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Strain depth profiles in thin films extracted from in-plane X-ray diffraction

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Thin films generally contain depth-dependent residual stress gradients, which influence their functional properties and stability in harsh environments. An understanding of these stress gradients and their influence is crucial for many applications. Standard methods for thin-film stress determination only provide average strain values, thus disregarding possible variation in strain/stress across the film thickness. This work introduces a new method to derive depth-dependent strain profiles in thin films with thicknesses in the submicrometre range by laboratory-based in-plane grazing X-ray diffraction, as applied to magnetron-sputtering-grown polycrystalline Cu thin films with different thicknesses. By performing in-plane grazing diffraction analysis at different incidence angles, the in-plane lattice constant depth profile of the thin film can be resolved through a dedicated robust data processing procedure. Owing to the underlying intrinsic difficulties related to the inverse Laplace transform of discrete experimental data sets, four complementary procedures are presented to reliably extract the strain depth profile of the films from the diffraction data. Surprisingly, the strain depth profile is not monotonic and possesses a complex shape: highly compressive close to the substrate interface, more tensile within the film and relaxed close to the film surface. The same strain profile is obtained by the four different data evaluation methods, confirming the validity of the derived depth-dependent strain profiles as a function of the film thickness. Comparison of the obtained results with the average in-plane stresses independently derived by the standard stress analysis method in the out-of-plane diffraction geometry validates the solidity of the proposed method.

1. Introduction

Thin films and multilayers typically present a high and strongly non-uniform strain distribution across their depth, resulting in large residual stress levels (Abadias *et al.*, 2007; Chason *et al.*, 2002). Various kinetic models have been proposed to describe the stress generation mechanisms during the different stages of thin-film growth, for example, due to island nucleation and growth, due to island coalescence and grain boundary formation ('zipping'), and due to the incorporation of adatoms into grain boundaries during the post-coalescence growth stage (Chason *et al.*, 2012). The growth stresses in functional thin films and multilayers affect their thermal (Moszner *et al.*, 2016; Druzhinin *et al.*, 2019; Cancellieri *et al.*, 2016), chemical (Delph & Jaccodine, 1999) and mechanical properties (Streitz *et al.*, 1994; Wen *et al.*, 2007). Hence fundamental knowledge on stress generating and relaxation mechanisms in thin films and multilayers is needed to tune their functional properties.

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Residual thin-film stresses are normally measured and quantified by an average strain (as averaged over the film thickness) using common X-ray diffraction (XRD) methods, such as the $\sin^2\psi$ method for polycrystalline samples or the crystallite group method for textured materials (Welzel *et al.*, 2005). However, most thin films and multilayer systems possess depth-dependent strain (stress) gradients, which depend on the growth and processing conditions, self-organization phenomena during grain growth and post-deposition treatments like thermal annealing (Abadias *et al.*, 2018). The functional properties of thin films and multilayers are in fact governed by the out-of-plane gradients of stress and not by the average stress through the thin film. However, it is rather challenging to access stress gradients (in real space) as a function of depth below the film surface, especially for film thicknesses in the submicrometre range. The depth-dependent stress gradient in deposited films can be estimated from the incremental stress with increasing film thickness (*i.e.* the amount of stress being added to the film as it grows), as measured by real-time *in situ* wafer curvature techniques (Abadias *et al.*, 2014). However, such a methodology assumes that the newly added stress for each finite thickness increase does not affect the accumulated stresses in the already formed film region, which is only valid if relaxation and/or redistribution of accumulated stresses during film formation are kinetically frozen. Typically only dedicated nano-diffraction setups at few synchrotron facilities worldwide are suited for probing depth-dependent stress gradients in thin films and nanomultilayers (Keckes *et al.*, 2012; Stefanelli *et al.*, 2013). However, synchrotrons have limitations in terms of instrument accessibility, *in situ* growth and processing possibilities, and sample dimensions.

In most cases, analysis to extract the strain profile is performed on micrometre-thick films using standard out-of-plane diffraction at fixed or variable penetration depths (Fischer *et al.*, 2014; Klaus & Genzel, 2013). A variable penetration depth is normally achieved by varying the tilt angle ψ , like in the case of the traditional $\sin^2\psi$ method (Cullity, 1956), where each ψ corresponds to a different penetration depth. However this method has two limitations:

(1) The probing depths of typical inorganic solids, such as a metal or oxide, can be varied in the range of a few micrometres by adjusting the incidence angle in the range of $0.5\text{--}5^\circ$ (employing Cu radiation). Very thin films are therefore not accessible.

(2) Only polycrystalline materials showing a random orientation of crystallites can be investigated. Highly textured layers diffract only at specific ψ angles and, consequently, the penetration depth cannot be controlled.

