

TEXTURE DETERMINATION IN HIGHLY STRESSED PVD THIN FILMS

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ABSTRACT

Growth texture and residual stress in TiN thin films on 304 stainless steel were studied by XRD in parallel beam configuration. The high residual stress deeply influenced texture determination by conventional methods based on pole figures. *Area maps* (collections of θ - 2θ patterns at regular steps of ψ -tilting) were used to properly assess the mixed [211]/[111] growth mechanism in the nitride thin film, and for a detailed study of the residual stress analysis within the coating and outer layers of the substrate. The residual stress trend in the TiN thin film was studied considering data from (111) and (200) reflections, in order to avoid the effects of the fibre texture on the mechanical anisotropy. In particular, a residual stress gradient of the in-plane stress component was obtained for the thin film, whereas average in-plane stresses were calculated for the Martensitic layer at the thin film - substrate interface and for the outer layers of the substrate Austenitic phase underneath. It was also proposed that the use of Area Maps can be extended to study thickness and layer sequences, as well as microstrain and domain size effects connected with profile width and shape, in order to provide a detailed picture of thin film and interface features.

INTRODUCTION

Thin films produced by Physical Vapor Deposition (PVD) techniques are frequently characterized by intense residual strain fields and preferred growth orientations. Fibre texture is typically produced when no epitaxial relationship is possible between substrate and thin film material (for instance, with polycrystalline or amorphous substrates, or with amorphous buffer layers); the detailed features of the fibre texture depend on several deposition parameters, first of all deposition temperature (as compared with the melting point of the thin film material), but also on the film thickness and growth kinetic [1].

This type of microstructure exhibits properties that are markedly different from both epitaxial and random polycrystalline thin films: in particular, the anisotropy in the mechanical (as well as other) properties, although different from that of a single-crystal, becomes an important feature. In such conditions, the use of conventional XRD methods developed for bulk material characterization, can lead to rather unclear or even wrong results if due attention is not given to the strong correlation between residual strain and texture.

Previous work already pointed out the effect of preferred orientation on the residual stress analysis of fibre textured stabilized zirconia thin films [2]. In that case, it was shown how the X-ray Elastic Constants (XECs) should be corrected on the basis of the experimentally measured pole density. On the other hand, the strain-texture correlation can also be important for a qualitative assessment of texture, an apparently simple task that is frequently necessary in thin film studies.

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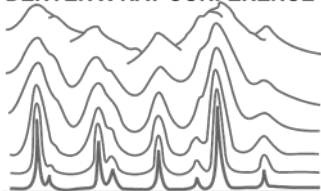
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When a high residual strain field is present, conventional pole figures cannot be used, since the 2θ peak position considerably changes with ψ -tilting (according to the axis labelling used in X-ray residual stress analysis); instead, an extended 2θ range should be collected at different (ϕ, ψ) sample orientations. This measurement strategy can be easily adopted in the technologically relevant case of fibre textured thin films, where the necessary information can be obtained by mapping the 2θ - ψ space at a fixed ϕ value. In this way, a correct preferred orientation can be evaluated together with the residual strain data given by peak position changes with the ψ -tilting. As shown in the present work, this procedure was particularly useful to disclose the [211] orientation in (fcc) TiN thin films sputter-deposited on stainless steel substrates (the (211) peak is extinct for a fcc), and to provide a detailed picture of the residual stress field in both thin film and interfacial substrate layers. The procedure, as described in the present work, can be easily extended to the study of other non-epitaxial thin films.

EXPERIMENTAL

The studied TiN thin film samples (nominal thickness 1 μm) were sputter-deposited on 304 stainless steel substrates; details on the deposition process, as well as details of application as wear-resistant coatings, are reported elsewhere [3].

