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We have developed a kinetic model for residual stress generation in thin films grown from energetic vapor fluxes, encountered, e.g., during sputter deposition. The new analytical model considers sub-surface point defects created by atomic peening, along with processes treated in already existing stress models for non-energetic deposition, i.e., thermally activated diffusion processes at the surface and the grain boundary. According to the new model, ballistically induced sub-surface defects can get incorporated as excess atoms at the grain boundary, remain trapped in the bulk, or annihilate at the free surface, resulting in a complex dependence of the steady-state stress on the grain size, the growth rate, as well as the energetics of the incoming particle flux. We compare calculations from the model with in situ stress measurements performed on a series of Mo films sputter-deposited at different conditions and having different grain sizes. The model is able to reproduce the observed increase of compressive stress with increasing growth rate, behavior that is the opposite of what is typically seen under non-energetic growth conditions. On a grander scale, this study is a step towards obtaining a comprehensive understanding of stress generation and evolution in vapor deposited polycrystalline thin films. Published by AIP Publishing.

I. INTRODUCTION

Intrinsic stresses are an inherent feature in polycrystalline thin films and play a significant role in the reliability and functionality of thin film based devices.1–3 Hence, a fundamental understanding of the mechanisms that govern stress generation and evolution is paramount for the development of knowledge-based strategies for stress management and engineering. The difficulty in achieving this understanding is compounded by a wide number of deposition techniques that are available to experimentalists for modifying the properties of the resulting films. Mechanisms that are active in the deposition of atoms with thermal energy (e.g., evaporation and electrodeposition) may be modified by the addition of energetic species, typically encountered in plasma-based processes (e.g., sputtering, ion-beam assisted deposition, pulsed laser deposition, and arc evaporation).4

In situ wafer curvature techniques5–8 have provided valuable data for researchers to correlate stress evolution with kinetic conditions (i.e., temperature, atomic mobility, and growth rate) during island nucleation and coalescence as well as during continuous film formation. For thermal deposition, various mechanisms have been proposed to explain the development of tensile9 and compressive6,10–12 stress at different stages of the growth, the compressive-tensile-compressive stress transition with thickness,8 and the effect of grain growth.5,6,13,14 Among the mechanisms for compressive stress generation, atom insertion into grain boundaries has been gaining credibility based on a number of recent experiments8,10,15,16 and theoretical studies.17 An example is the kinetic model developed by Chason et al.18 that describes the stress evolution under different conditions (described further below). It is based on combining the atom insertion mechanism for compressive stress with a mechanism for tensile stress generation due to grain boundary formation.9 The model focuses on describing the stress that is generated at the triple junction where two adjacent grains meet to form new elements of grain boundary. Agreement of model predictions with measurements using both evaporation and electrodeposition18–20 has been demonstrated.

For energetic deposition, the energy and flux are critical additional parameters that can alter the stress evolution.2,21,22 The presence of the energetic species may affect the surface and/or bulk of the growing film.23 Surface processes enhance adatom mobility23,24 and may contribute to additional incorporation of atoms into grain boundaries.25,26 Interaction with the bulk of the film may result in atomic “peening” which induces point defects and compressive stresses,27–30 but also causes collision induced densification of the grains31 and the grain boundaries.32 While many effects of the mechanisms described above are well documented in the literature, the combined effect of non-energetic (i.e., thermally activated) growth processes and ballistically activated ones on the stress evolution is not known. Moreover, it has been proposed that the stress-inducing effects from energetic bombardment act independently from and are additive to those emanating from growth (i.e., nucleation, coalescence, grain boundary formation, and densification), so that the resulting steady-state stress is the superposition of all these contributions.33 This provides motivation for extending the existing
model for growth-induced stress\textsuperscript{18} to include the effects of energetic species.

