Atomistic Simulations of Metallic Cluster Coalescence

Andrew R. Takahashi, C.V. Thompson, W.C. Carter

***Abstract*—A new computational method is introduced to investigate the stresses developed in the island-coalescence stage of polycrystalline film formation during deposition. The method uses molecular dynamics to examine the behavior of clusters of atoms both in free space and on substrates. Continuum treatments used in previous models may not be applicable at small length scales or low dimensionality. In atomistic simulations, the effects of surface diffusion, bond straining and defect formation can be directly studied. TEM experiments will be used to evaluate the validity of the simulation model.**

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

I. Introduction

The study of stresses in thin films is becoming increasingly important as microelectronic and micromechanical thin film devices must meet more aggressive performance goals. The intrinsic stresses developed during deposition of thin films can lead to yield loss due to stress voiding or failure to meet property specifications, or due to reliability failures later in the product life cycle.

The stresses developed in the thin films have been shown [1] to depend on the earliest stages of growth. For films growing by an island mechanism, coalescence of isolated islands into a continuous network is thought to play a large role in stress development. Hoffman originally proposed that crystallites growing on a substrate could spontaneously strain in order to form a grain boundary[2]. While this process results in an increase in strain energy, the overall energy is reduced by replacing two grain surfaces with a single grain boundary. In Hoffman's analysis, the distance at which islands would spontaneously "zip" to form a finite grain boundary was based on atomic size considerations and the average stress, $\langle\sigma\rangle$, generated was given by

$$\langle s \rangle = \frac{E}{1-n}\frac{\Delta}{(2a)}, \tag{1}$$

where E is Young's modulus, n is Poisson's ratio, a is the grain radius, and Δ is the largest gap which could spontaneously close by forming a grain boundary.

This model was further developed by Nix and Clemens to show that the stresses and extent of grain boundary formation could be related to the surface energy, grain boundary energy, mechanical properties, and island size without explicitly introducing atomic size arguments [3]. To illustrate the concept, crystallites were modeled as hexagonal prisms. By equating the energy of the configuration prior to zipping to the energy after zipping, Nix and Clemens obtained an expression for the largest gap that could spontaneously be closed during grain boundary formation.

$$\Delta_{\max} = \left[4a\left(2g_{sv} - g_{gb}\right)\frac{1-n}{E}\right]^{1/2}, \tag{2}$$

where g_{sv} is the interfacial energy between the solid and vapor, and g_{gb} is the grain boundary energy. Using this estimate for the gap size gives

$$\langle s \rangle = \left[\left(\frac{1+n}{1-n}\right)E\frac{\left(2g_{sv} - g_{gb}\right)}{a}\right]^{1/2}. \tag{3}$$

Nix and Clemens also considered 2-D elliptical grains. In this case, the grain boundaries were modeled as a series of cracks and the Griffith fracture criteria was used to estimate the stresses. This approach is suggested by previous work by Chiu and Gao in an analysis of the stresses present during surface roughening [4]. The stress intensity factor, K, for this case is

$$K = \frac{1}{1+n}\langle s \rangle\sqrt{a}. \tag{4}$$

The stress can be related to the length of grain boundary formed by

$$\langle s \rangle \approx \frac{1}{6}\frac{E}{(1-n^2)}\left(\frac{z_0}{b}\right)^2, \tag{5}$$

where z_0 is the length of grain boundary formed and b is the maximum height of the film. The zipping distance can be predicted in terms of the material properties as

$$\frac{z_0}{b} \approx \left[\frac{36(1-n)(1+n)^3\left(2g_{sv} - g_{gb}\right)}{Ea}\right]^{1/4}. \tag{6}$$

Taking the specific case of a hemispherical grain, the model of Nix and Clemens predicts a stress of 3.9 GPa for typical values of silver and an island radius of 300 Å. This value of stress is roughly an order of magnitude higher than the stresses observed from experiment [5]. Maximum tensile stresses in fcc metals at room temperature are typically of the order of 100 MPa. Because the model equates the energy of

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the final structure to the initial structure rather than minimizing the total energy, the model calculates the maximum zipping distance rather than an equilibrium distance. The resulting stress estimate is an upper bound to the actual stress. The assumption that the islands are all of the same size at the point of coalescence also biases the estimate to higher stress values. Another possible reason for overprediction is that the model neglects any stress relaxation that occurs during growth.

Seel *et al* further developed this model by calculating coalescence stresses using finite element methods (FEM) [5]. Using FEM, stresses were calculated as a function of the island size and zipping distance. From these numerical simulations, the stress generated during coalescence was found to be proportional to $a^{-0.814}$. A separate simulation was used to generate realistic island growth structures through simulation of island nucleation, growth, and impingement.

During the simulation of film formation, the stresses in the islands were calculated based on the FEM results. The film formation simulation also included a stress relaxation term,

$$\langle \dot{s} \rangle = -\frac{C_0}{h^3}\langle s \rangle \exp(-Q/kT), \tag{7}$$

where C_0 is a materials dependent constant, h is film thickness, Q is activation energy for the rate-limiting diffusive process, either grain boundary or surface diffusion, k is Boltzmann's constant and T is temperature. The simulated stress-thickness vs. thickness curves qualitatively agreed with the experimental data. The simulated peak tensile stress and experimental peak tensile stress were approximately 70 MPa at room temperature. This prediction is in significantly better agreement with experiments than the prediction of the Nix and Clemens model.

