Effect of adatom surface diffusivity on microstructure and intrinsic stress evolutions during Ag film growth

D. Flötotto,¹ Z. M. Wang,^{1,a)} L. P. H. Jeurgens,^{1,b)} E. Bischoff,¹ and E. J. Mittermeijer^{1,2}

¹Max Planck Institute for Intelligent Systems (former Max Planck Institute for Metals Research), Heisenbergstraße 3, D-70569 Stuttgart, Germany

²Institute for Materials Science, University of Stuttgart, D-70569 Stuttgart, Germany

(Received 11 January 2012; accepted 17 July 2012; published online 16 August 2012)

The effect of the adatom surface diffusivity on the evolution of the microstructure and the intrinsic stress of thin metal films was investigated for the case of growth of polycrystalline Ag films on amorphous SiO₂ (a-SiO₂) and amorphous Ge (a-Ge) substrates, with high and low Ag adatom surface diffusivity, respectively. The surface diffusivity of the deposited Ag adatoms on the a-Ge substrate is suppressed also *after* coalescence of Ag islands due to the continuous (re)segregation of Ge at the surface of the growing film as evidenced by *in-situ* XPS. An assessment could be made of the role of adatom surface diffusivity on the microstructural development and the intrinsic stress evolution during film growth. As demonstrated by *ex-situ* TEM and *ex-situ* XRD, the Ag films grown on the a-SiO₂ and a-Ge substrates possess strikingly different microstructures in terms of grain shape, grain size, and crystallographic texture. Nevertheless, the real-time *in-situ* stress measurements revealed a compressive → tensile → compressive stress evolution for the developing Ag films on both types of substrates, however on different time scales and with stress-component values of largely different magnitudes. It was concluded that (i) the microstructural development of metallic thin films is predominated by the *surface* diffusivity of the adatoms and (ii) the intrinsic stress evolution is largely controlled by the developing microstructure and the grain-boundary diffusivity. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4746739>]

I. INTRODUCTION

Thin films find numerous applications in modern engineering systems, such as surface coatings and micro-electro-mechanical systems. During fabrication and processing of these thin film systems, both *intrinsic* (i.e., arising during film growth) and *extrinsic* (i.e., induced after film growth; e.g., upon cooling/heating due to differences in thermal shrinkage/expansion of the various system components) residual stresses can arise. On the one hand, these residual film stresses can deteriorate the system's mechanical performance during operation, by causing excessive deformation, leading to fracture and/or spallation. On the other hand, the mechanical, electrical, and magnetic properties of the film system may benefit from the controlled adjustment of the film stresses (cf. Refs. 1 and 2). Thus, a fundamental, comprehensive understanding of the operating mechanisms of residual stress formation during thin film growth and operation is of great technological importance.

In recent years, the stress evolution during growth of a polycrystalline metal film, e.g., Ag, Cu, and Au films on amorphous substrates (typically SiO₂), has been studied, in particular by real-time stress measurements.^{3–12} As a result, two archetypes of the intrinsic stress evolution for the Volmer-Weber type of growth¹³ of polycrystalline metal films were identified, depending on the homologous temperature, $T_h = T_s/T_m$, of the deposited metal (where T_s and T_m denote

the substrate temperature during film growth and the melting temperature of the metal, respectively, $T_h = T_{\text{substrate}}/T_{\text{melting}}$).¹⁰ For the deposition of metals at *high* homologous temperatures (and thus for a relatively high atomic diffusivity in the evolving substrate/film system), as holds for, e.g., Ag film growth at room temperature, the average film stress during continued film growth is initially compressive, then becomes tensile, and subsequently becomes compressive again.^{5,9,10} Metal film growth at *low* homologous temperatures (with a correspondingly *low* atomic diffusivity in the evolving substrate/film system), as holds for, e.g., Fe film growth at room temperature, only results in the development of average film stresses of tensile nature.^{10,14} Each of the above described intrinsic stress evolutions is characterized by the development of specific film microstructures: Films grown at high homologous temperatures develop columnar grain morphologies, whereas films grown at low homologous temperature form fine, equiaxed grain morphologies (cf. the so-called structure zone model of thermally evaporated films¹⁵).

However, as demonstrated in the present paper, a general classification of stress and microstructure evolutions during metal film growth on the basis of solely the homologous temperature is very misleading, because the atomic diffusivity in the evolving film/substrate system comprises a number of also concurrent transport processes of the deposited metal (ad)atoms: i.e., diffusion along the parent substrate and developing film surfaces, along the grain boundaries and within the bulk of the growing film. As shown in this paper, it is essential to disclose the contribution of each of the different atomic transport processes to

^{a)}Author to whom correspondence should be addressed: Electronic mail: z.wang@is.mpg.de.

^{b)}Present address: Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, 8600 Dübendorf, Switzerland.

both the microstructural development and the generated stress.

