Stress tuning in sputter-grown Cu and W films for Cu/W nanomultilayer design

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Stress tuning in sputter-grown Cu and W films for Cu/W nanomultilayer design

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ABSTRACT
Controlling growth stresses during thin film fabrication is of paramount importance to solve reliability issues during operation of functional thin films in harsh environments. A combination of different methods for thin-film stress determination, such as \textit{in situ} wafer curvature and \textit{ex situ} x-ray diffraction, is usually required to reveal and tailor growth stresses in thin film systems, as well as to extract interface stress contributions in multilayered coatings. In this article, the tuning of intrinsic growth stresses in thin films of Cu and W, as grown by magnetron sputtering, was performed by varying the Ar pressure and gun power during thin-film deposition. The average growth stress in Cu and W thin films could be tuned between tensile and compressive. Next, the thus obtained knowledge on stress engineering of Cu and W single layers was applied to investigate the corresponding intrinsic stresses in Cu/W nanomultilayer coatings, for which interface stress was found to play an important role.

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I. INTRODUCTION
Stress in thin films and multilayers can reduce the performance or even lead to failure in technical applications, through mechanisms such as cracking, buckling, or delamination.\textsuperscript{1,2} In some circumstances, however, stress is desirable since it can be exploited to enhance specific properties of coatings, such as conductivity,\textsuperscript{3} thermal stability,\textsuperscript{4,5} mechanical strength, or magnetic properties.\textsuperscript{6,7} For this reason, assessing and controlling the stress state of thin films and coatings are of primary technological importance.

Physical vapor deposition (PVD), in particular, magnetron sputtering, is a widely used technique for the fabrication of thin films and multilayers, which allows the specific design of alternating layers with precise properties and microstructure.\textsuperscript{8-10} In thin polycrystalline films, where the primary growth mode is Volmer–Weber (VW),\textsuperscript{11} stress is generated during the growth itself, hence it is denoted as \textit{intrinsic stress} or \textit{growth stress}. Many studies have investigated the stress-generation mechanisms during thin-film growth to find the connection between growth and stress with the aim of properly controlling and optimizing the intrinsic stress. This would allow us to relate the stress to growth conditions, microstructure, and material parameters and serve as a guide for thin-film growth.\textsuperscript{12-14} A big step forward in the fundamental understanding of internal stress has been achieved with the introduction of substrate-curvature-based stress measurement techniques, such as the Multi-beam Optical Stress Sensor (MOSS).\textsuperscript{15} This setup allows direct access to the evolution of the average film stress during film growth. The “stress-thickness” vs “thickness” curve obtained displays a three-stage trend following either a “compressive-tensile-tensile” or a “compressive-tensile-compressive” evolution with increasing film thickness, depending on the melting temperature and the adatom diffusivity of the deposited material. The former trend, on the one hand, is commonly observed in high-melting temperature metals with a relatively low atomic mobility (e.g., Ta, W, Cr, and Fe), i.e., the type I materials.\textsuperscript{14,16} The latter trend, on the other hand, is typical of low-melting temperature metals with a relatively high atomic mobility (e.g., Cu, Al, Ag, and Au), also known as type II materials. The first compressive stage, shared by both types of materials, is associated with island formation during VW growth, often denoted as the pre-coalescence stage.\textsuperscript{17} The second stage associated with tensile stress generation is also shared by both types of materials, and it is attributed to the coalescence of individual grains into a laterally continuous film (i.e., the “zipping” of grain boundaries).\textsuperscript{16,17} The third stress evolution stage is
associated with the post-coalescence regime of VW growth, and it is sometimes denoted as the steady-state stage if the stress-thickness product is linear. It leads to a different stress evolution for the two types of materials. For type II materials, incremental compressive stress during the post-coalescence stage can be the consequence of the diffusion of surface adatoms into the grain boundaries of the developing film or of an atomic peening process. For type I materials, the energy of the arriving adatoms and their atomic mobility on the film surface is generally much lower and, consequently, the above-mentioned compressive stress-generating mechanisms are partially or completely blocked. Hence, the film may not reverse the stress sign, and it retains a tensile stress state, as incorporated during the coalescence stage.

