

Weak temperature dependence of stress relaxation in as-deposited polycrystalline gold films

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During deposition of polycrystalline gold thin films, a compressive stress develops that reversibly changes during interruptions of growth. One model for this mechanism posits that this reversible stress change is related to adatom diffusion into and out of grain boundaries and recent work has established a relationship between the reversible stress and grain size. In the current study, the dependencies of the relaxation of the compressive stress during growth interruptions on the initial stress and substrate temperature have been studied. Stress was measured *in situ* during growth and during interruptions in growth. The stress relaxation over a fixed time was found to be proportional to the stress when growth was terminated and the effect of temperature was found to be very weak. These results suggest that grain-boundary diffusion is not a factor in the stress relaxation.

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During the deposition of polycrystalline metallic films that nucleate and grow by the Volmer-Weber mechanism, stress is observed to evolve in stages. It is generally agreed that an initial tensile stress develops due to elastic strain associated with grain-boundary formation during island coalescence.¹⁻⁴ Under conditions of high atomic mobility, during continued growth of the continuous film the stress state becomes less tensile and often becomes compressive. This compressive stress state has been shown to change reversibly, in the tensile direction, during interruptions of growth.⁵⁻⁹ Chason *et al.*⁷ have argued that the compressive stress develops due to adatom trapping at grain boundaries with the reversible component due to out-diffusion from the boundaries near the surface. Spaepen⁵ has suggested that the reversible changes are the result of out-diffusion of adatoms trapped between impinging ledges on growth surfaces. Friesen and Thompson⁸ have suggested that the reversible changes are associated with differences in surface defect densities on growth and equilibrium surfaces, though recent molecular-dynamics simulations indicate that the stresses associated with surface defects are not high enough to support this argument.¹⁰ Koch⁹ has suggested that reversible changes in the surface curvature of grains might be responsible for reversible stress changes during growth interruptions with a change in surface shape occurring through surface diffusion during interruptions. As these mechanisms should exhibit very different temperature dependencies, experimental measurement of the kinetics of relaxation with respect to temperature should help identify the most likely explanation of this phenomenon.

The polycrystalline films used in this study were 99.99+% pure gold deposited on cantilevers cleaved from silicon-nitride-coated (100) silicon wafers. The low-stress 33-nm-thick silicon-nitride layers were grown using chemical vapor deposition. Substrates were cleaved into rectangular cantilevers and supported at one end. Gold deposition was carried out in an ultrahigh-vacuum electron-beam evaporation system with a base pressure of 2×10^{-10} Torr. A quartz-crystal monitor (calibrated using atomic force microscopy) was used to monitor deposition rates. The first 30 nm of each gold film was deposited at 0.1 nm/s. Deflection of the end of the cantilever was monitored *in situ* during deposition 3.4 cm from the support using the capacitance measured be-

tween a stationary 5 mm² circular plate and the curving substrate. Tip deflections as small as 1 nm could be measured at a rate of 100 Hz and were converted to stress and strain using Stoney's equation.¹¹ Temperature values were measured using an in-stage thermocouple. Differential thermal expansion of the films after cooling from the measurement temperature to room-temperature matched expected values from the thermocouple within 10%. The substrate temperature of each film was held constant at the deposition temperature for the duration of each stress measurement. Figure 1 shows a representative stress-thickness curve for a gold film deposited at 0.1 nm/s at room temperature. In this figure, h_{peak} is defined as the film thickness at which the derivative of the stress-thickness curve becomes negative. $\sigma-h_i$ is defined as the stress thickness when deposition is first interrupted with σ_i being the same quantity divided by the total film thickness at the point of interruption, denoted h_{int} .