XRD measurements were done on a Philips X'Pert MRD. The instrument geometry was based on a parallel beam produced by a multicapillary collimator (divergence $<0.3^\circ$) in the incident beam, parallel plate collimator and a graphite flat crystal analyser in the diffracted beam. As recently pointed out by a dedicated work [4,5], the use of the multicapillary optics greatly enhanced the quality of the diffracted signal, both in terms of an increased diffracted signal intensity and in terms of a very limited error in peak position with sample ψ -tilting, even at low 2θ values (30 – 50°), which are of great interest for thin film studies. In addition, the instrumental component of profile broadening was almost unaffected by sample ψ -tilting, and was clearly smaller than that observed with a conventional cross-slit collimator. All these features make the parallel beam set-up extremely convenient for simultaneous stress/texture studies, as compared with a conventional geometry, like that used by the Schulz's method [6].

RESULTS AND DISCUSSION

Figure 1 shows the XRD pattern (in conventional Bragg-Brentano geometry) for a TiN thin film deposited by reactive sputtering on a 304 (Austenitic) stainless steel substrate. Besides the reflections from Austenite (A), further peaks can be attributed to a Martensite (M) phase, formed on the surface of the substrate by the mechanical polishing done before deposition. The intense reflection at $2\theta \sim 36.3^\circ$ can be attributed to the (111) planes of the fcc (NaCl-type) TiN phase; also the (222) TiN peak is observed in the pattern.

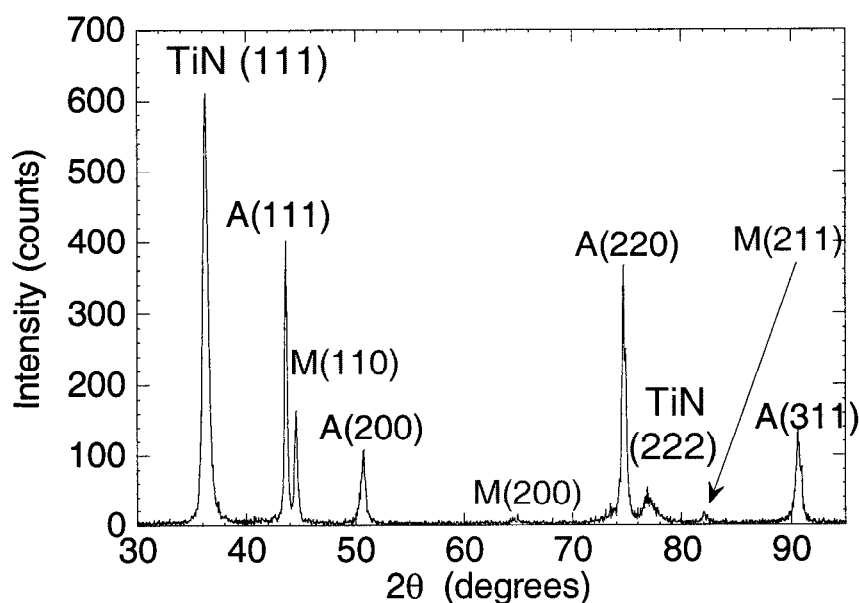


Figure 1. XRD pattern (Bragg-Brentano geometry) of a TiN thin film on 304 s.s.. Miller indices are reported for the reflections from the present phases: TiN (titanium nitride), A (austenite) and M (martensite)

On the basis of this information, we might tentatively conclude that the TiN thin film grew along a direction close to [111]. However, a more conclusive evidence is generally sought by

means of pole figures, to assess both the correct growth direction and the possible presence of in-plane ordering. Figure 2a shows the (111) TiN pole figure, collected at $2\theta=36.3^\circ$, according to the peak position given by Figure 1. A [111] fibre texture should give a signal (distributed along a 360° ring) at a ψ -tilting of 70.5° . To find this feature, we need to change considerably the 2θ position: if we collect the pole figure at $2\theta=37.1^\circ$, the ring at about 70° is visible (Figure 2c), even if the pole at $\psi=0^\circ$ is not present anymore. Finally, Figure 2b shows an intermediate result, as obtained for $2\theta=36.7^\circ$. In this case, the 'ring' is at approximately 65° , and a weak maximum is found at $\psi=0^\circ$.

