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THICKNESS DETERMINATION OF THIN POLYCRYSTALLINE FILM BY GRAZING INCIDENCE X-RAY DIFFRACTION

J. Lhotka[a], R. Kuzel[a], G. Cappuccio[b,c] and V. Valvoda[a,*]

[a] *Faculty of Mathematics and Physics, Charles University, 12116 Prague 2, Czech Republic*
[b] *Istituto di Strutturistica Chimica, CNR, C.P. 10, I-00016 Montelibretti Sc., Italy*
[c] *Laboratori Nazionali di Frascati, INFN, C.P. 13, I-00044 Frascati, Italy*
** Corresponding author, Fax +420 2 2491 1061, e-mail address: valvoda@karlov.mff.cuni.cz*

Abstract

Three methods of thickness measurement based on absorption of X-rays in thin films were tested on polycrystalline titanium nitride film deposited on tungsten carbide substrate. The intensities of three reflections from each material were measured in the incidence range from 3° to 35° of the primary beam. After experimental correction for texture effects, data from the TiN film, the WC substrate or from their ratio were fitted by known functions using least squares routines. The substrate reflection intensities were found to be the most suitable for determining the thickness of the overlaying thin film. The average thickness of TiN film (2.00 ± 0.16 μm) determined from the substrate reflections was in fair agreement with the average value obtained from optical microscopy (2.2 ± 0.8 μm). The use of substrate reflections is generally preferable unless their intensities are spoiled by statistical errors (e.g., low intensity, grain size effect, texture etc.). The method based on the ratio thin-film/substrate reflection intensities is not complicated by correlation of the least square parameters but suffers strongly from accumulated experimental errors.

Keywords: Titanium nitride; X-ray diffraction; Thickness determination

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1) INTRODUCTION

X-rays can be used to estimate thin film thickness either through scattering on interfaces or through absorption in a thin-film material. Reflectivity curves obtained in symmetrical scans at low diffraction angles show periodic patterns from which the thickness of the film can usually be determined with a better-than-1% accuracy. However, the applicability of this method is restricted to thicknesses smaller than about 0.5 μm and to very flat surfaces and interfaces.

The method of X-ray absorption in a thin film is based on the path length of the X-ray beam inside the film. The path length changes with any change in the incidence angle of the primary beam. The effect is especially strong at low angles of incidence when almost whole surface area of the sample is illuminated. The applications of this approach reported in literature [1] are usually limited to measurements of reflections from the thin film only, neglecting the fact that the intensity of the substrate reflections is also affected by the absorption in the thin film in similar way. The ratio of intensities of reflections from both materials (when both are crystalline) can be in principle utilized for such purposes, too.

We used a sample of TiN thin film [2] deposited on WC substrate to test the three absorption methods. The choice of sample was influenced by the following requirements. The nominal thickness of the film should be between 0.5 and 10 μm. Both components should preferably be crystalline with well-defined composition. At least two reflections from the thin film and two from the substrate should be measurable. Grain size effect (which can strongly affect the measured intensities) should be almost negligible and the effect of texture easy to determine.

Another problem, already know from our previous experiments, was the correlation of parameters refined by least squares, which is critical when using data from one material only. Therefore, this problem was investigated in detail.

2. THEORETICAL BACKGROUND

General formula for diffracted intensity of sample volume V as a function of the Bragg angle θ and of the angle α of incidence of the beam on a flat sample surface is:

$$\mathrm{I} = \mathrm{C} \cdot \mathrm{L}(\theta)\mathrm{P}(\theta)\mathrm{A}(\alpha,\theta,\mathrm{t})\frac{|\mathrm{F}_{\mathrm{hkl}}|^2}{\mathrm{V}_\mathrm{c}^2}\mathrm{Vn}_{\mathrm{hkl}}\mathrm{T}(\alpha,\theta), \qquad (1)$$

where $L(\theta)$ is the Lorentz term, $P(\theta)$ polarization term, F_{hkl} structure factor, V_c volume of the elementary cell and n_{hkl} is multiplicity of crystallographic plains {*hkl*}. *C* is a multiplicative factor which is constant for one experimental set-up and is the same for all measured samples. $A(\alpha,\theta,t)$ is the absorption term and $T(\alpha,\theta)$ is texture term. Only the term $A(\alpha,\theta,t)$ contains information on the thickness *t* of the film. Absorption factor for a thin film of thickness *t* is given by formula [see Refs. 3,4]

