The effect of thermal treatment on the stress state and evolving microstructure of Cu/W nano-multilayers

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The functionality and reliability of nano-multilayered devices and components are largely affected by the stress evolution during fabrication, processing, and operation. The impact of thermal treatment on the stress state and evolving microstructure of Cu/W nano-multilayers, as deposited on different substrates (i.e., Si(001), Al₂O₃-C, and Al₂O₃-R) by magnetron sputtering, was investigated by *in-situ* high temperature X-ray diffraction and high-resolution scanning electron microscopy. The as-deposited Cu and W nanolayers exhibit an out-of-plane orientation relationship according to Cu $\langle 111 \rangle \parallel$ W $\langle 110 \rangle$. On the Al₂O₃-C and Al₂O₃-R substrates, the Cu/W nanomultilayers also develop a pronounced in-plane texture given by Cu $\{111\}\langle 10\bar{1} \rangle \parallel$ W $\{110\}\langle 00\bar{1} \rangle$. The stress state of the Cu nanolayers in the as-deposited state and upon heating, investigated *ex-situ*, is largely imposed by the accumulated stresses in the much stiffer W nanolayers. In the as-deposited state, the W nanolayers exhibit a much larger in-plane compressive stress than the Cu nanolayers (i.e., -3.5 GPa versus -1.5 GPa), which both mainly originate from growth stresses generated during the deposition process. The growth stresses in the as-deposited Cu nanolayers are relaxed after annealing at 500°C . Relief of compressive stresses in the W nanolayers is accompanied by grain coarsening which only occurs upon degradation of the nano-multilayered structure. The degradation of the periodic layer structure proceeds in the range of $750 - 900^\circ\text{C}$ and is independent of the substrate.

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I. INTRODUCTION

Multilayered architectures, which comprise a periodic alternation of different single- or multiple-elemental layers, are a versatile and promising route to tailor the properties and/or durability of functional materials in various application areas, such as those related to optical, magnetic, and electronic devices, tribology, and mechanical engineering.¹ If the thicknesses of the alternating layers are reduced to the nano-scale, the resulting properties will be governed not only by the combined properties of the individual layers constituents but in particular, also by the structural, physical, and chemical characteristics of the internal interfaces, which include both phase and grain boundaries.² The combination of nano-confinement and interfacial effects in such nano-multilayered (NML) systems may be exploited to optimize specific material properties, such as mechanical strength, reflectivity, pre-melting or superheating behavior, or corrosion resistance.³ However, NML architectures are intrinsically thermodynamically unstable and typically exhibit large residual stresses, which may deteriorate their long-term stability under harsh operation conditions (e.g., elevated temperatures, complex loading conditions).⁴

NML architectures can be straightforwardly synthesized by Physical Vapor Deposition (PVD) techniques with precise control of, e.g., individual layer thicknesses, modulation periodicity, and chemical composition. The PVD process parameters constitute a “palette for the materials scientist” to

tailor the materials properties down to the nanometer scale.^{5,6} Magnetron-Sputtering (MS) is one of the most common non-equilibrium PVD growth methods. The MS parameters, such as target power, pressure, and substrate bias, can be effectively varied to tailor the microstructure (i.e., layer morphology, interface structure, defect density, growth stresses) and thereby the functional properties.⁷ For most applications (optoelectronics, magnetism, etc.), it is highly desirable to design NMLs with atomically sharp interfaces and limited residual growth stresses to ensure device reliability. However, in specific cases, the stress state in MS layers can also be exploited, for example, to induce the preferred magnetization direction,⁸ or in the case of epitaxial stress, to adjust the bandgap of semiconductors.⁹ Elastic anomalies in NMLs are generally correlated with the extreme strain states of the layer constituents due to interfacial stress.^{7,10} NML-based devices and components, which are subjected to thermo-mechanical loading during processing and/or service, require an in-depth understanding of the evolution of thermal stresses and microstructural transformations during heating to ensure their long-term durability. Depending on the as-deposited microstructure, complex stress gradients with localized intensity maxima at the internal interfaces may arise during heating.¹¹

