Kinetics and magnitude of the reversible stress evolution during polycrystalline film growth interruptions

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(Received 19 May 2015; accepted 25 July 2015; published online 7 August 2015)

During the deposition of polycrystalline thin films, often intrinsic compressive stresses develop, which reversibly change in tensile direction once the deposition process is interrupted. Up to date, the underlying mechanism of such reversible stress changes during growth interruptions have been controversially discussed, mainly because the correlations between the growth conditions, the developing film microstructure and the reversible stress change were still largely unclear. The present study has experimentally established the separate effects of the pre-interruption deposition rate and the average lateral film grain size on both the magnitude and the kinetics of the reversible tensile stress rise during polycrystalline film growth interruption. To this end, *real-time in situ* substrate-curvature measurements were performed during polycrystalline Ag growth and upon subsequent growth interruptions for well-defined and controlled *adjusted* microstructures. It is shown that the magnitude of the reversible tensile stress rise during growth interruption is predominantly governed by the grain-boundary density, while the rate of the tensile stress rise during growth interruption increases with increasing pre-interruption deposition rate and increasing (lateral) Ag grain size. These phenomena can be rationalized by taking deposition-rate and lateral-grain-size dependent surface morphological developments into account. © 2015 AIP Publishing LLC.

[<http://dx.doi.org/10.1063/1.4928162>]

I. INTRODUCTION

Thin film systems are widely applied in advanced technologies such as microelectronics, optoelectronics, catalysis, and functional surface coatings for enhanced corrosion and wear resistance. During the fabrication of these thin film systems, intrinsic stresses often develop. These intrinsic stresses can pronouncedly influence the functional (mechanical, electronic, and magnetic) properties of the thin film systems.^{1–5} Controlled functionalization of thin film systems thus requires fundamental and comprehensive knowledge of the underlying mechanisms of intrinsic stress generation during film growth.

Most polycrystalline metal films grow according to a Volmer-Weber mode: Initially isolated islands nucleate on the substrate surface, which subsequently grow, impinge, and coalesce to form a laterally closed film during continued film deposition. These successive, partly overlapping stages of the developing film morphology are typically accompanied by the accumulation of intrinsic film stresses: (i) During island growth, compressive stresses parallel to the substrate surface can evolve as a result of surface-stress effects;⁶ (ii)

the coalescence of islands results in the formation of grain boundaries and induces an in-plane tensile stress component;^{7,8} and (iii) the post-coalescence intrinsic stress evolution strongly depends on the deposition conditions. For the combination of relatively high atomic mobilities and low deposition rates, in-plane compressive stresses are accumulated during thickening of the continuous film. If the deposition process is interrupted, the in-plane stress changes in tensile direction. Upon resuming the deposition process, the stress returns to its pre-interruption value as if the preceding growth interruption has not occurred.^{9,10} Despite the enormous number of experimental and theoretical studies on the development of intrinsic film stresses during the past decades, the underlying mechanism for the post-coalescence compressive stress development and, in particular, the so-called reversible stress evolution upon growth interruption and resumption is still controversially discussed.^{9–23} The reversible stress change upon growth interruption and resumption has been attributed to (i) an alternating surface stress originating from a change in surface defect concentration,^{10,11} (ii) trapping and release of excess adatoms at interstitial surface sites/ledges,¹² (iii) out-diffusion of adatoms from the grain boundaries, as driven by a chemical potential gradient near the film surface,¹³ or (iv) reversible changes in the surface-shape of individual grains.^{14,15} All these models attribute the reversible stress change to processes that occur in the near-surface region, but every model predicts strikingly different dependencies of the magnitude and the kinetics of the tensile stress rise on the growth conditions and on the film microstructure. Evidently, experimental

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investigations of the kinetics of the reversible tensile film-force rise with respect to the film growth conditions and the film microstructure, such as deposition rate and lateral film grain size, are essential to identify the underlying mechanism(s) and to eventually arrive at a unified, quantitative model description.