It is clear from these results that conventional pole figures cannot be used in this case. The reason is the intense residual stress field, that is responsible for a considerable change in peak position with sample ψ -tilting. Even if the fibre-like nature is clear, a proper evaluation of the growth texture needs a simultaneous evaluation of peak position and intensity. To this purpose we can collect θ - 2θ patterns at regular steps of ψ -tilting, in order to produce a ψ - 2θ Area Map. As discussed in the following, this type of data collection and representation is of great help to understand texture and residual stress, as well as other important features in fibre textured thin films.

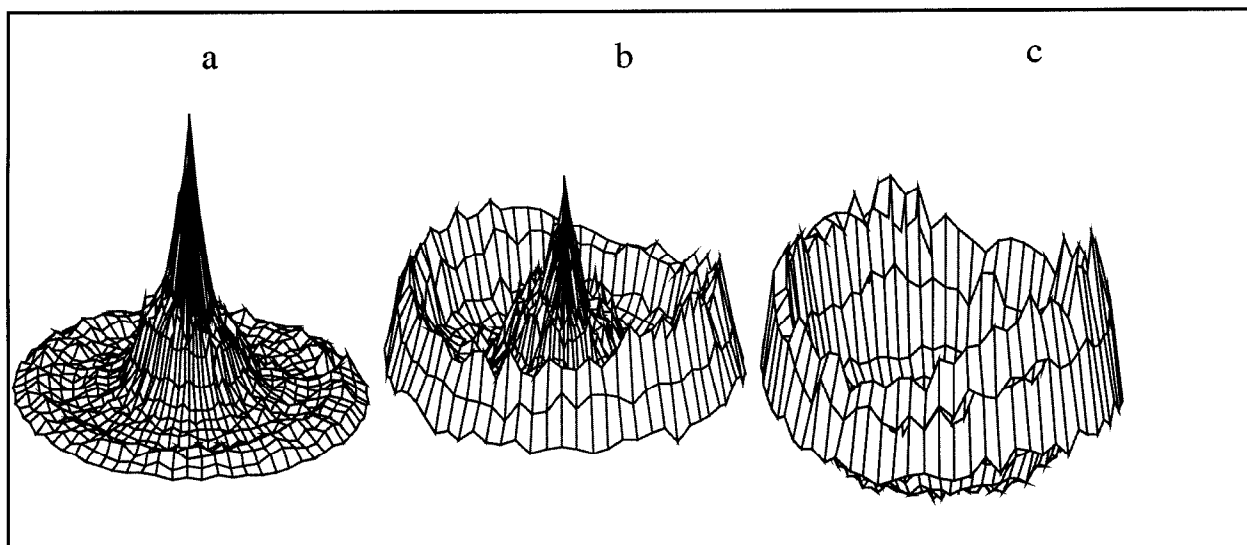


Figure 2. (111) TiN pole figures at $2\theta=36.3^\circ$ (a), 36.7° (b) and 37.1° (c).

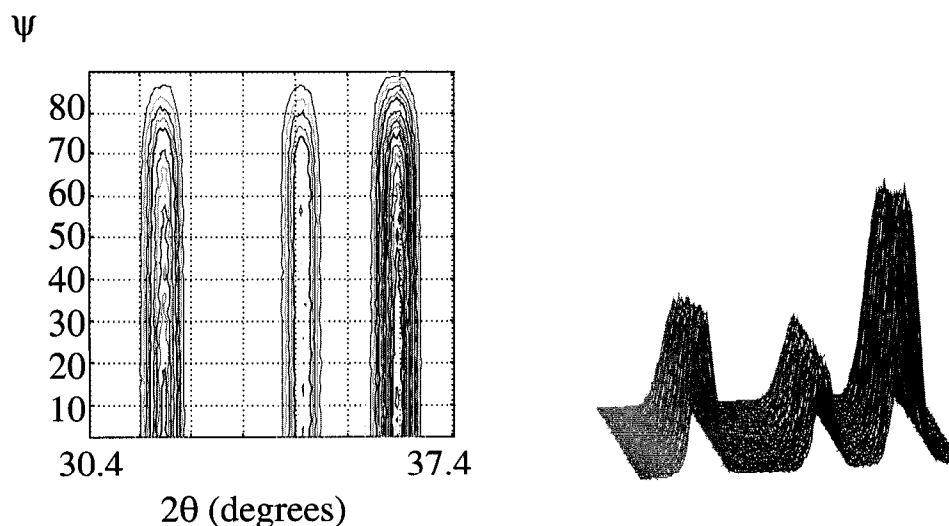


Figure 3. Area map for a zinc oxide powder sample. (100), (002) and (011) peaks.