In this study, the intrinsic stress evolution and the microstructural development during growth of polycrystalline Ag films on amorphous SiO₂ and amorphous Ge (a-Ge) substrates, by thermal evaporation under identical growth conditions, were investigated in a comparative manner. Ag/SiO₂ and Ag/a-Ge are important thin film systems for next-generation photovoltaic devices using plasmonic light trapping.^{16,17} Recognizing that Ag atoms have very different surface mobilities on a-Ge and on a-SiO₂ substrates (at the same substrate temperature),^{18,19} this study aims at an assessment of the particular role of the surface diffusivity for the development of the intrinsic stress and the microstructure during film growth.

II. EXPERIMENTAL

A. Thin film growth

The experiments were carried out in a customized, multi-chamber UHV system (base pressure $<3 \times 10^{-8}$ Pa) for *in-vacuo* specimen processing (e.g., cleaning and annealing), thin-film deposition by molecular beam epitaxy (MBE), and *in-situ* analysis by XPS.

Square-shaped ($13.9 \times 13.9 \text{ mm}^2$) Si (001) wafers (thickness: $100 \mu\text{m}$) covered with a native amorphous oxide layer were ultrasonically cleaned successively in acetone and isopropanol. Next, the Si(001) wafers were loosely mounted in an especially developed specimen holder for the *in-situ* stress measurements (see below), such that the wafer could bend freely in all directions during film deposition: this implies that the specimen holder is put in upside-down position during film deposition, so that the wafer is only held by gravity (i.e., resting on a three point-contact at the outer edges of the wafer). After introduction into the UHV system, the wafers were first preliminary degassed at 200°C for 1 h in the fast-entry lock (base pressure $<10^{-6}$ Pa) and, subsequently, thoroughly degassed at 400°C for 1 h in the MBE chamber under UHV conditions (base pressure $<3 \times 10^{-8}$ Pa). *In-situ* XPS analysis (see below) evidenced that adventitious carbon is the only contaminant on the degassed wafer surfaces. After cooling down to room temperature, Ag thin films were grown on the freshly degassed Si(001) wafer surfaces at about 50°C (with the native amorphous SiO₂ film preserved) by thermal evaporation of pure Ag ($>99.995\%$) from a Al₂O₃ crucible using a high-temperature effusion cell (type HTC-40-10-1700-WK-SHP by Createc GmbH, Germany). The Ag deposition rate used in the present study was 3.9 nm/min and 2.1 nm/min and was determined in separate runs by (*ex-situ*) measurements of the film thickness after different deposition times with a Veeco DekTak profilometer.

In another series of experiments, a 30 nm thick a-Ge film was deposited *in-situ* onto the degassed Si(001) wafer, prior to the deposition of the Ag film (by the same procedures as described above), by thermal evaporation of pure Ge ($>99.999\%$) from a pyrolytic graphite (PGR) crucible using a high-temperature effusion cell (type HTC-40-2-250-WK-SH by Createc GmbH, Germany).

The two different types of substrate surfaces (a-SiO₂ and a-Ge), as employed for the subsequent (identical) Ag films deposition steps, will be further designated as “Ox/Si” substrate and “Ge/Ox/Si” substrate, respectively.

To investigate the microstructures of the Ag films at various stages of deposition by *ex-situ* TEM (see Sec. II C), Ag films were also deposited by evaporation for different deposition times (following the above procedures) on degassed 9 nm-thick amorphous Si membranes covered with native SiO₂ (SiMPore Inc.) as well as on degassed 9 nm-thick amorphous Si membranes covered with a 30 nm thick a-Ge layer.

B. In-situ stress analysis

To monitor in real time the stress-induced change in substrate curvature during film deposition, the multi-source MBE side-chamber is equipped with a multi-optical stress sensor (MOS) system²⁰ (k-space Associates) using a 3×3 array of parallel laser beams, which is aligned at normal incidence to the sample surface (i.e., single-port configuration). According to the Stoney equation,²¹ the measured change in substrate curvature is proportional with the film force per unit of lateral width, i.e., the product of the thickness-averaged film stress and the mean film thickness. From a plot of the film force vs. the film thickness, the following two quantities can be obtained: (i) The thickness-averaged film stress at deposition time t is given by the measured film force at time t divided by the mean film thickness at time t and (ii) The slope of the film-force curve at time t will be further designated as the incremental stress; its value is determined by the combined effects of instantaneous stress in the newly deposited part of the film and the (possible) stress change in the underlying (already deposited) film.

C. Microstructural analysis

1. TEM

The deposited Ag films (of thicknesses in the range of 3 nm–100 nm) on the prepared Ox/Si and Ge/Ox/Si TEM membranes (see Sec. II A) were removed from the UHV system directly after growth and then immediately put into a Philips CM 200 transmission electron microscope (operating at an acceleration voltage of 200 kV) for microstructural analysis in planar view.