In the present study, the reversible stress evolution in polycrystalline Ag films upon growth interruption and resumption has been investigated for a wide range of lateral film grain sizes and, at the same time, as a function of the pre-interruption deposition rate. It is revealed that the magnitude of the tensile stress rise upon growth interruptions is predominantly governed by the grain-boundary density, while the kinetics of the stress evolution depends on both the grain-boundary density and the pre-interruption deposition rate. The observed dependencies of the kinetics of stress evolution during growth interruption on grain-boundary density and pre-interruption deposition rate are *not* the result of correspondingly different intrinsic stress states before the growth interruption. It is suggested that the observed effects are the result of deposition-rate and lateral grain-size dependent surface-morphology developments.

II. EXPERIMENTAL PROCEDURE

Thin Ag film growth was carried out in a customer-designed ultrahigh vacuum (UHV) system (base pressure $< 3 \times 10^{-10}$ mbar) by thermal evaporation of pure ($>99.995\%$) Ag on 200 μm thin, (native, amorphous) SiO_2 covered, Si(100) wafers. Prior to thin film deposition, the square-shaped substrates were ultrasonically cleaned successively in acetone and isopropanol, loosely mounted in a specimen holder such that the substrate could bend freely in all directions, and degassed at 200 °C in UHV. After cooling down to room temperature, Ag was thermally evaporated from an Al_2O_3 crucible using a high temperature effusion cell. All deposition rates used in this study were calibrated from separate experiments by measuring the film thickness after different deposition times with a Veeco DekTak profilometer. To monitor the intrinsic stress evolution during Ag film growth and upon growth interruptions, real-time *in-situ* substrate-curvature measurements were performed using a multi-optical stress sensor (MOS; k-space Associates).^{18,24} According to the Stoney's equation, the measured substrate-curvature change is proportional to the film force f (i.e., the force per unit width acting on the film parallel to the substrate), which can be given as the product of thickness-averaged film stress and film thickness. Extrinsic thermal stresses, arising from radiation-induced temperature changes due to opening and closing the shutter in front of the effusion cell, have been characterized in a separate set of experiments using an empty Al_2O_3 crucible. All data reported in this study have been corrected for these extrinsic thermal stresses.

To study the effect of the film microstructure and, in particular, the effect of the grain-boundary density on the tensile stress change during growth interruptions, six Ag film specimens of different lateral (parallel to the film surface) grain sizes were prepared as follows. The first two sets of

specimens were prepared by continuous deposition of Ag on the amorphous SiO_2 surface with deposition rates of 0.034 nm/s (sample B) and 0.618 nm/s (sample C), respectively. At a film thickness of 145 nm, the Ag growth was interrupted for 900 s. For the third and fourth sets of specimens, a 30 nm amorphous Ge layer was deposited *in-situ* on the SiO_2 surface (see above) prior to Ag film growth by thermal evaporation of pure (99.999%) Ge from a pyrolytic-graphite crucible at room temperature. Subsequently, Ag was deposited with deposition rates of 0.034 nm/s (sample E) and 0.618 nm/s (sample D), respectively. Again, Ag film growth was interrupted at a film thickness of 145 nm for 900 s. Note that the presence of amorphous Ge significantly retards the Ag adatom surface diffusivity during Ag film growth, and thus, the grain-boundary density increased pronouncedly as compared to Ag film growth on a SiO_2 surface.¹⁸ For the fifth specimen (sample A), initially, a 100 nm thick silver film was deposited on the amorphous SiO_2 surface with a deposition rate of 0.034 nm/s. Next, the specimen was annealed for 1 h at 160 °C in UHV to promote grain growth in the Ag film. After cooling down to room temperature, the thus-obtained coarse-grained Ag layer was used as a template for further growth of 45 nm Ag at a deposition rate of 0.034 nm/s. At a total film thickness of 145 nm, the Ag deposition was interrupted for 900 s. The above described procedures result in five polycrystalline Ag films with distinctively different average lateral grain sizes in the range of 63 nm–436 nm (see Sec. III A). Finally, also a 100 nm thick epitaxial Ag film (sample F) was prepared by deposition of Ag on a thoroughly cleaned Si(100)– 2×1 surface at room temperature. The as-deposited Ag film was annealed for 2 h at 160 °C, and subsequently cooled to room temperature. The thus prepared epitaxial Ag film, with an orientation relationship to the Si substrate given by $\text{Ag}(100) \parallel \text{Si}(100)$ with $\text{Ag}[1 \bar{1} 0] \parallel \text{Si}[1 \bar{1} 0]$ (as determined by XRD measurements), was used as a template for further growth of 45 nm Ag with a deposition rate of 0.034 nm/s. At a total film thickness of 145 nm, the Ag deposition was interrupted for 900 s.