Apart from the above restrictions, nondestructive analysis of the depth-dependent lattice parameter (and thereby the strain) is only possible by using various incidence angles of the X-ray beam. However, in order to derive the actual strain profile across the thickness from the measured average in-plane atomic distances, whose depth distribution has different weight at each incidence angle, a dedicated deconvolution procedure is needed. Different methods can be used to

convert average strain values at different incidence angles into a discrete or continuous residual strain (stress) depth profile $\sigma(z)$, *i.e.* finding the inverse Laplace transform of the measured $\sigma(\mu)$, where μ denotes the X-ray inverse penetration depth (proportional to the absorption coefficient) for a given incident angle (Genzel *et al.*, 2013; Genzel, 1996). This is usually done by least-squares fitting the Laplace transform of a trial function. However, all these methods can have multiple solutions for the depth-dependent stress profile and thus no unique solution of $\sigma(z)$ can be found. This is due to the uncertainties with respect to the measurement and the assumptions made during the evaluation, since the inverse Laplace transform is an ill-posed problem. In most cases, the execution of the inverse Laplace transform is successfully done by assuming a specific ansatz for the $\sigma(z)$ curve (Benediktovitch, Ulyanenkova *et al.*, 2014), which implies foreknowledge of the functional form of the strain depth profile. However, in this case, the application to very thin films (maximum hundreds of nanometres in thickness) is excluded as the probing depth achievable by varying ψ lies in the micrometre range and therefore the acquisition of enough discrete data points at different depths, as required for a robust strain deconvolution procedure, is not possible.

In-plane grazing-incidence diffraction (IP-GID) (Benediktovitch, Feranchuk & Ulyanenko, 2014; Pietsch *et al.*, 2004) can overcome the above-mentioned challenges by probing diffracting lattice planes that are oriented near-normal to the film surface, since the scattering vector $\mathbf{q}$ lies in-plane, parallel to the film surface (see Fig. 1). IP-GID results in an X-ray incident beam traveling a long distance inside the thin film and thus high diffraction intensities for thin films can be obtained (Yasaka, 2010).

Notably, for textured films only a few specific reflections can be measured using IP-GID (analogously to the standard Bragg–Brentano out-of-plane measurement of single crystals and textured materials, where only diffraction planes parallel to the surface give rise to constructive interference and hence to the appearance of reflections). However, the corresponding probing depth can be gradually increased up to a few hundred nanometres below the film surface through a tiny stepwise increase of the incidence angle (Neuschitzer *et al.*, 2012;

Figure 1
In-plane noncoplanar diffraction geometry, where the scattering vector lies in the plane parallel to the sample surface. The (220) planes in polycrystalline [111]-textured Cu are perpendicular to the surface.

Kobayashi, 2010). An average value of the in-plane lattice spacing (and thus strain) at different probing depths can then be obtained by measuring the in-plane lattice spacing at different grazing incident angles.

In the following, laboratory-based IP-GID is applied to polycrystalline {111}-textured Cu thin films with different thicknesses in the range of 20–300 nm, to measure the in-plane reflections at different probing depths (by varying the incident angle). We present an innovative and robust procedure to derive the depth profile of the in-plane lattice parameter for these submicrometre-thick films. To this end, the Bragg scattering vectors, as obtained at different incident angles for the in-plane reflections, are used to extract consistently the in-plane lattice parameter depth profile through two different independent procedures: (a) fitting the XRD data with the direct Laplace transform of a generic series, whose coefficients are adjusted by a least-squares method, and (b) finding the inverse Laplace transform of the data by solving the associated linear system resulting from the Laplace transform of the generic series, through a suitable reduction of the rank of the associated matrix operator. For each of these approaches we have tested both power series and Fourier series to derive the continuous strain depth profile. The multiple procedure proposed is necessary to confirm unambiguously the uniqueness of the derived strain profile.

2. Experimental methods

2.1. Thin-film preparation

Cu thin films were grown on sapphire, Al_2O_3 , single-crystal (0001) substrates (Crystec) by direct current magnetron sputtering from a pure Cu 99.99% target at room temperature, at 100 W power. The substrates were RF-cleaned at 100 V for 2 min prior to the deposition. The as-grown Cu single layers have nominal thicknesses of 20, 50, 150 and 300 nm. A nanoporous Cu film was obtained by oxidizing the 300 nm-thick Cu thin film in air at 548 K for an hour and subsequently fully reducing it in 5 vol.% H_2 /95% Ar at 573 K for 90 min.

2.2. XRD characterization

A Bruker D8 instrument in out-of-plane and point focus geometry was applied to perform stress analysis of the highly textured films based on the crystallite group method (CGM) (Cancellieri *et al.*, 2016; Welzel *et al.*, 2005). The as-deposited Cu thin films [face-centered cubic (f.c.c.), $Fm\bar{3}m$, $a_{\text{Cu}} = 3.615 \text{ \AA}$] have a pronounced {111} fiber texture (Unutmazsoy *et al.*, 2020). Accordingly, the $\bar{1}11$, 200, 220 and 331 reflections were measured at specific tilt angles ψ (depending on the texture). The lattice parameter a derived from each reflection [$a = d_{(hkl)}(h^2 + k^2 + l^2)^{0.5}$] was then plotted versus $\sin^2\psi$. The average in-plane stress was derived from the slope of the line through the compliance coefficients (Clemens & Bain, 1992).