2. XRD

The crystallographic texture and grain/crystallite size of the Ag films on the Ox/Si and Ge/Ox/Si substrates were determined by recording (*ex-situ*) XRD ψ -scans (pole-figure sections) and θ - 2θ -scans employing a Pro Philips X'Pert MRD diffractometer operating with Cu- $K\alpha$ radiation. The average grain sizes parallel and perpendicular to the film surface (further designated as lateral grain size and perpendicular grain size, respectively) were deduced by single-line analysis (after correction for instrumental broadening)^{22,23} from the measured Ag {111} and Ag {222} reflections, both recorded at specimen tilt angles of 0° and 70.53° . The Bragg peaks were fitted with a pseudo-Voigt function (i.e., a convolution of a Cauchy and a Gaussian profile) using the

PROFILE FIT software from the manufacturer, employing linear background subtraction and a $K\alpha_2/K\alpha_1$ intensity ratio of 0.5.²⁴ Within the single-line analysis, the Cauchy component of the diffraction line profile is only due to finite crystallite size, whereas the Gaussian component results from microstrain. Within the experimental accuracy, the Gaussian contribution (i.e., the microstrain) in the Ag films grown on the Ox/Si and Ge/Ox/Si substrates was negligibly small.

3. XPS

The occurrence of surface segregation of Ge during growth of the Ag films on the Ge/Ox/Si substrates (as discussed in Sec. III D) was investigated by *in-situ* XPS measurement of the Ge 3d and 2p core-level spectra before Ag deposition as well as after cumulative Ag film deposition steps (corresponding to Ag film thicknesses of 20, 50, 90, 140, 210, and 310 nm). The XPS analysis was performed using a Thermo VG Thetaprobe system employing monochromatic Al- $K\alpha$ radiation ($h\nu = 1486.68$ eV; beam spot size of 400 μm), while operating the radian lens (i.e., a 180°-spherical-sector-analyzer with an exceptionally large angular acceptance range of 60°) in the so-called “standard” lens mode by simultaneously collecting all photoelectrons over the detection angle range between 23° and 83° (with respect to the specimen surface normal; i.e., the central detection angle equals 53°).²⁵ An angle-resolved-XPS (AR-XPS) measurement was performed also at an Ag film thickness of 50 nm in the so-called “parallel” data acquisition mode, by detecting the photoelectrons simultaneously over the angular detection range from $\alpha = 23^\circ$ to $\alpha = 83^\circ$ in eight ranges of 7.5° each (α is the center of the corresponding angular detection range with respect to the sample-surface normal).²⁵

The total Ge 3d and Ge 2p primary zero loss (PZL; see Ref. 26) intensities ($I_{\text{Ge } 3d}$ and $I_{\text{Ge } 3p}$) were obtained from the integrated area of the background-corrected Ge 3d and 2p

spectra (applying a Shirley-type background), as recorded from the Ge/Ox/Si/substrate before and after various Ag deposition steps. The surface coverage by Ge in monolayers (MLs; one atomic layer in Ge(111) taken as 0.327 nm) after each Ag deposition step was calculated from the PZL intensity ratios $I_{\text{Ge } 3d}^\infty/I_{\text{Ge } 3d}$ and $I_{\text{Ge } 3p}^\infty/I_{\text{Ge } 3p}$, as resolved from the measured Ge 3d and Ge 2p spectra of the bare substrate (i.e., $I_{\text{Ge } 3d}^\infty$ and $I_{\text{Ge } 3p}^\infty$) and the Ag-covered Ge/Ox/Si/substrate (i.e., $I_{\text{Ge } 3d}$ and $I_{\text{Ge } 3p}$), respectively, according to the procedures described in Ref. 26. The values for the effective attenuation lengths (EALs) of the detected Ge 3d and Ge 2p photoelectrons, as required in the thickness calculations, equal 2.992 nm and 0.899 nm, respectively (see Ref. 25 and references therein). Note that the average information depth of the XPS analysis (as given by $3\lambda \cdot \cos \alpha$) is in the range of 8–1 nm and 2.5–0.3 nm with increasing angular detection range from $\alpha = 23^\circ$ to $\alpha = 83^\circ$ (see above) for the detected Ge 3d and Ge 2p photoelectrons, respectively.

III. RESULTS

A. *In-situ* stress analysis

The measured film force and the calculated thickness-averaged stress (i.e., film force divided by mean film thickness) during Ag film growth on the Ox/Si and Ge/Ox/Si substrates (at a deposition rate of 3.9 nm/min) are shown as function of the mean film thickness in Figs. 1(a) and 1(b), respectively. On both substrates, the developing Ag films show a compressive $\rightarrow$ tensile $\rightarrow$ compressive stress evolution, which is typical for Volmer-Weber type of film growth of metals with a high atomic diffusivity at the deposition temperature (i.e., for deposition at high homologous temperatures), as holds for Ag deposition at room temperature (see Sec. I).⁹ The durations (i.e., the thickness ranges) of the successive stress stages, as well as the corresponding magnitudes of the developed stresses, are distinctly different for both substrates (compare Figs. 1(a) and 1(b)): (i) For Ag film

FIG. 1. Film force and thickness averaged stress of Ag films deposited at a deposition rate of 3.9 nm/min on (a) Ox/Si and (b) Ge/Ox/Si substrates. The stages corresponding to the thicknesses where TEM analyses were made (see Figs. 3 and 4) have been marked with red circles.