In the present study, we describe a kinetic model that combines mechanisms of film growth kinetics and energetic bombardment into equations for the steady-state stress under different conditions. The energetic processes are divided into ones that occur at the grain boundary (by ballistic densification) and those that occur in the bulk of the film (by trapping of bombardment-induced defects). The resulting model enables us to calculate the dependence of the stress on the growth rate and pressure during deposition as well as the grain size in the film. These calculations are bench-marked against \textit{in situ} stress measurements in sputtered Mo films in which the grain structure and characteristics of the energetic vapor fluxes are varied systematically and independently.\textsuperscript{34,35} Good agreement is found using reasonable values for the adjustable model parameters, paving the way towards a comprehensive understanding of stress evolution in both thermal and energetic deposition of polycrystalline films.

II. EXPERIMENTAL RESULTS

The work described here is motivated by recent measurements of stress in Mo films using real-time wafer curvature in which film structure and process parameters were systematically varied to determine their effect on film stress evolution. In the first set of experiments, the stress was measured during DC magnetron sputter (DCMS) deposition using different growth rates (from 0.05 to 0.3 nm/s) and Ar working pressures (from 0.11 to 0.43 Pa). Some of these results have been presented in Ref. 34 where additional details of the growth conditions can be found. The values of the steady-state stress as a function of growth rate is shown in Fig. 1. The corresponding pressure for each set of growth rates is indicated in the figure. Note that the solid lines in the figure are the result of calculations from the model that is described in Sec. III. Several important features can be seen in Fig. 1. The stress becomes more compressive/less tensile at lower pressures for the same growth rate. Such an increase in compressive stress at lower pressures during sputtering has been seen in many systems\textsuperscript{22} but is often only reported for a single growth rate. The simultaneous measurement of the growth-rate dependence is an important feature of these data, which shows that the stress becomes more compressive/less tensile at higher growth rates for the same pressure. This is in contrast to thermal growth where the stress generally becomes more tensile at higher growth rates.\textsuperscript{6,8} The grain size of the Mo films in this deposition series was characterized after growth with atomic force microscopy (AFM) and cross-sectional transmission electron microscopy (TEM). The analysis showed that the grain size did not vary significantly with thickness or processing conditions and had an average value of 50 ± 10 nm. Thus, any effect of grain growth on the stress can be ruled out. The latter is further supported by the observation that there is no stress evolution/relaxation after growth is interrupted, behavior that is typically observed for metal systems with low-adatom mobility (e.g., Mo grown at room temperature which corresponds to a homologous temperature (T/T\textsubscript{m}) of \textasciitilde0.10).\textsuperscript{36}

In the second set of experiments, Magnfalt \textit{et al.} measured the dependence of the steady-state stress on the grain size (L) for a fixed growth rate and pressure, as described in Ref. 35 where additional details of the deposition and analysis can be found. The films were deposited using high power impulse magnetron sputtering (HiPIMS) at a working pressure of 0.24 Pa and an average deposition rate of 0.051 nm/s using a pulsed frequency of 100 Hz and a pulse-width of 50 \textmu s. HiPIMS is a pulsed ionized sputtering method that is known to lead to intense bombardment\textsuperscript{37} of the growing films by both metal and working gas ions. The use of different deposition methods explains why the stress is not the same for similar values of the pressure, growth rate, and grain size in the data shown in Figs. 1 and 2. The grain size was varied by depositing 200 nm thick Mo films over different Mo\textsubscript{1-x}Si\textsubscript{x} seed layers\textsuperscript{38} and characterized with AFM and cross-sectional TEM. The magnitude of the stress versus the grain size is shown in Fig. 2 (the solid line is a fit to the model described in Sec. III). The stress becomes more

![FIG. 1. Measurements of steady-state stress vs. growth rate in sputtered Mo films. The different symbols correspond to different values of the growth pressure as indicated in the figure. The solid lines are fits to the model described in the text.](image1)

![FIG. 2. Measurements of steady-state stress vs. grain size for Mo films deposited by HiPIMS at an average rate of 0.051 nm/s and pressure of 0.24 Pa. The solid line is a fit to the model described in the text.](image2)
compressive at smaller grain sizes, consistent with previous observations of stress in sputtered Mo films for which the densification of grain boundaries was proposed as a stress generating process under energetic deposition conditions.26

III. KINETIC MODEL FOR STRESS DURING ENERGETIC DEPOSITION

The measured dependence of the stress on the growth rate, pressure, and grain size establishes several different phenomena that must be accounted for by a model for energetic deposition. In this section, we describe the different mechanisms that are included in the model that allow it to account for these observations. In the subsequent sections, the model predictions are compared with the experimental data from Sec. II, and the values of the model parameters are discussed.