Cu/W nano-composites and NMLs have received increasing interest in the last decade.^{12–14} The high thermal conductivity of Cu and the low thermal expansion coefficient of W make Cu-W composites attractive for thermal management applications. The Cu-W system is highly immiscible due to the different crystal structures of Cu and W (fcc vs. bcc), their lattice parameter mismatch (15% difference), and

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their positive mixing enthalpy (+36 kJ).¹⁵ Hardness and mechanical properties of Cu/W NMLs were found to be dependent on the multilayer period. Thermal treatment of Cu/W architectures above 200 °C results in a drastic reduction of the hardness.¹⁴ The breaking of the NML periodic structure at high temperature has been investigated by means of Scanning Electron Microscopy (SEM) and X-ray diffraction (XRD).¹⁶ The thermal degradation of the Cu/W NML's structure into a nanocomposite structure was found to be rate-determined by W diffusion along internal interfaces (i.e., grain- and phase-boundaries). However, the role of intrinsic (growth) and thermally induced stresses in the NML degradation upon heating is not yet clarified. Elastic properties of W in Cu/W multilayers have been investigated in the past,¹⁷ finding unusually high values for the stress tensor. The high compressive stress state in W was attributed to an interfacial effect.¹⁸ For Cu/W multilayers, the level of growth stress in the constituent layers (i.e., in the as-deposited state) can be very different. The in-plane stress in the W layers is always highly compressive (up to −5 GPa), independently of the thickness and layer period.^{12,17,19} On the contrary, the alternating Cu layers were seen to exhibit different stress states in the range from −0.5 to +2.8 GPa (i.e., from compressive to highly tensile), depending on the thickness and on the deposition conditions.²⁰ Notably, the substrate can also influence the stress state of the multilayer. A systematic and comprehensive study on the impact of thermal treatments on the internal stress state and evolving microstructure in Cu/W NML on different substrates is still missing, but of fundamental and technological interest. Most importantly, not only the average stress state in the Cu/W NML but also the stress levels in the individual Cu and W nanolayers should be monitored as a function of the heating temperature. XRD provides a powerful method to independently determine both the microstructural characteristics (e.g., phase constitution, texture, and grain size) and the residual stress states of each multilayer constituent independently (in our case Cu and W). In the following, the microstructure of Cu/W NMLs as deposited on different substrates by MS is accessed by *in-situ* high temperature XRD (HT-XRD) and high resolution SEM (in planar and cross sectional view). Moreover, the change in the stress state and the structure imposed during heat treatment from room temperature (RT) up to 900 °C is revealed.

II. EXPERIMENTAL METHODS

A. Sample preparation

Cu/W NMLs were deposited on 2 in. epi-polished α -Al₂O₃ and Si single-crystalline substrates (sapphire-R (1 $\bar{1}$ 02), sapphire-C (0001), and Si (001) +15 nm of Si₃N₄ wafers, see Table I) by DC unbalanced magnetron sputtering in a high vacuum chamber (base pressure <10^{−8} mbar) from two 2 in. targets of pure W (99.95%) and Cu (99.99%) confocally arranged and operated at 200 W. The insertion of the Si₃N₄ layer before W deposition prevents the formation of tungsten silicide observed when W is grown directly on the Si substrate.²¹ Before insertion in the deposition apparatus, the sapphire substrates were ultrasonically cleaned using acetone and

TABLE I. Substrates and layers orientations (in NML) and thermal coefficients.^{22,23}

Material	Bulk thermal coefficients (10 ^{−6} / K)	Orientation
Al ₂ O ₃ -R substrate	8	(1 $\bar{1}$ 02)
Al ₂ O ₃ -C substrate	8	(0001)
Si substrate	2.49	(001)
Cu	16.5	(111)
W	4.3	(110)

ethanol. Prior to deposition, possible surface contaminant on the α -Al₂O₃ substrates (mostly adventitious carbon) was removed by Ar⁺ sputter cleaning for 5 min applying a RF bias of 100 V. First, a 25 nm-thick W buffer layer was deposited on the sputter-cleaned substrate. Next, 100 repetitions of alternating Cu and W layers with an individual (nominal) thickness of 5 nm were deposited on top. For the stress measurements, the as-prepared samples were isothermally annealed *ex-situ* at different temperatures (400, 500, 600, 650, 700, 750, and 800 °C) for 100 min in a vacuum (<10^{−5} mbar).