Evidently, the above-stress-generating mechanisms are also governed by deposition parameters (e.g., pressure, magnetron power, and temperature) because they act directly on the energy of sputtered adatomic species impinging on the film surface. A variation of deposition parameters can lead to higher or lower incremental stresses during film growth and may even reverse the sign of the average film stress in the post-coalescence regime. Thus, extreme scenarios are possible, like type II materials displaying tensile stress and type I materials displaying compressive stress in the steady-state regime. Many investigations of the effect of the growth conditions on stress evolution during film growth have been reported in literature, involving many different materials and deposition parameters. However, very few works exist on stress evolution during alternating deposition of two different materials, thus creating additional internal interfaces, as it is the case for multilayer structures. A comprehensive characterization of different internal and interface stress contributions in multilayer systems requires the combined application of the stress curvature method with x-ray diffraction (XRD) techniques, since each method measures different types of stress. On the one hand, XRD determines the stress originating from the strain in the crystal lattices of the constituting crystalline phases, and interface stresses do not contribute to the diffracted intensity of compounds like CuSi or WSi; on the other hand, the presence of amorphous silicon nitride prevents the films to inherit a crystalline texture from the parent substrate, which will affect the stress evolution during film growth. In this way, the deposited layers develop their own texture independently of the crystal orientation of the parent substrate. Films are deposited from two targets, on the intrinsic stress state generated in Cu and W thin films grown by DC-magnetron sputtering.

Samples tend to develop compressive stress under low Ar-pressures and high gun powers. Indeed, these growth conditions promote the arrival of more energetic adatoms on the substrate, consequently intensifying compressive-stress generation mechanisms, i.e., atomic peening and atomic diffusion into grain boundaries. Vice versa, opposite conditions will favor the development of a tensile stress. W and Cu are fully immiscible and representative of the aforementioned type I and II materials: tungsten, which has a high melting temperature and a low diffusivity, and copper, which has a low melting temperature and high-diffusivity material. The thus-obtained knowledge of the dependence of single-phase metal films on stress-deposition parameters is applied to investigate the stress state in Cu/W multilayers. In situ stress data are compared with XRD-derived stress to determine the amount of interface stress. This work opens the path toward the production of Cu/W nanomultilayers with controlled stress states, highly relevant for reliability issues in microelectronic applications.

## II. EXPERIMENTAL METHODS

### A. Sample production

Cu and W thin films have been grown with an AJA DC-magnetron sputtering setup (AJA International Inc.) in a ultrahigh vacuum chamber with a base pressure of $5 \times 10^{-7}$ Pa. The substrates used are Si (100) squares (edge 1 cm, thickness 200 μm) with a 90-nm-thick a-SiN$_x$ film on top. Prior to deposition, they have undergone three cleaning steps in an ultrasonic bath in acetone, ethanol, and isopropanol and a fourth step inside the sputtering chamber, consisting of a 2-min-long RF sputter cleaning with an Ar-pressure of 2 Pa at 50 W power. The choice of growing films on a-SiN$_x$ and not directly on Si has two motivations: on the one hand, the a-SiN$_x$ buffer layer acts as a diffusion barrier to prevent the diffusion of atoms from the film into the substrate (Cu is particularly reactive with Si) and, thus, block the formation of compounds like CuSi or WSi; on the other hand, the presence of amorphous silicon nitride prevents the films to inherit a crystalline texture from the parent substrate, which will affect the stress evolution during film growth. In this way, the deposited layers develop their own texture independently of the crystal orientation of the parent substrate. Films are deposited from 2"-diameter W (99.95% of purity) and Cu (99.99% of purity) confocally arranged targets, which have been presputtered for 2 min before every deposition. The target–substrate distance is 10 cm, and every deposition has been performed at room temperature. The parameters controlled to tune the stress state are the Ar-pressure, with values ranging from 0.267 to 2.667 Pa, and the applied power, with values ranging from 30 to 150 W. The growth rates have been measured prior to every deposition with a Bruker Dektast XTL profilometer.

### B. Stress measurements

In situ stress measurements have been performed with a k-Space multi-beam optical stress sensor (MOSS, k-Space Associates Inc.), which is an optical technique to monitor the substrate curvature during film growth. It allows to determine the stress-thickness product, $\sigma \times h$ by Stoney’s equation:

$$\sigma \times h = \frac{M_s h_i^2}{6 \rho}$$  \hspace{1cm} (1)$$

where \(1/\rho\) is the substrate curvature, $M_s$ is its bulk modulus, which is 180.5 GPa for Si, and $h_i$ is its thickness, which is 200 μm. The effect of the SiN$_x$ overlayer on the mechanical response of the
substrate can be neglected because its thickness (90 nm) is negligible compared to that of the Si (200 μm). From $\sigma \times h$ values, the average stress in the film, $\sigma$, and the incremental stress, $\sigma_i$, can be estimated. The former by dividing by the film thickness, $h$, i.e., $\sigma = \frac{\sigma h}{h}$, the latter by calculating the derivative, i.e., $\sigma_i = \frac{d(\sigma h)}{dh}$.