$$A_{TF}(\alpha,\theta,t) = \frac{1}{\mu_{TF}}\frac{\sin\beta}{\sin\alpha+\sin\beta}\left(1-\exp\left(-\mu_{TF}t\left(\frac{1}{\sin\alpha}+\frac{1}{\sin\beta}\right)\right)\right) \qquad (2)$$

and the absorption factor for the substrate is:

$$A_{SUB}(\alpha,\theta,t) = \frac{1}{\mu_{SUB}}\frac{\sin\beta}{\sin\alpha+\sin\beta}\exp\left(-\mu_{TF}t\left(\frac{1}{\sin\alpha}+\frac{1}{\sin\beta}\right)\right) \qquad (3)$$

The angles α, β and θ are defined in Fig. 1, μ is the linear absorption coefficient of the thin film (TF) or the substrate (SUB). Since $L(\theta)$, $P(\theta)$, F_{hkl}, V_c, n_{hkl} can be expressed exactly from theory, we can rewrite formula (1) as:

$$I_{hkl}(\alpha) = C_{hkl} A(\alpha, \theta, t) T(\alpha, \theta) \qquad (4)$$

where C_{hkl} is constant for each reflection *hkl*. The aim is to obtain function $A(\alpha,\theta,t)$ because it is then straightforward to obtain thickness from equation (4) using e.g. least-square fitting. However, first we have to measure the texture function $T(\alpha,\theta)$.

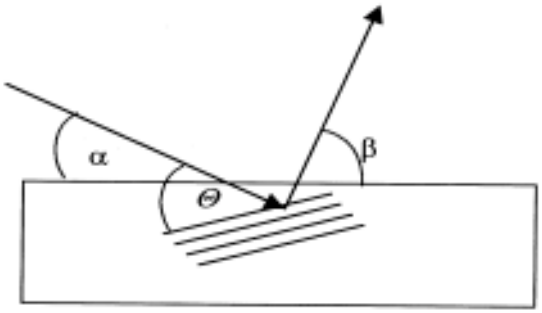

Figure 1 – Definition of angles by means of diffraction of X-rays on a set of crystallographic planes inclined at the angle θ-α with respect to the surface of a flat sample.

3. EXPERIMENTAL AND DATA EVALUATION

Polycrystalline thin film of titanium nitride of the thickness of about 2 μm deposited on a tungsten carbide substrate was used to test the method. First, the sample was investigated by the Debye-Scherrer method and the images obtained confirmed the expected small grain size of both the thin film and the substrate crystallites.

X-ray diffraction data were collected on a Seifert XRD-7 powder diffractometer using asymmetric diffraction geometry of the almost parallel beam conditioned by the 0.4° Soller slits assembly. The divergence slit was 0.15 mm wide, so that the irradiated area on the surface was smaller than the sample size (12.7 mm) for angles α greater than 3°. We believe that this is a reasonable compromise between the requirement of low cross section of the X-ray beam and sufficiently high intensity. Reflections WC(001), WC(100) and WC(101) of the substrate and TiN(111), TiN(200) and TiN(220) of the thin film were measured with Cu K_α radiation at 18 different angles α of incidence between 0.5° and 35° (Fig. 2). We tried to cover the whole range of all possible angles of incidence between zero and 2θ, where θ is a Bragg angle for certain reflection.

Texture measurements were done with Co K_α radiation using the "knife" Eulerian cradle equipped with the χ-tilt, i.e. with the axis of rotation lying on the sample surface and perpendicular to the Θ–axis of the goniometer [5]. Data were obtained at 15 different tilt angles χ to cover the interval of angles α already measured in parallel beam geometry. The relation $\alpha = \theta - \chi$ was used when correcting the data measured at different α angles for the texture effect.