growth on Ox/Si, the initial compressive and subsequent tensile stress maxima are reached at thicknesses of 9 nm and 67 nm, respectively (Fig. 1(a)). For Ag film growth on Ge/Ox/Si, the initial compressive and subsequent tensile stress maxima are reached at much smaller thicknesses of 3 nm and 6 nm, respectively (Fig. 1(b)). (ii) The average stress attained at the tensile maximum is more than two times smaller for the Ag film growing on Ox/Si than for the Ag film growing on Ge/Ox/Si (i.e., 11 MPa versus 23 MPa). (iii) The subsequent incremental compressive stress (i.e., the slope of the film force curve) is much smaller for the Ag film growing on Ox/Si than for the Ag film growing on Ge/Ox/Si (i.e., -19 MPa versus -103 MPa at thickness ranges of 80 nm–115 nm and 15 nm–40 nm, respectively). In addition, reversible stress relaxations are observed during Ag film growth interruptions on both the Ge/Ox/Si and the Ox/Si substrate (see Fig. 2). The amount of relaxed stress is much larger for the Ag film grown on the Ge/Ox/Si substrate than on the Ox/Si substrates (i.e., 50 MPa versus 13 MPa at a thickness of 130 and 140 nm and, respectively).

B. Microstructural evolution

The development of the microstructure of the Ag films was investigated by plan-view TEM (cf. Sec. II). TEM micrographs of the Ag films of various thicknesses on the Ox/Si and Ge/Ox/Si substrates are shown in Figs. 3 and 4, respectively (The stages of film growth pertaining to these micrographs have been indicated by circles and the characters in Fig. 1 showing the film force vs. thickness behavior). Indeed (cf. Sec. III A), Ag film growth on both types of substrate proceeds by a Volmer-Weber-type growth mode, as characterized by successive (partially overlapping) stages of island nucleation, island growth and island impingement.

Well separated, predominantly single-crystalline Ag islands occur for the (nominally) 9-nm thick Ag film on Ox/Si (see Fig. 3(a)). The Ag islands start to impinge at a thickness of 25 nm, resulting in the formation of grain boundaries within the now much larger islands (Fig. 3(b)). Island

coalescence progresses upon continued Ag deposition and, consequently, the grain-boundary density increases with increasing thickness (see Fig. 3(c) pertaining to a thickness of 45 nm) until the Ag film becomes practically closed at a thickness of 67 nm (Fig. 3(d)). After formation of a closed Ag film (further referred to as the onset of the post-coalescence stage), the film microstructure does not change significantly upon further growth (Fig. 3(e)): Only a very slight increase of average grain size (i.e., by grain growth) is observed in the post-coalescence stage (cf. the TEM micrographs of the 67-nm and 100-nm thick Ag films shown in Figs. 3(d) and 3(e), respectively).

The above described stages of growth occur at much smaller thicknesses during Ag film growth on the Ge/Ox/Si substrate. Island coalescence already takes place at a (nominal) Ag thickness of only 3 nm (see Figs. 4(a) and cf. Fig. 3(b)). At a film thickness of 6 nm, the Ge/Ox/Si substrate is largely covered by small Ag nano-grains with an average grain size of 10 nm (see Fig. 4(b)). Already at a film thickness of 25 nm (Fig. 4(c)), the Ag film is completely continuous, containing very fine Ag grains, with an average size of 21 nm, which increase slightly in size by grain growth during the post-coalescence stage to 25 nm for the 45 nm thick Ag film (Fig. 4(d)).

C. Texture and grain morphology

The texture (preferred orientation) of the Ag films on the Ox/Si and Ge/Ox/Si substrates was investigated by XRD: The Ag film on the Ox/Si substrate shows a strong and sharp $\{111\}$ fiber texture, as evidenced by the occurrence of dominant peaks at $\psi = 0^\circ$ and 70.5° in the Ag $\{111\}$ ψ -scan (pole-figure section; see Fig. 5) recorded at $2\theta = 38.2^\circ$, which is expected for polycrystalline thin films of fcc metals due to the relatively low surface energy of $\{111\}$ orientated grains.²⁷ The small peak at $\psi = 56^\circ$ can be ascribed to twinning on (111) planes, inclined with respect to the surface, of the $\{111\}$ fiber texture component, leading to a texture component with (511) planes parallel to the film surface.

On the contrary, the Ag film grown on the Ge/Ox/Si substrate is almost *texture-less*; i.e., the Ag grains are randomly oriented (see dotted line in Fig. 5).

The average grain/crystallite size and grain/crystallite morphology in the Ag films were determined by XRD line-profile analyses (see Sec. II). It follows that the Ag film on the Ox/Si substrate possesses a columnar grain structure: for the 205 nm thick Ag film, the average lateral (= parallel to the surface) grain size is 43 nm and the average perpendicular (to the surface) grain size is 89 nm.²⁸ The Ag film on the Ge/Ox/Si substrate exhibits an equiaxed nano-grain structure with equal average lateral and average perpendicular sizes: for the 280 nm thick Ag film the lateral and perpendicular grain sizes are 19 nm, in accordance with the TEM analysis (see Fig. 4).

D. Ge surface segregation during Ag deposition on the Ge/Ox/Si substrate

The Ge 3d and Ge 2p photoelectrons are detectable for the Ag films grown on the Ge/Ox/Si substrate at Ag

FIG. 2. Film force evolution of Ag films deposited at a deposition rate of 2.1 nm/min on the Ox/Si substrate (red) and the Ge/Ox/Si substrate (black). Upon interrupting the Ag film growth (see arrows in the figure), reversible stress relaxations are observed for both films.