The approach that we use is to add the effects of energetic particles to the model by Chason et al.18 for stress during non-energetic (i.e., thermal) thin film growth (hereafter referred to as the growth model). The growth model uses rate equations to describe the stress generated at the top of the grain boundary (triple junction) that forms between two adjacent islands as they grow to intersect with each other. Details can be found in Refs. 8 and 18, so only the main result is presented here. The model predicts that the stress in each layer depends on the rate at which the triple junction moves up (which for a uniform, fully coalesced film is the same as the average growth rate, \( R \))

\[
\sigma_{\text{growth}} = \sigma_C + (\sigma_f(L) - \sigma_C) e^{-\beta f/R L}. \tag{1}
\]

In Eq. (1), \( \sigma_f(L) \) is a tensile stress that is generated due to the formation of new segments of grain boundary. Based on the mechanism proposed by Hoffman,9 we assume that it depends on \( 1/L^{1/2} \). \( \sigma_c \) is a compressive stress that is generated by insertion of atoms into the grain boundary, driven by the non-equilibrium chemical potential of mobile adatoms on the surface. The exponential term depends on the effective diffusivity of atoms from the surface into the grain boundary \( (D_{gb}) \), the rate at which the grain boundary height is changing \( (R) \) and the grain size \( (L) \). \( \beta \) is a parameter that depends on the concentration of mobile defects and the mechanical properties of the layer. Whether the energetic particle effects may also modify the kinetic parameters in the growth model is considered in Sec. V.

For energetic (e.g., sputter) deposition, we propose the addition of two processes based on mechanisms suggested by others as well as our experimental results. The first is related to collision-induced densification of the structure near the grain boundary and the second is due to the introduction of mobile defects in the bulk of the film (i.e., not at the grain boundary). A schematic of the geometry for the additional energetic effects is shown in Fig. 3, where the spacing between grain boundaries is set equal to \( L \). A defect (black circle) is created at a depth \( l \) from the surface. This depth is expected to depend on the energy of the incoming particle (sputtered atom, backscattered gas neutral, or accelerated ion), which is in turn determined by the material system, deposition method, and working gas pressure in the chamber. The rate of defect creation is equal to \( c f \), where \( f \) is the flux of energetic particles and \( c \) is the number of defects generated per particle. The diffusivity of the resulting defect is defined as \( D_l \). A key element of the model is that the surface is moving upward at a constant rate \( R \) due to deposition. The shaded area (with width approximated to be proportional to \( l \)) represents the region in which the energetic species will enhance densification near the grain boundary (e.g., through incorporation of atoms into more favorable sites or accommodation of ballistically induced defects such as interstitial atoms or implanted species), leading to compressive stress according to the mechanisms described by Magnfelt et al.26 We consider it to be a diffusion-less process by which atomic collisions knock the atoms into more energetically favorable sites in this region. The complex interactions involved in ballistic processes are simplified into a mechanism that assumes that any energetic atom hitting within this range of the grain boundary will induce additional compressive stress in the layer with a magnitude that depends on the particle’s energy. Because the process does not involve diffusion, it will depend only on the number of energetic particles per deposited atoms (i.e., the ratio \( f/R \)). The net effect of all these processes is incorporated into the following term:

\[
\sigma_{\text{energetic}} = A_o \times (l/L). \tag{2}
\]