Stress has also been measured ex situ by means of XRD with a Bruker D8 diffractometer operating in a Bragg–Brentano and point focus geometry at 40 V and 40 mA, with an incident radiation wavelength of 1.5406 Å, which is the Cu Kα1,2 line. The method used to determine the stress is a modified version of the sin²ψ-method, also known as the Crystallite Group Method (CGM).32 The CGM accounts for the texture in the grown thin films, i.e., a [111] out-of-plane texture for Cu (fcc crystal lattice) and a [110] out-of-plane texture for W (bcc crystal lattice). The elastic constants for the data analysis are taken from Ref. 33.

### III. EXPERIMENTAL RESULTS AND DISCUSSION

#### A. Tungsten stress tuning

Several depositions were performed at a fixed applied power of 80 W and different Ar-pressures (0.267, 0.533, 0.8, and 1.333 Pa) to investigate the effect of the Ar-pressure on the intrinsic stress generated in sputter-grown W films. The related stress-thickness evolutions, measured in situ using MOSS during film growth, are reported in Fig. 1(a). A clear trend is observed. On one side, high Ar-pressures are associated with positive values and slopes of stress-thickness due to tensile stress generation. On the other side, low Ar-pressures, as 0.267 Pa, are associated with negative values and slopes due to compressive stress generation.

The role of the applied target power on stress evolution was investigated by performing three depositions at constant intermediate Ar-pressure of 0.533 Pa and at different gun powers of 30, 80, and 150 W. Positive stress-thickness values and slopes were measured at low gun powers (30 and 80 W) because of the build-up of tensile stress. By contrast, negative stress-thickness values and slopes were found at high gun powers, as a result of compressive stress development during film growth.

The general trends that can be derived from these data are of two kinds. On one hand, low Ar-pressures and high gun powers are favorable conditions for compressive stress generation, and, on the other hand, high Ar-pressure and low gun powers promote the build-up of tensile stress. Both trends can be explained by invoking concepts such as atomic peening and adatom energy, whereas atomic diffusion into grain boundaries can be ruled out, being negligible in type I materials. Indeed, when a high power is applied to the target, W atoms detach with high energy. Moreover, they undergo few collisions along their path toward the substrate if the Ar-pressure is low, hence retaining most of their kinetic energy. Therefore, low Ar-pressure and high gun power are parameters specific for highly energetic adatoms, which intensify the atomic peening mechanism and the consequent compressive stress generation. When the applied power is not high enough or the Ar-pressure overcomes a certain threshold, W atoms do not have enough energy to effectively contribute to the atomic peening process. As a consequence, the compressive stress generation is less pronounced and films develop a tensile intrinsic stress, as predicted for type I materials (see Introduction). A similar trend has been observed for other refractory metals,34–36 including W,37 as well as for other type I materials like iridium38 and ZrN.39 X-ray diffractograms have been acquired on two W films of identical thickness (50 nm), which have been grown at different Ar pressures to obtain opposite stress states. Both W films have a preferred [110] out-of-plane growth direction (in-plane, the grains are approximately randomly oriented, i.e., films express a fiber texture). In Fig. 2, the diffraction peak (110) of W is shown; the peak position is shifted in two opposite directions as compared to its theoretical position for the strain-free state (as obtained from a bulk W powder;40 as marked with a solid vertical line), which confirms the opposite stress state of the two films. The corresponding average stresses in the W films have been quantified from diffraction data by application of the CGM method and can be
TABLE I. Tabulated values of the average total stresses of the substrate/W-film assemblies, as determined by substrate-curvature, \( \sigma_{\text{SC}} \), before and after relaxation at the end of deposition and the corresponding average stresses in the W film by XRD, \( \sigma_{\text{XRD}} \). The data refer to 50-nm-thick W films that were sputter-deposited at a constant power of 80 W but at different Ar pressures. An Ar-pressure of 0.267 Pa results in a compressive stress state, whereas an Ar pressure of 0.8 Pa induces a tensile stress state.

<table>
<thead>
<tr>
<th>Stress State</th>
<th>( \sigma_{\text{SC}} ) (GPa)</th>
<th>( \sigma_{\text{XRD}} ) (GPa)</th>
</tr>
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<tbody>
<tr>
<td>W compressive</td>
<td>(-0.79 \pm 0.04)</td>
<td>(-2.0 \pm 0.1)</td>
</tr>
<tr>
<td>W tensile</td>
<td>(0.68 \pm 0.02)</td>
<td>(1.40 \pm 0.06)</td>
</tr>
</tbody>
</table>

Compared to the average total stresses in substrate/film systems, as determined from the substrate curvature, see Table I.

