Understanding the intrinsic compression in polycrystalline films through a mean-field atomistic model

Enrique Vasco1, María J Ramírez-Peral1,2, Enrique G Michel2,3,4 and Celia Polop2,3,4

1 Instituto de Ciencia de Materiales de Madrid, CSIC, Sor Juana Inés de la Cruz 3, 28049, Madrid, Spain
2 Departamento de Física de la Materia Condensada, Universidad Autónoma de Madrid, 28049, Madrid, Spain
3 Condensed Matter Physics Center (IFIMAC), Universidad Autónoma de Madrid, 28049, Madrid, Spain
4 Instituto Universitario de Ciencia de Materiales Nicolás Cabrera, Universidad Autónoma de Madrid, Madrid 28049, Spain

E-mail: enrique.vasco@csic.es

Received 8 July 2020, revised 2 October 2020
Accepted for publication 14 October 2020
Published 17 November 2020

Abstract

Mullins’ theory predicts the buildup of adatoms during surface diffusion at the edges of grooves where grain boundaries emerge to the surface of a polycrystalline film. However, the mesoscopic nature of this theory prevents the identification of the atomic-scale physical mechanisms involved in this phenomenon. Here, we interpret the buildup of adatoms in atomistic terms through a mean-field rate-equation model and demonstrate both its kinetic nature and its impact on the intrinsic stress in these systems. Furthermore, the model provides estimates of the surface profile of intrinsic stress, of its typical mean values, and of the dependence of stress on temperature and deposition flux for different growth stages. These estimates agree well with reported experimental results obtained from recent advances in nanoscale mapping of mechanical stresses on the surface of polycrystalline films.

Keywords: stress and mechanical properties of thin films, surfaces and polycrystals, growth and surface kinetics, atomistic modeling and simulation

(Some figures may appear in colour only in the online journal)
of the groove (or gap [10]) where the GBs emerge to the surface. The kinetic nature of the phenomenon is probed and used to estimate the resulting profile of intrinsic stress under conditions of high atomic mobility. This description allows us to explain the dependence of the intrinsic stress on the deposition parameters, in order to address the large body of experimental evidence reported so far.

1.1. Review of the mesoscopic Mullins’ theory

In this study, we assume a surface, which is initially in equilibrium, evolving under deposition conditions. As previously discussed in [5, 6], the equilibrium profile $h_r$ in the vicinity of a GB counteracts the surface gradient of the balance $\nabla h$ between interfacial tensions along the GB groove profile (from the GB triple-junction to far-from-the-GB free surface). This causes the stress normal to the surface (i.e. $\delta h$) to be cancelled. The equilibrium profile $h_r(r)$, where $r$ denotes the position, can be approximated by the expression [11]:

$$h_r(r) = 1.77h_{GB} \text{erfc}(m_0(r-r_{GB}))/1.77h_{GB}$$

(1)

where $h_{GB}$ is the GB triple-junction depth measured from the average height of the surface $h$ (which corresponds to the film thickness), $\text{erfc}(x)$ denotes the integral of the complementary error function, $m_0 = \tan^{-1}(\gamma_{GB}/2\gamma_e)$ is the equilibrium surface slope at the GB triple-junction and $r_{GB}$, the GB position ($r_{GB} = 0$ hereafter). The nature of the equilibrium profile $h_r(r)$ in equation (1) is discussed in [12–14].

Under deposition conditions far from equilibrium, the surface profile $h(r,t)$ evolves according to the mesoscopic Mullins’s equation [11, 14]

$$\frac{1}{\Omega} \partial_t h(r,t) - \langle h \rangle = \nabla_s \cdot \nabla h(r,t),$$

(2)

driven by a surface diffusion current $\mathbf{J} = -\phi \nabla_s \mathbf{h}$, $\mathbf{J}$ is biased by the gradient of the surface curvature $\nabla_s h$ (driving force) where $\kappa \propto \nabla^2 h$; $\phi$, the diffusive mobility of adatoms, corresponds to the kinetic constant of $\mathbf{J}$; and the minus sign considers the curvature sign convention [6]. Surface curvature provides an estimate of the local surface chemical potential in terms of relative density of dangling bonds $n_{\text{GB}} \propto \kappa$. Thus, $\mathbf{J}$ flows from the concave regions (where the density of dangling bonds is lower) towards convex ones (with higher density) through the flat areas.