As the changes in stress and strain were still significant hours after deposition was halted (see Fig. 5), data were compared to the expected stress and temperature relationships for power-law creep,¹²

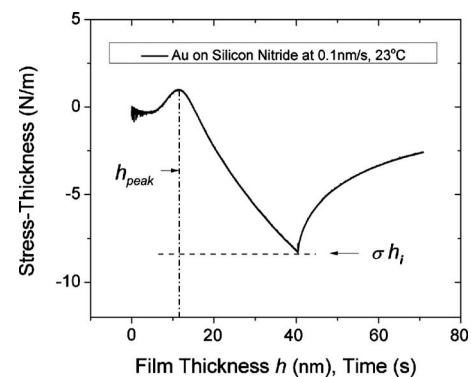


FIG. 1. Representative stress-thickness curve for gold deposited on amorphous silicon nitride. h_{peak} is defined as the film thickness at which the derivative of the stress-thickness curve becomes negative. $\sigma-h_i$ is defined as the stress thickness at the conclusion of deposition with σ_i being that quantity divided by the total film thickness h .

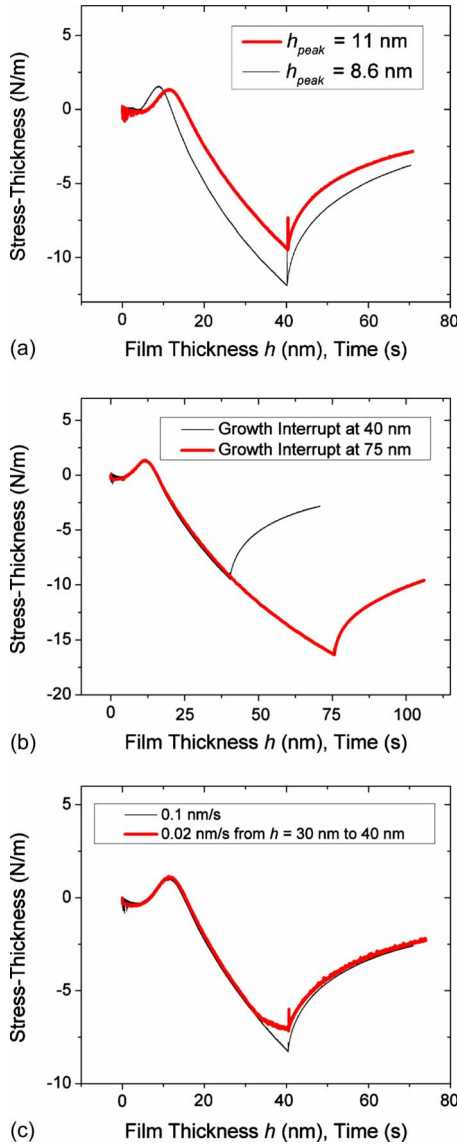


FIG. 2. (Color online) Experimental methods for changing σ_i . (a) Shifting h_{peak} , (b) changing h_{int} , and (c) changing R after $h=30$ nm.

$$\frac{d\varepsilon}{dt} = C\sigma^n \exp\left(\frac{-E_a}{kT}\right), \quad (1)$$

with ε the film strain, C a constant with units of $s^{-1} Pa^{-n}$, σ the average stress, E_a the activation energy for the rate-limiting creep process, and T the absolute temperature. As the stress under study was intrinsic, σ could not be directly varied by applying a force. Therefore, the relationship between $d\varepsilon/dt$ and σ immediately after deposition was interrupted was measured. $d\varepsilon/dt$ was approximated by the change in strain over the first second of relaxation. This strain was calculated by dividing the average stress change over that second by the biaxial modulus of bulk gold, 130 GPa. Substitution of the biaxial modulus for (111)-textured gold, 189 GPa, would lead to a rescaling of σ_i , but would not change the general conclusions that will be reached. The

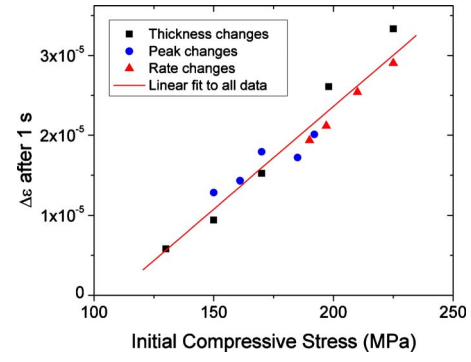


FIG. 3. (Color online) Dependence of the strain change after one second as a function of initial compressive stress.

stress at the beginning of the relaxation, σ_i , was substituted for the applied stress in Eq. (1).