B. XRD

The Bruker D8 Discover X-ray diffractometer, operated in Bragg-Brentano geometry, was applied to measure 2-theta (2 θ) scans and stress state for the as-deposited and annealed samples. To access the texture, pole figures of Cu <111> and W <110> family of planes were recorded on samples grown on different substrates. Stress and texture measurements were recorded at RT on *ex-situ* annealed samples. HT-XRD experiments were performed with a PANalytical X'Pert PRO MPD X-ray diffractometer with a gas-tight Anton Paar XRK-900 heating chamber equipped for heating and gas feeding (5850 TR, Brooks instrument), applying a H₂/N₂(g) gas mixture of 5 vol. % H₂ (99.999%, Messer) in N₂ (99.999%, Messer) at a flow rate of 100 ml/min. Diffraction patterns (2 θ range of 10°–90° step size of 0.026°; using Cu K $\alpha_{1,2}$ radiation, at 40 kV and 40 mA) were recorded during heating and cooling (from RT to 900 °C and back). To enhance the surface sensitivity (i.e., to increase the signal contribution from the top layers of the NML), separate Grazing Incidence XRD (GI-XRD) measurements were performed applying the same thermal ramp, while fixing the incidence angle at 10° and recording the entire diffractograms from 20° – 80°. For more details on the measurement geometries of the XRD experiments, see [supplementary material](#).

C. SEM analysis

High-resolution SEM analysis was performed in plain and in cross sectional views using a Hitachi S-4800 instrument equipped with a Bruker XFlash 6|60 energy dispersive X-ray (EDX) detector. Cross-sectional cuts were prepared by using a Hitachi IM4000 Ar ion milling system applying an acceleration voltage of 6 kV, a discharge voltage of 1.5 kV, and a swing angle of $\pm 30^\circ$.

D. Residual stress analysis

The most common XRD method for stress-analysis is the so-called $\sin^2 \psi$ method,²⁴ which is based on the

variation of the diffraction peak position with $\sin^2 \psi$, ψ being the angle between the normal to the diffracting planes and the surface normal (see [supplementary material](#)). However, for highly textured materials (as is the case for the studied NMLs), the so-called Crystallite-Group Method (CGM) is more appropriate.²⁵ The CGM is a special case of the $\sin^2 \psi$ technique. It differs mainly in the fact that it explicitly takes into account the texture of the sample, rather than using X-ray elastic constants to account for the geometrical distribution of the crystallites. It also assumes that on average every crystallite (having the same orientation) is exposed to the same stress. Elastic analysis via Hookes law relates the strain to the stress tensor (and vice versa) through stiffness or compliance tensors.^{26,27} In the case of textured films, it is assumed that all crystallites having the same orientation form a unique crystal. This implies that every crystallite shows the same stress state (Reuss averaging scheme). Due to its specific geometry, a thin film deposited onto a substrate is free to expand or contract along the film normal direction. Thus, the stress in this direction and shear components that involve the normal direction are equal to zero ($\sigma_{33} = \sigma_{13} = \sigma_{23} = 0$). Moreover, an equal-biaxial stress state is often observed ($\sigma = \sigma_{11} = \sigma_{22}$), consequently all in-plane shear components are also zero. Hence, uniaxial stress and rotational symmetry have been assumed for the Cu layers and the $\{111\}\langle 2\bar{1}1 \rangle$ CGM was used to determine the stress. The W interlayers contain a distinct polycrystalline component (besides the textured component; see Sec. III) and therefore both methods have been applied to determine the respective stress state: i.e., the $\sin^2 \psi$ analysis was performed on the basis of the (211) reflection, where the CGM was performed on the basis of the $\{110\}\langle \bar{1}12 \rangle$ group of reflections. The stress values for W, as presented in Sec. III, refer to the CGM only, although similar values (within the error bars) have been found with the $\sin^2 \psi$ method, see [supplementary material](#) for details. This result is indeed expected for α -W because it is elastically isotropic.