Considering the surface slope constraints at the GB triple-junction and away from GB (namely, $\partial_t h(r,t)|_{r \rightarrow r_{GB}} \rightarrow m_0$ and $\partial_t h(r,t)|_{r \rightarrow \infty} \rightarrow 0$, respectively) (see figure 6 of [6]), the solution of the Mullins equation causates the initial equilibrium profile to evolve into a kinetic state. This state is characterized by the mass accumulation at the edges on both sides of the GB groove [5, 6, 11]. In atomistic terms: (a) this mass accumulation can be understood as the buildup of adatoms with volume $\Omega$, while (b) the slope constraint models the existence of local gradients in the density of steps between surface terraces. The physical mechanisms underlying mass accumulation are difficult to identify from the numerical solution of the mesoscopic model that involves a partial fourth-order differential equation (equation (2)). This fact, together with experimental difficulties in detecting mass accumulations in steep regions near the GB groove by Atomic Force Microscopy (AFM), does not allow us to rule out the existence of mathematical artifacts a priori.

We infer the following from the mesoscopic model [5, 6]:

The continuity equation (left part of equation (2)) predicts that the accumulation must be induced by a non-null surface divergence $\nabla_s \cdot \mathbf{J}$, which can be attributed to local changes in both the effective local rate of surface diffusion $\mathbf{J}$ and/or the diffusion driving force $\nabla_s \cdot (\nabla h) \neq 0$ along the profile of the GB groove:

$$\nabla_s \cdot \mathbf{J} = -\nabla_s \phi \cdot \nabla_s k - \phi \nabla_s \cdot \left( \nabla_s k \right)$$

(3)

In the case of the Mullins-type diffusive profile, the mass accumulation at the edges of the GB grooves has been ascribed to the decrease in the diffusive mobility of the adatoms as they diffuse towards the GB triple-junction. Plausibly and in agreement with the results in [9], diffusive mobility falls within the groove as the density of step-edge barriers to cross increases. This effect would reduce interlayer transport, forcing the diffusing adatoms to meet and nucleate reversibly. On the other hand, although the surface curvature ‘diverges’ at the GB triple-junction, causing the density of dangling bonds to reach a long-range maximum, the constrictions of the surface slope limits the transport throughput (see the effective local rate of surface advance in figure 6 of [6]). This causes the gradient of superficial curvature to remain roughly constant ($\nabla_s k \approx \text{const.}$) along the groove profile such that its divergence is minimized. In practical terms, the second term in equation (3) is much smaller than the first, and thus $\nabla_s \cdot \mathbf{J} \propto -\nabla_s \phi$.

In this context, a microscopic interpretation of the profile of the GB groove in terms of terraces and steps (vicinal surfaces), rather than the blind distribution of dangling bonds, helps us to identify the physical mechanisms involved in the phenomenon of mass accumulation induced by the Mullins-type diffusion on the surface of polycrystalline solids. As we know today [5, 6, 8], this phenomenon underlies the origin of the intrinsic stress experienced by these systems during their lifespan.

2. Model, results and discussion

2.1. Atomistic approach to growth by step-flow

By applying the law of conservation of mass, the evolution of the surface profile (in equation (2)) can be rewritten in atomistic parameters as:

$$\frac{1}{\Omega} \partial_t h(r,t) = F - \partial_t n_1(r,t)$$

(4)

where $n_1(r,t)$ is the density of diffusing monomers (i.e. mobile single adatoms), which are deposited from a flux $F$ and incorporated into the film bulk at the growth rate. Thus, equation (4) distinguishes between the deposition rate $F$ (atoms deposited per unit of time and area) and the growth rate $\partial_t h$ (thickness variation over the unit of time) through $n_1(r,t)$ evolution,
which is described according the following kinetic rate equation:

\[ \partial_t n_1 = F - D_s n_1 \text{step} - D_s \left[ 1 - \left( \frac{\lambda}{\xi} \right)^2 \right] n_1^2 + \beta D_s \nabla^2 n_1, \quad (5) \]

where \( D_s \) is the intralayer monomer diffusion coefficient, \( n_{\text{step}} = \frac{1}{2} \left( \sqrt{2} / \partial h (r, t) - 3/4 \right)^{-1} \) denotes the step density in a vicinal surface comprising fcc (111) terraces separated by indistinguishable A and B steps \([15]\), \( \lambda/\xi \) corresponds to the diffusion length-to-grain size ratio, and \( \beta \) is a kinetic parameter described below. Since metal (111) planes exhibit the highest close-packing and lowest energy cause most polycrystalline metal films to grow [111]-textured with high roughness (following a Volmer-Weber mode), it makes sense to use a (111) vicinal surface as a generic growth scenario.