Before discussing the Area Maps for the present case of study, it is interesting to look at the result obtained for a sample with zero strain and random domain orientation (no texture). Figure 3 shows the Area Map for a zinc oxide powder sample, in the region of the most intense reflections of the hexagonal structure: (100), (002) and (011). The lack of residual strain is demonstrated by the constant peak maximum position, whereas the absence of any texture is indicated by the constant intensity of peak maxima (in agreement with the standard [7]). The last feature is strictly true up to $\sim 65^\circ$ ψ -tilting. Above this value a defocusing correction is necessary, mainly to account for the increasing fraction of beam spread out of the sample and of the limited area read by the diffracted beam optics.

An interesting feature, in part due to the incident beam multicapillary collimator used in the present study, is the width of the observed reflections, that is a constant with the ψ -tilting. This is of help to collect useful data even at high ψ -tilting, and also for a possible use of that valuable part of information associated with peak width and shape (*Line Profile Analysis*).

Figure 4 shows two area maps for the studied thin film sample: they refer to the (111) TiN peak (a) and to a cluster of peaks belonging to both film and substrate (b): (200) TiN, (111) A and (200) M. In Figure 4a we can clearly see how, due to the residual strain, the (111) peak shifts toward higher 2θ angles with the ψ -tilting; this clearly demonstrates the problem of measuring a peak intensity at a fixed peak position (like in pole figure measurements). As a further feature, the pole at $\psi=0^\circ$ is stretched toward increasing tilting angles; from the 3D picture, two 'shoulders' at $\psi \sim 15\text{-}20^\circ$ are visible. At high ψ -tilting, broad poles are present around $60\text{-}65^\circ$.