III. RESULTS AND DISCUSSION

A. XRD analysis of the as-deposited Cu/W NMLs

The W $\{110\}$ and Cu $\{111\}$ pole figures, as measured from the Cu/W NMLs deposited on the Al_2O_3 -C, -R and Si(001)/ $[\text{Si}_3\text{N}_4]_{15\text{nm}}$ substrates, are given in Fig. 1. The common central peak at $\psi = 0^\circ$ corresponds to the preferential growth direction of $[111]$ for Cu and $[110]$ for W. For all three substrates, a ring of maximum intensity occurs at $\psi = 60^\circ$ for W (corresponding to the angles between the

W(110) and W(011) planes) and at $\psi = 70.53^\circ$ for Cu (corresponding to the angles between for the Cu(111) and Cu(11 $\bar{1}$)). This implies that all the NMLs exhibit the same out-of-plane orientation relationship according to $\text{Cu}\{111\} \parallel \text{W}\{110\}$ independently of the type of substrate. This is expected, since the Cu $\{111\}$ and W $\{110\}$ planes constitute the most densely packed planes of lowest surface energy. For the NMLs deposited on sapphire substrates (-C and -R), the intensity rings at $\psi = 60^\circ$ for W and $\psi = 70.53^\circ$ for Cu exhibit 6 high intensity poles: see Figs. 1(a) and 1(b), respectively. This denotes a coherent interface between Cu and W with a crystallographic orientation relationship according to: $\text{Cu}\{111\}\langle 10\bar{1} \rangle \parallel \text{W}\{110\}\langle 00\bar{1} \rangle$. Moreover, 3 additional poles at $\psi \sim 35.3^\circ$ and 4 poles at $\psi \sim 45^\circ$ are clearly distinguishable in Figs. 1(a) and 1(b), respectively, as indicated with white arrows. This weaker, second texture component arises from the epitaxial relationship of the first 25 nm thick W layer in contact with the single-crystalline Al_2O_3 substrate. Consequently, the W buffer layer does not develop a $\{110\}$ out-of-plane texture, like the subsequently deposited W nanolayers on Cu. The W layer directly in contact with the substrate presents a $\{111\}$ out-of-plane texture on the 6-fold symmetric Al_2O_3 -C surface and a $\{100\}$ out-of-plane texture on 4-fold symmetric Al_2O_3 -R surface.^{28,29} Subsequent growth of Cu and W nanolayers on the first epitaxial W buffer layer then proceeds along the preferred directions of $[111]$ for Cu and $[110]$ for W (corresponding to the most densely packed planes of lowest surface energy) and results in the same in-plane texture of the Cu/W NML on Al_2O_3 -C and Al_2O_3 -R (see above). The Si(001) substrate is covered with an (predominantly) amorphous Si_3N_4 buffer layer, which hinders the formation of a preferred crystallographic orientation relationship between the single-crystalline substrate and the 25 nm-thick W bottom layer during growth. Consequently, the subsequent W and Cu layers do not inherit a distinct in-plane texture during growth, resulting in a fiber-texture or random in-plane orientation.¹³

B. Microstructure of the as-deposited and heat-treated Cu/W NMLs by SEM

SEM micrographs of the as-deposited and heat-treated NML are shown in Fig. 2, both in plain and cross-sectional views. The surface of the as-deposited NMLs is very uniform and exhibits a grain-like morphology (as originating from the waviness of the deposited nanolayers; see Ref. 16) with no evidence of cracks, voids, and/or delaminations (Fig. 2(a)). In the cross-sectional view, the 25 nm thick W bottom layer and the periodicity of the alternating Cu/W layers with individual (nominal) thicknesses of 5 nm each are clearly resolved (Fig. 2(b)). The deposited nanolayers are relatively uniform in thickness adjacent to the substrate but become less uniform in thickness (i.e., wavier) towards the surface. The surface morphology (in planar view, Fig. 2(c)) and layered structure (in cross-sectional view, Fig. 2(d)) of the Cu/W NML are largely changed after the temperature treatment up to 900°C , see Figs. 2(c) and 2(d). First, the original stratified structure has completely degraded into a nanocomposite structure, consisting of globular W particles embedded in a

FIG. 1. Pole figures of W $\{110\}$ and Cu $\{111\}$ on (a) Al_2O_3 -C, (b) Al_2O_3 -R, and (c) Si substrates. The white arrows indicate the second W(111) and W(100) orientations present in Al_2O_3 -C and -R substrates, respectively.