\( A_o \) is not calculated explicitly but will be used as an adjustable parameter to compare the model with the data. We expect that it depends on the energy (or the pressure), growth rate, and flux of energetic species. For this work, we assume that \( f/R \) does not change with the growth rate for each pressure so that we can use one value of \( A_o \) for fitting the model to the data (as described below). In future work, the dependence on \( f \) and \( R \) could be investigated experimentally by comparing, e.g., stress during sputtering with different magnetic field configurations. The linear dependence on \( l/L \) is used here to approximate the fraction of the impinging energetic particles that induce stress in the grain boundary region relative to the bulk of the film. For grain sizes that become comparable to or less than \( l \), we would not expect this approximation to remain valid. Hence, additional modeling of the stress inducing effects of energetic particles near the grain boundaries (e.g., by molecular dynamics) is needed in order to develop a better understanding of how this term depends on the grain size.
The second mechanism that we consider for stress generation by energetic particles is due to the point defects that get trapped in the film, consistent with the X-ray diffraction measurement of the film stress state.\textsuperscript{39,40} Defect creation is an inherent part of the other models discussed in the literature, but we also include the subsequent kinetics of defect annihilation at the free surface. The following differential equation for the average defect concentration \((C)\) describes the balance of defect creation and annihilation:

\[
\frac{dC}{dt} = \frac{1}{l} (c_{\text{in}} - CR) - \frac{C}{\tau_s}.
\]  

(3)

The first term on the right-hand side corresponds to introduction of defects into the layer (at a depth \(l\) and a rate \(c_{\text{in}}\)) while it is growing (at rate \(R\)). In the absence of diffusion, the steady-state concentration will be \(c_{\text{in}}/R\). The second term corresponds to the rate at which these defects annihilate at the surface, determined by the characteristic time \(\tau_s\) necessary to diffuse to the surface. Defects that do not escape to the surface in this time are assumed to eventually become immobile and remain trapped in the layer (in the form of self-interstitials or clusters). The characteristic time for a defect to reach the surface is complicated by the fact that there is a moving boundary condition (i.e., the distance to the surface is increasing at rate \(R\)). We take this into account by equating the diffusional distance with the distance to the moving surface

\[
\sqrt{D_s \tau_s} = l + R \tau_s.
\]  

(4)

Solving this Eq. (4) yields

\[
\tau_s = \frac{l}{R} \left[ \alpha - 1 - \sqrt{1 - \left( \frac{2}{\alpha} \right)} \right],
\]  

(5)

where \(\alpha = D_s/(2R)\), provided that \(\alpha > 2\). In the steady-state regime (i.e., \(dC/dt = 0\)), the concentration of defects in the layer is given by

\[
C_{ss} = \frac{c_{\text{in}}}{R} \frac{1}{1 + \frac{l}{R \tau_s}}.
\]  

(6)

For values of \(\alpha\) that are less than 2 (e.g., high growth rates or low defect diffusivity), the rate of annihilation at the surface goes to zero and all the defects are retained, i.e., \(C_{ss}\) saturates at \(c_{\text{in}}/R\). We describe the stress-induced effect of defect trapping in the bulk as

\[
\sigma_{\text{bulk}}^{\text{energetic}} = \left(1 - \frac{l}{L}\right) \sigma_o C_{ss},
\]  

(7)

where the term \(\sigma_o\) represents the stress per defect retained in the bulk. The factor \((1 - l/L)\) is present because we assume that the bulk stress effect is proportional to the fraction of energetic particles that are not within a distance \(l\) of the grain boundary. By combining Eqs. (1)–(7), the following expression for the steady-state stress during sputter deposition or deposition with energetic species can be derived:

\[
\sigma_{ss}^{\text{spat}} = \sigma_{\text{growth}} + \sigma_{\text{energetic}}^{\text{grain}} + \sigma_{\text{energetic}}^{\text{bulk}}
\]

\[
= \left[ \sigma_C + (\sigma_T - \sigma_C) e^{-\frac{\phi}{kT}} \right] + A_o (l/L)
\]

\[
+ \left(1 - \frac{l}{L}\right) \left( \frac{B_o}{1 + \frac{l}{R \tau_s}} \right),
\]  

(8)

where we have replaced the constant \(\sigma_o c_{\text{in}}/R\) with a single parameter \(B_o\). Each term in Eq. (8) has a different dependence on \(R\) and/or pressure which plays a role in reproducing the complex behavior seen in the experiments.