To study the effect of the pre-interruption deposition rate on the tensile stress change during growth interruption for an about constant lateral grain size (i.e., an about constant grain-boundary density; see Sec. III A), Ag film growth of specimens A–E was resumed with an *altered* deposition rate after the first growth interruption of 900 s at a film thickness of 145 nm; see above. For the samples A, B, and E, the deposition rate was increased (from 0.034 nm/s before the first growth interruption) to 0.184 nm/s after the first growth interruption, to deposit additional 70 nm of Ag. After a second growth interruption of 900 s at a film thickness of 215 nm, deposition was again resumed at an even higher deposition rate of 0.618 nm/s to deposit yet additional 70 nm of Ag. For specimens C and D, the experiments were performed in the reverse order, i.e., the deposition rate between the first and second growth interruption was decreased from 0.618 nm/s to 0.184 nm/s to deposit additional 70 nm of Ag. After a second growth interruption of 900 s at a film thickness of 215 nm, deposition was again resumed at an even lower deposition rate of 0.034 nm/s, to deposit yet additional

70 nm of Ag. The courses of the successive Ag film depositions and growth interruptions for specimens A–E are shown in Fig. 2.

The microstructure of the deposited polycrystalline Ag films was investigated directly after completion of the film deposition by a DME DualScope atomic force microscope (AFM) equipped with a Si tip (curvature radius < 10 nm) and operating in tapping mode. For each specimen, the average lateral grain size was determined by line analysis of several representative AFM images of different sizes and averaging over at least 200 grains. The lateral size of the grains is given by the average linear intercept length between adjacent grain boundary grooves on the test lines multiplied by a factor of $4/\pi$.²⁵

III. RESULTS

A. Ag film microstructure: Lateral grain sizes

Representative AFM images of the five polycrystalline Ag films at the final film thickness of 285 nm show that the described preparation procedures (see Sec. II) indeed result in the formation of Ag films with distinctively different lateral grain sizes (see Fig. 1). The average lateral grain sizes of specimens A, B, C, D, and E at the end of the experiments are 436 nm, 196 nm, 136 nm, 100 nm, and 63 nm, respectively. Grain growth during thickening of polycrystalline Ag films has been reported to occur at relative low temperatures,²⁶ and separate sets of AFM measurements indicate that the lateral grain sizes of the polycrystalline Ag films might have increased slightly during the course of the experiments (i.e., during the successive Ag deposition steps and growth interruptions). However, for the specimen with the smallest average in-plane grain size (specimen E), which experiences the largest driving force for grain growth by reduction of the grain-boundary area,²⁷ the average lateral grain size increased by at most 9% during the whole course of the experiment. Hence, despite the possible slight increase of the lateral grain size during the course of the experiments, specimens A–E represent a well distinguishable set of specimens with different grain sizes. In the following, the specimens are distinguished by their average grain sizes determined at the final film thickness of 285 nm.

B. Intrinsic stress evolution during deposition

The film-force evolutions during alternating intervals of Ag growth at different deposition rates and subsequent

growth interruptions (see Sec. II) are shown in Fig. 2 for the specimens A–E of distinctly different lateral average grain size. The film-force curves as measured during growth of the polycrystalline Ag films can be described as follows: (i) The *thickness-averaged stress* distinctively differs for the five polycrystalline Ag films, being tensile for the specimen with the largest lateral grain size (specimen A) and descending down to highly compressive for the specimen with the smallest grain size (specimen E). (ii) For each experiment, the slope of the measured film-force vs thickness curve (further denoted as the *incremental stress*) is negative during any time of Ag deposition and, accordingly, predominantly compressive stress contributions are generated during film growth. (iii) For most of the experiments, the incremental stress before the growth interruptions becomes more (less) compressive with decreasing (increasing) deposition rate. Such trend is in accordance with previous experimental observations^{13,20} and model calculations²³ of the intrinsic stress evolution during polycrystalline film growth at room temperature. Note that, in agreement with Ref. 20, the variation of the incremental stress in the Ag film with a change in deposition rate is rather small and that, not for all experiments, a truly constant (steady-state) incremental stress is attained within the deposition time before the next growth interruption.