FIG. 2. Typical (a) planar and (b) cross-sectional SEM images of a Cu/W multilayer in the as deposited state. (c) Planar and (d) cross-sectional SEM images of similar sample after HT-XRD (after 900 °C thermal ramp). In the insets in (a) is shown a magnified section of the top most surface. The inset in (b) is a magnified section of a faceted particle.

Cu matrix (Fig. 2(d)). Second, the originally smooth NML surface has been partially covered by faceted protrusions. EDX analysis (not shown here) revealed that the individual surface protrusions mainly consist of Cu, in accord with Ref. 16. The outward migration of Cu from the NML interior to the outer surface, forming faceted nanocrystallites, is attributed to a stress-assisted driving mechanism, as discussed in the following.

C. HT-XRD analysis of the Cu/W NMLs during heating

The measured 2θ -scans in the selected range from 30° to 48°, as recorded from the NMLs during heating up to 900 °C and during subsequent cooling to RT, are shown in Fig. 3. The intensity modulation in the XRD pattern, also indicated as satellite peaks, is characteristic for periodic layer structures as multilayers.³⁰ The satellite peaks are compatible with calculated diffractograms of a superlattice exhibiting Cu{111} and W{110} textures: see Ref. 16 for details. The evolution of

the satellite peaks as a function of temperature is displayed in Fig. 3. Despite the different textures of the first W buffer layer and the subsequently deposited Cu/W NML sequence, the diffracted intensity modulation (typical of an ordered periodic structure in the as-deposited state) vanishes completely during heating in the temperature range between 750 and 900 °C, independently of the parent substrate (see Fig. 3).

This is indeed an unexpected and surprising result recognizing that the different substrates not only induce different textures of the deposited NML (see Sec. III A) but also possess different thermal expansion coefficients (see Table I). The thermal expansion coefficient of Al₂O₃ is almost a factor of 3 larger than that of Si. Nevertheless, NML degradation takes place in the same temperature range for all studied substrates, which suggests that the degradation of the NML structure upon annealing is not governed by thermally induced stresses due to the thermal expansion mismatch between the substrate and the NML; i.e., other mechanisms such as internal stresses should be called into play.

FIG. 3. HT-XRD measurements on (a) Al₂O₃-C, (b) Al₂O₃-R, and (c) Si substrates. The arrows indicate the temperatures where the degradation of the multilayer structure occurs.

FIG. 4. *In-situ* high temperature GI-XRD pattern of Cu/W multilayers. The temperatures are indicated on the right axis. The peak of Cu (200) appears at a temperature of $\sim 750^\circ\text{C}$ indicated with a star (*).

Various possible explanations for multilayer degradation occurring at elevated temperatures have been proposed.³¹ For immiscible systems like Cu and W, capillary forces can drive layer recession to reduce the (excess) Gibbs energies associated with internal interfaces (i.e., phase and grain boundaries). Thermal grooving of grain boundaries initiates layer pinch-off when the upper and lower grooves of the same grain boundary merge. In Ref. 16, the pinching of the W-layer by Cu is indeed observed. Stress effects are thought to play an important role in determining such morphological instabilities of multilayers.³² In particular, the lattice misfits at incoherent and semicoherent interfaces between phase A and B in an A/B NML can induce coherency stresses within the alternating nanolayers in the GPa range. Internal stresses can also have a dramatic effect on the directional coarsening of precipitates in alloys. The evolution of the residual stresses upon thermal treatment of Cu and W layers will be presented in Sec. III D.

The NMLs grown on Si and $\text{Al}_2\text{O}_3\text{-R}$ substrates were also analyzed during heating and subsequent cooling by *in-situ* high temperature GI-XRD (see Fig. 4). The as-deposited NMLs on the $\text{Al}_2\text{O}_3\text{-C}$ and $\text{Al}_2\text{O}_3\text{-R}$ exhibit similar textures