The IP-GID analysis was performed using a Bruker D8 Discover diffractometer (Cu $K\alpha$ radiation), equipped with a special tilt stage for single-crystal alignment and for grazing

incidence in- and out-of-plane diffraction. The X-ray tube was rotated by 90° to move the diffraction vector in plane, parallel to the film surface, giving access to the reflections of crystallographic lattice planes which are oriented near-normal to the film surface (Fig. 1). Owing to the preferred {111} texture of the Cu films, when performing an in-plane diffraction scan in the adopted IP-GID geometry, only the reflections perpendicular to the {111} family of planes can be accessed, *i.e.* the Cu 220 reflections. The in-plane diffraction experiment consisted in acquiring 2θ scans at different incident angles, α , ranging from 0 to 2° .

In this particular geometry, illustrated in Fig. 1, the diffracted beam is also detected at low angles and the sample surface lies almost on the same plane as the measurement (planar geometry). During the scan, the film sample is rotated to an angle ϕ around its normal, while the detector is rotated around the same axis to an angle $2\theta = 2\phi$.

3. Extraction of strain profiles from IP-GID

3.1. Low-angle incidence X-ray diffraction

The in-plane diffraction reproduces the Bragg–Brentano geometry for the planes near-normal to the film surface, with an in-plane component $q_{\parallel} = 4\pi \sin(\phi) \cos(\alpha)/\lambda$ and a small out-of-plane component $q_{\perp} = 4\pi \sin(\phi) \sin(\alpha)/\lambda$ for the momentum transfer vector for a given X-ray wavelength λ . The intensities of incident and diffracted beams are attenuated along their paths through the material. This attenuation is characterized by the linear absorption coefficient μ , which depends on both the film composition and the wavelength of the incident radiation. The intensity attenuation across a material obeys the following relation:

$$I(l) = I_0 \exp(-\mu l), \quad (1)$$

where l is the traveled length along the beam path and I_0 the incident intensity. Equation (1) is the starting point for the calculation of the dependence of the collected intensity as a function of the angle of incidence α and the film thickness t . The procedure is the same as for the calculation of the absorption correction of diffracted intensity in reflective geometry (Maslen, 2006). Note that, in reflective geometry, the plane defined by the incident and collected beams is perpendicular to the film surface, while for in-plane diffraction this is no longer the case. Nevertheless, the procedure is not affected since, for absorption, only the length of the beam path through the film enters the calculation. Thus, we can use the same schematics as for reflective geometry.

The path length l , the incidence angle α and the depth z are related through

$$z = l \sin(\alpha). \quad (2)$$

Thus, the infinitesimal contribution to the diffracted intensity at depth z reads

$$dI(z) = A \frac{2\mu I_0}{\sin(\alpha)} \exp\left[\frac{-2\mu z}{\sin(\alpha)}\right] dz, \quad (3)$$

where A is a dimensionless constant taking into account the fraction of the energy irradiated in the diffracted direction. The factor 2 in the exponential function corresponds to the attenuation along the total length path of incident and collected beams in the interior of the sample. The collected intensity is then obtained by integrating equation (3) over the entire film thickness t :

$$I(\alpha, t) = A \frac{2\mu I_0}{\sin(\alpha)} \int_0^t \exp\left[\frac{-2\mu z}{\sin(\alpha)}\right] dz \\ = AI_0 \left\{ 1 - \exp\left[\frac{-2\mu t}{\sin(\alpha)}\right] \right\}. \quad (4)$$

The measured peak intensity of a given in-plane Bragg reflection as a function of the angle of incidence should obey equation (4). Linear absorption coefficients μ are calculated by combining two kinds of tabulated data (Arndt *et al.*, 2006): the mass attenuation coefficient μ/ρ for a given radiation wavelength, and the material density ρ .

To understand this effect, let us examine the above equations. In equation (1) the absorption coefficient μ is an inverse length or, in other words, $1/\mu$ is a characteristic length over which the intensity decays roughly by a factor of 3. This means that, according to equation (2), the diffraction is probing the material essentially over a depth of $\sin(\alpha)/\mu$. The obtained experimental values for the interplanar distances are thus a sort of weighted average of the varying distances across the whole film.