Equation (5) corresponds to the easiest form of kinetic rate equation able to consider the following processes: The first term takes into consideration that the flux feeds evenly the monomer density; the second and third terms account for the decay in \( n_1 \) by monomer capture by steps and monomer capture by other monomers, respectively. The fourth term considers the monomer diffusion driven by surface gradients of \( n_1 \), which corresponds to the thermodynamic potential involved in the Fick’s first law \( \dot{j} = -D_s \nabla n_1 \). The ability of the fourth term to homogenize spatially the monomer density is controlled by \( \beta \). Equation (5) assumes low growth temperatures, such that the re-evaporation is negligible. Figure 1(c) offers a visual description of the atomic parameters involved in the model.

Figure 1(a) displays the equilibrium profile (black curve) in the vicinity of a GB with \( n_{01} = 0.3 \) \([16]\), along with its densities of (111) steps \( n_{\text{step}} \) (red curve) and dangling bonds according to Mullins’ equation \( n_{db} \propto \nabla^2 h \), dashed green curve). As revealed from the \( n_{\text{step}} \) profile, the steps are concentrated within the GB groove. \( n_{\text{step}} \) remains nearly constant close to the GB triple-junction where the surface slope is constrained to \( n_{01} \) (gray line) and decreases towards the grain surface. Note that the \( n_{\text{step}} \) profile differs greatly from the \( n_{db} \) profile, as considered by the Mullins’ theory \([11]\) that predicts an accumulation of dangling bonds at the GB triple-junction where the surface curvature diverges. Since in the polycrystalline films, the intrinsic stress relaxes (down to residual levels of two-three orders of magnitude lower) under low surface mobility conditions (e.g. at room conditions), the initial surface profiles (at \( t = 0 \) shown below are taken to be similar to \( h_{GB} \)-normalized equilibrium profiles [i.e. \( h (r, t = 0) = h_c (r) / h_{GB} \)]. This is because major differences between initial and equilibrium profiles would imply high residual levels of stress (see discussed in section 2.2).

By inserting equation (5) in equation (4), the local rate of surface advance is described as follows:

\[ \frac{1}{\Omega} \partial h = D_s n_1 n_{\text{step}} + D_s \left[ 1 - \left( \frac{\lambda}{\xi} \right)^2 \right] n_1^2 - \beta D_s \nabla^2 n_1, \quad (6) \]

The first term in equation (6) corresponds to growth by step-flow within the GB groove (i.e. steps capture diffusing monomers). The second term accounts for second nucleation on the grain top (diffusing monomers meet each other), and the third one correlates spatially the rates of the two first terms through the monomer density.

The factor \( 1 - \left( \frac{\lambda}{\xi} \right)^2 \) in the second term evaluates the probability of second nucleation on the grain top. For grain sizes much larger than the diffusion length \( \lambda \) the contribution of the monomers to the step-flow is proportional to the number of atoms landing in the \( \lambda \)-wide strip near the GB (where \( n_{\text{step}} \) is higher), and then the monomer current is \( j_t \sim F \lambda (\lambda/\xi) \). Otherwise, all the deposited monomers contribute with \( j_t \sim F \xi \). In accordance with the law of conservation of mass, the probability of second nucleation can be estimated from the relative difference between these two cases \( \sim [F \xi - F \lambda (\lambda/\xi)] / F \xi \). In principle, the diffusion length is effectively limited by the grain size, so that \( 1 - \left( \frac{\lambda}{\xi} \right)^2 \) is ranged between 0 and 1 (i.e. without and with second nucleation, respectively).

On the other hand, the kinetic parameter \( \beta \) (in the third term of equation (6)) ranges between two limiting cases: \( \beta \approx 1 \) corresponds to a kinetic limitation-free stage where the surface diffusion is much faster than the monomer capture and cancels any gradient of the monomer density. Otherwise, \( \beta < 1 \) corresponds to an aggregation-limitation diffusion that characterizes kinetically limited growth. The interlayer transport delayed by step-edge barriers and/or reversible nucleation would be, potentially, the major kinetic limitations in these systems.