and therefore only the $\text{Al}_2\text{O}_3\text{-R}$ was chosen for a comparison with Si. The temperature range of $750 - 900^\circ\text{C}$ for NML degradation during heating is confirmed by the GI-XRD analysis. Despite the strong textures of the W and Cu layers, a weak polycrystalline component is detected in the *in-situ* GI diffractograms of the Cu/W NMLs, as associated with the W(211) reflection. Other W reflections (i.e., except for W(110) and W(211)) are too weak to be detected. Strikingly, the disappearance of the satellite structure coincides with the appearance of the Cu(200) reflection, as attributed to the outflow of confined Cu from the interior of the NML to the outer surface, forming Cu crystals with a random in-plane orientation (resulting in a polycrystalline texture): see Sec. II C and related discussion in Ref. 16. The average grain size of W, as estimated from the FWHM (using the Scherrer formula) of the W(211) peak, is plotted as a function of temperature in Fig. 5(a). It follows that NML degradation with Cu outward migration is accompanied by abrupt grain coarsening of W in the range of $750 - 900^\circ\text{C}$. The resulting W grain size remains nearly constant during subsequent cooling down to RT. The relative change of the W(211) plane spacing ($d_{(211)}$) with respect to the bulk spacing (d_0), i.e. $(d_{(211)} - d_0)/d_0$, is shown in Fig. 5(b). It follows that the lattice expansion does not follow an ideal thermoelastic behavior during heating; i.e., irreversible plastic deformation occurs during heating. The lattice expansion follows the expected nominal slope upon cooling from 900°C to RT.

D. Stress analysis of the Cu/W NMLs after thermal treatments

The average residual stress in the Cu and W layers on $\text{Al}_2\text{O}_3\text{-R}$ and Si substrates, as determined by the CGM (see Sec. II D), is plotted as a function of the annealing temperature in Fig. 6(a). In the as-deposited state, the Cu and W nanolayers possess a large compressive average in-plane stress of roughly -1.5 GPa and -3.0 GPa , respectively, on the $\text{Al}_2\text{O}_3\text{-R}$ substrate. On the Si substrate, similar values for the compressive stress have been found in Cu whereas a more pronounced compressive stress was found in W ($\sim -4\text{ GPa}$). W is much stiffer than Cu and hence the much larger compressive growth stress in the W nanolayers will be largely superimposed on the much softer Cu nanolayers. Indeed the lattice of a Cu monolayer in contact with W fully adjusts to the W lattice parameter.^{33–35} The Cu(111)/W(110) interface between the alternating W and Cu layers (corresponding to the boundary plane between the

FIG. 5. *In-situ* (a) W grain size evolution and (b) $d_{(211)}$ expansion as a function of temperature. Investigations on Si and sapphire-R substrates are shown.

FIG. 6. (a) Residual stress analysis of Cu and W layers on an Al_2O_3 -R substrate plotted as a function of the annealed temperature. The red points (circle) are the results on the same study carried out on a Si substrate. The dashed lines are guide to the eyes. Error bars are derived from the linear fit of the lattice parameter as a function of $\sin^2 \psi$. The shadowed region represents the temperature window where the Cu outflow is observed by SEM. In panel (b) and (c), corresponding SEM pictures for a 500 °C annealed samples are shown in planar and cross sectional views, respectively.

most densely packed atomic planes of W and Cu; see Sec. III A) also has the lowest energy and is thus thermodynamically preferred.³³ In accord with the above discussion, it may be assumed that any changes in the stress state of the W nanolayers during growth and subsequent heating will be largely imposed to the confined Cu nanolayers. Indeed, as reflected in region I in Fig. 6, the course of the stress evolution upon heating is *qualitatively* similar for Cu and W. The as-deposited Cu nanolayers possess an average in-plane compressive stress of -1.5 GPa, which is fully released upon heating up to 500 °C (see the regions I and II in Fig. 6(a)). The in-plane compressive stress in the as-deposited W layers is significantly larger, i.e., -3.5 GPa. It is not yet fully released upon heating up to 500 °C and the W layers still possess a large compressive stress of -2 GPa at 500 °C (see region II in Fig. 6(a)). Here, it is emphasized that the residual stresses and the corresponding SEM pictures in Fig. 6(a) were acquired at RT, i.e., after annealing. Accordingly, a stress-free state at RT not necessarily implies a stress-free state at the respective annealing temperature. However, assuming that the W nanolayers superimpose their stress on Cu and considering the relatively small thermal mismatch

