

# Metallic Cluster Coalescence: Molecular Dynamics Simulations of Boundary Formation

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**Abstract**—During the evaporative deposition of polycrystalline thin films, the development of a tensile stress at small film thicknesses is associated with island coalescence. Several continuum models exist to describe the magnitude of this tensile stress but the coalescence stress becomes significant at small enough thicknesses to draw the continuum models into question. For nanometer-sized islands, we perform atomistic simulations of island coalescence to determine if the atomistic methods and continuum models are mutually consistent. The additional detail provided by the atomistic simulations allows for study of the kinetics of island coalescence and the treatment of different crystallographic orientations. We find that the atomistic simulations are consistent with the continuum models. We also note that the atomistic simulations predict extremely fast coalescence times and include the possibility of island rotations during coalescence.

**Index Terms**—modeling, simulation, stress, thin films

## I. INTRODUCTION

THE recent utilization of microelectromechanical systems (MEMS) in high performance technological applications has increased the reliability and performance requirements for the micro-elements that compose these systems. Polycrystalline metallic films are critical components for several MEMS applications. Considering that these components often operate in environments with high thermal, electrical, and mechanical stresses, performance enhancements could depend strongly on the existing internal stress state and microstructure of the thin films. Still, the earliest stages of film formation can only be described in a general sense with continuum models and simulations.

While for many applications the continuum models are adequate, the increasing demands of the microelectronics industry are constantly pushing for higher device density and smaller device dimensions. As the device dimensions shrink,

the trend moves toward thinner polycrystalline films as the micro-elements. In the future, device dimensions will become small enough such that the critical size is beyond the validity of the continuum models. As the device dimensions approach this range, the size scales of interest become small enough for full atomistic simulations to be tractable. Simulations on the atomic scale provide a level of kinetic and structural detail that continuum models cannot reproduce.

Since the performance and reliability of MEMS can depend strongly on the microstructure and internal stress state of thin films, a clear understanding of stress and structure development at the early stages of film growth is required. The standard compressive-tensile-compressive behavior seen in high mobility materials is well-known and the observed tensile stresses are generally attributed to an island coalescence process[1]. The addition of strain energy in small islands to compensate for the excess surface energy provides an intuitive argument for how and why such a process would occur[2,3,4,5]. While the general energetics of the process are understood, many of the details of island coalescence are not examined in further detail. Most notably, the effects of material anisotropy are not included and the continuum models do not account for whether the type of boundary formed during the island coalescence has a significant effect on coalescence behavior. These continuum theories also do not consider whether continuum assumptions are still valid for particle arrangements consisting of thousands rather than millions of atoms.

The following sections will focus on the origin of the tensile stress during polycrystalline film formation. First, the theory and relevant experimental verification will be presented as background and then the additional contributions made available by the atomistic modeling will be outlined. Recent simulations of island coalescence will be reviewed and the results will be compared with other researchers' work on sintering and free space coalescence.

## II. BACKGROUND

### A. Continuum Modeling

The first model for tensile stress developed during the early stages of film formation was proposed by Hoffman[2]. In

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Hoffman's model, the average stress in the island could be characterized by the elastic properties of the island and the separation distance between the islands just before impingement. This critical distance was determined based on atomic size considerations. The volume average stress  $\langle \mathbf{S} \rangle$  was given as

$$\langle \mathbf{S} \rangle = \frac{E}{1-\mathbf{n}} \frac{\Delta}{2a} \quad (1)$$

where  $E$  is the Young's modulus,  $\mathbf{n}$  is the Poisson's ratio,  $a$  is the island radius, and  $\Delta$  is the distance which islands will strain in order to form boundaries.

The Hoffman model was later analyzed by Nix and Clemens[3]. Nix and Clemens used an energetic rather than an atomistic argument in order to determine the maximum strain generated in coalescing islands. By examining an energy balance between surface energy and strain energy contributions, Nix and Clemens derived the maximum strain due to impingement and coalescence as

$$\Delta_{\max} = \left[ 4a(2\mathbf{g}_{sv} - \mathbf{g}_{gb}) \frac{1-\mathbf{n}}{E} \right]^{1/2} \quad (2)$$

where  $\mathbf{g}_{sv}$  and  $\mathbf{g}_{gb}$  are the surface energies of the solid-vapor interface and grain boundary, respectively.