C. Intrinsic stress evolution during film growth interruption

For the polycrystalline Ag films with average in-plane grain sizes between 436 nm and 100 nm (specimens A–D), the tensile film-force rises that occur during successive growth interruptions at film thicknesses of 145 nm, 215 nm, and 285 nm are practically fully reversed upon resuming growth (see Figs. 2(a)–2(d)). Evidently, the tensile film-force changes during growth interruptions of 900 s are associated with a reversible stress-generation mechanism. Processes which lead to non-reversible film-force changes,^{14,16,19} such as grain growth and recrystallization, do not significantly contribute to the film-force evolution during the growth interruptions. For the polycrystalline Ag film with the smallest in-plane grain size of 63 nm (specimen E), growth interruptions at film thicknesses of 145 nm, 215 nm, and 285 nm also result in tensile film-force rises, but, in this case, the film force is not fully reversible and does not return to its (extrapolated) pre-interruption value upon resuming growth (see Fig. 2(e)). This suggests that for specimen E, grain

FIG. 1. Representative AFM images of the surfaces of the polycrystalline Ag film specimens A–E with a film thickness of 285 nm. The different preparation procedures (see Section II) result in distinctively different average in-plane (lateral) grain sizes of 436, 196, 136, 100, and 63 nm for specimens A, B, C, D, and E, respectively. Note that the AFM images have been taken at different magnifications, i.e., the scale bars are different.

FIG. 2. Film-force evolutions during polycrystalline Ag film growth of specimens A-E with altered deposition rates (of either successively 0.034 nm/s, 0.184 nm/s, and 0.618 nm/s for specimens A, B, and E or successively 0.618 nm/s, 0.184 nm/s, and 0.034 nm/s for specimens C and D), and growth interruptions at film thicknesses of 145 nm, 215 nm, and 285 nm, respectively. For specimens A–D, growth interruptions result in tensile film-force changes which are practically fully recovered upon resuming growth. For specimen E, the film-force evolution upon growth interruption is not completely reversible owing to the occurrence of slight grain growth during growth interruptions (see text).

growth might have occurred during the growth interruptions of 900 s, as already indicated in Sec. III A. Note that in general a decreasing in-plane grain size and an increasing deposition rate lead to an enhanced development of a tensile stress component during growth,²³ and thus, the film-force curve might not reach its pre-interruption value upon continued film growth with an altered deposition rate. As a result, the stress change upon growth interruption then seems to be non-reversible. This effect is in particular pronounced during the course of the experiment for specimen E with a relatively small average in-plane grain size. For continued Ag deposition at a *constant* deposition rate of 0.036 nm/s on an amorphous Ge covered substrate surface (i.e., with a similar small average lateral grain size as specimen E), the film-force curve upon growth resumption practically reaches the (extrapolated) pre-interruption value, i.e., results in nearly reversible behavior of the film-force evolution (see dashed curve in Fig. 2(e)).

1. Magnitude of the stress change

The observed tensile film-force rises during successive growth interruptions, Δf , have been plotted in Fig. 3 as function of the interruption time for all six Ag film specimens of different average grain size and for different pre-interruption deposition rates of 0.034 nm/s, 0.184 nm/s, and 0.618 nm/s. It follows that the *magnitude* of the tensile film-force rise during growth interruption depends strongly on the average in-plane grain size. To enable a more direct comparison for the specimens of different grain size, the corresponding Δf values are also plotted in Figs. 4(a)–4(c) as a function of the interruption time for different pre-interruption deposition rates. The polycrystalline Ag film with the smallest grain size of 63 nm (specimen E) shows the largest tensile film-force rise and the polycrystalline Ag film with the largest grain size of 436 nm (specimen A) the smallest. No significant film-force rise occurs during growth interruption for the epitaxial Ag(100) film, which contains no (high-angle) grain boundaries. The here established trend of increasing Δf with decreasing in-plane grain size of the Ag films is in accordance with observations for polycrystalline and homoepitaxial Au films,²¹ as well as with the evaluation of the experimental data for homoepitaxial Ag and Cu growth¹¹ (as revised in Ref. 21) where no film-force rise occurred.