In fact, the experimental measurement of in-plane lattice spacings d relies on the determination of the position of the corresponding Bragg reflection in the Fourier space: $q = 2\pi/d$. The measured intensity is the sum of intensity contributions from the whole film. Thus, the position of the resulting peak in q space is an average over all these contributions, weighted by the local intensity contribution originating at each depth. But, strictly speaking, the weighted average of the peak position's maxima is not the position of the resulting peak maximum but the center of gravity of the contributing peaks. However, for small differences δq with respect to the peak width, the position of the maximum is a very good approximation. As we shall see, in our case the approximation is justified since the maximum spread in q vectors is about $1.5 \times 10^{-2} \text{ \AA}^{-1}$, while the peak width in q space is about $6.5 \times 10^{-2} \text{ \AA}^{-1}$. The peak positions for our analysis have been derived by a Gaussian fit function which reproduces the peak shape well (see supplementary materials). In this geometry, as also reported in a similar experiment on textured materials (Vlasenko *et al.*, 2018), the peak broadening is very pronounced (more than 1.5° corresponding to $1.5 \times 10^{-2} \text{ \AA}^{-1}$ in q space). In our case, the in-plane geometry imposes a very large instrumental broadening, which determines the large FWHM in the peaks. However, for the presented analysis, we considered only the peak position.

The corresponding weighting function $\omega_\alpha(z)$ can be derived directly from equation (3), the infinitesimal contribution to the diffracted intensity at depth z , after normalization:

$$\omega_\alpha(z) = \frac{I(z)/dz}{I(\alpha, t)} = \frac{2\mu}{\sin(\alpha)} \frac{\exp[-2\mu z/\sin(\alpha)]}{1 - \exp[-2\mu t/\sin(\alpha)]}. \quad (5)$$

The average in-plane value of the q vector at a given incidence can be written as

$$\bar{q}(\alpha) = \int_0^t \omega_\alpha(z) q(z) dz, \quad (6)$$

where $q(z)$ is the depth profile of the in-plane peak position. Equation (6) is the Laplace transform of the actual profile $q(z)$, defined in the finite interval $[0, t]$. The goal of the method proposed in our work is to obtain the depth profile $q(z)$ by inverting equation (6) for the most general case.

The ill-posed nature of the inverse Laplace transform makes its numerical application to experimental data quite complex. Indeed, good results can be expected only when a data function is available in a closed analytic form (Craig *et al.*, 1994). Conversely, when the data are taken in a restricted domain and affected by experimental errors, the instability associated with inverting discrete data is increased. In the case of smooth profiles, and when a particular analytic dependence can be justified, one can attempt to fit the experimental data using the direct Laplace transform of a trial function by adjusting a few parameters. However, there are no universal numerical recipes for the general case.

In the present study, we propose two different approaches to obtain the strain profile from the in-plane GIXRD measurements. Both approaches rely on generic series expansions of the strain profile to be derived. The first approach is based on the Laplace transform of a series expansion, whose coefficients are adjusted by a fit of the data using a least-squares Monte Carlo procedure. The second one consists in the solution of the linear system resulting from the Laplace transform of the series, with a suitable reduction of the rank of the matrix produced by equation (6) in order to avoid overdetermination. In this work we will only consider power and Fourier series within each approach.

3.2. Series expansions of the $q(z)$ profile

3.2.1. Power series. The peak position profile $q(z)$ is written as a power series of the depth z measured from the film free surface:

$$q(z) = \sum_{n=0}^N Q_n z^n. \quad (7)$$

Inserting equation (7) into the integral of equation (6) we obtain

$$\bar{q}(\alpha) = \sum_{n=0}^N Q_n I_n(\alpha), \quad (8)$$

where the $I_n(\alpha)$ functions are defined by

$$I_n(\alpha) = \int_0^t \omega_\alpha(z) z^n dz. \quad (9)$$

The I_n s obey a simple recursion relation. Integrating equation (9) by parts, we obtain

$$I_n(\alpha) = \frac{nI_{n-1}(\alpha)}{\beta} - \frac{t^n \exp(-\beta t)}{1 - \exp(-\beta t)}, \quad \beta = \frac{2\mu}{\sin(\alpha)}, \quad (10)$$

with $I_0(\alpha) = 1$ for all values of α .

3.2.2. Fourier series. The $q(z)$ profile is defined, in principle, within the interval $[0, t]$. Using simply the interval length t for the fundamental mode (period) will introduce many higher harmonics due to the singularities at the borders. In order to avoid these difficulties, some symmetry conditions, which need to be validated *a posteriori*, can be imposed on the Fourier expansion. Assuming strain profiles with a linear behavior close to the substrate ($z = t$) and a smoothly rounded shape close to the free surface ($z = 0$), one can restrict the Fourier expansion to single parity functions (e.g. cosine) and consider a fundamental period of $4t$:

$$q(z) = \sum_{n=0}^N Q_n \cos(nKz), \quad K = \pi/(2t). \quad (11)$$

Proceeding as before, we insert equation (11) into the integral of equation (6) to obtain equation (8), where, now, the $I_n(\alpha)$ functions correspond to the Fourier expansion:

$$I_n(\alpha) = \int_0^t \omega_\alpha(z) \cos(nKz) dz. \quad (12)$$

Integrating equation (12) by parts in two steps, we obtain the $I_n(\alpha)$ functions for the Fourier case:

$$I_n(\alpha) = \frac{1 + [(nK/\beta) \sin(n\pi/2) - \cos(n\pi/2)] \exp(-\beta t)}{[1 + (nK/\beta)^2][1 - \exp(-\beta t)]}, \quad (13)$$

$$\beta = \frac{2\mu}{\sin(\alpha)}.$$

Alternatively, equation (13) can be written in terms of the unit imaginary number (i) as

$$I_n(\alpha) = \frac{1 - \Re[i^n(1 + inK/\beta)] \exp(-\beta t)}{[1 + (nK/\beta)^2][1 - \exp(-\beta t)]}. \quad (14)$$