Using this estimate for the strain, the average stress is given by

$$\langle \mathbf{S} \rangle = \left[ \left( \frac{1+\mathbf{n}}{1-\mathbf{n}} \right) E \frac{(2\mathbf{g}_{sv} - \mathbf{g}_{gb})}{a} \right]^{1/2} \quad (3)$$

Assuming 2-D elliptical islands, the average stress can be approximated by

$$\langle \mathbf{S} \rangle \approx \frac{1}{6} \frac{E}{(1-\mathbf{n}^2)} \left( \frac{z_0}{b} \right)^2 \quad (4)$$

where  $z_0$  is the length of boundary formation and  $b$  is the height of the island.

Combining the previous two equations gives an estimate of the zipping length as

$$\frac{z_0}{b} \approx \left[ \frac{36(1-\mathbf{n})(1+\mathbf{n})^3 (2\mathbf{g}_{sv} - \mathbf{g}_{gb})}{Ea} \right]^{1/4} \quad (5)$$

Seel et al.[4] followed up on the Nix and Clemens work but with more focus on the precise contributions of strain energy and surface energies. Rather than using the approximations and simplifications of the Nix and Clemens model, Seel et al. performed finite element method(FEM) calculations of the stress and strain in the islands. In conjunction with a film formation simulation including diffusional creep, the FEM simulations of Seel et al. qualitatively reproduced the shape of the stress-thickness vs. thickness curves and also quantitatively matched the maximum experimental tensile stress. In the analysis of coalescing cylinders, Seel et al. found that the

zipping distance was proportional to  $r^{0.675}$  instead of  $r^{3/4}$  as predicted by the Nix & Clemens model.

Freund and Chason presented an analytical model based on Hertzian contact theory. Hertzian contact theory is often invoked in the analysis of nanoindentation with a spherical indenter tip. By modifying the theory to include the effects of cohesion and applying the new theory to arrays of spheres, cylinders, and disks, a process similar to island impingement and coalescence was described. In this model, the volume-averaged stress is dependent on the shape and dimensionality of the islands.

$$\frac{\langle \mathbf{S} \rangle^{(N)}}{E} = A_N \left( \frac{\mathbf{g}_{sv} - \frac{1}{2}\mathbf{g}_{gb}}{Ea} \right)^{c_N} \quad (6)$$

$A_N$  and  $c_N$  are dimensional dependent constants. In the case of coalescing spherical bodies,  $c_N$  is equal to 1 and  $A_N$  is equal to 4. The corresponding zipping length is given as

$$z_0 \approx 3.41 \left( \frac{(1-\mathbf{n}^2)(2\mathbf{g}_{sv} - \mathbf{g}_{gb})}{pE} \right)^{1/3} a^{2/3} \quad (7)$$

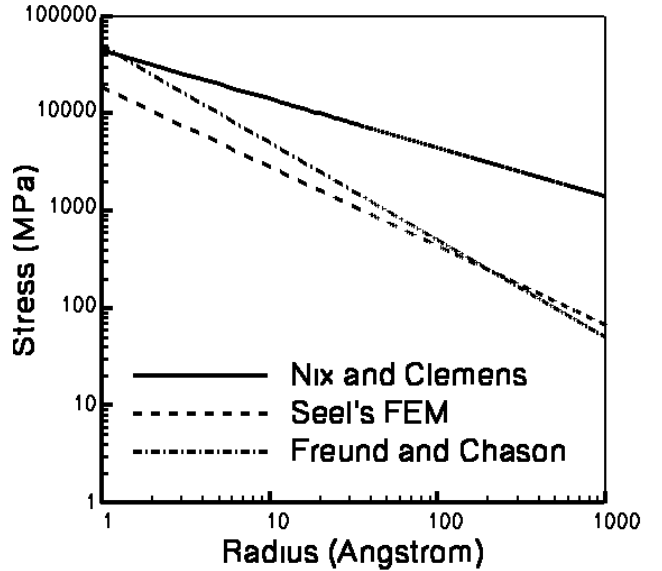


Figure 1: Comparison of the predicted values of maximum tensile stress based on the continuum models