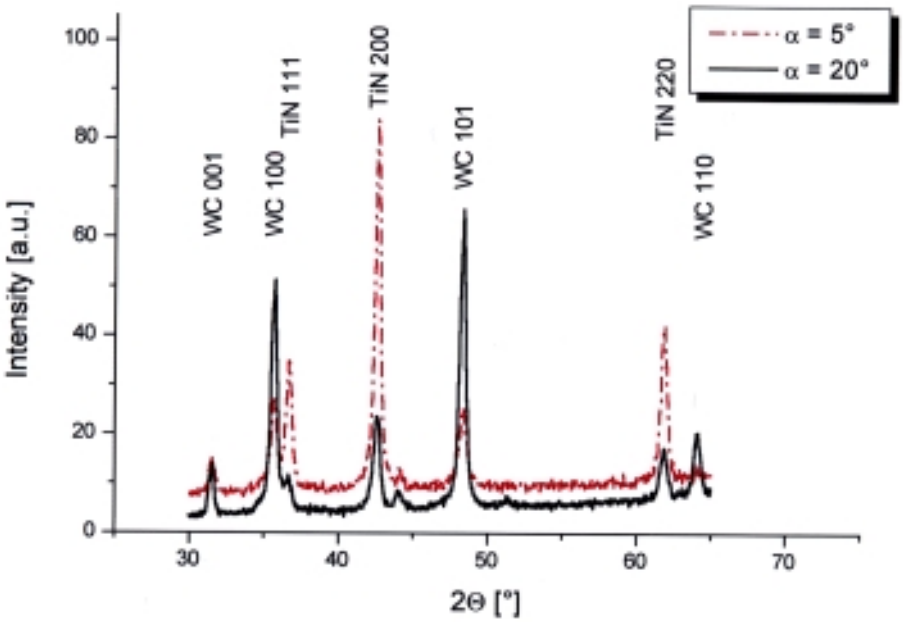

Figure 2 – Examples of X-ray diffraction patterns recorded at two angles of incidence, $\alpha = 5^{o}$ and 20^{o}.

Depending on the diffraction data used, thickness can be evaluated in three ways: (i) from the thin film only, (ii) from the substrate only, (iii) from the ratio thin-film/substrate diffraction data. Texture correction of the parallel beam (PB) data is done by dividing the measured reflection intensities by the χ-scan data:

$$R_{hkl} = \frac{I_{hkl}^{PB}(\alpha,\theta)}{I_{hkl}^{\chi}(\chi(\alpha),\theta)} = \frac{C^{PB} \cdot L(\theta)P(\theta)A^{PB}(\alpha,\theta,t)\frac{|F_{hkl}|^2}{V_c^2}Vn_{hkl}T(\alpha,\theta)}{C^{\chi} \cdot L^{\chi}(\theta)P^{\chi}(\theta)A^{\chi}(\chi(\alpha),\theta,t)\frac{|F_{hkl}|^2}{V_c^2}Vn_{hkl}T(\chi(\alpha),\theta)} \tag{5}$$

$$R_{hkl} = \frac{C^{PB}}{C^{\chi}}\text{const.}A^{PB}(\alpha,\theta,t)$$

The absorption factor A^{χ} for χ-scan changes only slightly with χ and can be treated as a constant. We do not have to consider the other members of the ratio because they are constant for certain reflections, so the following formula was used to fit the measured data:

$$R(hkl) = C\frac{\sin\beta}{\sin\alpha+\sin\beta}\left(1-\exp\left(-\mu_{TiN}t\left(\frac{1}{\sin\alpha}+\frac{1}{\sin\beta}\right)\right)\right) \text{ for TiN-thin film,} \tag{6a}$$

$$R(hkl) = C\frac{\sin\beta}{\sin\alpha+\sin\beta}\left(\exp\left(-\mu_{TiN}t\left(\frac{1}{\sin\alpha}+\frac{1}{\sin\beta}\right)\right)\right) \text{ for WC substrate,} \tag{6b}$$

$$\beta = 2\theta - \alpha.$$

where *C* and *t* are free parameters. When using the ratio of TiN and WC intensities we have a chance to eliminate the unknown constant *C*. However, differences in the structure factor and the Lorentz-polarization factor values both for reflections and for differences caused by using different wavelengths in α- and χ- scans must be taken into account. Hence, there remains only one free parameter, the thickness *t*, for the fitting.

Cross-sectional optical microscopy was used to check the X-ray results (Fig. 3). The sample was cut by a diamond saw and direct image of the cross-section was observed and registered on a polarization microscope with physical magnification of 1600x. Several tens of point couples were analyzed using the Adobe Photoshop. The distances between the points along the surface were kept constant. An average thickness of 2.2 ± 0.8 μm was found.