Clearly, the average stress values determined by the two methods are very different. In particular, the average stress in the W phase, as probed by XRD, is systematically larger than the average total stress of the substrate/film assembly, as measured by wafer curvature: i.e., \(-2 \text{ vs } -0.79 \text{ GPa}\) for the tensile state and \(1.40 \text{ vs } 0.68 \text{ GPa}\) for the compressive state, respectively. This kind of discrepancy between the two methods is well documented in the literature and typically attributed to the contribution of stress stored at interfaces, which is not probed by XRD.35,41–43 The two methods are indeed complementary: with XRD, only the crystalline contribution to stress is measured, whereas all sources of stress, originating from crystalline and non-crystalline regions, contribute to the curvature of the substrate.26 Only combining both stress-measurement techniques the stress stored at interfaces can be derived as difference between the stress derived with the two methods.

![Graph showing intensity vs. 20 (deg) for W(110) peaks acquired by XRD scans performed on two 50-nm-thick W films deposited at Ar-pressures of 0.267 and 0.8 Pa.](image)

Denoting \( \sigma_{\text{inter}} \) as the stress stored at the internal interfaces (which can be grain boundaries and/or the substrate-film interface), then \( \sigma_{\text{SC}} = \sigma_{\text{XRD}} + \sigma_{\text{inter}} \). It then follows that \( \sigma_{\text{inter}} \) compressive \( = 1.2 \pm 0.1 \text{ GPa} \) and \( \sigma_{\text{inter}} \) tensile \( = -0.73 \pm 0.06 \text{ GPa} \). Note that the sign of the stress stored at the interfaces is opposite to the sign of \( \sigma_{\text{XRD}} \), thus contributing to a relaxation of the overall stress state of the substrate/film assembly.

B. Copper stress tuning

An analogous study was conducted to tailor the stress in Cu thin films by controlled variations of the target power and Ar pressure. The stress-thickness curves obtained by the in situ wafer curvature are shown in Figs. 3(a) and 3(b). We note that the measurements are nosier than the ones for W as stress-thickness values are lower for Cu due to different material stiffnesses. The intrinsic noise of the measurements appears then more pronounced. Here, it is noted that the measured wafer response, once the growth is stopped, is not shown. Cu, contrary to W, undergoes a stress-relaxation stage at the end of deposition. Consequently, the ex situ stress state of the as-deposited Cu film after removal from the sputtering chamber differs from that obtained in situ at the end of the deposition process (but before growth interruption). This stress-relaxation during growth interruptions is well known44 (an example is also shown in the inset of Fig. 5).

In Fig. 3(a), the stress-thickness curves, as measured during Cu depositions at different Ar pressures (0.267, 0.667, 1.333, 2, and 2.667 Pa) and constant target power of 80 W, are shown. “High pressure—tensile stress” and “low pressure—compressive stress” relationships can be identified, analogously to W. The curves pertaining to constant Ar pressures of 0.267 and 0.667 Pa are superimposed, despite the fact that the Ar pressure is doubled. Moreover, the highest tensile stress occurs in the film grown at 2 Pa [see Fig. 3(a)] and not in the one grown at an even higher pressure of 2.667 Pa, although the latter condition results in highest incremental stress.

Cu has a much high deposition rate as compared to W for similar target powers and Ar pressures (here: the Cu deposition rate of 0.3 nm/s is roughly 5 times higher than that of W for similar deposition conditions). Consequently, the reflectance of the substrate/film assembly changes within few seconds from a relatively low reflectance for the bare insulating Si/a-SiN\(_x\) substrate \((R = 0.118.744 \text{ at } \lambda = 558 \text{ nm} \text{ for } \text{Si}_x\text{N}_y\)) to a very high reflectance for the Cu metal \((R = 0.647.37 \text{ at } \lambda = 558 \text{ nm})\). As a result, the intensity of reflected laser beams for the substrate-curvature measurement (as captured by the camera) rapidly approaches saturation during the initial deposition stage, which obscures the detection of the initial compressive stress stage during the very short pre-coalescence regime (even though an automated intensity regulation of the reflected beam is implemented). Still, a tensile maximum associated with grain coalescence (albeit very small) can be observed for all deposition conditions studied. Incremental compressive stress is generated during transition to the post-coalescence stage.

The films grown at 0.267 and 0.667 Pa maintain a compressive stress until the end of their deposition: indeed they reach a steady compressive stress state due to an approximately constant incremental stress of \(-0.03 \text{ GPa}\) during the post-coalescence stage. Pletea et al.46 and Navid et al.47 have observed similar trends for Cu grown at low...
Ar pressures. The compressive stress generation was ascribed to the atomic peening mechanism in one case\textsuperscript{46} and to the diffusion of adatoms into the film grain boundaries (to lower their chemical potential) in the other case.\textsuperscript{35} Both mechanisms result in a larger incremental compressive stress with increasing adatom energy, as achieved by lowering the Ar pressure (thus decreasing the number of collisions in their path from the target to the substrate; see above).