Fig. 1 shows a comparison of the predicted tensile stress values for each continuum model based on the parameters for Ag given in Table I. Clearly, the Nix and Clemens model predicts much higher values for the stress than the Seel et al. results and the Freund and Chason model. The size range where island coalescence occurs is on the order of 100 Angstroms. In this range, the Freund and Chason predictions and the FEM results are similar.

TABLE 1: TYPICAL VALUES FOR THE ENERGETIC AND ELASTIC PROPERTIES OF AG

<i>Young's modulus, (GPa)</i>	<i>Poisson ratio</i>	<i>Surface energy, (J/m<sup>2</sup>)</i>	<i>Grain boundary energy, (J/m<sup>2</sup>)</i>
87.3	0.354	1.5	0.47

### B. Atomistics

The atomistic simulations described in this proceeding are performed using molecular dynamics(MD) methods[6,7]. In classical MD simulations, the complexity of fully quantum-mechanical interactions between ions and electrons is abandoned in favor of a closed form potential which approximates these effects. Instead of being forced to solve the Schrodinger equation for each atom and electron, the use of semi-empirical potentials allows the complex problem to be reduced to a simple many-body problem in Newtonian mechanics. In the present method, the equations of motion are integrated in time using a fifth order Gear predictor-corrector algorithm[8]. Energy conservation to better than  $1 \times 10^{15}$  is achieved with a time step of approximately 2.5 fs.

The many body potential used to model the atomic interactions is the Rosato, Guillope & Legrand(RGL) potential for Ag[9,10]. This class of potentials is derived from the second moment approximation to the tight binding(SMA-TB) model and the functional form of the potentials is identical to the potentials derived by the embedded atom method(EAM). The RGL potential has fewer fitting parameters than the standard EAM potentials but still manages to achieve good agreement with the elastic and thermal properties of Ag while only requiring explicit tracking of interactions up to third nearest neighbors. The equivalent SMA-TB potential for Ni requires tracking of up to fifth nearest neighbor interactions in order to accurately approximate the elastic and thermal properties of the bulk. The SMA-TB potentials were selected for this study due to their simplicity of form and ability to produce consistent thermal and mechanical properties. EAM formulations require too many fitting parameters and two-body potentials fail to capture the details of the elastic properties accurately.

For simplicity, interactions of the atoms with the substrate are achieved through the use of a Lennard-Jones wall. The Lennard-Jones wall provides the normal forces required to bind the islands to the substrates but the flat surface has no means of applying traction forces. This interaction means that the clusters simulated on Lennard-Jones walls are essentially simulations of islands on traction-free substrates.

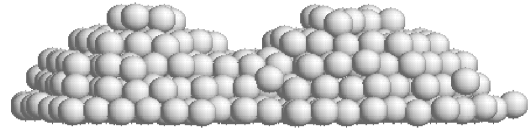
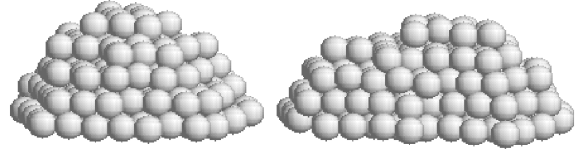


Figure 2: Coalescence of hemispherical Ag islands on a traction-free substrate. The top image is the initial condition of the islands on the Lennard-Jones substrate. The bottom image is the structure after coalescence.

### III. RESULTS

We have focused on Ag as a model system for simulations. Ag has been shown to act as a high mobility material and also has weak interactions with amorphous SiO<sub>2</sub> substrates. For this system, the Lennard-Jones wall provides an analogy for the SiO<sub>2</sub> interaction with Ag. Fig. 2 is a representative illustration of islands on the Lennard-Jones substrate both before and after coalescence.