To quantify the experimentally established correlations of the magnitude of the tensile film-force rise with the grain-boundary density, as well as with the pre-interruption deposition rate, the value of the tensile film-force rise after 900 s of growth interruption, $\Delta f_{900\text{ s}}$, has been plotted as function of the inverse grain size (which is proportional to the grain-boundary density, i.e., the grain boundary length per unit area of film surface) for all growth interruptions (see Fig. 5). It follows that $\Delta f_{900\text{ s}}$ increases about *linearly* with increasing grain-boundary density, irrespective of the pre-interruption deposition rate or respective film thickness (see also Fig. 3). This implies that the grain-boundary density is the *decisive factor* which controls the magnitude of the reversible film-force rise during growth interruption, whereas the pre-interruption deposition rate plays, if at all, only a

FIG. 3. Tensile film-force changes during growth interruptions, Δf , as function of interruption time for five polycrystalline Ag films of different average in-plane (lateral) grain size as well for the epitaxial Ag(100) film, and for pre-interruption deposition rates of 0.034 nm/s, 0.184 nm/s, and 0.618 nm/s, respectively. All film-force curves have been corrected for *extrinsic* (thermal) stresses, arising from radiation induced temperature changes due to closing the shutter in front of the effusion cell, by subtracting the experimentally established thermal stresses (see Section II) from the measured data. For all Ag films of different grain size, the rate of tensile film-force rise at the beginning of growth interruption increases with increasing pre-interruption deposition rate. Note that for all experiments, growth interruptions of 900 s were performed at Ag film thicknesses of 145 nm, 215 nm, and 285 nm, but the sequence of the applied deposition rates was different (cf. Sec. II; specimens A, B, and E vs C and D).

minor role. It is important to note that this statement only holds for the asymptotically approached final value Δf_{900s} . Strictly speaking, a direct comparison of the magnitude of the film-force rise for specimens of different grain size and/or for different pre-interruption deposition rates is only justified if the tensile film-force rises follow similar rate kinetics. As shown in the following, this is not the case for the polycrystalline Ag films under study, and at smaller interruption times, a plot similar to that presented in Fig. 5 can be misleading.

2. Kinetics of stress change

The experimentally established tensile film-force rises during growth interruptions (see Fig. 3) disclose that, for all Ag films of different average grain size, the *kinetics* of the tensile film-force rise significantly depends on the pre-interruption deposition rate. For each Ag film with a given average grain size, the kinetics follows a characteristic behavior. For the highest pre-interruption deposition rate applied in the present study (i.e., 0.618 nm/s), the rate of the film-force rise is initially very fast. As a result, for most polycrystalline specimens, Δf practically attains a constant value within an interruption time of 900 s. With decreasing pre-interruption deposition rate, the initial rate of film-force rise decreases. For the lowest pre-interruption deposition rate applied in this study (i.e., 0.034 nm/s), the initial rate of the film-force rise is considerably lower and decreases more gradually than in the case of the higher pre-interruption

deposition rates. As a result, for most of the polycrystalline specimens, Δf does not attain a constant value within an interruption time of 900 s. A similar trend of an accelerated initial rate of tensile film-force rise during growth interruption with increasing pre-interruption deposition rate is also evident from the data in Ref. 10 (but left undiscussed there).

The *kinetics* of the reversible tensile film-force rise depends not only on the pre-interruption deposition rate but also on the Ag grain size. By normalizing the film-force curves, $\Delta f(t)$, with respect to their values at the end of the respective growth interruption, Δf_{900s} (see Figs. 4(d)–4(f)), it is disclosed that, for the lowest pre-interruption deposition rate, the film-force curves exhibit rather similar kinetics (there is a slight tendency of an increasingly faster tensile film-force rise at the beginning of growth interruption with increasing grain size): see Fig. 4(d). With increasing pre-interruption deposition rate, the kinetics of the film-force rise become faster (see above). This behavior becomes more pronounced for thin films with larger lateral grain sizes (see Figs. 4(e) and 4(f)). Since the value of Δf_{900s} increases roughly linearly with increasing grain-boundary density and does not significantly depend on the pre-interruption deposition rate (cf. Fig. 5), the normalized values $\Delta f(t)/\Delta f_{900s}$ can be considered as being proportional to the film force released per unit grain boundary length at the film surface.²⁸

