Origin of Compressive Residual Stress in Polycrystalline Thin Films

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(Received 16 August 2001; published 29 March 2002)

We present a model for compressive stress generation during thin film growth in which the driving force is an increase in the surface chemical potential caused by the deposition of atoms from the vapor. The increase in surface chemical potential induces atoms to flow into the grain boundary, creating a compressive stress in the film. We develop kinetic equations to describe the stress evolution and dependence on growth parameters. The model is used to explain measurements of relaxation when growth is terminated and the dependence of the steady-state stress on growth rate.

DOI: 10.1103/PhysRevLett.88.156103 PACS numbers: 68.60.Bs, 68.55.–a

Wafer curvature measurements [1] have enabled the measurement of residual stress evolution in a large number of systems [2–7]. For high surface mobility films that grow by a Volmer-Weber mechanism, it is well established that the evolution of the residual stress typically occurs in alternating stages of compressive, tensile, and compressive growth [2,4,5,8]. An example is shown in Fig. 1 for the room temperature growth of Ag on glass in which the measured curvature has been converted into the product of the average film stress and the film thickness using Stoney's equation [1]. During the early stages of nucleation, before the film has coalesced, the film stress is compressive. This has been attributed to the effect of surface capillary forces on the isolated cluster [9,10]. At the point of island coalescence, a tensile stress develops which is associated with the formation of grain boundaries [2,7,11–13].

After further growth to form a fully continuous film, the tensile stress is observed to decrease. For the high mobility films that are the subject of this work, the average stress keeps decreasing until it changes sign from tensile to compressive so that this effect is more than just a relaxation of the tensile component [2,4,5]. The compressive stress ultimately reaches a steady-state value that depends on the growth conditions. When growth is interrupted at this stage, a rapid relaxation of the compressive stress is observed, but upon resumption of growth, this relaxation is fully reversed and the same compressive stress value is reestablished [4,5]. Grain boundaries have been shown to play an important role in the compressive stress generation since Pd films deposited onto polycrystalline Pt became compressive, while those deposited on monocrystalline Pt remained tensile [14].

Understanding the origin and reversible relaxation of the compressive stress in this third stage of growth is the topic of this Letter. We propose that the compressive stress is a consequence of the nonequilibrium state of the thin film surface during deposition. In the presence of the growth flux, the chemical potential of the surface is higher than it would be if the surface were in equilibrium. Raising the chemical potential on the surface provides a driving force that causes the flow of atoms into the grain boundary. The incorporation of excess atoms into the grain boundary creates a compressive stress in the film. Since the compressive stress raises the chemical potential of atoms in the grain boundary, the driving force for additional flow decreases with increasing stress and eventually a steady state is achieved. Within this framework, the compressive stress is regarded as a consequence of a thermodynamic driving force provided by the supersaturation of the surface. This differs from previous models that propose kinetic mechanisms for the compressive stress

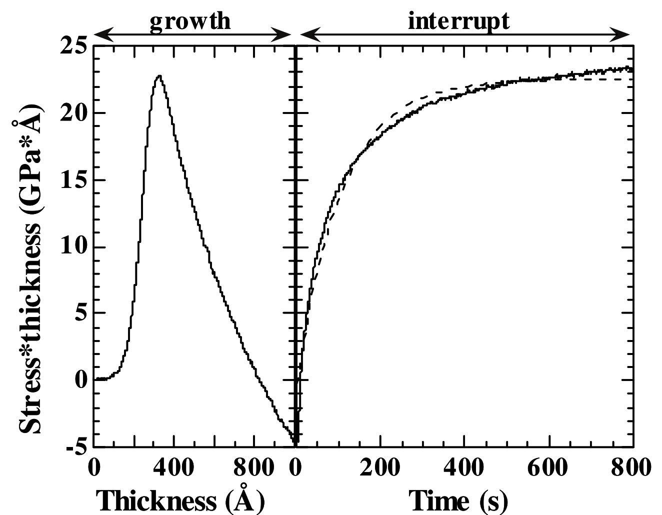

FIG. 1. Evolution of the product of average film stress and thickness during room temperature deposition of Ag on a glass substrate. The change in sign corresponds to alternating stages of compressive, tensile, and compressive stress during deposition. The interrupt corresponds to relaxation of the film stress after the growth flux is terminated. The dashed line corresponds to exponential relaxation with parameters determined from a least squares fit.

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based on trapping of adatoms [8] or surface-stress-related effects [10].

On the basis of this model, we derive here a simple one-dimensional kinetic equation to calculate the flux of atoms from the surface into the grain boundary and the resulting film stress. A schematic of the growing polycrystalline film is shown in Fig. 2. We assume that the individual grains of length L have coalesced into a continuous film so that the height of the film is a uniform value h. The grain boundaries are shown as the shaded region in the figure and the arrows represent the fact that atoms can move reversibly between the surface and the grain boundary. R is equal to the rate of growth dh/dt which is proportional to the growth flux, J. The atomic volume is Ω and we define the atomic spacing a as equal to $\Omega^{1/3}$.