The simulated clusters exhibit three critical stages of behavior. First, an incubation stage occurs where the interaction forces between the two clusters are communicated to the cluster as a whole. Then the clusters rapidly approach each other in a rigid fashion as the attractive forces overcome the random thermal motion in each cluster. Finally, a boundary is formed which is the lowest energy configuration attainable by the clusters. Further boundary formation would require enough thermal energy to displace surface atoms near the neck in a manner that would fill the neck. The three stages of behavior are shown clearly in Fig. 3.

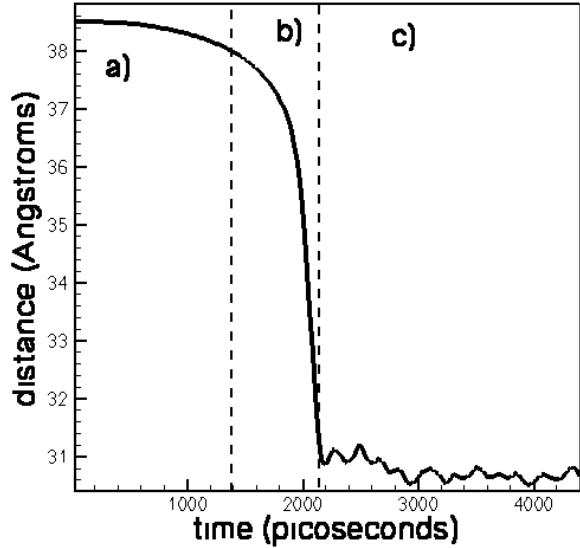


Figure 3: Sample coalescence data showing center of mass distance between two clusters. Region a) shows the period where the clusters are beginning to feel the attractive pull between islands. Region b) is the period of rapid coalescence and region c) is the period when a stable neck has formed.

The metrics used to identify the coalescence behavior of islands are primarily the following: coalescence time, coalescence velocity, potential energy, boundary length, shrinkage, and rotations during coalescence. Radial distribution functions (RDF's) are also used in a limited extent to determine the crystallinity of structures but the high proportion of surface atoms makes the interpretation of the RDF ambiguous.

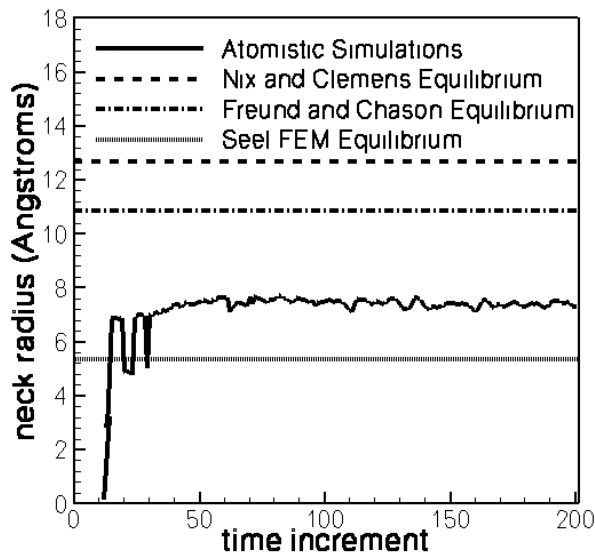


Figure 4: Neck radius vs. time data showing that the atomistic simulations are similar in magnitude to the Freund & Chason model and the Seel et al. FEM results.

Fig. 4 and Fig. 5 show the boundary length evolution during island coalescence. Fig. 4 depicts small clusters coalescing in free space and shows that the boundary formation occurs

rapidly and stabilizes quickly. Fig. 5 shows the same behavior for hemispherical islands on a Lennard-Jones substrate.