FIG. 3. Bright field plan-view TEM images taken at characteristic stages of Ag film growth (with a deposition rate of 3.9 nm/min) on Ox/Si substrate. The images correspond to mass equivalent Ag film thicknesses of (a) 9 nm, (b) 25 nm, (c) 45 nm, (d) 67 nm, and (e) 100 nm. For (a)–(e), see Fig. 1(a).

FIG. 4. Bright field plan-view TEM images taken at characteristic stages of Ag film growth (with a deposition rate of 3.9 nm/min) on Ge/Ox/Si substrate. The images correspond to mass equivalent Ag film thicknesses of (a) 3 nm, (b) 6 nm, (c) 25 nm, and (d) 45 nm. For (a)–(d), see Fig. 1(b).

FIG. 5. XRD ψ -scans (pole-figure sections) recorded for the Ag 111 reflection (at $2\theta = 38.2^\circ$) of Ag films deposited on Ox/Si and Ge/Ox/Si substrates. The {111} planes parallel to the surface, representing the fibre-texture component for the Ag film on the Ox/Si substrate, give rise to peaks at $\psi = 0^\circ$ and 70.5° . The peak at $\psi = 56^\circ$ can be ascribed to twinning on {111} planes, inclined with respect to the surface, of the {111} fiber texture component leading to a texture component with {511} planes parallel to the film surface. The Ag film on the Ge/Ox/Si substrate is practically texture-less.

thicknesses as large as 310 nm, i.e., very much larger than the information depths of the XPS analyses (see Sec. II). This indicates that, during the Ag film growth, Ge segregation to the Ag film surface takes place (this process can be driven by lowering of the surface energy²⁹).

In order to disclose whether the segregated Ge atoms are located homogeneously at the Ag film surface or rather agglomerated at the Ag grain boundaries or at the surface/grain-boundary junctions, an AR-XPS measurement was performed at an Ag film thickness of 50 nm. As revealed by the AR-XPS results shown in the inset of Fig. 6, the ratio of the asymmetry-factor-corrected (see Ref. 25) photoelectron intensities of the Ge 3d and Ag 3d peaks increases with increasing detection angle α (relative to the sample-surface normal) from 26° to 72° . The increase of the photoelectron-intensity ratio is proportional to the inverse of $\cos(\alpha)$ (see inset of Fig. 6). Such $1/\cos(\alpha)$ dependence, as predicted by theoretical models for submonolayer surface adsorption systems,³⁰ thus confirms that the segregated Ge is exclusively located at the growing Ag film surface rather than at the Ag grain boundaries or at the surface/grain-boundary junctions. This observation is consistent with the thermodynamic recognition that Ag and Ge are fully *immiscible* at room temperature³¹ (i.e., a large *positive* enthalpy of intermixing exists) and therefore, Ge atoms tend to stay at the low-coordination Ag surface sites rather than at high-coordination Ag grain-boundary sites.

The surface coverage by the segregated Ge layer, expressed in monolayers (MLs) and as separately estimated from the measured Ge 3d and Ge 2p photoelectron intensities (see Sec. II), has been plotted as function of the Ag film thickness in Fig. 6. Although the EALs (and thus the information depths; see Sec. II) of the detected Ge 3d and Ge 2p photoelectrons are different (3 nm vs. 0.9 nm, see Sec. II), the values determined for the thickness of the segregated Ge layer at the surface of the Ag film, on the basis of the separate resolved Ge 3d and Ge 2p photoelectron intensities, are

FIG. 6. Surface coverage by the segregated Ge (given in monolayers (MLs); 1 ML equals the thickness of one atomic (111) layer of Ge), as separately determined from the resolved Ge 2p and Ge 3d photoelectron intensities, as function of Ag film thickness. The inset shows the ratio of the asymmetry-factor-corrected intensities of the Ge 3d and Ag 3d peaks, $I_{\text{Ge 3d}}/I_{\text{Ag 3d}}$, as function of the detection angle α at a Ag film thickness of 50 nm. The ratio increases proportionally to $1/\cos(\alpha)$, indicating that the segregating Ge atoms are located at the top surface of the Ag film.

similar. The results show that the Ge surface coverage during Ag deposition is well below 1 ML; it gradually decreases from about 0.7 ML to 0.2 ML for an increase in Ag film thickness from 20 nm to 310 nm. Evidently, Ge from the Ge/Ox/Si substrate (see Sec. II) segregates to the Ag film surface at the onset of Ag deposition. This initially segregated Ge layer then continuously resegregates to the film surface during continued deposition. The observed decrease of the Ge surface coverage with increasing Ag film thickness (see Fig. 6) can be explained by a partial incorporation of the initially segregated Ge atoms underneath the surface during continued film growth due to a lower Ge segregation rate as compared to the Ag deposition rate.