We define the chemical potential on the surface as

$$\mu_s = \mu_s^0 + \delta\mu_s , \quad (1)$$

where μ_s^0 is the chemical potential of the surface adatoms in equilibrium with the solid and $\delta\mu_s$ is the increase in chemical potential due to the impinging deposition flux. The deviation from equilibrium, $\delta\mu_s$, may result in a supersaturation of adatoms on the surface, nucleation of new clusters, or increased surface step density, but the details of how this rise in chemical potential comes about are not important for this model. The essential feature is that the surface is at higher chemical potential during growth than it would be at equilibrium. This assumption is consistent with experimental observations [15] and kinetic Monte Carlo simulations [16] that show surfaces relax to smoother morphologies or lower adatom densities when the growth beam is turned off if there is sufficient surface mobility. It is important to note that $\delta\mu_s$ corresponds to the difference in the surface chemical potential under two different conditions (equilibrium conditions and growth conditions). It is not the chemical potential difference between the surface and the vapor.

The chemical potential in the grain boundary is

$$\mu_{\text{gb}} = \mu_{\text{gb}}^0 - \sigma\Omega , \quad (2)$$

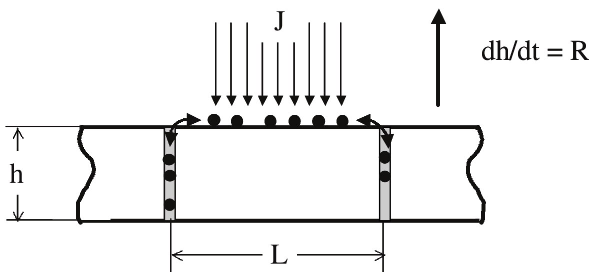

FIG. 2. Schematic of model for flow of atoms into the grain boundary during film growth. The surface chemical potential is raised above the equilibrium value by the nonequilibrium growth flux. Addition of atoms to the grain boundary results in compressive stress which raises the grain boundary chemical potential.

where μ_{gb}^0 is the chemical potential of the unstrained grain boundary at equilibrium and σ is the normal stress acting across the grain boundary [17] (using the convention that tensile stress is positive). The difference in chemical potential between the surface and grain boundary is

$$\Delta\mu = \mu_s - \mu_{\text{gb}} = \Delta\mu_0 + \delta\mu_s + \sigma\Omega , \quad (3)$$

where $\Delta\mu_0 = \mu_s^0 - \mu_{\text{gb}}^0$. $\Delta\mu_0$ corresponds to the difference between the surface and grain boundary chemical potentials in the absence of growth and can incorporate effects such as nonequilibrium grain shapes. The magnitude of $\Delta\mu_0$ is expected to be small. Note that $\Delta\mu$ depends on the growth conditions (through $\delta\mu_s$) and on the film stress. If $\Delta\mu$ is positive, atoms will flow into the grain boundary from the surface. Defining N_{gb} as the number of extra atoms added to the grain boundary due to this flux, a kinetic rate equation relates the rate of atoms flowing into the grain boundary $\frac{\partial N_{\text{gb}}}{\partial t}$ to the driving force $\Delta\mu$:

$$\frac{\partial N_{\text{gb}}}{\partial t} = 2C_s\Gamma[1 - e^{-\Delta\mu/kT}] \cong 2C_s\Gamma\frac{\Delta\mu}{kT} . \quad (4)$$

The approximate linear form assumes that $\Delta\mu \ll kT$. The factor of 2 is present because there are surfaces on either side of the grain boundary that contribute atoms to it. We define C_s as the concentration (fractional coverage) of mobile atoms on the surface, equal to $N_s\ (a/L)$, where N_s is the number of mobile atoms on the surface of each grain. Γ is a kinetic parameter corresponding to the transition rate between the surface and the grain boundary. We have assumed that there is rapid transport across the surface and gain boundary so that there is no concentration gradient on the surface or in the grain boundary. Refinements of this model will include concentration gradients to allow there to be diffusive fluxes and nonuniform film stress, but here we assume uniform concentration to simplify the analysis without changing the fundamental mechanisms.