Compressive stress generation by the diffusion of Cu into film grain boundaries also rationalizes the observed post-deposition stress relaxation of the Cu films. Namely, the chemical potential gradient at the film surface is lowered as soon as the deposition is interrupted; the driving force can, thus, be reversed, driving the incorporated grain-boundary adatoms back to the film surface, resulting in the relief of compressive film stress. Pletea et al., instead, attributed the post-deposition stress relaxation to the movement of dislocations.

The films grown at higher pressures, i.e., at 1.333, 2, and 2.667 Pa, only exhibit an incremental compressive stress during the onset of the post-coalescence stage (i.e., following the tensile maximum obtained during the coalescence stage). Subsequently, the slope of the stress-thickness curve becomes reversed due to the generation of incremental tensile stress. The reversal in incremental film stress from compressive to tensile for relatively high Ar pressures during the post-coalescence stage has also been documented by Pletea et al.\textsuperscript{46} and Navid et al.\textsuperscript{35} A possible explanation for this striking phenomenon has been given by Yu and Thompson,\textsuperscript{47} attributing the compressive-to-tensile stress turnaround to grain coarsening during the post-coalescence stage. Grain coarsening during film thickening reduces the grain boundary density and thereby the number of sinks for surface adatoms to lower their chemical potential, thus suppressing the generation of compressive stresses.

Stress turnaround can find another explanation in those films that grow according to the zone T of Thornton’s model.\textsuperscript{11} Indeed, the growth of these films is characterized by an overgrowth of some grains, which can successively coalesce, thus introducing a second tensile stage. Figure 4 can help to visualize this mechanism.
The first stages of the growth of films belonging to the zone T are analogous to those of other films’ growth, i.e., grains nucleation and coalescence. The coalescence in the first stage is marked with red dashed circles in the figure and is responsible of tensile stress at the beginning until the tensile peak. Subsequently, compressive stress generation mechanisms cause the negative slopes observed in depositions at 1.333, 2, and 2.667 Pa. However, zone T films differ from other films because some grains grow faster than others. The preferential growth is determined by the energetically more favorable crystallographic orientation of some grains, which then exhibit a faster growth rate. Eventually, these grains can shade other slower grains, blocking their growth. Upon further thickening of the film, the overgrown grains zip with each others, hence causing a second coalescence stage. This second coalescence stage is marked with solid blue lines in Fig. 4 and is responsible of tensile stress generation, causing a minimum in stress-thickness curves, which then continue toward tensile values. This mechanism would still comply with the proposition by Yu and Thompson, since subsequent adatoms arriving at the film surface would experience a lower accessible number of grain boundaries for inward diffusion and compressive stress generation.

As already noticed, tensile stress is measured in films deposited at higher Ar-pressures, i.e., 1.333, 2, and 2.667 Pa [see Fig. 3(a)]. Indeed, at high Ar-pressures, the mean energy of adatoms decreases because of scattering with Ar atoms or ions. Less adatom energy implies less surface mobility and less diffusion into grain boundaries, hence favoring the tensile stress. However, the highest tensile stress is measured in the film deposited at 2 Pa not at 2.667 Pa. Indeed, when the pressure is further increased, surface roughness and film porosity may develop because of inter-columnar voids formation. The change in microstructure can then also influence the build-up of a higher tensile stress. Moreover, a maximum achievable tensile stress is somehow expected as stress cannot diverge indefinitely as the pressure is increased. Indeed, at very high Ar-pressures, the adatoms mobility and the growth rate are very low, hence favoring the development of a disordered microstructure, characterized by small grains, voids, and Ar and O interstitials. All these structural defects offer to the film many opportunities to relax its stress state, consequently hindering stress build-up. In this work, a pressure of 2.667 Pa appears to be analogous to those of other films with the two methods are similar, being both close to zero. This is attributed to post-deposition stress relaxation. In Fig. 3(b), the stress-thickness curves are shown for three depositions performed at a constant Ar pressure of 2 Pa and target powers of 80 and 150 W as well as for two depositions at a constant pressure of 2 Pa and target powers of 80 and 150 W. It follows that all the films grown at a constant Ar pressure of 0.267 Pa develop a compressive stress state, whereas the films grown at a constant pressure of 2 Pa result in a tensile stress state. This indicates that for Cu thin-film deposition, a variation of Ar pressure has a much larger impact on the stress evolution than a proportional change of the applied power of similar magnitude.