IV. DISCUSSION

A. Effect of the adatom surface diffusivity on the microstructural evolution

At the onset of the deposition process, the nucleation of Ag islands on the parent a-SiO₂ and a-Ge surfaces competes with the further growth of already nucleated Ag islands (by trapping diffusing Ag adatoms in their vicinity). The activation energy for diffusion of Ag is significantly higher on the a-Ge surface than on the a-SiO₂ surface (0.45 eV vs. 0.32 eV)^{18,19}; hence the average diffusion length of Ag adatoms is much smaller on the parent a-Ge surface than on the parent a-SiO₂ surface (for the same substrate temperature). Consequently, growth of already existing Ag islands by adding Ag adatoms by surface diffusion, as compared to the formation of new islands, is less pronounced on the a-Ge surface than on the a-SiO₂ surface. Hence, for the parent a-Ge surface, and as compared to the parent a-SiO₂ surface, the combination of a relatively low diffusivity of the Ag adatoms and the (correspondingly) higher initial density of islands promotes the formation of a closed Ag film with

relatively small grain size, in accordance with the experimental observations (see Sec. III). This smaller grain size upon film coalescence implies a much higher grain-boundary density of the Ag film on the Ge/Ox/Si substrate in the post-coalescence stage (as compared to the Ox/Si substrate): compare Figs. 3(d) and 4(b).

The differences in the microstructural evolution of the Ag films on both substrates cannot only be ascribed to the *initial* difference in surface mobility of the Ag adatoms on the *parent* Ox/Si and Ge/Ox/Si substrates at the onset of the deposition (as discussed above), but also evolve by a maintained difference in surface diffusivity of the Ag adatoms on the *developing* Ag film surfaces upon continued film growth during the post-coalescence stage (see what follows).

The activation energy of 0.1 eV (Ref. 18) for diffusion of Ag on Ag(111) surfaces is significantly lower than the aforementioned activation energies of 0.32 eV and 0.45 eV for Ag diffusion on the a-SiO₂ surface and the a-Ge surface, respectively. Consequently, the diffusion length of Ag adatoms on the Ag film surfaces on the Ox/Si substrate is large enough to allow the continuous incorporation of the Ag adatoms in existing grains, preferentially those with an energetically favored {111} plane parallel to the film surface. The Ag film grown on the Ox/Si substrate thus develops a columnar grain morphology with a strong and sharp {111} texture. This type of microstructure, developing at a homologous temperature of $T_h = 0.3$, is compatible with the Zone II-type of microstructure developing at homologous deposition temperatures in the range of $T_h = 0.3$ – 0.5 , according to the Structure Zone Model.¹⁵

The absence of such a columnar microstructure for the Ag film grown on the Ge/Ox/Si substrate at the *same homologous temperature* of $T_h = 0.3$ can be understood as follows: The submonolayer of (re-)segregating Ge at the Ag film surface (see Fig. 6) significantly retards the surface diffusion of the Ag adatoms also during the post-coalescence stage, thereby promoting continued nucleation of new Ag grains during film growth. Furthermore, since grain growth in Ag thin films at temperatures of $0.2 T_m$ – $0.3 T_m$ is predominantly controlled by surface diffusion of Ag atoms,^{15,32} the significantly reduced surface diffusion by segregating Ge further hinders the occurrence of growth of the already formed Ag grains. As a consequence, the Ag film on the Ge/Ox/Si substrate develops a fine, equiaxed grain morphology without texture. In the absence of the continuous suppression of the Ag adatom surface diffusivity by the Ge (re-)segregation effect, such textureless films, exhibiting an equiaxed grain morphology, only develop at significant lower homologous temperatures, $T_h < 0.2$ (pertaining to the Zone I-type of microstructure of the Structure Zone Model¹⁵).

B. Effect of adatom surface diffusivity on the intrinsic stress evolution

As revealed by the measured stress evolutions and the corresponding TEM observations of the developing film microstructure during Ag film growth on the Ox/Si and Ge/Ox/Si substrates (compare Figs. 1(a) and 3, as well as Figs. 1(b) and 4), the generation of compressive stress during

the initial stage of film deposition correlates with the nucleation and growth of isolated islands on the parent substrate surfaces (e.g., see Figs. 1(a) and 3(a)). The generation of compressive (intrinsic) stress during island growth can be attributed to the presence of a (positive) surface stress that acts on an individual island and the strength of the adhesion of the individual island with the substrate, as follows.^{33,34} For an *unconstrained* island, the acting surface stress induces an equilibrium lattice spacing of the island that is lower than that of the corresponding bulk metal; the value of this equilibrium lattice spacing increases with increasing island size. Upon increasing (lateral) island size atomic rearrangements at the island/substrate interface become increasingly difficult. As a result, the increase of the *strived-for* equilibrium lattice spacing during island growth is associated with the development of a compressive stress component in the island parallel to the island/substrate interface.

As the deposition proceeds, the isolated islands grow and coalesce, thereby forming grain boundaries. The interatomic forces acting across the developing grain boundaries induce a tensile stress component in the film parallel to the film surface (e.g., see Figs. 1(a) and 3(b)–3(d)); the magnitude of this component of generated tensile stress is proportional with the amount of formed grain boundaries per unit area of film. The grain-boundary density is much larger for the growing Ag film on the Ge/Ox/Si substrate than on the Ox/Si substrate (see Secs. III B and III C) and, consequently, the average tensile stress component emerging during film coalescence is considerably larger for the film on the Ge/Ox/Si substrate (as compared to the Ag film on the Ox/Si substrate): compare Figs. 1(a) and 1(b). For both films, the end of the island-coalescence stage (i.e., the stage at which a closed Ag film has formed) corresponds well with the occurrence of the tensile stress maximum (compare Figs. 1(a) and 3(d) and Figs. 1(b) and 4(b)).