3.2.3. Extraction of the profile. The Q_n coefficients have to be extracted in order to enable the reconstruction of the $q(z)$ profile with equations (7) or (11). In the following we consider two different approaches: (1) the fit of the experimental $\bar{q}(\alpha)$ data using a least-squares Monte Carlo approach and, (2) the solution of the linear system resulting from equation (8). In this section, we illustrate the different procedures, applying them to a 50 nm-thick Cu thin film grown on sapphire (0001) (the fits for other Cu thicknesses are presented in the supplementary material). The Cu film has a {111} texture, and the measured in-plane diffraction peak is 220 with an interplanar distance $d_{(220)} = 1.278 \text{ \AA}$ in the unstrained case.

3.2.4. Least-squares fit. This procedure consists of adjusting the coefficients Q_n to fit the measured profiles $\bar{q}(\alpha)$ with equation (8). In this work we used an in-house least-squares Monte Carlo procedure that converges in less than 10^7 iterations with a simple MATLAB code. In Fig. 2(a) we illustrate the result of the $\bar{q}(\alpha)$ fitting procedure using a power series as given in equation (7). We found the contribution of the z^n terms for $n > 3$ negligible in the adjustment. The profile of $q_{(220)}$ is reconstructed using equation (7). The depth profile of the corresponding interplanar distance is then deduced from the $q(z)$ profile as $d = 2\pi/q$, and is depicted in Fig. 3(a).

The same procedure as above was implemented using the Fourier series defined in equation (11) for the $q(z)$ profile. The results are depicted in Figs. 2(b) and 3(b).

For the Fourier series, we found again only a few terms contributing to the profile: harmonic coefficients for $n > 3$ are negligible in the adjustment. Both series expansions (power and Fourier series) allow reasonable fits to the average $\bar{q}$ data. Furthermore, the profile reconstructions obtained through these two clearly different sets of functions are quite similar, constituting a mutual validation of the fits and, hence, of the global approach.

3.2.5. Solving the linear system. Equation (8) can be rewritten in matrix form as

$$\bar{\mathbf{q}} = \mathbf{A}\mathbf{Q}, \quad (15)$$

Figure 2
(a) Least-squares fit of the average peak position $\bar{q}_{(220)}$ as a function of the incident angle α for the power series approach applied to 50 nm Cu. (b) Least-squares fit of the average peak position $\bar{q}_{(220)}$ as a function of the incident angle α for the Fourier series approach. The dashed line indicates the nominal bulk value.

Figure 3
(a) Calculated in-plane $d_{(220)}$ as a function of the distance from the substrate for the power series approach for 50 nm Cu. (b) Calculated in-plane $d_{(220)}$ as a function of the distance from the substrate for the Fourier series approach for 50 nm Cu. The dashed line indicates the nominal bulk value.

where $\bar{\mathbf{q}}$ is the vector formed with the M data values collected at successive incident angles α_m , $\mathbf{Q}$ is the vector formed with the N coefficients in the series expansion of the profile and A is the $M \times N$ matrix defined as follows:

$$A_{mn} = I_n(\alpha_m). \quad (16)$$

The matrix representation of equation (14) is

$$\begin{pmatrix} \bar{q}_1 \\ \vdots \\ \bar{q}_m \\ \vdots \\ \vdots \end{pmatrix} = \begin{pmatrix} A_{11} & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & A_{mn} & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot & A_{MN} \end{pmatrix} \begin{pmatrix} Q_1 \\ \vdots \\ Q_n \\ \vdots \\ \vdots \end{pmatrix}. \quad (17)$$

Looking at the matrix expression, one would be tempted to fix the order of expansion for the profile at $N = M$, so as to obtain a square $M \times M$ matrix and solve the corresponding linear system using the maximum available data points. However, the obtained square matrices are rarely invertible and, when they are, their condition number is very high and the results are unphysical. This is not surprising for an ill-posed problem as we discussed before. In addition, the rank of these $M \times M$ matrices is much lower than their dimension. In other words, we are dealing with overdetermined systems. This can be understood considering the evolution of the weighting function $\omega_\alpha(z)$ [equation (5)] when increasing the incidence angles α_m .