IV. COMPARISON OF THE MODEL WITH EXPERIMENTAL RESULTS

To compare the predictions of Eq. (8) with the data in Figs. 1 and 2, we use a non-linear least-squares fitting routine to find the optimum values of the model parameters. Because there is a large number of potential fitting parameters in the model, we introduce some constraints (described below) to produce a self-consistent set of values with a much reduced number of free parameters. We then perform a global optimization of all the free parameters over the entire set of data. Although this makes the agreement between the data and the fitting results slightly less ideal for each data set, it helps to ensure that the fitting procedure produces physically reasonable values that are consistent across all the different data.

The full set of parameters used to calculate the model values is shown in Table I, with those used for each of the data sets labeled as DCMS and HiPIMS. The ellipses are used to show which parameters were kept the same for the different data sets. As shown in Table I, we required that there is a single set of values for the parameters \(\sigma_C(L), \sigma_C, \text{ and } D_s\) for all the measurements, since we do not expect these to vary greatly over the measured range of processing conditions. Note that the tensile stress due to grain boundary formation \((\sigma_T(L))\) depends inversely on the square root of the grain size. The value shown in the table (4.24 GPa) is the value of \(\sigma_T\) for a grain size of 50 nm. The value of \(\sigma_T\) for other values of \(L\) can be obtained by multiplying 4.24 GPa by \((50 \text{ nm}/L)^{1/2}\). The parameter \(\beta D_{\text{eff}}\) is assumed to have one value for all DCMS conditions and allowed to have another value for the HiPIMS conditions. This was done to recognize the fact that HiPIMS has a different energetic component than DCMS and, therefore, potential effect on the effective surface diffusivity. The parameters related to the DCMS data that depend on the energetic component of the deposition \((A_o, B_o, \text{ and } l)\) are expected to have different values for each pressure studied. However, since we assume that the ratio \(f/R\) does not change with the growth rate, we use the same value of each of these parameters for the different growth rates at each pressure. To ensure a reasonable dependence on the pressure, we assume that the energy of the particles in the DCMS data is proportional to \((P_x, P)\), where \(P_x\) is a single value of the threshold pressure used for all the data. This makes the higher pressure measurements correspond to less energetic particles. We constrain the parameters \(A_o, B_o, \text{ and } l\) so that they depend linearly on the pressure (and hence
energy): $A_o = A_o^* (P_o - P)$, $B_o = B_o^* (P_o - P)$, and $l = l_o^* (P_o - P)$. Therefore, we have reduced 12 of the possible fitting parameters for the DCMS data to 4 (i.e., $A_o^*$, $B_o^*$, $l_o^*$, and $P_o$). The results shown in Table I correspond to the values of $A_o$, $B_o$, and $l$ calculated for each pressure from these fitting parameters. The values of these parameters for the HiPIMS data are allowed to be different from their DCMS counterparts.

The results of the fitting for the DCMS data are shown as the solids lines in Fig. 1. The calculations appear to capture many of the features of the measured stress, i.e., stress becomes more compressive at lower pressures for the same growth rate, and more compressive/less tensile stress is observed at higher growth rates for the same pressure. The model also predicts that the stress should become more compressive/less tensile at the lower growth rates although the data do not cover a wide enough range to confirm this. To illustrate the contribution of the individual terms in Eq. (8) to the total stress, we plot each term in Fig. 4 as a function of growth rate using the parameters obtained from fitting the DCMS data measured at 0.24 Pa. The different lines correspond to the contributions of $\sigma_{\text{growth}}$, $\sigma_{\text{gb}}$, and $\sigma_{\text{bulk}}$, and the total calculated stress, $\sigma_{\text{sputt}}$, as indicated in Fig. 4.

The growth term in the model ($\sigma_{\text{growth}}$) produces tensile stress, which is typical for the low atomic mobility of Mo. The stress from this term becomes more tensile at higher growth rates, which is not what is seen in the DCMS experiments. However, $\sigma_{\text{bulk}}$ becomes more compressive at higher growth rates as more defects get trapped in the layer by a faster moving surface. This term is therefore able to counterbalance the growth stress contribution and explain the more compressive stress seen at high growth rates. The $\sigma_{\text{gb}}$ contributes a compressive stress that is larger for lower values of the pressure. In the model, this component of the stress does not depend on the growth rate as we assume here that the ratio of $f/R$ is constant.

