STRESS EVOLUTION DURING VOLMER-WEBER GROWTH OF THIN FILMS

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ABSTRACT

Most films grow through a process in which isolated crystals nucleate on a substrate and then grow to impinge and coalesce to form continuous films. This type of growth is known as the Volmer-Weber mode for film growth, and is the process through which most polycrystalline and many epitaxial films form. In all cases, the properties of the films are strongly affected by the fundamental mechanisms of film formation; nucleation, growth, and coalescence, as well as post-coalescence film thickening. In polycrystalline films, these mechanisms affect the final distributions of grain sizes, orientations, and shapes [1]. These microstructural characteristics, in turn, affect magnetic, electrical, optical, mechanical and other properties of the films. The fundamental processes of film formation and growth also profoundly affect the residual stress in films. In this paper, recent experimental and experimental work focused on understanding the correlation of the evolution of structure and stress during Volmer-Weber growth of films is reviewed, with a focus on growth of polycrystalline films.

1. INTRODUCTION

During polycrystalline film formation, crystals nucleate with different crystallographic orientations such that grain boundaries are formed when the islands grow to impinge and coalesce [Fig. 1]. These boundaries have an excess free energy, γ_{gb}, that is a function of the orientations of the two crystals as well of the boundary plane, and have average values of order $0.1 J/m^2$. The excess free energies of the free surfaces of the crystals, γ_f, also have values that depend on the orientation of the surface relative to the crystal lattice, but have average energies of order $1 J/m^2$. There is an excess free energy associated with the substrate surface, γ_s, and the island-substrate interface, γ_i, which have energies of order $1 J/m^2$ and in the range of 0.1 to 1 J/m^2, respectively. For a given island, the forces associated with the surfaces and interface balance [Fig.2], and the island surface will contact the substrate surface at an angle θ, where $\gamma_s = \gamma_i + \gamma_f \cos(\theta)$. There will be a similar equilibrium force balance for the free surfaces and grain boundaries.

Figure 1

Figure 2

The average grain size at impingement, defined as $r_i = (A/\pi)^{1/2}$, where A is the average in-plane area, depends on the relative rates of island nucleation, I (#/area-time) and growth, G (length/time). The growth rate is also governed by the distance, δ, over which atoms adsorbed on the substrate surface can diffuse to a growing island, which depends on the adatom diffusivity on the substrate surface, $D_{a,s}$. The adatom diffusivity has a temperature dependence of the form $D_{s,o} \exp(-Q_a/kT)$, where $D_{s,o}$ is a temperature-independent constant, k is Boltzman's constant, and Q_a is called the activation energy for adatom diffusion.
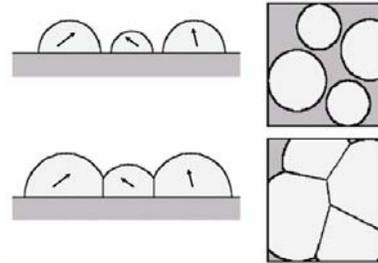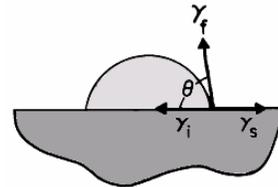
While the nucleation rate is not a direct function of δ, the fraction of the substrate available for nucleation does depend directly on δ. It can be shown that r_i can be approximated by

$$r_i \approx 0.676 \ \delta + 0.602(G/I)^{2/3}.$$

When $D_{a,s}$ is low, δ is small, and $r_i \sim 0.0602(G/I)^{1/3}$. As the deposition temperature is increased, r_i generally increases [2].

Once islands have coalesced, further film thickening generally occurs by further growth of existing crystals rather than nucleation of new islands. This leads to two broad categories of structures; columnar grain structures for which the grain size through the thickness of the film is larger than the grain size in the plane of the film [Fig. 3a], and equiaxed grain structures [Fig. 3b]. The latter develop when grain boundaries are mobile, leading to grain growth during and after coalescence. The mobility of grain boundaries is closely linked to the ability of atoms to self-diffuse along or across a boundary. This is characterized by a diffusivity, D_{gb}, that has a temperature dependence $D_{o,gb} \exp(-Q_{gb}/kT)$, where $D_{o,gb}$ is a temperature independent-constant and Q_{gb} is known as the activation energy for grain boundary self-diffusion. The grain boundary mobility generally directly scales with D_{gb}.