In Fig. 4 we show a logarithmic plot of $\omega_\alpha(z)$ for increasing values of α , corresponding to the example of the Cu thin film with $t = 50$ nm. For values of the incident angle above 0.8° , the distribution looks almost flat and the different curves are hardly distinguishable. This means that, except for the first four weighting functions, the XRD experiment is probing the whole film with a sort of arithmetic average. Furthermore, the linear equations corresponding to these rows in the $M \times M$ matrix are not linearly independent. To avoid over-determination, we have to reduce the dimensions of the matrix and truncate the profile series expansion accordingly.

Although there are many ways to implement this reduction, we propose to proceed in order to enable the use of all available experimental points. The procedure is as follows:

(a) Choose an order N for the q -profile series expansion, i.e. the highest power z^N or the last harmonic $\cos(NKz)$. The coefficient's vector $\mathbf{Q}$ is then reduced to N components.

(b) Construct a matrix $\tilde{A}$ by first suppressing the columns for $n > N$ of the former matrix A , then average the $(M - N + 1)$ consecutive rows starting from row 1, then from row 2 and so on, until row N . After this procedure one will have a square $N \times N$ matrix.

(c) The same averaging procedure as above has to be applied to the data vector $\bar{\mathbf{q}}$ to obtain a new data vector with N components.

After completing the reduction (vector and matrix), if the dimension of the matrix corresponds to its rank, we can safely use equation (14) to solve the linear system by inverting the matrix $\tilde{A}$. But, of course, we have to evaluate first the rank of the $M \times M$ matrix A , and choose $N \leq \text{rank}(A)$. In practice, we start with a lower rank and increase it until the matrix condition number becomes too high, or until the resulting

Figure 4
Logarithm of the weighting function $\omega_\alpha(z)$ for different values of the incident angle α .

profile lacks physical sense. In the following, we illustrate this procedure by applying it to the same sample as above: a 50 nm Cu thin film grown on sapphire (0001).

The example discussed here corresponds to the $q(z)$ profile taken as a generic power series. The number of data points in the considered sample is $M = 12$, while $\text{rank}(A) = 4$. In Fig. 5,

we show the evolution of the $\bar{q}(\alpha)$ solution and the reconstructed $d_{(220)}$ profile for different values of N : (0, 1, 2 and 3), corresponding to ranks (1, 2, 3 and 4) for the reduced matrix. As expected, there are no solutions with reasonable condition numbers for $\text{rank}(\tilde{A}) > 4$. In fact, the condition numbers grow from 1 at rank = 1, up to 10^{11} at rank = 4. These high values

for the condition numbers have to be expected when dealing with ill-posed problems. However, despite the good agreement of the solution with the experimental $\bar{q}(\alpha)$ data for rank = 4, considering the unphysical shape of the resulting interplanar distance profile, we choose $N = 2$ (rank = 3) as the optimal solution, for which the condition number is 7.7×10^6 . Note that, despite the marked difference between the two approaches, the results from the least-squares optimization and the solution of the linear system are surprisingly similar.

The same procedure has been tested with the Fourier expansion. The behavior is quite similar and the outputs are as follows: $\text{rank}(A) = 8$, the condition numbers grow from 1 at rank = 1, up to 8×10^{14} at rank = 7. The optimal solution was found, the same as before, for rank = 3, with a condition number of 5×10^3 . The optimal solution is depicted in Fig. 6. Again, the consistency with the least-squares optimization procedure is remarkable. Furthermore, the solution of the linear system corresponding to the reduced matrix $\tilde{A}$ (and data vector) has an extra advantage: the averaging procedure in blocks of consecutive rows (and data vector components) results in a smoothing that makes the solution more robust against experimental errors.

In summary, the consistency between the four approaches considered here allows us to confidently consider the results obtained for the profiles thus obtained. However, owing to the intrinsic difficulties related to the inverse Laplace transform, none of these approaches would be sufficient on its own.

Figure 5
Evolution, within the power expansion approach, of the linear system solution $\bar{q}(\alpha)$ and its associated $d_{(220)}$ profile reconstruction for a reduced matrix: rank = 1 in (a), rank = 2 in (b), rank = 3 in (c) and rank = 4 in (d). The dashed line indicates the nominal bulk value.

Figure 6

Optimal linear system solution within the Fourier expansion approach: $\bar{q}(\alpha)$ (a); associated $d_{(220)}$ profile reconstruction (b). The dashed line indicates the nominal bulk value.

Figure 7

(a) In-plane diffractogram of Cu 300 nm film. The most intense reflection is from (220), perpendicular to the {111} texture. (b) Cu(220) peak variation with the different incidence angles. S = substrate; the star denotes the $K\beta$ contribution.

4. Results and discussion

4.1. In-plane strain analysis

In this section we report the in-plane lattice constants derived from the Bragg peak positions measured at different incident angles α .