All the Cu films grown in this study develop a [111] out-of-plane texture, according to the energetically preferred [111] growth direction of fcc metals. The measured Cu(111) Bragg peak for a compressive and tensile state of the Cu film is compared in Fig. 5 (for a Cu film thickness of 50 nm grown with a target power of 80 W and an Ar pressure of 0.267 and 2 Pa, respectively). Despite the different growth conditions and the opposite stress states generated during deposition, the (111) peak position is identical for the two films and very close to its theoretical value for the strain-free bulk Cu metal. The ex situ stress analysis of both the Cu films with the CGM method indicates a slightly tensile stress state, despite the different deposition conditions and the different stress generated during the film growth. This is explained by the observed stress relaxation of Cu films after growth interruption, as exemplified in the inset of Fig. 5. In Table II, the stress values from curvature and XRD are compared. In this case, the stresses derived with the two methods are similar, being both close to zero. This is due to, as aforementioned, to stress relaxation occurring after stopping Cu deposition (i.e., growth interruption).

### C. Application to Cu/W nanomultilayers

With the knowledge acquired on the stress evolution of W and Cu metal films, Cu/W nanomultilayers (NML) were fabricated. They are constituted of 10 repetitions of a Cu/W bilayer unit with individual Cu and W layer thicknesses of 10 nm: see Fig. 6.

<table>
<thead>
<tr>
<th>Material</th>
<th>σ_{SC} (GPa)</th>
<th>σ_{XRD} (GPa)</th>
</tr>
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<tbody>
<tr>
<td>Cu compressive</td>
<td>−0.04 ± 0.02</td>
<td>0.17 ± 0.06</td>
</tr>
<tr>
<td>Cu tensile</td>
<td>0.05 ± 0.02</td>
<td>0.18 ± 0.07</td>
</tr>
</tbody>
</table>

FIG. 5. (111) Bragg peaks acquired by XRD for 50-nm-thick Cu films as grown under conditions that develop a compressive (0.267 Pa) and a tensile (2 Pa) stress state during deposition. In the inset, an example of the substrate curvature measured during and after deposition is shown, indicating pronounced post-deposition stress relaxation.
The substrate is the same as used for the single Cu and W films, i.e., a 200μm-thick Si(100) (square 1 × 1 cm²) wafer with a 90 nm a-SiNₓ barrier layer and a 25 nm W buffer layer (as freshly deposited prior to NML deposition). The alternating depositions of a 10-nm-thick Cu layer and a 10-nm-thick W layer were performed at an Ar-pressure of 0.533 Pa and a power of 80 W. These specific conditions were chosen because they combine compressive Cu with tensile W (from pure single layer deposition shown before) in the attempt to achieve an almost stress-free NML. However, by simply considering the in-plane lattice mismatch between the bulk Cu [111][10-1] and W[110][00-1], Cu is expected to be always under high tensile stress (>20%). The stress-evolution of the corresponding NML is shown in Fig. 7. In line with our previous W thin film study [see Fig. 1(a)], the W buffer layer that forms directly on a-SiNₓ develops a tensile stress state. On the contrary, deposition of a 10-nm-thick W layer on a previously deposited 10-nm-thick Cu layer results in the generation of compressive stress. Only the onset of each deposition step of W on Cu induces incremental tensile stress (σ = 5 GPa); further growth results in incremental compressive stress (σ = −1.6 GPa). As discussed above, tensile stress generation during VW growth of type I metals can be attributed to grain coalescence, whereas subsequent incremental compressive stress arises from atomic peening. Strikingly, the tensile maximum is reached much faster for W deposited on Cu (i.e., at around 1–2 nm) than for W deposited on a-SiNₓ (i.e., at around 5–10 nm). From a kinetic viewpoint, the atomic mobility of W adatoms on the Cu surface may be lower than that of W on the a-SiNₓ surface, which promotes island nucleation and grain coalescence, resulting in a shorter precoalescence stage. Alternatively, a purely thermodynamic explanation may be given, as follows. It may be assumed that W surface adatoms preferentially condense on step edges of the previously deposited Cu layer, which obscures the precoalescence stage associated with (isolated) island nucleation and growth (see Introduction), especially if the surface of the previously deposited Cu layers is pretty rough. Indeed, an initial precoalescence stage associated with incremental compressive stress is not observed for the deposition of W on Cu [note: it has been observed for the deposition of W on the atomically flat a-SiNₓ, see Fig. 1(a)]. Moreover, if the sum of the surface energies of Cu and W is higher than the Cu/W interface energy (both per unit area), an overall increase in Cu/W interface area at the expense of Cu and/or W surface area will be energetically preferred. Consequently, W film coalescence will be promoted on the rough Cu surface as compared to the atomically flat a-SiNₓ surface, generating tensile stress (similar to the aforementioned grain-boundary “zipping” mechanism). An analogous explanation has been given for Cu/Ag multilayers where new grains nucleating on an underlying polycrystalline layer zip with previously deposited grains, generating tensile stress. Hence, the different stress evolutions for W on a-SiNₓ and polycrystalline Cu suggest that the “superposition principle” is not valid in nanomultilayer films. In other words, the dependence of growth stress on deposition parameters for single metal films cannot be directly transferred to tune the stress evolution in the corresponding multilayer structures.