(a)

(b)
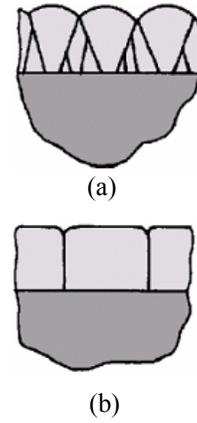
Figure 3

2. STRESS EVOLUTION DURING FILM GROWTH

There now exists a large body of literature on in-situ measurements of stress evolution during Volmer-Weber growth of crystalline films [3-4]. In-situ stress evolution is generally observed by monitoring deflection of a cantilever onto which a film is deposited. The deflection of the tip of a cantilever can be related to the curvature of the cantilever, κ, which in turn can be related to the product for the film stress and thickness of the film, σh. When the film is thin compared to the cantilever, σh is given by Stoney's relation [5],

$$\sigma h = h_c^2 E_c \kappa / 6(1 - \nu_c),$$

where h_c, E_c and ν_c are the thickness, Young's modulus, and Poisson's ratio of the cantilever.

There are generally two types of behavior, characteristic of high and low mobility materials [6]. Figure 4 schematically illustrates results obtained from in situ measurements for both classes of materials. The experimentally measured value, σh, can be related to an average stress $\sigma_{av} = \sigma h/h$, though caution must be exercised when applying this concept to discontinuous films. The change of σh with δ(σh)/δh, is called the instantaneous stress, and is related to the surface stress of the film. In low mobility materials, a large tensile stress develops as the film forms, and is retained as the film thickens. In low mobility materials, a compressive stress is sometimes observed before a tensile stress develops, and as the film is further thickened after development of a tensile stress, a compressive stress develops.
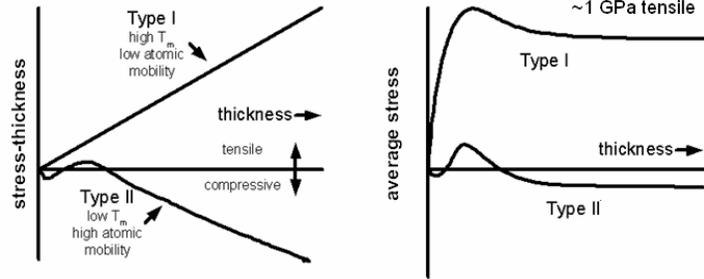
Figure 4

Tensile Stress

It has been demonstrated through microscopy at various stages of growth, that the development of a tensile stress is associated with the island coalescence process, with the peak tensile stress corresponding to the completion of the coalescence process [7].   The tensile coalescence stress has been attributed to the formation of grain boundaries during coalescence. It has been argued that as islands come into contact, boundary formation can occur through a 'zipping' process [Fig. 5] in which the free surfaces of the two islands are replaced by a grain boundary through an elastic distortion of the two islands. The energy gained through this process, $(2\gamma_s-\gamma_{gb})$, is balanced by the resulting tensile strain energy through an overall energy minimization. By considering a direct energy balance, Nix and Clemens [8] argued that the resulting stress for coalescing spherical-cap shaped islands with contact angle $\theta= 90^0$ scales with $(2\gamma_s-\gamma_{gb})/r_i$. Freund and Chason used Hertzian contact theory to argue that the average stress of such coalescing caps would be $<\sigma> = 2(2\gamma_s+\gamma_{gb})/r_i$. Seel et al [10] used finite element analyses of coalescing cylinders that gave results similar to those of Freund and Chason for $\theta= 90^0$, but could be extended to other contact angles [11].