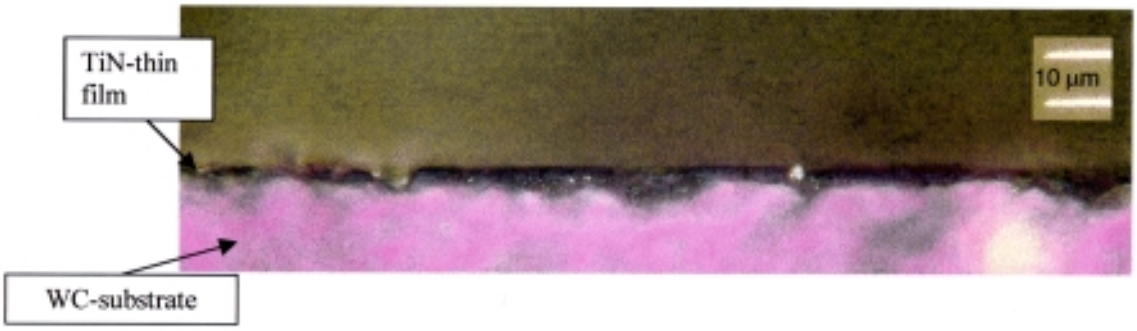

Figure 3 – Cross-sectional optical micrograph from polarization microscope**.**

4. RESULTS AND DISCUSSION

The results of the thickness determination are summarized in Tables 1–3. The texture analysis is reported in Fig. 4 and the fitting of the measured intensities by expressions (6) is shown in Figs. 5-7. Several methods of data evaluation were used. For example, the TiN data were analyzed by using integral intensities of reflections as well as peak heights. The reason for this was the smaller spread of data along the curves fitted to the χ-scans in the texture measurements compared with the integral intensity data. Table 1 compares the results of both approaches (the rather small thickness value of 0.31 μm, determined from integral intensities of the TiN(111) reflection, could originate from the strong overlap of this peak with the neighbouring WC(100) peak. In Table 2 we also compare results of the thickness determination obtained with and without texture correction of the α-scan data in order to estimate the effect of this correction. Finally, Table 3 reports results based on the assumption that the ratio of calculated scale factors is correct and so only one unknown parameter *t* is refined. The table also shows the results where a possible error in this ratio is assumed to be multiplicative and is described by a similar unknown parameter *C*, which is refined in the same way as in the two previous cases (TiN or WC reflections alone).

The average thickness of 2.00 ± 0.16 μm obtained from the WC substrate data with texture correction (see Table 2) is in reasonable agreement with the thickness estimated from the optical microscopy (2.2 ± 0.8 μm). On the other hand, the results obtained from TiN thin-film

data (Table 1, peak heights) are substantially lower, with the average thickness equal to 1.23 ± 0.12 µm. The thickness obtained from the intensity ratio of both materials strongly depends on the reflection couple used and ranges from 1.27 to 4.24 µm.

Table 1: Results of fitting of TiN - thin film data after texture correction

	t [µm]	Δt [µm]	Δt/t [%]	C	ΔC	ΔC/C[%]	χ2
peak heights							
111	**1.10**	0.12	10.8	44.6	2.5	5.5	1.20
200	**1.36**	0.13	9.4	44.6	2.1	4.4	1.61
peak intensities							
111	**0.31**	0.12	37.6	134.0	40.7	30.4	4.33
200	**1.28**	0.15	12.1	73.6	4.2	5.7	5.18

Table 2: Results of fitting of WC-substrate data.

	t [µm]	Δt [µm]	Δt/t [%]	C	ΔC	ΔC/C[%]	χ2
without texture correction							
001	**2.06**	0.15	7.2	9.0E+04	1.0E+04	11.3	0.08
100	**2.00**	0.11	5.7	3.5E+05	2.8E+04	8.0	1.01
101	**2.09**	0.10	4.7	2.6E+05	1.4E+04	5.4	1.09
with texture correction							
001	**2.11**	0.16	7.8	143	18	12.5	1.49
100	**1.87**	0.12	6.4	123	10	8.5	1.66
101	**2.03**	0.10	5.0	97	5	5.6	1.09

Table 3: Results of fitting of intensity ratio after texture correction using peak intensities.