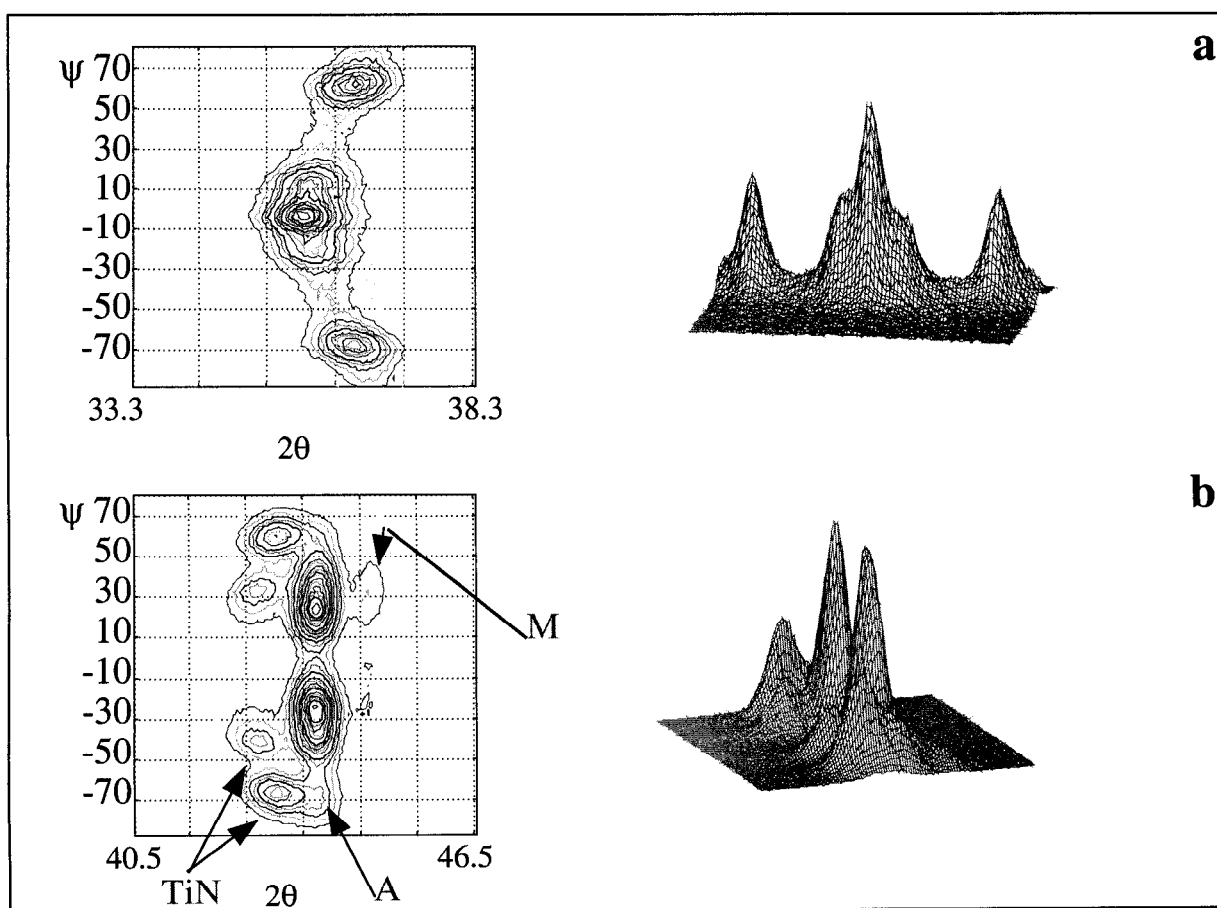


Figure 4. Area Maps for a TiN thin film deposited on 304 stainless steel. Region encompassing (111) TiN (a) and (200) TiN, (111)A, (110)M peaks (b). Corresponding 3D representations are rotated with respect to 2D maps for a better visibility of details.

These results are not compatible with a simple [111] texture. For a [111] texture, the (200) pole should be at $\psi=50.4^\circ$: looking at Figure 4b, we see quite a different picture, with a broad area between $\sim 20^\circ$ and $\sim 75^\circ$ where two maxima are found around 36° and 63° . These data can be interpreted by assuming a mixed texture, with two families of grains, grown along [211] and [111], respectively. This observation suggests the presence of twins resulting from a change in the stacking sequence of (111) planes in the fcc structure [6], probably due to the growth process under a high compressive in-plane stress. In addition, considering that a weak but measurable signal was observed at any ψ -tilting, a small fraction of random oriented grains is also present. Therefore, as a preliminary conclusion, we can indicate the validity of this approach to study the growth texture in highly stressed thin films; texture analysis can be extended on a quantitative level (pole density and ODF), by considering the distribution of peak intensity (or peak area) as a function of ψ , as obtained from the Area Maps, and assuming a cylindrical symmetry and using the suitable defocusing and thin film corrections.

Area Maps also provide a valuable tool for studying residual stress in fibre textured thin films. In fact, due to the axial symmetry, all of the necessary information is contained in the measured Area Maps, regardless of the ϕ orientation of the sample. Data concerning both the thin film (along two different crystallographic direction) and the substrate phases can be extracted from Figure 4.

As a preliminary consideration, we see that the observed data are symmetrical for positive and negative ψ -tilting (no ψ -splitting). Together with the information on the fibre-type nature of the texture, and the almost two-dimensional character of the thin film, this observation supports the hypothesis that a simple plane stress with axial symmetry can be assumed for our thin film samples, that is $\sigma_{11}=\sigma_{22}$, $\sigma_{33}=0$ and zero shear components.

Before using the peak shift data to calculate the residual strain and the residual stress field, it is important to point out the role of texture. It is well known that the elastic properties of crystalline materials are anisotropic, and this feature should be properly considered within any given mechanical model used to calculate the residual stress field from the observed residual strain data [8]. For this reason, if not measured experimentally, elastic constants need be calculated for the different crystallographic directions, starting from the single-crystal compliance or stiffness tensors [8]. This procedure introduces hypotheses on the mechanical coupling mechanism within the material and is always approximate and somewhat arbitrary in the choice of a model: common practice is to use Hill averages, i.e., XECs obtained as average of value calculated according to Voigt and Reuss models [8].