The results of fitting the HiPIMS data to the grain size dependence predicted by the model are shown by the solid line in Fig. 2. The dependence of the individual terms ($\sigma_{\text{growth}}$, $\sigma_{\text{gb}}$, and $\sigma_{\text{bulk}}$) on the grain size is shown in Fig. 5 to illustrate their separate contributions to the total calculated stress, $\sigma_{\text{sputt}}$. From Fig. 5, it can be seen that the grain size dependence of the calculated stress from the fitting is primarily due to the energetic grain boundary term ($\sigma_{\text{gb}}$). The other terms depend more weakly on $L$ over the measured range. The dependence of the non-energetic

| Pressure (Pa) | $L$ (nm) | $R$ (nm/s) | $\sigma_T$ (GPa) at $L=50$ nm | $\sigma_C$ (GPa) | $|D_{gb}|$ (nm²/s) | $D_t$ (nm²/s) | $P_o$ (Pa) | $A_o$ (GPa) | $B_o$ (GPa) | $l$ (nm) |
|--------------|----------|------------|-----------------------------|----------------|-----------------|-------------|----------|-------------|-------------|---------|
| **DCMS**     |          |            |                             |               |                 |             |          |             |             |         |
| 0.11         | 50       | varied     | 4.24                        | -1.60         | 0.28            | 7.2         | 0.83     | -144.7      | -46.0       | 1.45    |
| 0.17         | 50       | ...        | ...                         | ...           | ...             | ...         | ...      | -132.7      | -42.2       | 1.33    |
| 0.24         | 50       | ...        | ...                         | ...           | ...             | ...         | ...      | -118.7      | -37.7       | 1.19    |
| 0.43         | 50       | ...        | ...                         | ...           | ...             | ...         | ...      | -80.7       | -25.7       | 0.81    |
| **HiPIMS**   |          |            |                             |               |                 |             |          |             |             |         |
| 0.24         | varied   | 0.051      | ...                         | ...           | 1.29            | ...         | ...      | N/A         | -81.9       | -172.7  |

The calculated values are determined using the parameters for DCMS deposition at 0.24 Pa from Table I.

The calculated values are determined using the parameters for HiPIMS deposition from Table I.
growth stress ($\sigma_{\text{growth}}$) on $L$ may be at first somewhat surprising, since the tensile stress from grain boundary formation increases as the grain size decreases (i.e., $\sigma_f$ is proportional to $1/L^{1/2}$. However, this tensile stress is compensated by the additional compressive contribution from having more grain boundaries in which adatoms can be inserted. Experimental evidence for this can be found in the work of Koch et al. who showed that stress in Fe films becomes more compressive as grain size decreases. This agrees with the model but is not what would be expected from the Hoffman mechanism alone (further discussion can be found in Ref. 18). For very small values of $L$ such as in nanocrystalline materials, the stress-generating mechanisms in the model may not be valid but the limits require further experiments and simulations to be determined. For large values of $L$ (not shown in Fig. 5), the calculated stress is predicted to approach the value of $\sigma_{\text{bulk}}$ due to the decreasing contribution of processes occurring at the grain boundaries.

V. DISCUSSION

The agreement between the calculated stress and the data shows that the model is capable of reproducing the dependence on $R$, $P$, and $L$ seen in the experiments which incentivizes further pursuing this approach to modeling the stress. In this section, we discuss the values obtained for the fitting parameters and compare them with other measurements wherever possible to determine if they are reasonable. We also discuss the justifications for some of the mechanisms included in the model and describe other studies that are needed to test it.

The value for the effective diffusivity of the deposited Mo species ($\beta D_{\text{eff}} = 0.28 \text{ nm}^2/\text{s}$) is smaller than the values obtained from other studies of stress in higher mobility metals such as Cu grown by electrodeposition ($\beta D_{\text{eff}} = 174 \text{ nm}^2/\text{s}$). However, if we assume that the activation energy for diffusion scales roughly with the melting point, we might expect the effective diffusivity for Mo to be even lower relative to Cu than what is suggested by these values. This may indicate that the energetic effects on the surface are leading to enhanced (hyperthermal) diffusion. To determine this parameter with more accuracy, we would need to measure the stress at even lower growth rates, which was not attainable using our DCMS deposition system. The value of $\beta D_{\text{eff}}$ obtained from fitting the HiPIMS data is larger than the values for the DCMS data, as might be expected for the more intense bombardment. However, this value was obtained from the data measured at only one growth rate, and more data would be needed to confirm this. Note that, reasonably good fits can still be obtained if this parameter is held at the same value as for the DCMS data.