The incorporation of N_{gb} atoms into the grain boundary results in a compressive stress in the film. In addition, there is a tensile stress, σ_i, that develops as the planes in adjacent clusters grow together to form a grain boundary. We approximate this tensile component as being constant due to the cohesive attraction between atoms at the grain boundary [12]. The total stress in the film is then equal to

$$\sigma = \sigma_i - \sigma_0 N_{\text{gb}}\left(\frac{a}{h}\right), \quad (5)$$

where $\sigma_0 = E\alpha a/L$. σ_0 corresponds to the compressive stress that would result if an additional atom were added to each of the atomic planes in the grain boundary without changing the size of the grain. E is an elastic modulus and α is a geometric shape factor. This expression is consistent with Abermann's observation [18] that films with low surface mobility develop a residual tensile stress. In this case, atoms are kinetically limited from being incorporated into the grain boundary so that $N_{\text{gb}} = 0$.

Differentiating Eq. (5) enables us to relate the rate of change of σ to the number of atoms going into the grain boundary and the rate of increase in height (R) of the grain during growth. Using Eq. (4) to determine $\frac{\partial N_{\mathrm{gb}}}{\partial t}$ and substituting $\sigma_i - \sigma = \sigma_0 N_{\mathrm{gb}}(a/h)$, the rate of change of the stress is given by

$$\frac{\partial \sigma}{\partial t} = -\left(\frac{\sigma_0 a}{h}\right) 2C_s \Gamma \left(\frac{\Delta\mu_0 + \delta\mu_s + \sigma\Omega}{kT}\right) + (\sigma_i - \sigma)\frac{R}{h}. \qquad (6)$$

The stress always decays to a stable steady limit defined by $\partial\sigma/\partial t = 0$ with increasing time, and only this limit is examined here. The steady-state residual compressive stress is

$$\sigma_{ss} = \frac{\sigma_i \hat{R} - \sigma_0[(\Delta\mu_0 + \delta\mu_s)/kT]}{\hat{R} + (\sigma_0\Omega/kT)}, \qquad (7)$$

where we have defined $\hat{R} = R/(2aC_s\Gamma)$ as a normalized growth rate.

The dependence of the steady-state stress on the growth parameters can be determined directly from Eq. (7). According to the model, increasing the excess chemical potential on the surface $\delta\mu_s$ increases the compressive stress by driving more atoms into the grain boundary. Conversely, increasing the growth rate decreases the compressive stress by decreasing the fraction of atoms that can be incorporated into the grain boundary during growth (assuming that $\delta\mu_s$ does not change). In the following section, we compare the predictions of the model with measurements of stress evolution during Ag deposition.

As observed by several groups [2,4,5], when growth is interrupted the compressive stress rapidly relaxes (and may even revert to net tension) as shown in the second half of Fig. 1. This result can be understood in terms of the change in chemical potential on the surface due to the growth beam. Interrupting growth rapidly lowers the surface chemical potential as the surface relaxes (e.g., excess adatoms find stable sites on which to attach). When the surface chemical potential drops, atoms flow out of the grain boundary to the surface. The rate of change of the stress can be calculated from Eq. (6) using a value of zero for the growth flux. In this case, the model predicts that the stress will relax exponentially from its steady-state value. The measured relaxation kinetics are described well by an exponential as shown by the dashed line in Fig. 1. The relaxation rate from the model is equal to

$$\frac{1}{\tau} = 2C_s\Gamma\left(\frac{a}{h}\right)\left(\frac{\sigma_0\Omega}{kT}\right). \qquad (8)$$

Measurements of the relaxation of Ag films at room temperature provide a value for $1/\tau$ of $0.0093\ \mathrm{s}^{-1}$. Using parameters appropriate for this experiment ($\Omega = 1.7 \times 10^{-29}\ \mathrm{m}^3$, $h = 1 \times 10^{-7}$ m, $L = 1 \times 10^{-7}$ m, $\sigma_0 = 260$ MPa), we obtain an estimate for $2C_s\Gamma$ of $3.3\ \mathrm{s}^{-1}$.

Experiments indicate that the stress relaxation upon terminating growth is reversible [4,5]; i.e., when the growth flux is resumed, the compressive stress returns to the same value it had. This result is consistent with the dependence on the growth parameters expressed in Eq. (7) since resumption of the growth flux quickly reestablishes the surface excess chemical potential which drives atoms into the grain boundary and creates compressive stress.

The model also allows us to understand the effect on film stress of changing the growth rate without terminating it completely. Experimental measurements of the stress at different growth rates are shown in Fig. 3 for a Ag film at room temperature. In order to keep other parameters such as grain size constant, the growth rate was changed after the film had been grown into the steady-state compressive region. At the initial growth rate of 0.013 nm/s, a compressive stress of −38 MPa was obtained. The growth rate was then changed to 0.2 nm/s and the compressive stress decreased to a value of −16 MPa. When the growth rate was reduced to the previous value of 0.013 nm/s, the compressive stress reverted to the value of −38 MPa, and then back to −18 MPa when the growth rate was increased again. Note that we have estimated the average steady-state compressive stress by measuring the instantaneous slope of the stress thickness product, since Shull *et al.* [4] have shown that the average stress converges to the incremental stress for large film thickness.