The initial stress, σ_i , was varied at the beginning of each interrupt in the following ways. First, the thickness at which the peak tensile stress developed, h_{peak} , was varied from 8.5–11 nm by varying the background pressure up to 10^{-5} Torr using a leak valve flowing forming gas (5% H_2 , balance nitrogen). As h_{peak} decreased with increased pressure, the compressive stress at a given film thickness h increased. In this way, σ_i could be varied for a constant 40 nm film thickness at interruption and constant deposition rate. Second, the film thickness at the beginning of the interrupt, h_{int} , was varied from 40–200 nm while maintaining a constant deposition rate of 0.1 nm/s. σ_i was found to decrease as h_{int} increased. Finally, the deposition rate was changed to alter σ_i . After depositing the first 30 nm of gold at 0.1 nm/s, the deposition rate R was changed to values of 0.01, 0.02, 0.05, and 0.15 nm/s without interrupting deposition. The new rate R_2 was stable after approximately 15–20 s in each case. R_2 was then maintained until the total thickness of the gold film was 40 nm. σ_i was found to become more compressive as R_2 decreased. See Fig. 2 for representative stress-thickness data curves obtained using these methods. With these techniques, σ_i could be varied at room temperature from 70 to 225 MPa.

Figure 3 shows the initial strain relaxation rate versus σ_i . A linear dependence of ε_i on σ_i was found, independent of the method used to vary σ_i . As the temperature was maintained at room temperature during these measurements, the exponential term in Eq. (1) remained constant. The exponent n in Eq. (1) was therefore empirically determined to be 1 for the strain relaxation process.

Figure 4 shows ε_i versus σ_i for 50-nm-thick gold films deposited at 0.1 nm/s at 75 °C, 100 °C, and 150 °C. The results from Fig. 1 are also plotted for comparison. As the data points for elevated temperatures fell on or near the same line established at 25 °C, increasing the substrate temperature did not appear to have a significant effect on the initial relaxation rate.

To verify this result, stress relaxations were measured for 18 h after 50 nm gold depositions performed with silicon-nitride substrate temperatures of 25 °C, 100 °C, and 150 °C. The change in strain normalized by the initial stress after each interruption of deposition is plotted in Fig. 5. The

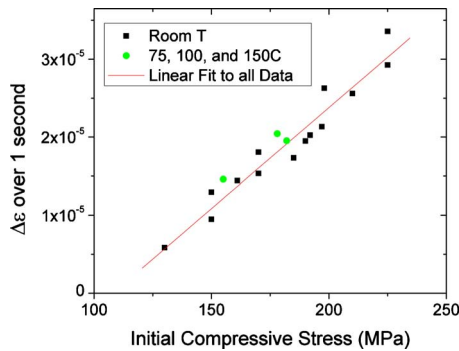


FIG. 4. (Color online) Dependence of strain change in gold films deposited on silicon nitride after one second on the initial compressive stress at temperatures of 75, 100, and 150 °C. Data from room temperature is included for comparison.

effect of temperature on the initial relaxation rate was determined by dividing the derivative of each curve, $d\epsilon/dt$, by the stress at each data point. From Eq. (1), this quantity should be $C \exp(-E_a/kT)$. At all temperatures, this value was $5 \pm 1 \times 10^{-16} \text{ s}^{-1} \text{ Pa}^{-1}$. The quantity $C \exp(-E_a/kT)$ was therefore essentially constant up to 150 °C ($E_a \leq 0.04 \text{ eV}$), in agreement with the results obtained by variation in σ_i .