The parameter for the diffusivity of the interstitial defects ($D_i$) is difficult to compare with other studies; the diffusivity of Mo interstitials is very complex and has been the subject of much research. The activation energy is reported to be very low ($\sim 0.01 \text{ eV}$) but there is less agreement about the actual value of the diffusivity needed for comparison with our result. The value from our fitting is in the range of some calculations but smaller than others, e.g., Pasianot et al. predict a value of $1260 \text{ nm}^2/\text{s}$ while Starikov et al. predict a value of $10^{10} \text{ nm}^2/\text{s}$. We do not know for certain that the defects controlling the stress are Mo interstitials. Although the concentration of Ar ions retained in the film is believed to be less than 1 at. %, this may still play a role in creating compressive stress. Therefore, we cannot say whether this is a reasonable value for the defect diffusivity. Comparison with measurements in other materials systems is needed to determine if these parameters of the model are reasonable.

The parameters $A_o$, $B_o$, and $l$ are assumed to depend linearly on the particle energy as an approximation. To relate the particle energy to the controllable processing parameter (pressure), we can consider the results of Monte-Carlo simulations using the SIMTRA code described in Ref. 34. The calculated average energy of sputtered Mo and backscattered Ar is found to decrease linearly with the pressure, which supports the linear pressure dependence of these parameters used in the model. Extrapolating the SIMTRA results to higher pressure predicts that the energy goes to zero at threshold pressures of 0.86 Pa and 0.69 Pa for Mo and Ar, respectively. These values are similar to the threshold value of $P_e = 0.83 \text{ Pa}$ obtained from fitting the stress data. The SIMTRA calculations also predict that the average energy of the Mo species is on the order of 20 eV. Calculations using SRIM Mo ions with energies of 10–100 eV yield an implantation depth of 0.2–0.6 nm. For 100 eV Mo, the most probable depth is 0.6 nm with a maximum of 1.5 nm and recoils occurring up to 2.5 nm. Since the reliability of SRIM at these low energies is questionable, the estimates of $l$ determined from the fitting (0.8–1.7 nm) seem to be reasonable. The fitting of the model to the data for each pressure used a single value for the range $l$. It is well known that the energetic particles deposit their energy over a distribution of depths. To determine if that affected the fitting results, determination of the parameters using a distribution of depths was also performed. This did not improve the quality of the fits, so it was not pursued further. The growth rate in the experiments is controlled by changing the power which may also affect the energy of the particles. SRIM and SIMTRA calculations confirmed that the change in deposited energy due to changing the target voltage is marginal compared to the changes induced by pressure.

In the model, we assume that $A_o$ is a diffusion-less term, i.e., the stress in $\sigma_{\text{gb}}$ is generated by ballistic collisions driving atoms into the grain boundary. This mechanism was arrived at only after considering an alternative diffusion-based mechanism where the grain boundaries act as sinks for diffusing defects. The diffusional mechanism was rejected because it predicts that all the atoms that do not go to the surface will ultimately go to the grain boundary, resulting in stress values being independent of grain size, which is in stark contradiction with the experimental results. Because the ballistic model was able to account for all the effects seen in the data, it was used here. However, further measurements of the grain size dependence at different growth rates and temperatures and atomistic modeling of stress-
generation near the grain boundary are needed to determine whether this assumption for $A_n$ is valid.