Figure 1(b) shows the evolution of the \( n_1 \) profile computed by integrating equation (5) for a kinetically limited growth by step-flow (i.e. with \( \beta = 0.01 \) and \( \xi = \lambda \)), \( n_1 \) profile (along x-axis) stabilizes to steady values in fractions of \( \mu s \) (y-axis), which are different inside \( n_1 \) (i.e. \( F / D_s n_{\text{step}} \)) and outside \( n_1 \) (i.e. \( F / D_s n_{\text{step}} \)) the GB groove. These values differ in several orders of magnitude (~two orders in our study for \( \xi/2 = 25 \) lattices), which indicates that monomer density is depleted within the GB groove, in agreement with the predictions of the classical growth theories \([19]\). This result rules out previous models that attributed the postcoalescence compression to the insertion/trapping of adatoms in GBs \([4, 20, 21]\) because since the GB groove is empty in monomers there is nothing to insert or capture. In this context, it is also interesting to note that Mullins’ theory predicted early that currents involving transport along GBs have a negligible effect on the material relaxation (see equation 15 in \([11]\)).

(Kinetically limited growth, \( \beta < 1 \)) figure 2(a) shows the local rate of surface advance by step-flow (first term in equation (6)), \( \partial h \)—dashed pink curve). The normalized profiles of densities of the involved species in this type of growth, namely, saturated \( n_1 \) (blue curve, for \( t \geq 10 \mu s \) according to figure 1(b)) and initial \( n_{\text{step}} \) (red curve taken from figure 1(a)) are also included. Since both densities have opposite behaviors (\( n_1 \) rises as we move away from the GB while \( n_{\text{step}} \) drops), \( \partial h \) exhibits a maximum where the product \( n_1 \times n_{\text{step}} \) is highest. In other word, \( \partial h \) is higher at the edge of the GB groove where both species coexist in moderate amounts. By way of comparison, the local rate of surface advance obtained from the slope-constrained Mullins’
Figure 1. (a) $h_{gb}$—normalized equilibrium surface profiles [$h(0) = h_e$, black curve] along with the density of A/B-undistinguishable (111) steps ($n_{step}$, red curve) and dangling bonds ($n_{db}$, dashed green curve) around a GB triple junction at $r_{gb} = 0$ (with $m_0 = 0.3$ [16], gray line).

(b) Evolution of the profile of the monomer density computed from equation (5) with $F = 0.5 \text{ nm min}^{-1}$ ($\approx 2 \text{ Ml min}^{-1}$), representative $D_x = 100 \mu \text{m}^2 \text{s}^{-1}$ at RT [17] ($\approx 1.6 \times 10^9 \text{ lattice}^2 \text{s}^{-1}$ for Au(111) with lattice parameter $a = 0.252 \text{ nm}$), $\beta = 0.01$ and $\xi = \lambda$ (i.e. kinetically limited growth by step-flow without second nucleation). (C) Schematic atomistic landscape of the model. Roman numbers denote the terms in equation (5): (I) deposition rate, (II) step-flow and (III) second nucleation. The dashed red curve traces the potential-energy profile of the surface including step-edge barriers.

The red curves display the evolution of $n_{step}$ profile before (solid) and after (dashed) the surface advance. The accumulation of material at the edge results from the meet and nucleation of the adatoms along the diffusion path towards the GB triple junction. This gives rise to the formation of small terraces with unstable steps where the monomer capture is reversible. Consequently, $n_{step}$ takes negative values to indicate that these sites correspond to delayed detachment sites (i.e. kinetic limitations as discussed above) rather than attachment sites.

The quick diffusion homogenizes spatially $n_{1}$ profile (along X-axis) in few $\mu$s (y-axis), as displayed in figure 3(b). In the absence of major kinetic limitations (e.g. $\beta=0.9$), growth in regions with higher $n_{step}$ prevails independently on the site...
positions/proximity. Consequently, the local rate of the surface advance \((\partial h—\text{dashed pink curve in figure 3(c)})\) reproduces well the shape of the normalized \(n_{\text{step}}\) profile (red curve in figure 3(c)). Note that both curves (dashed pink and red) exhibit a high degree of overlap.

Figure 3(d) shows the surface profile \([h(\Delta t)—\text{pink curve}]\) that results from the initial profile \([h(0)—\text{black curve}]\) considering the advance rate plotted in figure 3(c) after \(\Delta t = 1\) s [18] of kinetic limitation-free growth by step-flow. The procedure is as the one followed to obtain the data plotted in figure 2(b). However, the profile \(h(\Delta t)\) that results in this case does not exhibit mass accumulation at the edge of the GB groove. On the contrary, a comparison with the equilibrium profile \([h_e(\Delta t)—\text{dark-cyan curve}]\) corresponding to a similar deposited volume [22] reveals a good agreement between both. This agreement indicates that kinetic limitation-free growth does not modify the equilibrium condition between interfacial tensions (described by Laplace-Young equation) as expected.