Conventional X-ray Elastic Constants calculations are done by assuming a completely homogeneous material, with a random distribution of crystalline domain orientations. When the last condition is not fulfilled, like in the case of fibre textured thin films, suitable corrections must be introduced in the XECs calculation. Knowing the ODF, this can be done in a relatively simple way assuming the validity of the Reuss hypothesis of a constant stress within the thin film [3,9].

The point of interest to the present work is that it can be demonstrated that, for cubic materials, texture has no effect along two crystallographic directions: [hhh] and [h00], which are the soft and stiff direction, respectively. XECs along other directions are affected by texture to a degree that depends on the texture itself and on the anisotropy of the material (e.g., $A=2C_{44}/(C_{11}-C_{12}) = 1.2$ (Diamond), 2.87 (Au), 0.71 (TiN) [8-10]). Even if XECs in textured materials can be obtained, it must be recognised that calculations invariably need approximations; the effect of

texture on the $\sin^2\psi$ trend of the residual strain is a non-linearity, which can be rather difficult to separate from other possible sources of second order effects. First of all, and of interest to many practical cases like the present one, the presence of a gradient in the in-plane residual stress.

In summary, there are several reasons to rely mainly on data relative to (111) and (200) for a residual stress analysis: (a) no texture effects on the $\sin^2\psi$ trend: non-linear effects due to e.g., gradients, can be better resolved; (b) the maximum contrast between soft and stiff directions is considered, so that mechanical anisotropy effects are maximised; (c) both reflections are always relatively intense in cubic phases, and their 2θ positions sufficiently close that geometrical conditions (and possible aberrations) are similar.

From the Area Maps of Figure 4 (111) and (200) peak positions were obtained by profile modelling. Profiles were well reproduced by symmetrical functions, within the whole wide range of ψ -tilting considered; however, due to the errors that can be introduced at very high ψ -tilting values, especially concerning peak position [5], the residual strain analysis was limited to the range $-76^\circ < \psi < 76^\circ$. Residual strain as a function of $\sin^2\psi$ is reported in Figure 5a. Zero-strain interplanar distances were obtained from the XECs for any [hkl], by means of the condition:

$$\sin^2\psi_o = -\frac{2 \cdot \left(-\frac{\nu}{E} \right)}{\left(\frac{1+\nu}{E} \right)} = -\frac{2 \cdot \text{XEC}_2}{\text{XEC}_1} \quad (1)$$

that defines the ψ -tilting direction (ψ_o) along which the zero-strain interplanar distance is measured. It can be demonstrated that this relation holds for plane stress fields, and is approximate for other cases [8]. XECs, in turn, were obtained in the Reuss limit, from single-crystal stiffness: $c_{11}=625$, $c_{12}=165$ and $c_{44}=163$ GPa [10].

The elastic anisotropy is clearly demonstrated by the considerably different trend in Figure 5a, for the residual strain along [111] and [200], respectively. To calculate a residual stress value, the two sets of data along the different crystallographic directions were refined together, within a conventional $\sin^2\psi$ model, with XECs calculated for the two different directions. According to this procedure, a high compressive stress of -6.8 GPa was found.

However, the data in Figure 5a exhibit a little but measurable deviation from the linear trend of the conventional $\sin^2\psi$ model; the quality of the least square fitting could be considerably improved by considering a gradient effect in the in-plane stress, and taking into account also the finite thickness of the thin film. The detail of this procedure are described elsewhere [9,11]: the model is based on a simple assumption that the rotationally symmetric plane stress field ($\sigma_{11}=\sigma_{22}$, $\sigma_{33}=\sigma_{12}=0$) changes with depth below the thin film surface according to a (second order) polynomial law:

$$\sigma_{11}(z) = \sigma_{11,0} + A_{11,1} \cdot z + A_{11,2} \cdot z^2 + \dots \quad (2)$$