Although the Ag films developing on the Ox/Si and Ge/Ox/Si substrates exhibit strikingly different microstructures (see Secs. III B and III C), continued deposition during the post-coalescence stage results in the (re)appearance of a compressive stress component as well as reversible stress relaxations during Ag film growth interruptions for the Ag films on *both* types of substrates.

The present experimental findings, that Ag films with largely different adatom surface diffusivities (see the discussion in Sec. IV A) and strikingly different film microstructures exhibit, similarly, the emergence of a post-coalescence compressive stress component as well as reversible stress relaxations, allow a more sophisticated classification of stress-evolution behavior during polycrystalline film growth, which was so far simply based on the atomic mobility (i.e., the homologous temperature).^{9,10} A high adatom surface diffusivity and the development of a textured, columnar microstructure (which do not occur for the Ag film growing on the Ge/Ox/Si substrate) are evidently not decisive factors for the post-coalescence compressive stress generating mechanism.

The emergence of a post-coalescence compressive stress component for both types of Ag films can be reduced to the same denominator by departing from a concept proposed in Ref. 4. Recognizing the non-equilibrium nature of film

growth, the chemical potential of Ag adatoms at the film surface is significantly larger than that of Ag (ad)atoms in the film grain boundaries. Therefore, a reduction of Gibbs energy of the system during the post-coalescence growth stage can be realized by the transport of the adatoms from the supersaturated film surface into the film grain boundaries, in association with, first, the relaxation of the tensile stress contribution (see above discussion) and, subsequently, the buildup of a compressive stress contribution. This stress contribution can be significant provided the grain-boundary diffusion rate is large with respect to the layer-growth rate.

Because for the Ag film growing on the Ge/Ox/Si substrate, (re)segregated Ge atoms are exclusively located at the growing Ag film surface (see Sec. III D), only the Ag adatom surface diffusivity is suppressed, whereas due to the absence of Ge at the developing film grain boundaries, the grain-boundary diffusivity of Ag (ad)atoms is unaffected, thereby allowing operation of the same compressive stress generating mechanism as described above.

The above interpretation of the emerging post-coalescence compressive stress component as well as reversible stress relaxations during growth interruptions is moreover supported by the much larger value of the compressive stress contribution and the much larger value of relaxed stress observed for the fine-grained Ag film (i.e., the film on the Ge/Ox/Si substrate) as compared to the much coarser grained Ag film (i.e., the film on the Ox/Si substrate): -103 MPa versus -19 MPa and 50 MPa versus 13 MPa; cf. Figs. 1(a), 1(b), and 2.

V. CONCLUSIONS

The adatom surface diffusivity has a dramatic impact on the microstructural development of polycrystalline Ag films during growth at a homologous temperature of $T_h \approx 0.3$.

The Ag film deposited on the a-SiO₂ substrate possesses a columnar, surface-energy minimizing $\{111\}$ fiber textured microstructure, due to a relatively high Ag adatom surface diffusivity allowing incorporation of Ag adatoms in already existing grains during continued film growth.

The distinctly lower diffusivity of Ag adatoms on the a-Ge substrate (as compared to the a-SiO₂ substrate) enhances the initial nucleation of Ag islands and at the same time suppresses the growth of (initially) formed Ag islands on the parent substrate surface. The surface diffusivity of the Ag adatoms is also lowered *during thickening* of the laterally closed Ag film on the a-Ge substrate, due to the continuous and exclusive (re)segregation of Ge to the film surface. As a consequence of the thus maintained lower adatom surface diffusivity, continuous nucleation of new Ag grains takes place and a fine, equiaxed, texture-less, microstructure is formed.

The Ag films growing on both types of substrates, at similar conditions, both experience the development of compressive $\rightarrow$ tensile $\rightarrow$ compressive contributions of stress parallel to the film/substrate interface, albeit at different times and of different magnitudes.

Irrespective of the great differences in film microstructure, the various, successive stress-inducing mechanisms are

identified as (i) a positive surface stress in combination with a rigidity of the atomic structure at the island/substrate interface increasing with island size causes the initial compressive stress; (ii) the coalescence of the islands and the interatomic forces acting across the resulting grain boundaries lead to a tensile stress component; and (iii) the diffusion of adatoms into the grain boundaries of the growing film generate the final compressive stress contribution.

The much larger grain-boundary density of the Ag film growing on the a-Ge substrate corresponds with much larger stress contributions (ii) and (iii) as compared to those of the relatively coarse grained Ag film on the a-SiO₂ substrate.

The generally adopted classification of the stress and microstructure evolutions in a high and a low mobility type of growth only on the basis of the homologous temperature is (much) too crude. This study demonstrates that the microstructural evolution of metallic thin films is predominantly governed by the adatom *surface* diffusivity and that the intrinsic stress evolution is largely controlled by both the developing microstructure and the grain-boundary diffusivity.