At this point, we can provide a microscopic description of the surface kinetics underlying the phenomenon of mass accumulation at the edges of the GB grooves, which addresses the results of the mesoscopic model [6]. The adatoms diffuse from the grain tops towards the GB grooves where the density of dangling bonds is higher (this is the thermodynamic driving force of the process). However, their diffusive mobilities (that determine the kinetics of the process, i.e. its rate) are limited by the reversible aggregation to the closer steps (where \(n_{\text{step}}\) is negative in figure 2(b)). In other words, while the long-range gradient of the density of steps biases the flow of diffusing adatoms, the short-range gradients control the flow rate and, consequently, the short-term surface advance.

2.2 Intrinsic stress

Unlike the extrinsic stress in thin films, which is associated to lattice and thermal mismatches with the substrate, the intrinsic stress is attributed to unbalanced force fields that arise around discontinuities in the crystalline lattice of the films. In polycrystalline films, the lattices discontinuities playing major role in the generation of intrinsic stress are the GBs and the film surface. As discussed above, the Laplace-Young equation describes the balance between these two discontinuities at the GB groove, with the Laplace pressure being the resulting stress for small perturbations in the equilibrium profile (equation (1)). These perturbations must be understood in terms of changes in the chemical potential of the surface, which is estimated from its curvature \(\kappa\). Consequently, an intrinsic stress \(\sigma_N\) in the form of a Laplace pressure is generated from the Young-Laplace equation:

\[
\sigma_N(r,t)/\gamma_s = 2(k \kappa_g(r,t) - \kappa_e(r,t)),
\]

wherever the curvature \(\kappa_g\) of the surface profile that results from kinetically limited growth differs from the curvature \(\kappa_e\) of the surface profile that corresponds to kinetic limitation-free growth (that of equilibrium as demonstrated above), for a similar deposited volume.

Figure 4 shows the surface profiles generated after \(\Delta t = 1\) s-deposition under kinetically limited and not limited conditions (pink and green curves, respectively), whose curvatures (dashed curves) differ from each other. The orange curve plots this difference \((\kappa_g - \kappa_e)\), which according equation (7), provides an estimate of the local ratio of the normal stress \(\sigma_N\) to the surface tension \(\gamma_s\). For textured vicinal surfaces, formed by terraces with a preferential crystalline orientation, \(\gamma_s\) is roughly constant and then \(\sigma_N(r,t) \propto (\kappa_g - \kappa_e)\). The thus-estimated stress profile exhibits an oscillatory behavior with a prevailing compressive contribution at the edge of GB groove (here around \(r \approx 7.5\) lattice from GB triple junction), which gives rise to a main compression averaged over the surface profile. From the data in figure 4, \(\langle \sigma_N \rangle \approx 2(k \kappa_g - \kappa_e) \gamma_s \approx (\frac{\sigma_s}{\kappa_g}) \gamma_s/a \sim 2\%\) of \(\gamma_s/a\), with \(a\) denoting the lattice parameter. The typical features (oscillating behavior, spatial range and local magnitude) of this stress profile agree reasonably with those measured experimentally in Au and Cu polycrystalline films by AFM-related techniques [8]. Besides,
Figure 3. (a) $\beta$—dependence of the $n_1$ profile around a GB triple junction at $r = 0$ (with $m_0 = 0.3$ and $\xi = \lambda$) for growth by step-flow. $n_1$ profiles are normalized by their far-from-GB values (i.e. on the gain top). (b), (c) and (d) Show similar results to those displayed in figures 1(b), 2(a) and (b), respectively, for the same set of parameters, except $\beta = 0.9$. Dark-cyan curve in (d) corresponds to the surface equilibrium profile for a similar deposited volume.

Figure 4. Surface profiles (taken from figures 2(b) and 3(d)) resulting from kinetically limited (pink curve for $\beta = 0.01$) and kinetic limitation-free (green curve for $\beta = 0.9$) growths for the same deposited volume, together with their curvatures $\kappa_k$ and $\kappa_e$ (dashed curves of the same color), respectively. The difference between the curvatures $(\kappa_k - \kappa_e)$ is included (orange curve), together with its main value averaged over the surface profile.
As nucleation (with ∂ growth by (i) step-flow (with local rate of surface advance of the surface species (monomers and steps) involved in film bombardment with energy particles [also been observed in high surface mobility conditions that considered here. This is because intrinsic stress generation has inhomogeneity leading to shadowing, steering…) are not con- do not substantially alter surface diffusivity (e.g. its spatial parameters is more difficult to understand. On the other hand, compression. Conversely, the behavior of them, and consequently lower post-coalescence intrinsic com- gives rise to larger grains, a lower density of GB sites between forwardly from the dependence of the GB density on these parameters can be addressed straight-antly modifying their sizes. Consequently, later F (or T) and the average grain size (or the GB density) can be treated as independent growth parameters.