between W, Si, and Al_2O_3 -R (see Table I), any additional stress contribution generated during cooling (due to the thermal mismatch) should be relatively small. The marked region II from 450 – 600 °C in Fig. 6(a) denotes the temperature range for which the thermally activated migration of Cu from the NML interior to the outer surface occurs. In Fig. 6(b), the corresponding SEM analysis taken after annealing at 500 °C clearly shows the Cu outflow on the surface, in agreement with Ref. 16, while the multilayer periodic structure is still preserved, see Fig. 6(c). As evidenced for Cu/W (and in other systems³⁶), faceted Cu particles of different geometries and sizes appear on the outer surface after annealing (cfr. Fig. 2(c) and Ref. 16). The confined W nanolayers still possess an in-plane compressive stress state up to 600 °C. Acknowledging the higher mobility and ductility of Cu as compared to W,^{37,38} the resulting local stress gradients in the NML may drive Cu from the compressive stress regions in the interior of the NML to the stress-free surface. The stress-assisted outward migration of Cu apparently becomes thermally activated at 500 °C and terminates at around 600 °C and is succeeded by a gradual breaking down of the periodic NML structure.¹⁶ As shown in Ref. 16, the gradual degradation of the Cu/W NMLs into a nanocomposite structure at $T > 750$ °C is rate-determined by the thermally activated diffusion of W along internal interfaces (i.e., grain- and phase-boundaries). As demonstrated in the present study, the gradual degradation of the NML structure at $T > 750$ °C is accompanied by an enhanced relaxation of compressive stresses in the W nanolayers (see region III in Fig. 6). The compressive stress in W is fully relaxed at around 750 °C, while the Cu nanolayers initially develop a tensile stress state of $+1$ GPa at 600 °C (presumably imposed by W; see above), which gradually relaxes to zero at 900 °C. Surprisingly, the stress evolutions of Cu and W in the Cu/W NMLs are relatively independent of the parent substrate. Small differences can be found in the absolute stress values of Cu and W measured on Si and Al_2O_3 -R substrates although the overall trend with the annealing temperature is similar. In order to rationalize this puzzling result, the origin of the in-plane stress component will be investigated, in the following.

The total average stress in the multilayer, σ_{TOT} , can be deconvoluted into the so-called coherency stress (σ_{coh}) and substrate-interaction stress (σ_{SI})^{39,55,56}

$$\langle \sigma_{TOT}^{Cu,W} \rangle = \langle \sigma_{coh}^{Cu,W} \rangle + \sigma_{SI}^{Cu,W}. \quad (1)$$

The substrate-interaction contribution originates from the superposition of intrinsic growth stresses (due to the MS deposition process) and thermal stresses (originating from the thermal expansion mismatch). Film growth by low-temperature PVD methods generally proceeds by an island-growth mode, which results in the accumulation of compressive stresses after (closed) film formation (as also observed in the present study): see Refs. 40–45,54. Moreover, when high-energetic species (backscattered neutrals, sputtered atoms or accelerated ions) are involved, as is the case in the applied MS process, additional compressive stresses can be generated due to the incorporation of defects and impurities.⁴⁶ Moreover, other kinds of defects like atomic mixing in the nanometer scale at the Cu/W interface can also be present⁴⁷ (see [supplementary material](#)). These compressive

stress contributions are related to the growth (deposition) process and thus add to the growth stress contribution in Eq. (1). In addition, large coherency stresses (several GPa) may arise at solid-solid interfaces due to the lattice mismatch between the two sub-lattices, which may partially relax by the introduction of misfit dislocations above a certain critical thickness.^{44,48} For the Cu/W NML under study, the coherency stress in the alternating Cu and W nanolayers (of the same thickness) induces equal and opposite forces into the layer, i.e.,

$$\langle \sigma_{coh}^{Cu} \rangle = -\langle \sigma_{coh}^W \rangle. \quad (2)$$