Surface Energy γ_s Grain Boundary Energy γ_{gb}

substrate r_i

Figure 5

The 'zipping' process described above is likely to be responsible for the initial tensile rise observed in both high and low mobility materials. However, in high mobility materials, grain boundaries are mobile even during coalescence at room temperature, so that coalescence stresses are reduced through boundary motion and grain boundary diffusion. In low mobility materials, high tensile coalescence stresses are retained, and in the absence of grain boundary diffusion, excess free volume at unrelaxed newly-formed boundaries probably continues to contribute to a tensile stress as the film is thickened. It is likely, therefore, that the difference in low mobility and high mobility behavior is associated with grain boundary diffusivity.
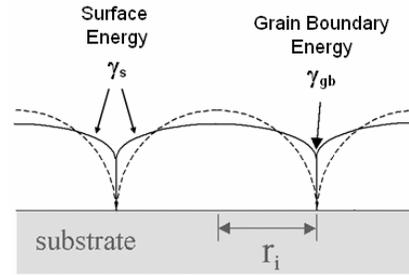
Compressive Stress

The origin of the pre-coalescence and post-coalescence compressive stress observed in high mobility materials is less clear. Aberman [6] proposed that the pre-coalescence stress is associated with the Laplace-Young effect, in that very small islands, having very high surface to volume ratios and corresponding high pressures, have smaller lattice parameters than their bulk counterparts. Cammarata and Srolovitz [12] argued that this small lattice parameter is at some point 'locked-in' due to traction with the substrate surface, and leads to the observed compressive stress as further island growth occurs. In a different approach, Spaepen [13] argued that if islands had a compressive surface stress, this would result in an apparent compressive film stress in the pre-coalescence regime. However, in a structurally relaxed state, most metallic surfaces have a tensile surface stress. It has been argued that the post-coalescence compressive stress might be associated with incorporation of excess material either in the lattice [13] or the grain boundaries [14].

Abermann and coworkers [4,7] observed that when growth is interrupted there is often an evolution in stress toward a tensile, or more tensile, state. Shull and Spaepen [15] made the further surprising observation that when growth is resumed after an interruption in growth, the stress returns to its pre-interruption level, and evolves as if the interruption had not occurred. Friesen and Thompson observed a similar reversible stress change during interruptions of Volmer-Weber growth before [16] and after coalescence [Fig. 6]. It was further found that the magnitude of the reversible stress change, $\Delta(\sigma h)_{rev}$, increased with the pre-interruption deposition rate in all regimes of Volmer-Weber growth; before, during, and after coalescence [17]. Also, the initial rate at which the stress changes when growth is resumed after an interruption, the initial instantaneous stress, is very high and significantly higher than the initial rate of change immediately after growth is interrupted [16-17].
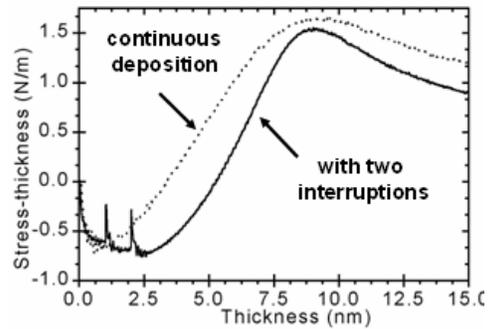
Figure 6

These observations led Spaepen [13] and Friesen and Thompson [16, 18] to propose that the reversible stress change is related to changes in the surface defect concentration on growing (dynamic) compared to equilibrium (static) surfaces. This is consistent with the observed asymmetry in the kinetics of the stress changes after an interruption and resumption of growth. When growth is resumed, surface defects quickly accumulate by direct adatom adsorption from the vapor phase. On the other hand, stress evolution during an interruption in growth requires diffusion of adatoms to ledges and over Ehrlich-Schwoebel barriers at ledge edges, and is therefore a slower process. Friesen et al [16-18] argued that the initial instantaneous stress is related to the effects of individual adatoms, and that the energy of interaction, or force dipole F_d, associated with an individual adatom can be related to the initial instantaneous stress and atomic volume Ω by

$$\partial(\sigma h) / \partial h = -F_d \Omega ,$$

so that in-situ, real-time stress measurements allow quantitative characterization of the effects of adatoms on surface stress. It was shown that measured values of F_d increase during deposition in the pre-coalescence regime (in which the measured F_d is a weighted average of the force dipole for interaction with the substrate and the film surface), and reaches a constant value after coalescence is complete.