Looking at the stress-thickness data acquired during the depositions of Cu layers, it is clear that the deposition of Cu on previously deposited W layers does not affect the overall substrate curvature, with a measured incremental stress of σ = 0.01 GPa. W is much stiffer than Cu (Young’s moduli are E_W = 407 GPa and E_Cu = 128 GPa) and, consequently, the thickening Cu layer cannot deform the underlying W/Cu stack and simply accommodates on it. However, a constant substrate curvature during growth does not imply a zero incremental stress. Namely, if the stack thickness, h, increases, σ must decrease in order to keep the product σ × h constant. In other words, the compressive stress of the substrate/NML assembly, on average, relaxes a little bit by tensile stress generation during the Cu layer deposition step. This also explains why, in these deposition conditions, the Cu does not grow with compressive stress, as expected from single-layer results, but the presence of the W interface hinders the building up of compressive stress.
In Fig. 8, a θ-2θ scan of the deposited Cu10 nm/W10 nm NML is shown (note the logarithmic scale on the y axis). Evidently, the NML grows with a preferential [110] out-of-plane texture for W and a preferential [111] out-of-plane texture for Cu (as for the single metal films). However, the (002) peak of Cu and the (211) peak of W can still be detected, which suggest a small, but distinct, randomly oriented polycrystalline contribution. The inset shows a zoom of W(110) and Cu(111) reflections in the 2-theta range between 36° and 45°. Some modulations in the diffractogram are visible; these so-called "satellite peaks" are typical of a superlattice structure, confirming the multilayered nature of our sample.51,52

Average stress values for W and Cu in the NML stack, as determined by XRD, are reported in Table III. The W layers in the NML stack exhibit an average compressive stress (despite the superimposed tensile stress in the 25-nm-thick W buffer layer underneath), in accordance with stress evolution during growth by the wafer curvature (see Fig. 7). The Cu layers have an average tensile stress state, albeit small, which is also in line with the wafer-curvature measurement.

A NML structure is characterized by a high density of interfaces, which play an important role in determining the overall stress state of the system. A general interface between two dissimilar solid phases will be associated with stress induced by the structural and/or chemical mismatch of the two solids at phase boundary plane (i.e., at the interface).53 In principle, both solids at each side of the interface can contribute to the resulting interface stress by adopting their crystal structure.54 However, as discussed above, W can be considered rigid with respect to Cu (see also Ref. 50). In this case, the interface stress can be well described by considering the reversible work per unit interface area needed to strain the softer phase (i.e., Cu) with respect to the rigid one (i.e., W). A corresponding change in the lattice parameter of the growing Cu layer can be achieved by elastic straining its crystalline lattice and/or by changing its misfit dislocation density at the interface.54 For a coherent (i.e., epitaxial) crystalline–crystalline interface, all lattice mismatch is accommodated fully elastically up to a certain critical layer thickness, commonly referred to as coherency strain. However, for systems with a very high initial lattice mismatch, like Cu [111][01-1] / W[110][-1-1] interface (1% along the a axis and 22% along the b axis),52 it is impossible to accommodate the interfacial lattice mismatch fully elastically, even for very small Cu layer thicknesses. Moreover, it is clear that in the Cu/W case, the mismatch is also anisotropic along the in-plane directions. It may, thus, be assumed that the lattice mismatch strain of the Cu/W interface is predominantly relaxed by creating a network of interfacial misfit dislocations in the growing Cu layer. The resulting interface stress then corresponds to the specific work associated with the change of the dislocation density in the Cu layer to relax the theoretical coherency strain originating from the initial mismatch between the as-deposited W layer and the unstrained Cu phase at the Cu/W interface.53,54 Here, it is noted that the as-deposited W layer may already contain "kinetically frozen" intrinsic growth strain depending on deposition conditions (see above), thereby affecting the resulting Cu/W interface stress. According to Ruud et al.,53,54 the average interface stress is proportional to the difference between the average stresses determined by XRD and from substrate curvature measurements, i.e.,