The growth stress model predicts that the stress should become more compressive at low growth rates (as shown by $\sigma_{growth}$ in Fig. 4). Although there is a decrease in the stress at the lowest measured growth rate and highest pressure, it was not possible to study lower growth rates that would confirm the increase in compressive stress. Other HiPIMS measurements (not shown here) also suggest that the stress becomes more compressive when the growth rate is decreased, but a corresponding increase in the particle energy at low growth rates cannot be ruled out as the cause of the stress change. Therefore, studies at lower growth rates are needed to test the model though it may be difficult to observe the compressive regime for low-mobility materials. Alternatively, measurements on higher mobility systems (e.g., Cu) might show the stress becoming compressive at more accessible growth rates. As pointed out by Koch, however, the effect of background oxygen impurities in the gas must be carefully considered in analyzing these experiments.

The range of validity for the model remains to be determined by comparison with experimental data, but it is also limited by the range of accessible processing conditions. Typically, the range of pressures is limited to less than 1 Pa for DCMS of metal films. However, at high pressures, most of the particles will be thermalized, so that the beneficial effects of “atomic peening” are no longer active. At high growth rates or high pressure, surface roughening and the development of porosity can occur that modifies the stress evolution. This is especially true for low-mobility metals like Mo. Therefore, the surface morphology should also be characterized to ensure that the films are relatively flat and dense if the results are to be compared with the model.

VI. SUMMARY AND OUTLOOK

The dependence of residual stress in films grown from energetic vapor fluxes, e.g., sputter deposited films, on the processing parameters and microstructure is complex. Although various trends have been identified in the literature, a comprehensive understanding of the ultimate stress that results from different conditions is not available. In the present study, we propose a kinetic model for the stress that includes effects of the growth processes and energetic particle bombardment. The model provides predictions of the dependence on the growth rate, pressure, and grain size that compare favorably with data in sputtered Mo films.

The goal of this work is to be able to explain the dependence of stress on multiple deposition conditions within a framework based on the underlying kinetic processes. For this reason, the physics behind the parameters in the model has been simplified in order to obtain analytical expressions that can be compared with experiments. In addition, the large number of parameters means that other values besides those shown here might also provide good fits to the data. Therefore, the results discussed here should not be taken as an exact treatment. Rather, the agreement between the model and experiments should be seen as evidence that supports the physical basis of the mechanisms included in it. This suggests that the approach of modeling the kinetic balance between different stress generating and relaxing mechanisms can be a useful way to develop a comprehensive understanding of stress evolution in films grown from energetic vapor fluxes. More fundamental calculations of the model parameters and potential additional mechanisms need to be performed to validate and refine the model. As importantly, more experimental studies of the stress that characterize and control all the important processing and microstructural parameters are needed. Nevertheless, the model presented here is able to explain the dependence of the stress on a number of deposition conditions within a computationally simple framework. It is our hope that this model will stimulate more experimental and computational studies to improve our ability to control and predict stress by tailoring the deposition conditions.

The kinds of studies that would be useful in the future are ones that isolate and quantify different mechanisms contributing to the stress evolution. For instance, comparison of stress in layers grown by non-energetic deposition (e.g., evaporation), energetic deposition (DCMS or HiPIMS deposition), and ion-assisted deposition (i.e., evaporation with a concurrent flux of energetic particles) would enable the effects of different components of the impinging particle fluxes to be quantified. Studying the stress over a range of deposition temperatures would enable the defect and atom mobilities to be modified, so that the effect of different terms in the model (such as the growth stress) could be increased relative to the energetic terms. Similarly, studying lower growth rates or higher mobility materials would enable the compressive stress due to non-energetic growth predicted by the model to be observed. Although stress evolution in many materials has been studied, in many cases, important parameters such as the grain size evolution have not been characterized so that the model cannot be compared directly with the measurements. Future studies that include a complete characterization of the processing conditions and the microstructure will be useful for testing and improving the model.

The model described in this work has been developed with the deposition of single component films in mind. However, there is an extensive interest in the growth of alloy films as well as reactive sputter-deposition of oxides and nitrides. These compounds typically exhibit high melting point and a refractory character, i.e., we expect that the model presented here would also apply for this class of materials. In the future, it would be desirable to have systematic studies of the stress evolution in multicomponent systems for different processing parameters (growth rate, pressure, and grain size) as well as the alloy composition and/or reactive gas pressure. Extension of the model to include these other effects can then be informed by the results of experiments in which the effects of different processing parameters have been individually studied.

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