In Fig. 7(a), an in-plane diffractogram of the Cu 300 nm sample is shown. The 220 peak is the most intense and visible, in accordance with the pronounced {111} (out-of-plane) texture usually obtained in f.c.c. metallic layers grown by magnetron sputtering. On measuring the same scan at different incidence angles, the position of the 220 reflection is moved about 0.5° towards lower diffraction angles when varying α from 0 to 1.6° [Fig. 7(b)]. For α values higher than 1.6° the 220 peak intensity is greatly reduced owing to the absorption.

This peak shift is the signature of a variation of the corresponding interplanar distances across the film thickness. In order to verify this statement, we performed the same experiment on a bare bulk substrate, where no variation of the lattice parameters should be measured as a function of the

incidence angle. The findings are reported in Fig. 8, where the sapphire 3030 reflection, perpendicular to the [0001] direction, is acquired at different α s. Although the peak intensity is strongly reduced by the change in the incidence angle, owing

Figure 8
3030 sapphire peak recorded at different α angles.

Figure 9

For the reduced, porous Cu film: (a) Cu(220) reflection and (b) the average in-plane $d_{(220)}$ measured at different α angles. The dashed line in (b) indicates the nominal bulk value.

to absorption, the position of the peak is not at all affected by the change in α . This indicates that any variation of the peak position with the incidence angle is a real signature of the different strain level across the depth, which is completely absent in the case of the bulk substrate.

To further demonstrate the validity of the experimental method to derive the strain depth profile, we performed the same measurement also on a reduced 300 nm Cu film. (Note that 300 nm is the initial thickness. After oxidation and reduction cycles the metal thickness is more than doubled.) The reduced metallic Cu appears completely relaxed (stress-free state) with randomly oriented crystallites, presenting also a porous microstructure (see supplementary material). In contrast with the case of Fig. 7(b) and in line with Fig. 8, where the peak position is α independent, the lattice parameter derived from in-plane diffraction does not change with the incidence angle [see Fig. 9(a)], keeping an almost constant value slightly above the nominal bulk value [Fig. 9(b)]. The sample is indeed completely relaxed with no internal stress gradient, as expected for a porous material. Here we also note that not only could the α values be varied up to 2.5°, probably

because of the lower absorption of the porous structure, but also the intensity of 220 is not affected by the incident angle variation. This indicates that the sample is porous (different density and different morphology with respect to the as-grown metallic Cu). This result corroborates the validity of the experimental method proposed to extract the strain gradient across the thickness of thin films and can then be implemented for thin {111}-textured Cu films of different total thicknesses of 20, 50, 150 and 300 nm, by analyzing the 220 peak variation.

Fig. 10 is a plot of the average in-plane Cu $d_{(220)}$ derived from the average peak positions as a function of the incidence angle. A simple inspection of the diffraction data reveals that all samples (from 20 to 300 nm) exhibit in-plane tensile strain at the film surface (*i.e.* small incidence angles). The thinner films (20 and 50 nm) seem to evolve to a weaker tensile strain more towards the interior of the film (higher incidence angle), their average value remaining above the unstrained bulk value. Conversely, the thicker films (150 and 300 nm) cross the bulk value and reach an asymptotic value in the compressive regime. In the next section, a detailed analysis is presented in order to derive a reliable strain depth profile for each Cu thickness.

Figure 10

Measured average in-plane $d_{(220)}$ as a function of the incident angle for different thicknesses of Cu films. The dashed line indicates the nominal bulk value.

4.2. Strain profile derivation: application of the models

The procedure described in Section 3, including the four versions of the in-plane lattice constant profile reconstruction, was implemented for all the samples. The obtained results are depicted in Fig. 11.

The profiles obtained have complex shapes and some unusual features. The over-relaxation of the in-plane lattice parameter for the 150 and 300 nm films was already shown in the $\bar{a}(\alpha)$ data obtained from low-angle diffraction (Fig. 10). However, the large compressive strain at the film–substrate interface and the non-monotonic evolution of the in-plane lattice parameters for all the films appearing in Fig. 11 could not have been guessed from the direct measurement. The application of the method proposed with the four approaches was then necessary to derive the actual in-plane lattice

parameter depth profile. As shown in Fig. 11, all four presented approaches give very similar results for each thickness, indicating the validity of the proposed method and that the obtained profiles reproduce the true lattice parameter variation across the thickness. This unexpected behavior is presumably related to the out-of-equilibrium deposition conditions. The role of interfaces on the intrinsic stresses in thin polycrystalline films has been addressed by many authors in recent decades, pointing to the complex correlation between growth conditions, relaxation mechanisms in quasi-coherent interfaces, grain shape and size, *etc.* (Gruber *et al.*, 2019). The observed non-monotonic stress depth profile could be the result of the gradual microstructural evolution during film growth, which includes a selective crystallographic orientation, columnar grain morphology, grain boundaries, grain coalescence and dislocation formation (Engwall *et al.*, 2016). In Cu thin films, consisting of relatively mobile atoms, it is also typically noted that one of the principal sources of stress generation is the incorporation of surface atoms during deposition (Chason *et al.*, 2012; Guduru *et al.*, 2003). The evolution (compressive–tensile–compressive) of the internal stress within the film thickness (final tensile stress for thin films and compressive stress for thicker films) during film growth (Chason *et al.*, 2002) is governed by the surface chemical potential, which determines the atom diffusion at the grain boundaries. Competition between film deposition rate and