The average residual strain can be related to the average stress as:

$$\langle \epsilon_\psi \rangle = [\text{XEC}_1 \cdot \sin^2\psi + 2 \cdot \text{XEC}_2] \langle \sigma_{11} \rangle \quad (3)$$

where the average is weighted over the exponential X-ray absorption law, and it is extended to the thin film thickness; for the average in-plane residual stress:

$$\langle \sigma_{11} \rangle = \frac{\int_0^t \sigma_{11} e^{-z/\xi} dz}{\int_0^t e^{-z/\xi} dz} \quad (4)$$

where t is the thickness and ξ is the information depth ($\sin\theta\cos\psi/2\mu$) and μ is the linear absorption coefficient.

By solving Eq.(4) with the residual stress trend of Eq.(1), it is possible to write Eq.(3) in a form suitable to model data like those of Figure 5a, where XECs, thickness, absorption coefficient and coefficients of Eq.(2) are parameters (fixed or to be refined by least squares).

The trend shown in Figure 5a (line) together with the experimental data (point) was obtained by least square fitting of Eq. (3), leading to the following in-plane stress:

$$\sigma_{11}(z) = -10.4 + 6.6 \cdot z + 4.7 \cdot z^2 \quad (\text{GPa}) \quad (5)$$

which is also reported in Figure 5b. Also film thickness was refined, to allow a better fitting and to compensate possible errors in thin film density that affect the exponential absorption law; the refined value, 0.99 μm , is in a good agreement with the nominal thickness of 1 μm .

The deviation from a constant stress value is not very large in the present case, and it is worth saying that the sensitivity of this method to slowly varying gradients is not very high. However, the present result is useful to illustrate the procedure, and the good agreement, within the proposed mechanical model, of the data collected along the two markedly different crystallographic directions: [111] and [200]. In addition, the good quality of the modelling suggests that the Reuss limit is adequate to this case.

Further information can be extracted from the Area Maps in Figure 4. From the data relative to the metal substrate phases, it was also possible to calculate the residual strain in both M and A phases [3]. The residual strain trend was linear for both phases, within the experimental accuracy, and considering typical values for steels for the elastic constants ($E=200$ GPa, $\nu=0.3$), the average stress in the two phases was -600 and -350 MPa in Martensite and Austenite, respectively. This further information, quite reasonable if we consider that the M phase is in direct contact with TiN and exhibits a higher yield strength than the A phase, can be of interest in tribological studies of protective coatings on steel components [3].

Area Maps contain other interesting types of information, that were not considered in the present study: film thickness, for instance, could be calculated by properly considering the ratio between integrated intensities from peaks belonging to the various present phases; in addition, a valuable information on the microstrain and size of coherently diffracting domains could also be obtained by using line profile data.

Future work will be necessary to devise a general procedure for the modelling of all the different features of Area Maps that were described so far, in order to formulate a detailed microstructural model of the thin film - substrate system.

