to get more insight. Values of β and σ_{PD} are taken as $\sim 40 meVÅ^{-1}$ and $\sim 50 Å s^{-1}$, respectively (Pai, 1997). Calculated result is shown in Fig. 1.1. Besides the surprisingly good match of overall reshaping process and time-scale, this simple continuum model reveals two additional features. First, a pinch-off at narrow neck is observed (see Fig. 1.1d). Secondly, step normal velocities at corners are overestimated in calculation (see Fig. 1.1b). The first observation is in fact a unique feature of peripheral diffusion mediated mass transport. If the reshaping is mediated by atom evaporation and condensation at step, the local mass flow is controlled by local curvature instead of its gradient along boundary. Simple geometric consideration shows self-crossing of island boundary is then prevented. This heuristic argument corroborates the finding of previous island diffusion study.

Discrepancy indicated by arrows in Fig. 1.1b could be due to either thermodynamic or kinetic reasons. This is clear from equation (1.1) in which the azimuthal dependence of β and σ_{PD} can both introduce the observed anisotropy. Since σ_{PD} requires knowledge of atomistic energetics as well as the boundary structure as a *priori*, it will be addressed by kinetic Monte Carlo simulation. Here we demonstrate, by incorporating an anisotropic β assuming Ising-like nearest neighbour interaction, the discrepancy can almost be fully addressed. Step normal velocity at corners is reduced because β is smaller there for a more open step structure. Figure 1.2 shows the result from the anisotropic continuum model.

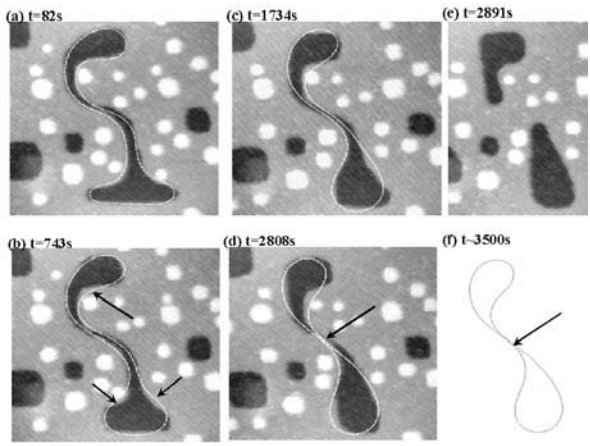

Figure 1.1 Reshaping sequence of a worm-like Cu vacancy cluster. Calculated cluster boundary within isotropic continuum model is overplotted as white solid lines. At time t~3500 sec, the calculated cluster boundary self-crosses, corresponding to the observed cluster pinching event.

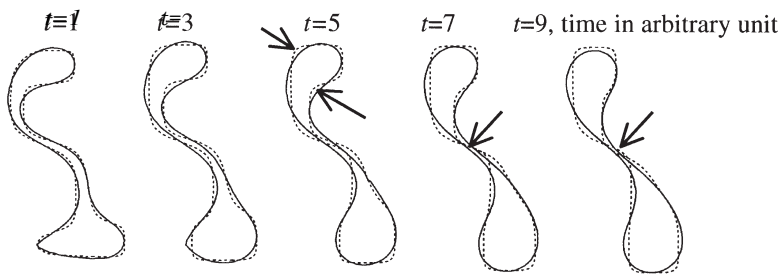

Figure 1.2 Comparison of calculated reshaping processes with either isotropic (solid line) or anisotropic (dotted line) step line tensions. Incorporation of lattice anisotropy properly accounts for the discrepancy of normal velocities at step corners.

2.2 Comparison with Kinetic Monte Carlo Simulation

There are several reasons to perform atomistic kinetic Monte Carlo simulation. As stated earlier, it is advisable to know at what scale the continuum model needs to be assisted or even replaced by atomistic modelling. Also, anisotropy introduced by

an angular-dependent σ_{PD} and thermal fluctuation effect can be properly addressed in such simulations.

Simulations were done for Ag(100) with energy barriers of edge diffusion, E_e, and NN bond strength, ϕ, taken from semi-empirical studies as E_e~0.26 eV and ϕ~0.26 eV (Pai, 2001; Cadilhe, 2000). An additional so-called "corner-rounding" barrier from next NN jump around corner sites is denoted as E_r. If E_r is neglected, the simulation corresponds to an isotropic mobility and the Ising-like line tension. A simulation on Ag(100) vacncy cluster (Pai, 2001) shows the above set of E_r and ϕ underestimates the reshaping time by a factor of over 200. To match proper time-scale between the experiment and the KMC simulation, one can reduce σ_{PD} by either introducing an extra E_r~0.16 eV or increase the kink-escape barrier $E_e+\phi$ to ~0.66 eV. The former case has a strong anisotropy in σ_{PD} whereas the later does not. Interestingly, simulations with these two routes show negligible differences in the overall reshaping process. Thus, KMC simulation does not yield a unique set of atomistic barriers. As for thermal fluctuations, we estimate the standard deviation of neck pinch-off time to be roughly 30% for a cluster ~20 nm in length. We could not, however, give a general criterion to describe quantitatively its effect. It seems necessary to address separately from cases to cases.

3 CONCLUSION

Detailed studies of post-growth kinetics on homoepitaxial Cu(100) and Ag(100) systems have revealed diffusion, coarsening and reshaping are consistently unified by peripheral mass transport. The prowess of continuum model is demonstrated by its quantitative agreement in shape relaxation and its successful prediction on island pinch-off events. Effects of atomistic structure, energetics, and thermal fluctuations are addressed through KMC simulations, allowing reasonable, though not unique, estimation of barriers involved in reshaping. W. W. Pai acknowledges support from NSC, Taiwan. D. J. Liu was supported by NSF grant CHE-0078596.

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