An alternative analytic model for coalescence stress was introduced by Freund and Chason, who applied Hertzian contact theory to interacting spheres [6]. Hertzian contact theory with cohesion allows the calculation of the forces acting across the contact area between spheres. Analyzing periodic arrays, Freund and Chason concluded that

$$\frac{\langle s \rangle^{(N)}}{E} = A_N \left(\frac{g_{sv} - \frac{1}{2} g_{gb}}{Ea} \right)^{c_N}, \tag{8}$$

where N is the dimensionality of the object in the array, A_N is a constant which depends on the dimension, and c_N is another dimension-dependent constant. For the case of a square array of coalescing hemispheres, c_N is 1. For typical values for silver with a grain radius of 300 Å, the Freund and Chason model predicts a stress of 170 MPa. This prediction is in better agreement with both experiments and the FEM calculations than the Nix and Clemens prediction. While the numerical result of Seel is closer to the experimental values, the Freund and Chason model has the advantage of being an analytical rather than numerical model. Also, Seel's numerical model uses a stress relaxation term but the atomic mechanism for relaxation remains unknown. Several possible mechanisms exist and each will give a different relaxation rate. In addition to surface and grain boundary diffusion, traction between the island and substrate may also affect the stress relaxation. Abermann pointed out that islands sliding on an interface may reduce stresses in silver[1]. Seel's FEM work supports this view and he states that dislocations moving along the grain-substrate interface could be a mechanism for sliding [5].

Work by Gao provides a framework for understanding how these dislocations could be formed. The stresses developed at the base of a grain boundary are representative of the stress concentrations present at a crack tip [4],[7]. With such high stresses, dislocations formed near the grain boundary/crack tip would relieve stress. These dislocations would presumably be nucleated at the grain boundary-substrate interface. If the dislocations lie in the plane of the substrate, dislocation motion along the interface could provide a mechanism for sliding.

Prior to the work by Gao, Rice had published a model for dislocation nucleation at a crack tip due to stress concentration and using the Peierl's concept of lattice resistance [8]. From the Peierl's concept, a periodic relation between shear stress and shear displacement is assumed. When the shear stress exceeds the Peierl's stress, a dislocation can be fully formed and moved away from the crack tip. In this model, dislocations would nucleate if

$$K_{II} = \sqrt{2\mu g_{us}/(1-\nu)}, \tag{9}$$

where K_{II} is the mode-II stress intensity factor, μ is the shear modulus, and g_{us} is the unstable stacking fault energy. The concept of an unstable stacking fault energy is a physical parameter introduced by Rice.

II. Stress Measurement and Prediction

The standard method for measuring the stresses developed in thin films is to use Stoney's equation [9], which relates the substrate curvature to the average stress in the film,

$$\sigma_{\text{film}} h_{\text{film}} = -\frac{1}{6}\left(\frac{E_{sub}}{1-\nu_{sub}} \right) h_{sub}^2 \Delta\kappa, \tag{10}$$

where $\Delta\kappa$ is the change in curvature. This method can also be used to calculate the stresses in multilayers by applying the principle of superposition. Substrate curvature is typically determined ex-situ using laser beam deflection techniques. Recently, a stress detection system for in-situ measurement has been developed in our research group and there is also

work being done to use piezoresistive cantilevers to measure deflection. In addition to having in-situ capabilities, these methods are expected to have a higher sensitivity than other methods currently available for thin film stress measurement.

The previously mentioned models for tensile stress generation during film formation all use a continuum approach. The continuum approach is convenient because stress is generally a continuum concept. However, the models fail to capture the atomistic processes during the zipping process. Understanding of these atomistic details will allow the development of models for the zipping rate, and, thus, how atomic rearrangement can lead to relaxation of the stresses generated in an island. The stress generation models discussed previously implicitly assume that zipping is the result of straining of the atomic bonds, without atomic rearrangement. Other atomistic mechanisms for zipping are possible and the relative effect of bond straining vs. atomic rearrangement can be determined with an atomistic model.

An atomistic model also provides a method for study of the effects of defects in the solids. These models can be used to predict defect nucleation and the effect of existing defects on the system behavior. A defect such as a grain-substrate interfacial dislocation can be generated and the defect stability and mechanical behavior can be studied. If these defects are present during island zipping, the extent of stress relaxation due to defect motion can also be predicted. Stress relaxation mechanisms by surface diffusion, grain boundary diffusion, and island shearing can also be observed in atomistic models.

III. Computation

A computational tool has been developed to simulate the process of island coalescence during the early stages of film deposition. As a first step to understanding the details of the final film microstructure and residual stress, this tool has been used to focus on the earliest stages of growth when the islands are just beginning to coalesce. By focusing on the atomic level details, the role of surface diffusion, internal plastic strain relaxation, and other transport mechanisms can be recognized. This tool may also provide insight into the grain boundary structure and texturing effects observed in the fully grown films. Also, retaining the trajectory of each atom should allow for easy identification of ordered defects such as dislocations. In this way, Rice's prediction of early nucleation of dislocations along the slip plane can be examined for (111) oriented fcc grains. In simulations, the presence of an extended defect could be detected by analyzing the coordination number of atoms near the defect.