The fact that the compressive stress should decrease when the growth rate is increased may not be immediately obvious, but it is consistent with our model. Under the conditions used in this experiment, the dominant effect of increasing the growth rate R is to increase the grain boundary height faster than atoms can be incorporated into the

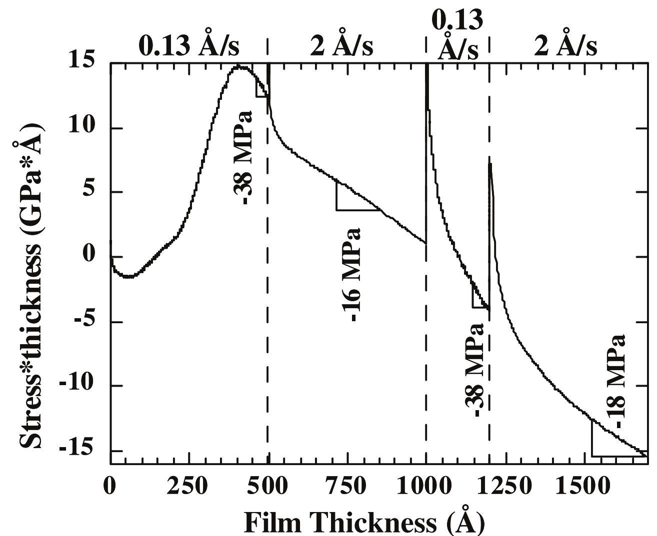

FIG. 3. Change in the stress-thickness product with the film growth rate. The film is initially grown at 0.013 nm/s until a compressive stress of −38 MPa is achieved. The growth rate is changed to 0.2, 0.013, and 0.2 nm/s at the points indicated in the figure. The resulting stress is indicated in the figure.

boundary. As a result, the fraction of atoms incorporated into the grain boundary actually decreases when the growth rate increases which lowers the compressive stress. We can explore this quantitatively using Eq. (7). We estimate σ_i to be 190 MPa [5] from the maximum measured tensile stress. Using the measured steady-state values of -38 and -17 MPa for growth rates of 0.013 and 0.2 nm/s, respectively, we determine values for the other parameters in Eq. (7). In this way, we obtain a value of $2C_s\Gamma = 6.5\ \mathrm{s}^{-1}$ which is in good agreement with the value of $3.3\ \mathrm{s}^{-1}$ obtained from the relaxation experiment described above. We also obtain a value for the parameter $(\Delta\mu_0 + \delta\mu_s)/kT$ equal to 0.16. In evaluating this expression, we assumed that $\delta\mu_s$ does not change with the growth flux, consistent with our expectations that the surface excess chemical potential is only weakly dependent on the growth flux at the high supersaturation present during Ag deposition. Note that the value for $\Delta\mu_0 + \delta\mu_s$ is consistent with our assumption that the excess chemical potential is small compared to the thermal energy.

As a final point, it is instructive to look at the limiting cases of Eq. (7) for the steady-state stress. For large values of $\hat{R}$ (which corresponds to either large growth rate or low surface mobility), the steady-state stress is equal to σ_i, the tensile stress produced by grain boundary formation. For small values of $\hat{R}$, the steady-state value is equal to $-(\Delta\mu_0 + \delta\mu_s)/\Omega$. In the limit of no flux, $\delta\mu_s$ is equal to zero and the calculated steady-state value is $-\Delta\mu_0/\Omega$. The relaxation experiment indicates that the steady-state stress with no flux can be tensile for Ag films (e.g., 23 MPa for the data shown in Fig. 1). Although this stress is significant, it corresponds to a value for $\Delta\mu_0$ of only -0.0025 eV. A negative value of $\Delta\mu_0$ could occur if inserting atoms at the grain boundary increases the grain boundary free energy because these atoms are bonded at less well-coordinated sites than those that initially formed the grain boundary (i.e., this would then increase μ^0_{gb}). It is also possible that the assumption of a constant concentration at the grain boundary is incorrect and kinetic limitations are preventing the layer from being completely relaxed. In this case, the stress throughout the film is not uniform. Refinements to the model are planned in order to investigate this further.

In summary, we have developed a model for the evolution of residual stress in polycrystalline films after coalescence has occurred. Driven by the impinging growth flux, the surface chemical potential is elevated relative to its equilibrium value. This drives excess atoms into the grain boundary inducing a compressive stress in the film. The model is able to account for observed relaxation in the films when growth is terminated and the effect of growth rate on the steady-state stress.

We are happy to acknowledge useful discussions with William Nix. Portions of this work were supported by the Brown University MRSEC program of the National Science Foundation under Award No. DMR-0079964 and the GM/Brown Collaborative Research Laboratory for Computational Materials Research. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract No. DE-AC04-94AL85000.

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