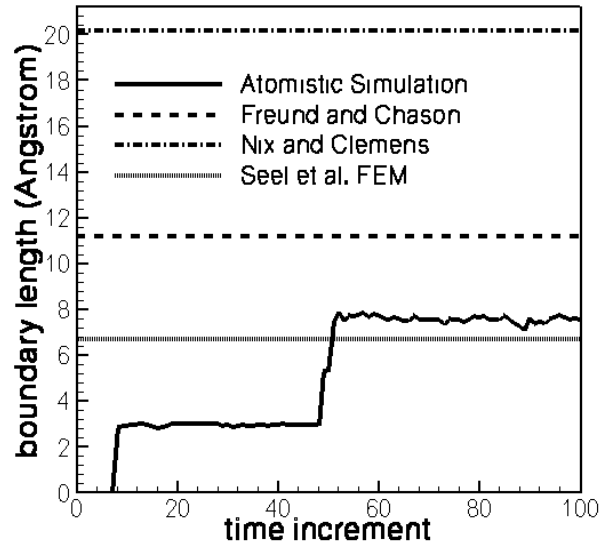


Figure 5: Boundary length comparison for coalescing hemispheres showing again that the atomistic simulation values are above the Seel FEM prediction and below the Freund and Chason prediction

We also note that since the MD simulations performed in this study are completely micro-canonical, the latent heat released during boundary formation is absorbed by the island in the form of heat. This absorption causes localized heating and in some high temperature cases, redistribution of atoms consistent with local melting is observed.

In order to expand the range of this study, we have started simulations of Ni. Ni is a system that can exhibit either low mobility or high mobility behavior. Because of the intermediate value of the atomic mobility activation energy, Ni behaves as a low mobility material below room temperature and transitions to a high mobility material at a few hundred degrees Celsius.

#### IV. DISCUSSION AND CONCLUSIONS

The simulations run for free-space cluster coalescence and coalescence on traction-free substrates show that the coalescence times occur on the order of nanoseconds. The boundary is formed both by island straining processes and atomic cascades to fill the neck region. This rapid boundary formation process is likely followed by subsequent boundary growth and migration due to diffusive processes. However, the timescales of the simulations does not allow for the observation of long-range diffusional events. Several other investigators have also shown that particles meeting in free-space will form boundaries and merge together on timescales much shorter than the timescales predicted by continuum theories. Zhu & Averbach attribute this rapid coalescence to the short diffusion distances and the enhanced diffusion near the neck[11]. Lewis et al. attribute the non-continuum like behavior to the presence of facets and faceting behavior in the

atomistic simulations which cannot be accounted for easily in the continuum models[12].

The time required to form a stable boundary is not strongly dependent on the mis-orientation of the clusters during the approach stage. For similarly sized clusters, the time required for coalescence varies by only 200 ps and this coalescence time is not strongly affected by temperature. However, at higher temperatures, the resolution of the data becomes more difficult due to more shuffling of atoms on the surface of the cluster.

For the simulations of clusters in free-space and clusters on traction-free substrates, the clusters have also been seen to experience large rotations. The degree of rotation is most noticeable for the clusters which are coalescing in free-space. For these clusters, no geometrical constraints exist and the clusters will rotate by significant amounts to find the lowest energy boundary. These rotations will often bypass boundary orientations which would normally be local energy minima. Instead, the clusters will perform a larger rotation to find the global minimum energy boundary(i.e. rotates into crystal registry). The larger changes in orientation are consistent with the study conducted by Zhu & Averbach on copper.

A simple analysis of the boundary length formed during coalescence shows that the atomistic simulations form a boundary with the same order of magnitude of boundary length predicted by the Freund & Chason model and the FEM results of Seel et al. For the small range of island sizes studied, the atomistic boundary lengths are always between the FEM predicted value and the Freund and Chason value. At larger island radii, the FEM and Freund and Chason model predictions will cross over, but atomic simulations in this size range have not yet been attempted due to the much greater computational cost. As expected, the oversimplified Nix & Clemens model overpredicts both the stress and boundary length.

The early results for the Ni potential show that the behavior is qualitatively the same with only very slight differences in the timescales required for each process. A more thorough study of the thermal behavior of Ni and the transition between low mobility and high mobility behavior is currently being pursued.

So far, the atomistic simulations have shown that the continuum approximations used in the FEM simulations and the analytical model of Freund & Chason are still applicable even at the nanometer length scale. The discrete nature of the atoms in the clusters do not appear to have a dramatic effect on the boundary length formed and presumably are consistent with the predicted stress values as well.

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