Quantitative agreement between reversible stress changes observed during interruption of Volmer-Weber growth of polycrystalline Cu and Ag films and results for homoepitaxial growth in the same systems [18], further support the idea that these reversible stress changes are associated with changes in surface properties rather than bulk (e.g. grain boundary) properties. The value of F_d measured for coalesced polycrystalline Ag and Cu films is the same as the value measured for epitaxial films (within experimental error), and both values are quantitatively consistent with expectations from embedded-atom molecular dynamics simulations [18].
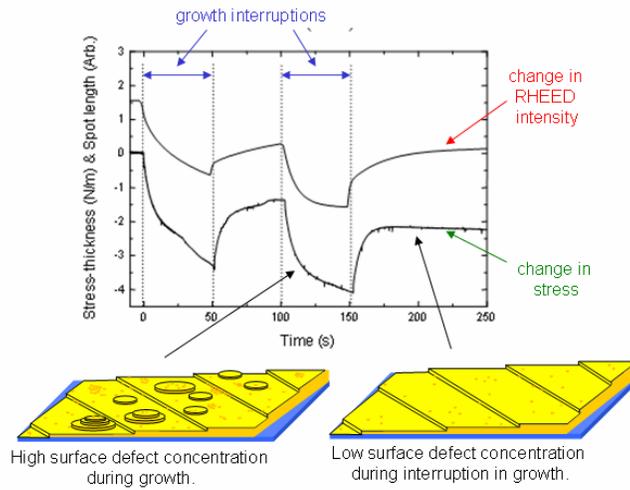
Figure 7: When growth (in this case homoepitaxial growth of Cu) is interrupted, there is an evolution toward a tensile stress state. When growth is resumed, the stress evolves back toward the pre-interruption level. This reversible stress evolution is correlated with changes in reflected high energy electron diffraction (RHEED) intensity, which indicates a correlation with changes in the atomic scale surface roughness [18].

In-situ, real time reflected high energy electron diffraction characterization of homoepitaxial growth surfaces of Ag and Cu were also characterized during growth and during interruptions in growth [18]. Reversible changes in the intensity of RHEED signals are known to correlate with atomic-scale changes in surface roughness. It was found that changes in the stress and surface roughness are correlated during interruptions in homoepitaxial growth of Ag and Cu [Fig. 7], further supporting the association of changes in surface stress with changes in surface structure, and suggesting that the net effect of the complex array of surface defects present during steady state growth (adatoms, ledges, kinks, and 2D clusters) causes a compressive surface stress (at least under the conditions of these experiments).

Effects of the Dynamic Surface State

The experiments reviewed above suggest that the dynamic (growing) surface of high mobility materials has a compressive surface stress. The magnitude of the surface stress would be a function of the deposition conditions (e.g. the deposition rate and temperature), and the adatom surface self diffusivity, $D_{a,f}$. In the pre-coalescence regime of Volmer-Weber, a compressive surface stress could lead to a net compressive 'film' stress through Spaepen's argument, outline above. In the post-coalescence regime, it might be expected that a net compressive surface stress would lead, through a local equilibrium, to a net compression in the growing layers. This would be mechanistically accomplished through inclusion of excess material as extra lattice planes (leading to dislocations) or interstitials in the bulk, or through the inclusion of excess material at grain boundaries.

3. SUMMARY AND CONCLUSIONS

Stress evolution during Volmer-Weber growth of thin films can lead to a net residual tensile or compressive stress. In polycrystalline films, tensile stresses are thought to be the result of grain boundary formation during the island coalescence stage and during post-coalescence growth. The magnitude of these stresses is expected to be a function of the island-size at coalescence (affected by the adatom diffusivity on the substrate surface $D_{a,s}$) and the ability of atoms to diffuse into grain boundaries and to accommodate energy minimizing rearrangements during growth (affected by the self diffusivity of atoms at grain boundaries D_{gb}). Compressive stresses are thought to be affected by the dynamic state of the growing surface, which can be in a compressive state even for materials that have tensile surface stresses in the equilibrium state. The stress state of the dynamic surface is also affected by the deposition conditions, as well as by the adatom surface self-diffusivity, $D_{a,f}$. The residual stress in films that grow via the Volmer-Weber mechanism is therefore seen to be closely related to both the micro- and nano-scale structure of the evolving films, and is affected by the intrinsic atomic mobility of the material (as characterized by $D_{a,s}$, D_{gb} and $D_{a,f}$) as well as the deposition conditions (especially the deposition temperature). In-situ, real-time stress measurements not only allow detailed characterization of stress evolution during film growth, but also provide a means for the characterization of the structure of dynamic growth surfaces.

4. ACKNOWLEDGMENTS

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