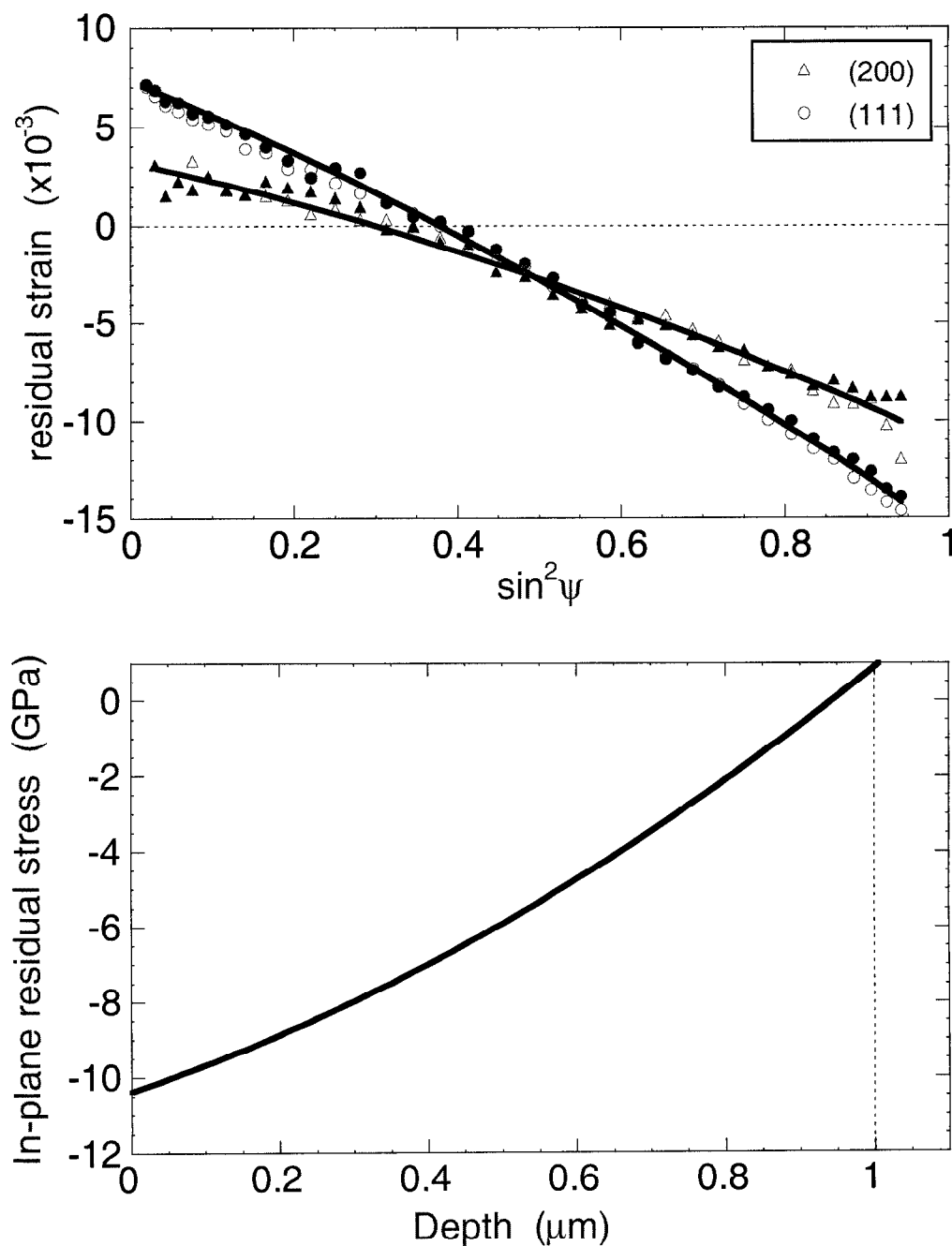


Figure 5. $\sin^2\psi$ plot for the TiN thin film, with data from (111) and (200) peaks, for both negative (open symbol) and positive (full symbol) ψ -tilting (a). The line is the result of the least square modelling of Eq. (3). The resulting trend of the in-plane residual stress is reported below (0=surface, 1=metal interface) (b).

CONCLUSIONS

In the presence of intense residual stress fields, like those frequently found in PVD thin films, a texture analysis based on conventional XRD methods can lead to wrong conclusions. In

the present case, concerning a TiN thin film deposited on a 304 s.s. substrate, conventional pole figures for the (111) TiN reflection were not of help, since the strong residual strain caused a large shift in the peak maximum with the ψ -tilting. The true [211]/[111] fibre texture could be disclosed only after a careful analysis, involving the use of *Area Maps*, made of θ -2 θ patterns collected at regular steps of ψ -tilting.

The collected Area Maps, including reflections from both thin film ((111) and (200)) and substrate ((111) Austenite and (200) Martensite), contained also a detailed information on the residual strain; it was shown how the in-plane residual stress in the thin film can be determined as a function of the depth below the surface. In addition, average values were found for the Martensitic layer at the interface and the outer layers of the Austenitic substrate. Considerable advantages are envisaged from the use of Area Maps for texture and residual stress determination in fibre textured thin films, including also information on the microstrain and domain size from line profiles, as well as film thickness.

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