WC	001	001	100	100	101	101
TiN	200	200	200	200	200	200
t [µm]	**4.24**	**2.58**	**1.27**	**1.61**	**-**	**2.18**
Δt [µm]	1.38	1.23	0.32	0.33	-	0.36
C	1 fixed	0.801	1 fixed	1.088	1 fixed	1.436
ΔC		0.079		0.039	poor fit	0.035
χ2	0.040	0.027	0.010	0.008		0.008

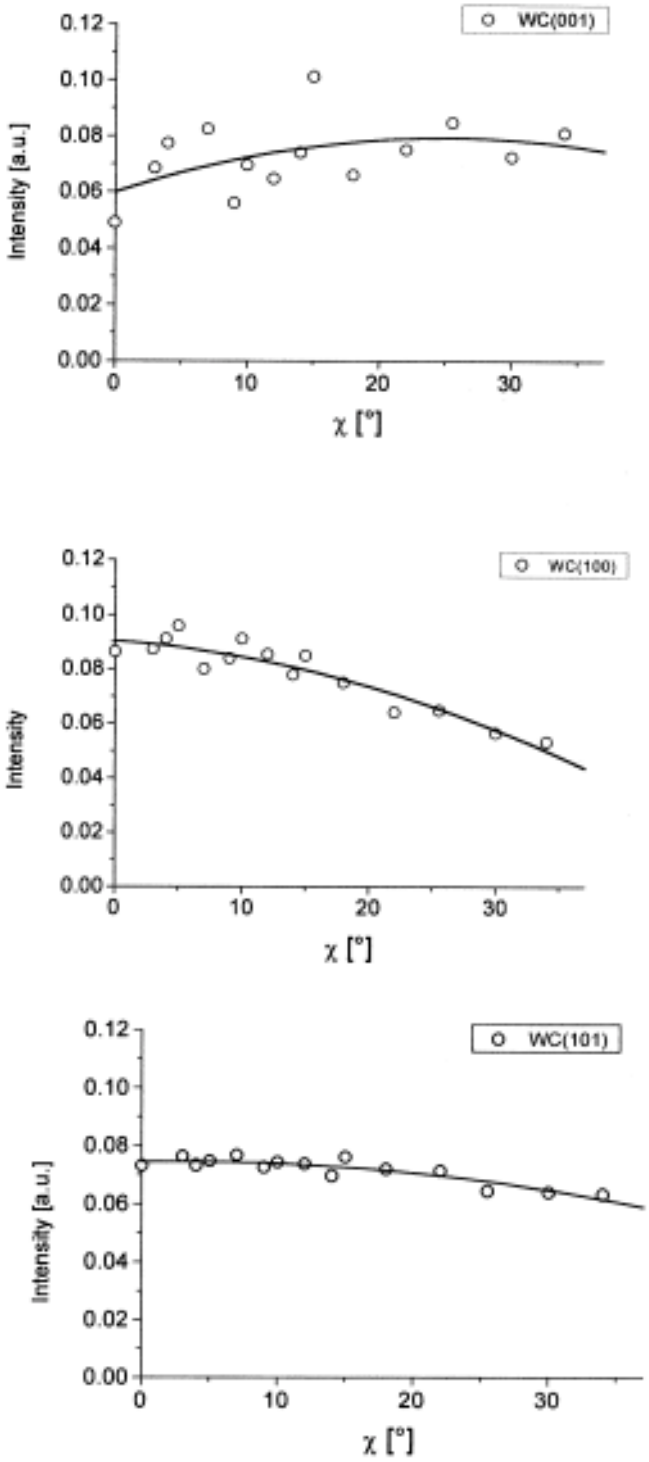

Figure 4 – Examples of texture determination of WC substrate from χ - scans. Experimental data are fitted by a polynomial of second order.