Based on the above considerations, the behavior of σN with the early growth parameters can be addressed straightforwardly from the dependence of the GB density on these parameters [28]. Thus for example, higher Tearly (lower Fearly) gives rise to larger grains, a lower density of GB sites between them, and consequently lower post-coalescence intrinsic compression. Conversely, the behavior of σN with the later growth parameters is more difficult to understand. On the other hand, dependence on intrinsic stress with flux characteristics that do not substantially alter surface diffusivity (e.g. its spatial inhomogeneity leading to shadowing, steering…) are not considered here. This is because intrinsic stress generation has also been observed in high surface mobility conditions that do not involve flux (e.g. by post-deposition annealing [16] and bombardment with energy particles [28]).

Figure 5(a) shows the λ/ξ—dependences of the densities of the surface species (monomers and steps) involved in film growth by (i) step-flow (with local rate of surface advance ∂h ∝ D1n1nstep at the edge of grain-boundary), and (ii) second nucleation (with ∂h ∝ D2[1 − (λ/ξ)2]n2 on the grain top). As λ/ξ decreases (from solid curve to increasingly dashed ones, according to arrows directions), the second nucleation prevails depleting the grain top of monomers. This is because the second nucleation implies the meet of several monomers, such that n1 decays at a rate of ∂h1 ∝ −n12 down to a steady value of n1 → √F/D2. Figure 5(b) shows the resulting surface profiles (h(r,t)—pink curves, which are calculated in a similar way to those displayed in figures 2(b) and 3(d)), together with the corresponding equilibrium profiles [h0(r,t)—green curves]. Such equilibrium profiles are estimated by assuming: (a) a similar deposited volume [22], and (b) a similar height far from the GB [i.e. h0(r → ∞,t) ≡ h0(r → ∞,t)]. The curvature values (like those displayed in figure 4) are not included in figure 5(b) for the sake of clarity. Instead, their differences are plotted [(κκ − κκ)—orange curves]. As λ/ξ decreases, the mass buildup on the edge of the grain-boundary groove is transferred to the grain top. This causes (not shown here—use figure 4 to follow the description) the minimum of curvature κκ of the resulting surface profile to shift towards the GB position, while the minimum of κκ is moving in the opposite direction. Thus, the curvature minima approach to each other, such that the overlap of the curvature curves results in a decrease in the minimum of their difference ⟨κκ − κκ⟩, as shown in figure 5(b).

According to equation (7), this implies a decrease in both the compression maximum max(σN) and its main value ⟨σN⟩.

Beyond the reported qualitative behavior of the intrinsic stress with the later deposition flux (namely, σN drops as Flater...
increases [29–31]), in this study, we aim to address the quantitative dependence between these two magnitudes. Figure 5(c) shows the $\lambda/\xi$—dependencies of $\max(\sigma_N)/2\gamma_s$ and $\langle\sigma_N\rangle/2\gamma_s$ (red and black symbols, respectively), which fit well to parabolic functions (dashed curves). Assuming that the behavior of these statistical values is representative of the intrinsic stress, and taking into account $\lambda^6 \sim D_j/F$, we get:

$$\sigma_N \sim (\lambda/\xi)^2 \sim (F_{\text{early}}/F_{\text{later}})^{2/3} \sim F_{\text{later}}^{-1/3}$$

where, as discussed above, $F_{\text{early}} = F(h \rightarrow 0)$ is the early-growth flux, determining the grain size $\xi$. The power-law dependence $\sigma_N \propto F_{\text{later}}$ (with $\alpha = -1/3$) in equation (8) is consistent with the later flux-dependences of the steady intrinsic stress $\sigma_N$ reported for moderated fluxes and submicron-sized grains [29–31], whose power-law exponents are ranged between $\alpha = -0.21$ and $-0.40$ as displayed in figure 5(d).

Equation (8) describes the effects of the flux on intrinsic stress for different stages of growth. Thus, while the early increase in flux raises the density of GBs around which the material under compression accumulates (i.e. $\sigma_N$ increases), the late postcoalescence increase in flux induces extra surface roughness that results in traction between crystalline-coherent surface features (i.e. $\sigma_N$ decreases [29]). However, the crossover between both regimes changes for 3D growths by Volmer-Weber mode owing to the kinetic roughening of the surface as the film grows [14]. Hence, early flux is not low enough to avoid second nucleation throughout deposition, and consequently late increases in flux are not necessary to induce extra-roughness and traction on grain surfaces. This effect may consistently explain the non-monotonic behavior of $\sigma_N$ vs. flux (with a maximum of compression for intermediate fluxes) reported in [28].