atom diffusion can generate large stress gradients along the film thickness. Once the deposition is stopped, along with the dislocation mobility in grains, trapping and releasing atoms at interstitial sites, additional flow of ‘extra’ atoms from grain boundaries can occur to release the compressive stress accumulated, driven by the chemical potential gradient near the film surface (Flötotto *et al.*, 2015). Although during the deposition the mean stress can be regularly accumulated and modified in a continuous way, the post-deposition stage will be responsible for a non-monotonic stress profile formation, as the elastic stress will relax towards the elastic energy minimum. The complex interplay between different forces and phenomena including elastic energy minimization by dislocation formation and mobility will result in the nonlinear strain profile (Chaudhari, 1979; Doerner & Nix, 1988; Lubarda & Kouris, 1996).

4.3. Comparison with CGM-derived stress

The average in-plane stress in highly textured films is normally derived with the CGM (Welzel *et al.*, 2005). This is usually carried out in a standard out-of-plane diffraction geometry at different tilt angles. The stress value derived with the CGM is an average stress tensor of the {211} <111> crystallite group in Cu{111}-textured films. However, from the CGM analysis, no information can be extracted on the depth

Figure 11

Reconstruction of in-plane lattice constant profiles with the four different approaches described in this work: (a), (c) least-mean-square fit and (b), (d) linear system solution for power series expansion (a), (b) and for Fourier series expansion (c), (d). The horizontal dashed line in each graph indicates the unstrained value for the Cu lattice constant.

Figure 12

Comparison between the in-plane average stress derived by the CGM using out-of-plane diffraction geometry and the in-plane stress averaged from the IP-GID extracted profile.

dependence of the stress. Moreover, a Reuss grain interaction model is assumed, *i.e.* the stress distribution is homogeneous in the specimen and the in-plane stress tensor is equal for all crystallites ($\sigma_{11} = \sigma_{22}$, $\sigma_{33} = 0$ and $\sigma_{ij} = 0$ with $i \neq j$).

For the plot in Fig. 12, the arithmetic average of the in-plane strain $\langle \epsilon \rangle$ for each sample was obtained from the corresponding strain profile and converted to an average stress by the following equation:

$$\langle \sigma \rangle = \langle \epsilon \rangle E / (1 - \nu), \quad (18)$$

where E is the Cu Young modulus (117 GPa) and ν is the Poisson ratio (0.3). The evolution of the average stress with the Cu thickness is very similar for both methods, confirming the validity of the present approach. Although the trend of the stress evolution in the two methods is almost identical, there is a discrepancy between the stress values. This could be because we have ignored the presence of gradient strain in the calculation of the stress, as we have assumed uniform strain in the sample. The in-plane stress tensor is in reality more complex for the taken frame of reference, *i.e.* it presents non-diagonal components $\sigma_{12} = \sigma_{21} \neq 0$ and inequality of the main components $\sigma_{11} \neq \sigma_{22}$.

5. Conclusions

We have presented a many-sided method to reliably derive the depth-dependent strain profile in copper thin films with different thicknesses. The laboratory X-ray diffractometer used in this study was especially equipped for an advanced in-plane diffraction experiment through a 90° rotation of the X-ray source and the incident beam optics, which brings the scattering vector in plane, parallel to the film surface. The strain depth profile was derived from the average peak positions measured at different incidence angles, by using four different procedures. These procedures includes power and Fourier series expansions, both treated in two different ways: (i) adjusting the series coefficients by fitting experimental data with their Laplace transform and (ii) performing an inversion

of the Laplace transform by solving the corresponding (properly regularized) linear system. These four variants yield essentially the same strain depth profiles for all considered samples, confirming the validity of the approach and of the results obtained. The extracted depth strain profile is non-monotonic and strongly thickness dependent, pointing to a complex interplay between the developing microstructure and the stress evolution during thin-film growth. The approach presented in this work to extract the strain depth profile of a thin film by a laboratory in-plane XRD measurement can be considered as a complementary method to the *in situ* measurement of the substrate curvature during growth (Gilardi *et al.*, 2019; Chason & Guduru, 2016). During film growth – from an initial island to a coalescence state – a dynamic evolution of the thin-film stress states and microstructure progression of the films is observed. During and after the film growth, stress relaxation mechanisms may occur, resulting in a different stress profile from the one monitored during the deposition. Therefore, the proposed method is useful for relating the resulting stress profile to the stress evolution during growth, in order to gain a fundamental understanding of functional thin-film technologies in real-life applications.

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