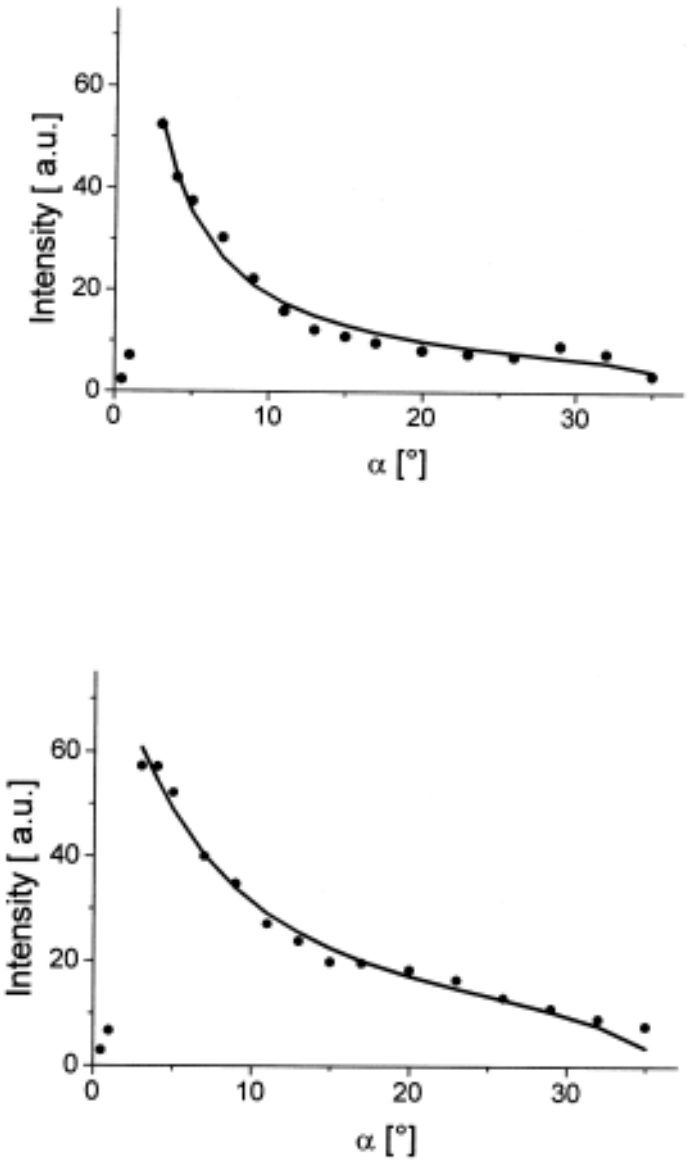

Figure 5 – Texture corrected intensities of TiN thin film reflections as a function of angle α of incidence of primary beam fitted by formula (6a); a) TiN (111), b) TiN (200).