3. Conclusions

We present an atomistic interpretation of the origin of the non-equilibrium morphology that forms at the edges of the grooves where adatoms accumulate during surface diffusion, according to Mullins’ theory. This non-equilibrium morphology is the result of kinetically limited growth by step-edge barriers and reversible nucleation/aggregation processes delaying interlayer transport. As it might be expected, the non-equilibrium morphology gives rise to a surface field of intrinsic stress, whose profile and mean values were estimated by means of the Young-Laplace equation. Once the mechanisms, growth modes (step-flow and second nucleation) and kinetic limitations are identified, we addressed the dependence of the intrinsic stress with the deposition parameters (namely, the deposition flux and temperature for different growth stages).

Finally, the atomistic interpretation presented here complements previous mesoscopic models (those of [5, 6], and also Mullins’ theory [11]) providing a comprehensive and multiscale understanding of the phenomenon of intrinsic stress generation in polycrystalline films and coatings. The kinetics of intrinsic stress in nanocrystalline films will be approached in forthcoming works.

Acknowledgments

This work was supported by the Ministerio de Economía, Industria y Competitividad (Spain) under Project No. FIS2017-82415-R; Ministerio de Ciencia, Innovación y Universidades (Spain) within the framework of UE M-ERA.NET 2018 program, under Project StressLIC (Spanish national subprojects PCI2019-103604 and PCI2019-103594). M.J.R.P. acknowledge support by Comunidad de Madrid under contract PEJ-2019-AI/IND-14228. E.G.M. and C.P. acknowledge financial support from the MICINN, through the ‘María de Maeztu’ Programme for Excellence Units in R&D (CEX2018-000805-M).

ORCID iD

Enrique Vasco https://orcid.org/0000-0002-0647-4499

References

[1] Floro J A, Hearne S J, Hunter J A, Kotula P, Chason E, Seel S C and Thompson C V 2001 The dynamic competition between stress generation and relaxation mechanisms during coalescence of Volmer–Weber thin films J. Appl. Phys. 89 4886–97
[2] Abadías G, Chason E, Keckes J, Sebastiani M, Gregory B, Etienne Barthel T, Doll G L, Murray C E, Stoessel C H and Martini L 2018 Review article: stress in thin films and coatings: current status, challenges, and prospects J. Vac. Sci. Technol. A 36 020801
[3] Koch R, Hu D and Das A K 2005 Compressive stress in polycrystalline Volmer-Weber films Phys. Rev. Lett. 94 146101
[4] Jagtap P and Chason E 2020 A unified kinetic model for stress relaxation and recovery during and after growth interruptions in polycrystalline thin films Acta Mater. 193 202–9
[5] Vasco E and Polop C 2017 Intrinsic compressive stress in polycrystalline films is localized at edges of the grain boundaries Phys. Rev. Lett. 119 256102
[6] Vasco E, Michel E G and Polop C 2018 Disclosing the origin of the postcoalescence compressive stress in polycrystalline films by nanoscale stress mapping Phys. Rev. B 98 195428
[7] Review Refs. [3, 4, 6] for a detailed description and discussion of previous models, which mostly point to the insertion/trapping of adatoms in the GB as the cause of intrinsic stress in polycrystalline films. These models fail to bridge the gap between macroscopic stress measurements and proposed atomistic mechanisms in the lack of experimental information on the nanoscale stress field
[8] Polop C, Vasco E, Perrino A P and Garcia R 2017 Mapping stress in polycrystals with sub-10 nm spatial resolution Nanoscale 9 13938–46
[9] Zepeda-Ruiz L A, Chason E, Gilmer G H, Wang Y, Xu H, Nikroo A and Hamza A V 2009 Understanding the relation between stress and surface morphology in sputtered films: atomistic simulations and experiments Appl. Phys. Lett. 95 151910
[10] Our ‘GB gap’ terminology used earlier in Refs. [5,6] to refer to the near-equilibrium shape of the hollow where the GB emerges to the surface, it is replaced by ‘GB groove’ to be consistent with Mullins’ theory [11]
[11] Mullins W W 1937 Theory of thermal grooving J. Appl. Phys. 28 333–9
[12] In Ref. [11], Mullins assumes that both the vapor pressure and the chemical potential of a surface depend linearly on its local curvature for small curvature approximations to the Gibbs-Thompson formula. From these assumptions and the Edward-Wilkinson and Nernst-Einstein relationships, Mullins determined the stationary surface profiles without and with diffusion in the vicinity of a grain boundary. The fact that these profiles are stabilized by the surface transport mechanisms against kinetic roughness [13,14] and the thermodynamic nature of the Gibbs-Thompson formula mean that the stationary profile without diffusion can be considered as an equilibrium profile.