This yields to the following expression for the total average stress:

$$\langle \sigma_{TOT} \rangle = 2\sigma_{SI}^{Cu,W}. \quad (3)$$

By employing Eqs. (1)–(3), the coherency stress in the constituent layers can be derived from the measured total average in plane stress. In Fig. 7, the thus obtained values for σ_{coh} for Cu and W are plotted as a function of the annealing temperature. A comparison of the values for the total stress and the coherency stress in W and Cu (i.e., compare Figs. 6 and 7, respectively) indicates that the σ_{coh} is significantly smaller than the total stress and, consequently, σ_{SI} is the dominant contribution to the total stress. Again assuming that the W nanolayers superimpose their stress on Cu and considering the relatively small thermal mismatch between W, Si, and sapphire (see above), it follows that σ_{SI} is dominated by the growth stress contribution (see Eq. (1)). Coherency stresses in the individual layers are thought to facilitate the degradation process, thereby lowering the effective activation temperature.^{31,49} In our findings, the contribution from coherency stresses is found to be smaller than that from growth stress and also similar on Si and sapphire substrates, in accordance with the experimental observation that NML degradation occurs within the same temperature range for the different substrates considered.

FIG. 7. Average coherency stress evolution for W and Cu sublayers grown on Si and Al₂O₃-R substrates. The lines are guides to the eye.

Finally, it is remarked that the conditions of the magnetron sputter process can be exploited to tailor the sputter-deposited microstructure (e.g., grain size, thickness, dislocation density, and point defects) and thereby the residual growth stress level.^{50–56} Different growth stress levels in the Cu/W NMLs may shift the thermal activation and rate kinetics of the NML degradation process, which would open new routes for microstructural engineering of NML systems for a broad range of applications.

IV. CONCLUSIONS

The impact of thermal treatment on the stress state and evolving microstructure of Cu/W nano-multilayers, as deposited on different substrates by magnetron sputtering, was investigated by *in-situ* high temperature XRD (HT-XRD) and high resolution SEM. The alternating Cu and W nanolayers grow along the preferred directions of [111] for Cu and [110] for W, which results in an out-of-plane orientation relationship according to Cu{111}||{110}, independently of the substrate. The Cu/W NML on Al₂O₃-C and Al₂O₃-R substrates also develops an in-plane texture according to Cu{111}⟨10 $\bar{1}$ ⟩||W{110}⟨00 $\bar{1}$ ⟩, as inherited from the epitaxy between the first W buffer layer and the single-crystalline Al₂O₃ substrate. Such an in-plane texture is absent for the Cu/W NMLs on the Si(001) substrate, because the amorphous Si₃N₄ interlayer prevents epitaxial growth of the first W buffer layer. The diffracted intensity modulation (i.e., satellite structure), typical of a periodically ordered NML structure, vanishes completely during heating in the temperature range of 750 – 900 °C, independent of the substrate. The disappearance of the satellite structure coincides with the appearance of the Cu(200) reflection (using surface sensitive GI-XRD), as attributed to the thermally activated and stress-assisted outflow of confined Cu from the interior of the NML to the outer surface. The NML degradation process is accompanied by abrupt grain coarsening of W in the range of 750 – 900 °C. The resulting W grain size remains nearly constant during subsequent cooling down to RT.

XRD stress analysis indicates that the stress state of the Cu nanolayers during deposition and upon heating is largely imposed by the accumulated stresses in the much stiffer W nanolayers. As result, the measured course of the stress evolution of Cu with annealing temperature is qualitatively similar for Cu and W. The as-deposited Cu nanolayers possess an average in-plane compressive stress of –1.5 GPa at RT, which is fully released after the annealing at 500 °C which coincides with the temperature where Cu outflow is detected on the surface. The W nanolayers exhibit a significantly larger in-plane compressive stress of –3.5 GPa at RT, which is only partially released after the annealing at 500 °C. Fast relaxation of compressive stresses in the W nanolayers only occurs upon degradation of the NML structure in the range of 750 – 900 °C, as accompanied by grain coarsening. The existence of high compressive stresses in the Cu and W nanolayers in the as-deposited state was found to originate mainly from growth stresses generated during the deposition process: i.e., the contribution of coherency stress in the Cu and W nanolayers on the total stress state is relatively small.

This study shed light on the role of stress in multicomposite, nano-multilayered materials subjected to thermal treatments. This work can be considered as the basis for further investigations on the effect of, e.g., layer thickness, layer sequence and deposition parameters on the microstructure, stress state, and thermal stability of Cu/W NML systems.

SUPPLEMENTARY MATERIAL

See [supplementary material](#) for the XRD geometries, stress data analysis in Cu and W layers, and the comparison of the $\sin^2\psi$ method with the CGM for W layers.

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