As follows from the above discussions, the kinetics of the reversible tensile film-force rise depends on *both* the pre-interruption deposition rate and the grain size. Two extreme combinations can be distinguished: (i) For a high pre-

FIG. 4. [(a)–(c)] Tensile film-force rises during growth interruptions as function of time (after correction for extrinsic thermal stresses) for Ag films with different average in-plane (lateral) grain sizes at pre-interruption deposition rates of (a) 0.034 nm/s, (b) 0.184 nm/s, and (c) 0.618 nm/s, respectively (same data as in Fig. 3 but grouped differently). [(d)–(f)] By normalizing the film-force curves with respect to their values at the end of the growth interruptions, i.e., Δf_{900s} , it is revealed that *both* the pre-interruption deposition rate and the in-plane grain size of the polycrystalline Ag films influence strongly the kinetics of the reversible tensile film-force rise.

interruption deposition rate (0.618 nm/s) and a relative large in-plane grain size (≥ 136 nm), more than 80% of Δf_{900s} occurs within the first 60 s of growth interruption. (ii) For a low pre-interruption deposition rate (0.034 nm/s) and relative

small in-plane grain size (of ≤ 100 nm), less than 40% of Δf_{900s} occurs within the first 60 s.

It is emphasized that the kinetics of the film-force rises are identical for successive growth interruptions pertaining to the same specimen (i.e., for a practically constant grain size) and applying the same pre-interruption deposition rate (not shown). Furthermore, the “here established” correlations of the kinetics of tensile film-force rise and (i) the pre-interruption deposition rate and (ii) the in-plane grain size are independent of both the film thickness at which the Ag deposition is interrupted and the sequence of the applied deposition rates (cf. specimens A, B, and E vs specimens C and D).

IV. DISCUSSION

The present study shows that both the magnitude and the kinetics of the reversible film-force rise upon growth interruption are largely *independent* of the film thickness at which film growth is interrupted. This suggests that the tensile stress rise during growth interruption is associated with processes occurring in the *near-surface region* of the film. This is in general agreement with all of the previously proposed mechanisms for the reversible tensile stress rise during growth interruptions of polycrystalline films, namely: (A) a reversible surface stress change owing to a change in adatom concentration;^{10,11} (B) trapping and release of excess adatoms at interstitial surface sites/ledges;¹² (C) out-diffusion of adatoms from the grain boundaries, as driven by a chemical

FIG. 5. Tensile film-force change after 900 s of growth interruption as function of the inverse in-plane grain size of the Ag films. For a certain grain size, Δf_{900s} significantly depends neither on the Ag film thickness at which the deposition is interrupted (i.e., 145 nm, 215 nm, and 285 nm, respectively) nor on the pre-interruption deposition rate (i.e., 0.034 nm/s, 0.184 nm/s, and 0.618 nm/s, respectively): the magnitude of the film-force change at the end of the growth interruption increases practically linearly with increasing grain-boundary density, with a slope of 5.6×10^{-5} N.

potential gradient near the film surface;¹³ and (D) reversible surface-shape changes of individual grains.^{15,29} However, as discussed in the following, the present experimental results, on the magnitude and the kinetics of the reversible tensile film-force rise and their dependencies on the pre-interruption deposition rate and the average grain size, are insufficiently described by the proposed models. Thereafter and finally, a possible qualitative understanding, compatible with both the previous and the new experimental data, is provided.

The present study evidences the decisive role of grain boundaries for the occurrence of the reversible tensile stress rise during polycrystalline film growth interruptions. The magnitude of the observed film-force rise during growth interruption decreases linearly with increasing lateral grain size (i.e., decreasing grain-boundary density); indeed, no film-force change is observed during growth interruptions of a practically single-crystalline epitaxial Ag film (see Figs. 4 and 5 and cf. Ref. 21). Furthermore, the present work discloses that the pre-interruption deposition rate plays only a minor role for the magnitude of the asymptotically approached, final value of the film-force rise. These experimental findings do not comply with the above-listed mechanisms A and B, because both essentially rely on the atomic defect concentration at the film surface, and thus predict a rather strong dependence of Δf on the pre-interruption deposition rate and, if at all, an only minor effect of the grain size on Δf .