Empirically, the stress relaxation rate over the first second can be described for the entire measured temperature range by the equation

$$\frac{\Delta\epsilon}{\Delta t} = 0.035\sigma_i - 3.6 \quad (2)$$

with σ_i in MPa and t in seconds. The lack of a significant temperature dependence indicates that the rate-limiting relaxation process was not lattice or grain-boundary diffusion and surface diffusion is also unlikely. These facts eliminate Coble and Nabarro-Herring creep.¹² The creep rate should be dependent on the dislocation density, which in bulk materials has been shown to be temperature dependent and proportional to σ^2 .^{12,13} Surface nucleation of dislocation loops has also been shown to have a power-law dependent on stress and dependent on film dimension in both modeling and experiments.¹⁴⁻¹⁷ The low activation energy and exponent

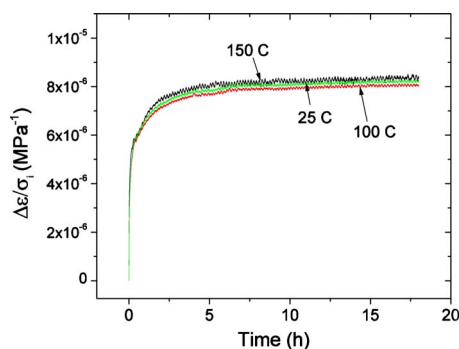


FIG. 5. (Color online) Strain changes in a 50-nm-thick gold film deposited on silicon nitride over 18 h at 25, 100, and 150 °C.

$n=1$ therefore additionally indicate that nucleation of dislocation loops was not the limiting reaction in this process. The results from this study also differ from isothermal relaxations measured in annealed silver films by Kobrinisky,¹⁸ in which deformation by temperature cycling led to high dislocation densities. Obstacle controlled glide then led to an expected temperature dependence that was not observed in this study. As obstacle controlled glide limited by dislocation-dislocation interactions should exhibit an activation energy of at least $0.2 \mu b^3$,¹² the very low E_a for the strain rates in these as-deposited films therefore indicates obstacle-free dislocation glide.

It is likely that grain growth has occurred during the long interruptions characterized in Fig. 5. Grain growth has recently been observed *in situ* during growth of Fe⁹ and Ag¹⁹ deposited under conditions in which reversible stress changes have been observed (room temperature in the case of Ag and Au). We also have evidence from *ex situ* transmission electron microscopy analysis that grain growth occurs over the time scale of the long-term experiments of Fig. 5.²⁰ Grain growth is a densification process that should lead to development of a tensile stress. However, grain growth is irreversible and is unlikely to contribute to the reversible stress change that is the focus of our discussion here. Grain growth also normally has an activation energy of about half the activation energy for grain-boundary diffusion.²¹ Given this, it would be surprising if grain growth significantly contributed to the behavior shown in Fig. 5. Having said this, instances of very low-temperature deformation-induced grain growth^{22,23} have been reported, suggesting a weak energy of activation for this form of grain growth.

The motion of pre-existing dislocations in as-deposited films has been suggested as an explanation of plastic deformation behavior in nanoindentation experiments in nanograined material at very low homologous temperatures^{22,23} and to explain differing responses to nanoindentation in as-deposited and annealed thin films.²⁴ Examination of literature data for long relaxations of intrinsic stress in sputtered copper²⁵ and evaporated iron⁹ also show very similar kinetics to those observed here. It is therefore possible that the rate-limiting process for relaxation of intrinsic stress in thin films is in many cases similar to that seen in nanoindentation experiments in nanograined materials. In this case, dislocation motion would occur during each interruption to relieve compressive stress that develops during resumed growth.