The simulation technique used to calculate the atomic motion is molecular dynamics (MD). In MD simulations, each atom obeys Newton's laws of motion in a variable potential. A particular material is modeled with an appropriately selected interatomic potential. For the purposes of this study, the Rose, Guillope, and Legrand potential for silver was used [10]. Previous studies using this potential obtained reasonable values for the surface energies and vacancy formation energy [11]. This potential is based on the second moment approximation to the tight binding model. For a single component system, the form of the potential is identical to the embedded atom method (EAM).

The simplest potential to use for MD would be the Lennard-Jones potential, but this potential is inadequate for the study of metals. Lennard-Jones models of metals predict the wrong type of surface relaxation and also fail in determining the appropriate shear modulus.

Since the grain boundary formation process is presumably related to the surface energies, the more accurate EAM potential is preferred. Similarly, modeling of the stresses developed during the coalescence process requires that the simulated system has the correct mechanical properties.

As an intermediate step in this study of island coalescence on a substrate, sintering simulations of two particles in free space were conducted. A process similar to island zipping was observed as the free-standing spheres formed a stable neck region. The analagous zipping process was found to occur in a time period of approximately 250 ps for a sphere radius of 11 Å. The structure prior to and after coalescence is shown as Figure 1. The results of the free cluster study can be compared with sintering theory and with other work performed on coalescence of atomic clusters. This step provides additional validation of the code and algorithm.

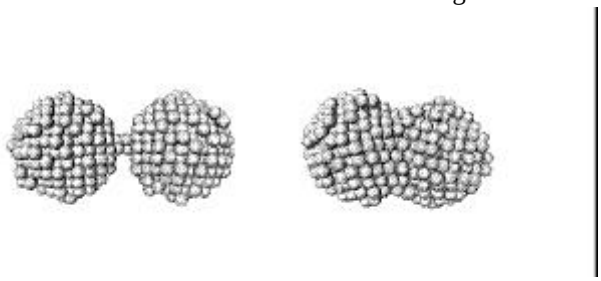

Figure 1: The picture on the left shows free-standing spheres prior to coalescence. The picture on the right shows the final configuration after coalescence has occurred.

Sintering simulations of periodic arrays have also been performed. In simulation of a 1-D periodic array, the formation of a boundary occurs in most cases but due to the constraint on position, the extent of boundary formation is not as large as observed for the free cluster simulation. A similar result is seen in simulations of clusters on a periodic square array.

IV. Work in Progress

Simulations that demonstrate the effect of substrate interactions with the islands are being conducted. Interactions with the substrate are assumed, for the sake of simplicity, to be of the form of a Lennard-Jones surface. A flat Lennard-Jones surface provides a reasonable model for a traction free interface. By perturbing the surface so that it has a periodic corrugation, a surface with resistance to shear can be simulated.

Additional methods of post-analysis of atomic trajectory data and localized rearrangement processes are also being explored. Classification of an event in the trajectory as diffusion, bond-straining or shear straining is difficult and, perhaps, subjective. Better criteria for atomic event classification are currently being developed and they include the time dependence of average coordination number, the average bond-length to nearest neighbors, and the distortion of the Voronoi cell about an atom.

Atomistic definitions for stress are also being evaluated to obtain more accurate estimates of the stress distributions within islands. Most MD simulations use a virial expression for the stress tensor. However, this expression is only well defined for a uniform and periodic system. A possible measurement of the stresses in the nonuniform case of coalescence of islands is a short time average of the local atomistic strain. Alternatively, a continuized force per area extrapolation can be used to estimate the stress if an appropriate area or appropriate continuization is selected for the calculation.

Experimental verification of the computer model is currently being planned. Verification will involve TEM observation of island structures with possible in-situ studies of island growth. The structures to be studied will be thin films and islands grown on micromachined silicon membranes. Similar membranes have been used to measure stresses in thin films [12] and to observe dislocations by TEM [13].

V. Summary

Using a MD approach, we have initiated a study of island coalescence and boundary formation. The interatomic potential selected is of the EAM type and is fitted to the properties of silver. Using this potential , we have observed boundary formation during the sintering of free particles and periodic arrays of particles. The formation of this boundary occurs very rapidly. In comparing free clusters with clusters constrained to a periodic lattice, the free clusters form the boundary at a faster rate.

As a continuation of this study, the coalescence of clusters with interactions with a substrate will be considered. Experimentally, the predictions of the simulation model will be weighed against TEM studies of coalescence and film growth.

The development of the simulation tool was motivated by a need to understand the atomistic mechanisms leading to stress development during the growth of thin films. The tool is also well adapted to studying atomistic mechanisms for boundary formation in general. We hope that the presence of such a tool will provide a means of gathering deeper insight into a variety of micro-structural and mechanical problems.

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