Only the proposed mechanisms C and D explicitly predict the observed linear increase of the *magnitude* of the reversible film-force rise with increasing grain boundary density. Both models ascribe the tensile stress rise during growth interruption to the relaxation of compressive stresses, which have accumulated exclusively in the vicinity of grain-boundaries during polycrystalline Ag film growth. Provided that the stress relaxation for an average grain-boundary is independent of the grain-boundary density, it immediately follows that the magnitude of the tensile film-force rise depends linearly on the grain-boundary density. The proposed mechanisms C and D, presuming a deposition-rate-independent excess chemical potential at the film surface, will now be discussed with reference to the present data on the *kinetics* of the reversible tensile film force rise and its magnitude.

A. Proposed mechanism C

It was proposed in Ref. 13 that during the post-coalescence growth stage, the chemical potential gradient between the supersaturated film surface and the film grain boundaries drives adatoms into the grain boundaries, thereby leading to the build-up of a compressive stress component. Upon growth interruption at $t=0$ (further designated as the onset of the growth interruption), the surface chemical potential is reduced. Consequently, excess adatoms diffuse out of the grain boundaries towards the film surface. Hence, the magnitude and the kinetics of the tensile stress rise should be governed by the intrinsic stress state at $t=0$, as determined by the combination of the deposition rate and the lateral grain size (cf. Sec. III B and Fig. 2), such that the magnitude and the rate of relaxation increase with increasing initial

value of compressive stress (i.e., a power-law-creep correlation). However, in the present study, neither a power-law-creep like correlation between the kinetics of Δf and the thickness-averaged stress at $t=0$, as reported in Ref. 19 (Ref. 30), nor a power-law-creep like correlation between the kinetics of Δf and the incremental compressive stress at $t=0$ could be established (cf. Figs. 2 and 3). For instance, for the polycrystalline specimen A, with the largest lateral grain size, the post-coalescence incremental compressive stress *decreases* with increasing pre-interruption deposition rate (cf. Fig. 2), whereas the rate of film-force change at the beginning of the growth interruption *increases* with increasing pre-interruption deposition rate. Moreover, the polycrystalline specimen A, which is in a net tensile state of stress, shows the fastest (relative to the value of Δf_{900s}) tensile film-force rise of all specimens, independent of the pre-interruption deposition rate.³¹ Therefore, (i) the kinetics of the stress evolution during growth interruption cannot be rationalized exclusively on the basis of different intrinsic stress states of the Ag films at $t=0$ and (ii) the proposed mechanism C does not comply with the more pronounced initial increase of Δf for higher deposition rates (see Fig. 3) and larger lateral grain sizes (see Figs. 4(e) and 4(f)).

B. Proposed mechanism D

The model proposed in Refs. 15 and 29 considers film-surface topographical developments, which are explicitly excluded in *mechanism C*. From the observation of surface-shape changes of individual grains during interruptions of polycrystalline film growth, it was suggested that the reversible tensile film-force rise results from deepening of grain-boundary grooves by surface diffusion (associated with the establishment of the equilibrium surface-shape of the grains), which thereby relieves compressive stresses originating from trapped adatoms at film grain boundaries in the near surface region of the film. In this case, the magnitude of the film-force rise per unit grain boundary unit length at the film surface (see Sec. III C 2) is controlled by the value of the initial compressive stress component at $t=0$ and the change of the depth of the grain-boundary grooves during growth interruption. Accordingly, the rate of compressive stress relaxation is controlled by the time evolution of the depth of the grain-boundary grooves. For a stress-free film, the depth of the grain-boundary groove evolving from an initially flat surface is proportional to $t^{1/4}$.³²

The morphology of the film surface that develops under quasi-steady-state conditions during deposition by continuous zipping of surface ledges of adjacent grains and simultaneous incorporation of adatoms into the film at grain-boundary grooves,²³ as well as the preferred equilibrium, final surface morphology obviously both depend on the deposition rate and the lateral grain size. Accordingly, the proposed mechanism D has to be advanced by implementing deposition-rate and lateral grain-size dependent surface morphologies, which evolve during growth and upon growth interruptions. Such an advanced model description can rationalize the increasing rate of film-force rise with increasing pre-interruption deposition rate, as observed in this study, as follows. During film