[13] Srolovitz D J 1989 On the stability of surfaces of stressed solids Acta Metall. 37 621–5

[14] Barabási A L and Stanley H E 1995 Fractal Concepts in Surface Growth (Cambridge UK: Cambridge University Press)

[15] González-González A, Sacedón J L, Polop C, Rodríguez-Cañas E, Aznárez J A and Vasco E 2009 Surface slope distribution with mathematical molding on Au(111) thin film growth J. Vac. Sci. Technol. A 27 1012–6

[16] Surface slope $m_0 = 0.3$ at the GB triple junction corresponds to a representative value taken within the measured range of border slopes in polycrystalline Au films by González-González A, Alonzo-Medina G M, Oliva A I, Polop C, Sacedón J L and Vasco E 2011 Morphology evolution of thermally annealed polycrystalline thin films Phys. Rev. B 84 155450

[17] Antczak G and Ehrlich G 2010 Surface Diffusion Metals, Metal Atoms, and Clusters (Cambridge UK: Cambridge University Press)

[18] The integration time $\Delta t = 1 s$ is estimated as $\Delta t \sim 1/\partial h = 1/D_j n_1 n_{as} \Omega$ with $D_j = 100 \mu m^2/s$ at RT [17], Au atomic volume $\Omega = 1.7 \times 10^{-29} m^3$, Au(111) lattice parameter $a = 0.252 \text{nm}$, and the steady profiles of $n_1(r)$ and $n_{as}(r)$ taken from figure 1

[19] Michely T, Krug J and Island M 2004 Atoms: Patterns and Processes in Crystal Growth Far from Equilibrium (Heidelberg Germany: Springer-Verlag)

[20] Yu H Z and Thompson C V 2014 Correlation of shape changes of grain surfaces and reversible stress evolution during interruptions of polycrystalline film growth Appl. Phys. Lett. 104 141913

[21] Saedi A and Rost M J 2016 Thermodynamics of deposition flux-dependent intrinsic film stress Nat. Commun. 7 10733

[22] The equilibrium profile $h_0(\Delta t)$ for a deposited volume of $F \Delta t$ follows equation 1 from considering $b_{cb} (\Delta t)$ as a fitting parameter to satisfy the condition $\int_0^\infty [h_0 (r, \Delta t) - h_0(r, 0)] \partial r = F \Delta t$. Consequently, for the comparison in figure 3(d): $\int_0^\infty [h_0 (r, \Delta t) - h_0(r, 0)] \partial r = \int_0^\infty \int_0^\infty [h (r, \Delta t) - h(r, 0)] \partial r$

[23] Mei J, Davenport J W and Fernando G W 1991 Analytic embedded-atom potentials for fcc metals: application to liquid and solid copper Phys. Rev. B 43 4653–8

[24] Shull A L and Spaepen F 1996 Measurements of stress during vapor deposition of copper and silver thin films and multilayers J. Appl. Phys. 80 6243–56

[25] Abermann R and Koch R 1985 The internal stress in thin silver, copper and gold films Thin Solid Films 129 71–78

[26] Grovenor C R M, Hentzell H T G and Smith D A 1984 The development of grain structure during growth of metallic films Acta Metall. 32 773

[27] Timoshenko G 1997 Mechanics of Materials (Boston USA: PWS Publications)

[28] Jamnig A, Pliaitsikas N, Sarakinog K and Abadias G 2020 The effect of kinetics on intrinsic stress generation and evolution in sputter-deposited films at conditions of high atomic mobility J. Appl. Phys. 127 045302

[29] Chason E, Sheldon B W, Freund L B, Floro J A and Hearne S J 2002 Origin of compressive residual stress in polycrystalline thin films Phys. Rev. Lett. 88 156103

[30] Del Vecchio A L and Spaepen F 2007 The effect of deposition rate on the intrinsic stress in copper and silver thin films J. Appl. Phys. 101 063518

[31] Flötotto D, Wang Z M, Jeurgens I P H and Mittemeijer E J 2015 Kinetics and magnitude of the reversible stress evolution during polycrystalline film growth interruptions J. Appl. Phys. 118 055305