In summary, the initial rate of strain relief of intrinsic compressive stresses in thin gold films deposited on amorphous silicon-nitride substrates has been shown to have a linear dependence on the initial stress and little or no dependence on temperature. These dependencies are consistent with an obstacle-free dislocation glide process for dislocations that exist in the as-deposited film so that dislocation generation is not required. These results are also consistent with the behavior of nanograined films under nanoindentation²²⁻²⁴ and with stress relaxations in thin films of other materials deposited by sputtering²⁵ and at other homologous temperatures.^{25,9} The lack of a significant temperature dependence also indicates that diffusion-based models

for generation and relaxation of the reversible compressive stress are unlikely to be correct. A new model consistent with this data will therefore be required to explain intrinsic compressive stresses and the accompanying relaxation.

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- ¹R. W. Hoffman, *Thin Solid Films* **34**, 185 (1976).
 - ²W. D. Nix and B. M. Clemens, *J. Mater. Res.* **14**, 3467 (1999).
 - ³S. C. Seel, C. V. Thompson, S. J. Hearne, and J. A. Floro, *J. Appl. Phys.* **88**, 7079 (2000).
 - ⁴L. B. Freund and E. Chason, *J. Appl. Phys.* **89**, 4866 (2001).
 - ⁵F. Spaepen, *Acta Mater.* **48**, 31 (2000).
 - ⁶R. C. Cammarata, T. M. Trimble, and D. J. Srolovitz, *J. Mater. Res.* **15**, 2468 (2000).
 - ⁷E. Chason, B. W. Sheldon, L. B. Freund, J. A. Floro, and S. J. Hearne, *Phys. Rev. Lett.* **88**, 156103 (2002).
 - ⁸C. Friesen and C. V. Thompson, *Phys. Rev. Lett.* **93**, 056104 (2004).
 - ⁹R. Koch, Dongzhi Hu, and A. K. Das, *Phys. Rev. Lett.* **94**, 146101 (2005).
 - ¹⁰C.-W. Pao, D. J. Srolovitz, and C. V. Thompson, *Phys. Rev. B* **74**, 155437 (2006).
 - ¹¹G. G. Stoney, *Proc. R. Soc. London, Ser. A* **82**, 172 (1909).
 - ¹²H. J. Frost and M. F. Ashby, *Deformation Mechanism Maps* (Pergamon Press, Oxford, 1982).
 - ¹³A. S. Argon, *Scr. Met. (Brno)* **4**, 1001 (1970).
 - ¹⁴M. F. Horstemeyer, M. I. Baskes, and S. J. Plimpton, *Acta Mater.* **49**, 4363 (2001).
 - ¹⁵V. S. Deshpande, A. Needleman, and E. Van der Giessen, *J. Mech. Phys. Solids* **53**, 2661 (2005).
 - ¹⁶L. Zuo, A. H. W. Ngan, and G. P. Zheng, *Phys. Rev. Lett.* **94**, 095501 (2005).
 - ¹⁷J. R. Greer and W. D. Nix, *Phys. Rev. B* **73**, 245410 (2006).
 - ¹⁸M. J. Kobrinsky and C. V. Thompson, *Acta Mater.* **48**, 625 (2000).
 - ¹⁹C. Polop, C. Rosiepen, S. Bleikamp, R. Drese, J. Mayer, A. Dimiyati, and T. Michely, *New J. Phys.* **9**, 74 (2007).
 - ²⁰J. Leib, R. Mönig, and C. V. Thompson, *Phys. Rev. Lett.* **102**, 256101 (2009).
 - ²¹D. Turnbull, *Trans. AIME* **191**, 661 (1951).
 - ²²K. Zhang, J. R. Weertman, and J. A. Eastman, *Appl. Phys. Lett.* **85**, 5197 (2004).
 - ²³K. Zhang, J. R. Weertman, and J. A. Eastman, *Appl. Phys. Lett.* **87**, 061921 (2005).
 - ²⁴E. T. Lilleodden and W. D. Nix, *Acta Mater.* **54**, 1583 (2006).
 - ²⁵M. Pletea, W. Bruckner, H. Wendrock, and R. Kaltofen, *J. Appl. Phys.* **97**, 054908 (2005).