¹L. B. Freund and S. Suresh, *Thin Film Materials* (Cambridge University Press, Cambridge, England, 2003).

²D. Sander, *J. Phys.: Condens. Matter* **16**, R603 (2004).

³R. Abermann and R. Koch, *Thin Solid Films* **129**, 71 (1985).

⁴E. Chason, B. W. Sheldon, L. B. Freund, J. A. Floro, and S. J. Hearne, *Phys. Rev. Lett.* **88**, 156103 (2002).

⁵J. A. Floro, S. J. Hearne, J. A. Hunter, P. Kotula, E. Chason, S. C. Seel, and C. V. Thompson, *J. Appl. Phys.* **89**, 4886 (2001).

⁶C. Friesen and C. V. Thompson, *Phys. Rev. Lett.* **89**, 126103 (2002).

⁷R. W. Hoffman, *Thin Solid Films* **34**, 185 (1976).

⁸R. Koch, *J. Phys.: Condens. Matter* **6**, 9519 (1994).

⁹R. Koch, *Surf. Coat. Technol.* **204**, 1973 (2010).

¹⁰R. Abermann, *Vacuum* **41**, 1279 (1990).

¹¹A. L. Del Vecchio and F. Spaepen, *J. Appl. Phys.* **101**, 063518 (2007).

¹²C. Friesen, S. C. Seel, and C. V. Thompson, *J. Appl. Phys.* **95**, 1011 (2004).

¹³Volmer-Weber type of growth involves that film growth proceeds by the initial nucleation of isolated islands on the parent substrate, which coalesce during continued deposition, thus forming a laterally-closed (continuous) film [M. Volmer and A. Weber, *Z. Phys. Chem.* **119**, 277 (1926)].

¹⁴G. Thurner and R. Abermann, *Thin Solid Films* **192**, 277 (1990).

¹⁵C. R. M. Grovenor, H. T. G. Henzell, and D. A. Smith, *Acta metall.* **32**, 733 (1984).

¹⁶H. A. Atwater and A. Polman, *Nature Mater* **9**, 205 (2010).

¹⁷V. J. Logeeswaran, N. P. Kobayashi, M. S. Islam, W. Wu, P. Chaturvedi, N. X. Fang, S. Y. Wang, and R. S. Williams, *Nano Lett.* **9**, 178 (2008).

¹⁸E. G. Seebauer and C. E. Allen, *Prog. Surf. Sci.* **49**, 265 (1995).

¹⁹H. C. Kim, T. L. Alford, and D. R. Allee, *Appl. Phys. Lett.* **81**, 4287 (2002).

²⁰E. Chason and B. W. Sheldon, *Surf. Eng.* **19**, 387 (2003).

²¹G. G. Stoney, *Proc. R. Soc., London* **82**, 172 (1909).

²²E. J. Mittemeijer and U. Welzel, *Z. Kristallogr.* **223**, 552 (2008).

²³T. H. de Keijser, J. I. Langford, E. J. Mittemeijer, and A. B. P. Vogels, *J. Appl. Crystallogr.* **15**, 308 (1982).

²⁴R. Delhez and E. J. Mittemeijer, *J. Appl. Crystallogr.* **8**, 609 (1975).

²⁵M. S. Vinodh and L. P. H. Jeurgens, *Surf. Interface Anal.* **36**, 1629 (2004).

²⁶L. P. H. Jeurgens, W. G. Sloof, C. G. Borsboom, F. D. Tichelaar, and E. J. Mittemeijer, *Appl. Surf. Sci.* **161**, 139 (2000).

²⁷C. V. Thompson, *Annu. Rev. Mater. Sci.* **30**, 159 (2000).

²⁸Due to the possible presence of stacking faults and twins, the average grain size (as determined by the single line analysis) has to be considered as a lower limit.

²⁹The surface energies of a-Ge and Ag at the growth (room) temperature are equal to 0.7 J/m² and 1.4 J/m², respectively [Z. M. Wang, J. Y. Wang, L. P. H. Jeurgens, and E. J. Mittemeijer, *Phys. Rev. B* **77**, 045424 (2008)]. The surface segregation of Ge atoms to the Ag film surface at these

strikingly low temperatures (i.e., room temperature) can occur because the (relatively strong) covalent bonds in the a-Ge substrate are weakened at the interface with the Ag film on top, as also observed in various metal-semiconductor contacts [A. Hiraki, *Surf. Sci. Rep.* **3**, 357 (1983)].

³⁰C. S. Fadley, *Prog. Surf. Sci.* **16**, 275 (1984).

³¹R. Olesinski and G. Abbaschian, *J. Phase Equilib.* **9**, 58 (1988).

³²R. Dannenberg, E. Stach, J. R. Groza, and B. J. Dresser, *Thin Solid Films* **379**, 133 (2000).

³³R. C. Cammarata, *Prog. Surf. Sci.* **46**, 1 (1994).

³⁴R. Abermann, R. Kramer, and J. Mäser, *Thin Solid Films* **52**, 215 (1978).