$$\sigma_{\text{SC}} - \sigma_{\text{XRD}} = \frac{2f}{\lambda}$$

where $\sigma_{\text{SC}}$ is the average stress derived from the substrate curvature and $\sigma_{\text{XRD}}$ is the average stress measured by XRD in the NML, i.e., the arithmetic average between the stress in W and Cu. For the Cu10 nm/W10 nm NML pertaining to Fig. 7, it follows that $\sigma_{\text{SC}} = -0.374 \pm 0.004$ GPa and $\sigma_{\text{XRD}} = \sigma_{\text{XRD}}(1) + \sigma_{\text{XRD}}(2) = -1.2 \pm 0.1$ GPa for a corresponding bilayer thickness $\lambda = 20.0 \pm 0.8$ nm. This results in a derived average interface stress of $f = 7 \pm 1$ J/m², which is in very good agreement with the interface stress of $f = 11.3 \pm 0.6$ J/m², as previously reported for Cu10 nm/W10 nm NMLs grown on the sapphire substrate at an Ar pressure of 0.45 Pa and a target power of 80 W for W and 100 W for Cu.5 High interface stress levels in the Cu/W NMLs was found to obstruct the expected grooving of W/W grain boundaries upon annealing at temperatures at the base of multilayer to nanocomposite transformation.56 Strikingly, the interface stress is much lower and reverse in sign for Ag/Cu NMLs (Ag and Cu are immiscible as W and Cu): $f = -3.2 \pm 0.4$ J/m².59 The sign of the interface stress directly relates to the sign of the substrate curvature.60 A positive interface stress induces a compressive stress inside the layers, causing concave bending. A negative interface...

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**TABLE III.** Average stress, $\sigma_{\text{XRD}}$, of Cu and W in a Cu10 nm/W10 nm NML, as measured by x-ray diffraction.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\sigma_{\text{XRD}}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W</td>
<td>$-2.5 \pm 0.2$</td>
</tr>
<tr>
<td>Cu</td>
<td>$0.13 \pm 0.1$</td>
</tr>
</tbody>
</table>

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stress induces a tensile stress inside the layers, causing convex bending. In summary, the overall stress state of the NML stack is governed by stiffer W layers. Hence, the intrinsic stress state in Cu/W NMLs, including the associated interface stresses, can only be effectively tailored by adjusting the stress in successively deposited W layers. Further research is ongoing to investigate in more detail whether the interface stress in Cu/W NMLs can be controlled by tuning the intrinsic stress in the individual W layers (using our knowledge on stress evolution of the single W films).

IV. CONCLUSIONS

The effect of the Ar-pressure and the applied power on the stress evolution in W and Cu thin films grown by DC magnetron sputtering has been investigated. It follows that a low Ar-pressure and a high power favor the development of compressive intrinsic stress, as more energetic adatoms arrive at the surface of the growing film, triggering atomic diffusion into grain boundaries (relevant mainly for Cu due to its relatively high atomic mobility) and/or atomic peening (more important in W due to its relatively low atomic mobility). Vice versa, for less energetic adatoms, as favored at high Ar-pressure and low applied power, these stress generation mechanisms are suppressed and the resulting thin films develop a tensile stress state. For Cu/W multilayers grown under similar conditions as their single film variants, the stress evolution is governed by the intrinsic stress in the successively deposited W layers. The stress in the softer Cu layers simply adapts to the stress state of the more rigid W layer underneath, resulting in a large interface stress contribution. The pre-coalescence stage is obsolete during NML deposition, as attributed to the preferred nucleation of new phase on step edges of the previously deposited layer (thus preventing isolated island formation and their subsequent coalescence). Consequently, the coalescence tensile stage is shorted as compared to single layer growth under similar conditions. Moreover, the resulting average stress state of W in the Cu/W NML is opposite to the one found for single W thin films (compressive instead of tensile). The respective interface stress contribution was determined from the difference in the average stress values, as determined by XRD (for both W and Cu) and by substrate curvature (for the substrate/overlayer system). The interface stress value is governed by the intrinsic stress in the successively deposited W layers. The stress in the softer Cu layers simply adapts to the stress state of the more rigid W layer underneath, resulting in a large interface stress contribution. The pre-coalescence stage is obsolete during NML deposition, as attributed to the preferred nucleation of new phase on step edges of the previously deposited layer (thus preventing isolated island formation and their subsequent coalescence). Consequently, the coalescence tensile stage is shortened as compared to single layer growth under similar conditions. Moreover, the resulting average stress state of W in the Cu/W NML is opposite to the one found for single W thin films (compressive instead of tensile). The respective interface stress contribution was determined from the difference in the average stress values, as determined by XRD (for both W and Cu) and by substrate curvature (for the substrate/overlayer system). The interface stress value is determined by XRD (for both W and Cu) and by substrate curvature (for the substrate/overlayer system). The interface stress value is determined from the difference in the average stress values, as determined by XRD (for both W and Cu) and by substrate curvature (for the substrate/overlayer system). The interface stress value is determined from the difference in the average stress values, as determined by XRD (for both W and Cu) and by substrate curvature (for the substrate/overlayer system). The interface stress value is determined from the difference in the average stress values, as determined by XRD (for both W and Cu) and by substrate curvature (for the substrate/overlayer system).

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are openly available in Zenodo at http://doi.org/10.5281/zenodo.6539318, Ref. 60.

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