deposition, the continuous zipping of surface ledges of adjacent grains results in the establishment of a relatively flat surface with shallow grooves at the grain boundaries. With increasing deposition rate, the zipping rate of surface ledges increases, which not only decreases the number of adatoms incorporating into the film at grain-boundary grooves²³ but also increasingly limits uphill diffusion. Hence, a more smooth film surface evolves for higher deposition rates. Furthermore, a higher deposition rate results in a higher density of surface defects and is therefore associated with a higher excess chemical potential at the surface (cf. mechanisms *A*^{12,20} and *B*^{10,11}). Consequently, a higher deposition rate results in a larger dihedral angle at the bottom of the grain-boundary grooves. This effect also contributes to the development of a smoother film surface for higher deposition rates. Upon growth interruption, the relatively shallow grain-boundary grooves formed during film deposition gradually deepen to attain their energetically preferred equilibrium shape/depth. The more shallow grooves, established at higher deposition rates, possess a higher driving force for grain-boundary grooving and will therefore deepen faster,³² causing an enhanced relaxation rate of the compressive stress component in the near surface region for higher pre-interruption deposition rates, as observed in the present study.

The experimental finding of an enhancement of the above described effect (i.e., increasingly faster tensile film-force rise at the beginning of growth interruption with increasing pre-interruption deposition rate) with increasing lateral grain size implies that films with larger average lateral grain sizes have less deep grain-boundary grooves at the film surface during deposition. However, not only the non-equilibrium depth of the grain-boundary grooves as formed under quasi-steady-state conditions during deposition but also the strived-for equilibrium depth of the grain-boundary grooves can depend on the lateral grain size.^{33,34} The gradual deepening of the grain-boundary groove by the combination of surface diffusion (on a short time scale) and grain-boundary diffusion (on a larger time scale) is likely influenced by the intrinsic stress state of the film and the surface-shape of the grains.^{34,35}

It can thus be concluded that an advanced model description of the kinetics of the tensile film-force rise during growth interruptions should incorporate dependencies of the compressive stress relaxation rate on the pre-interruption deposition rate and the average grain size, as resulting from different rates of grain-boundary grooving at the film surface upon growth interruption.

V. CONCLUSION

By combining Ag film with real-time *in situ* curvature measurements, the kinetics of the reversible tensile film-force change during polycrystalline film growth interruptions could be experimentally correlated with the pre-interruption deposition rate and the average lateral film grain size.

The reversible film-force (stress) change results from diffusional processes in the near-surface region of the film. The magnitude of the tensile stress rise during growth interruptions is predominantly determined by (and linearly

dependent on) the grain-boundary density; the pre-interruption deposition rate plays only a minor effect. The kinetics of the reversible tensile stress rise during growth interruptions is influenced by both the grain-boundary density and the pre-interruption deposition rate. The increasing rate of tensile stress rise at the beginning of the growth interruption with increasing pre-interruption deposition rate and increasing lateral grain size is *not* the result of different intrinsic stress states of the films before the growth interruptions, and no power-law-creep like correlation of the kinetics of the film-force rise and the film stress state before the growth interruption is observed.

Instead, the dependence of the kinetics of the reversible tensile stress rise on the pre-interruption deposition rate and the lateral grain size are attributed to the dependencies of the developing surface morphology on the deposition rate and the (lateral) grain-size: With increasing deposition rate, more shallow grain-boundary grooves evolve at the film surface during deposition, which then deepen faster upon growth interruption and, thus, lead to a faster tensile stress rise upon growth interruption for higher pre-interruption deposition rates. The enhancement of this effect with increasing grain size implies that the grain-boundary grooves during deposition are less deep for larger grain sizes.

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³⁰It is noted that in Ref. 19 the pre-interruption deposition rate and/or the average lateral film grain size was altered to modify the thickness-averaged compressive film.

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might potentially influence the kinetics of the post-growth film-force rise. However, the development of such a stress gradient, i.e., here an enhancement of the stress gradient with an increasing compressive stress in the very-near surface region with increasing deposition rate and increasing lateral grain size, is inconsistent with reported model calculations (P. R. Guduru, E. Chason, and L. B. Freund, *J. Mech. Phys. Solids* **51**, 2127 (2003); T. K. Bhandakkar, E. Chason, and H. Gao, *Int. J. Appl. Mech.* **1**, 1 (2009)).

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