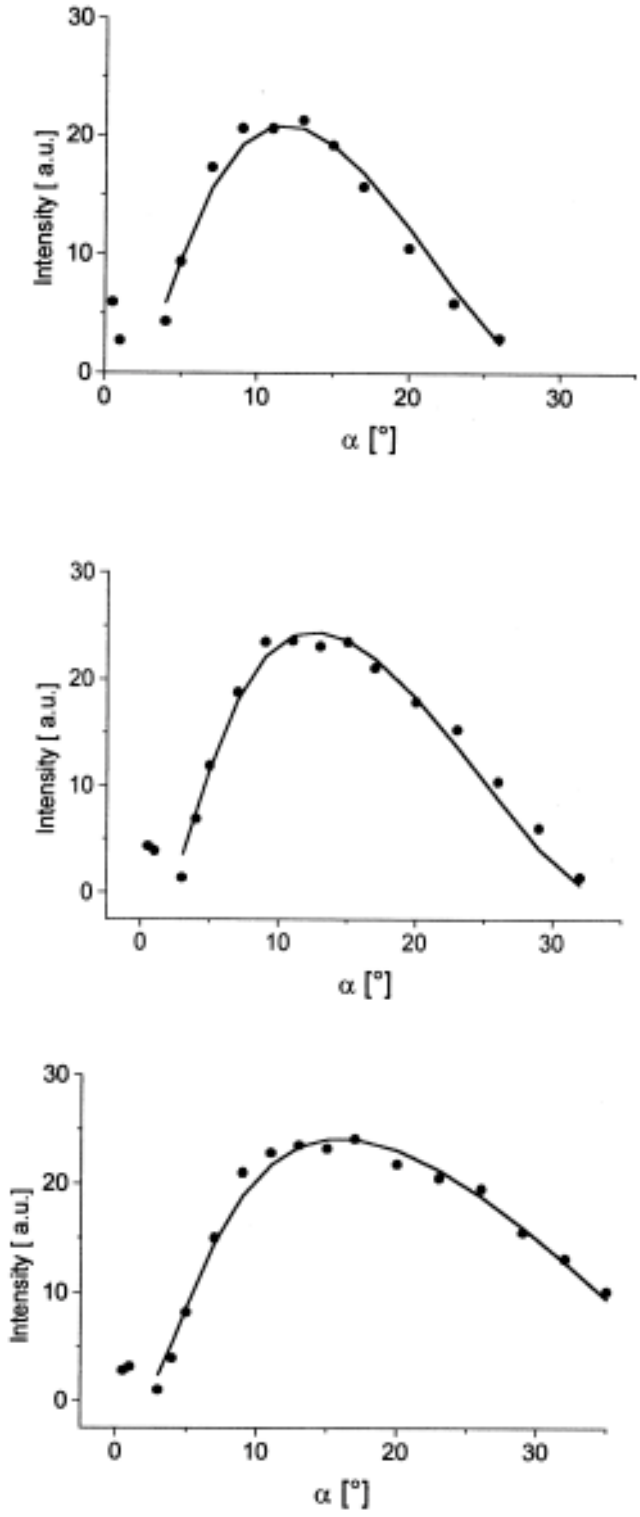

Figure 6 – Texture corrected intensities of WC substrate reflections as a function of angle α of incidence of primary beam fitted by formula (6b); a) WC(001), b) WC(100), c) WC(101).

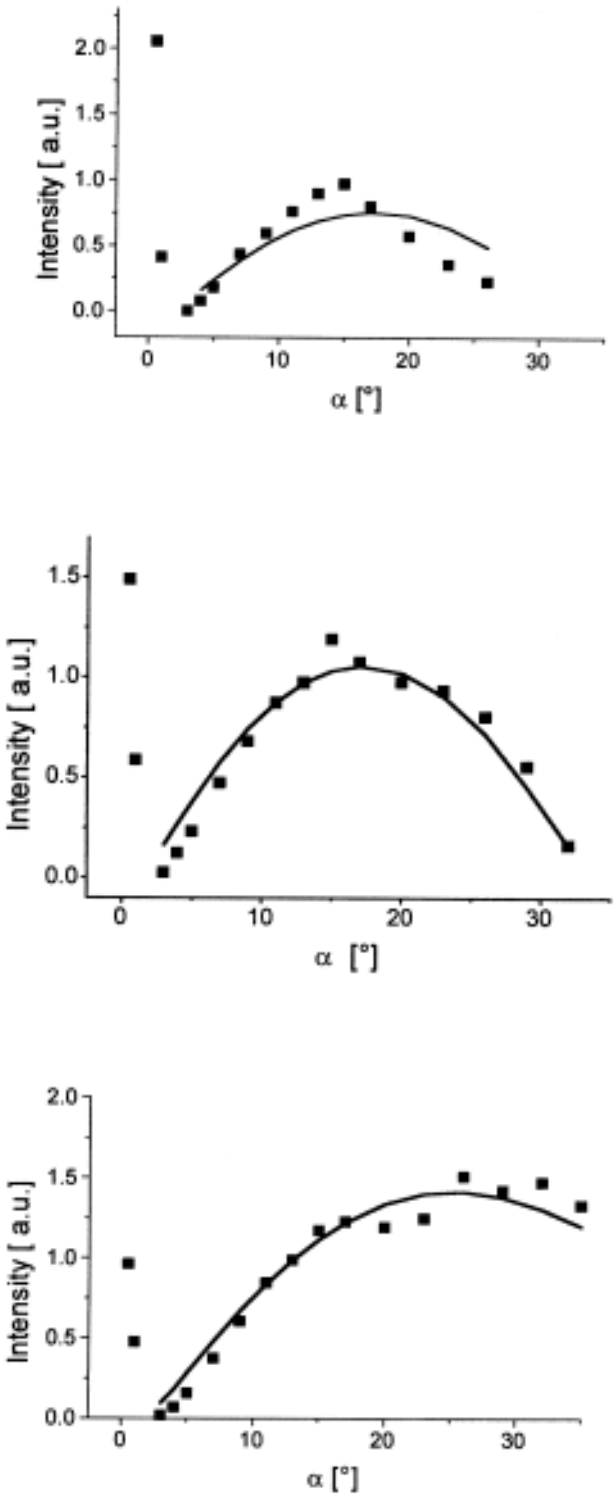

Figure 7 – Ratio of intensities fitted by the ratio of functions in (6);
a) WC(001)/TiN(200), b) WC(100)/TiN(200), c) WC(101)/TiN(200).

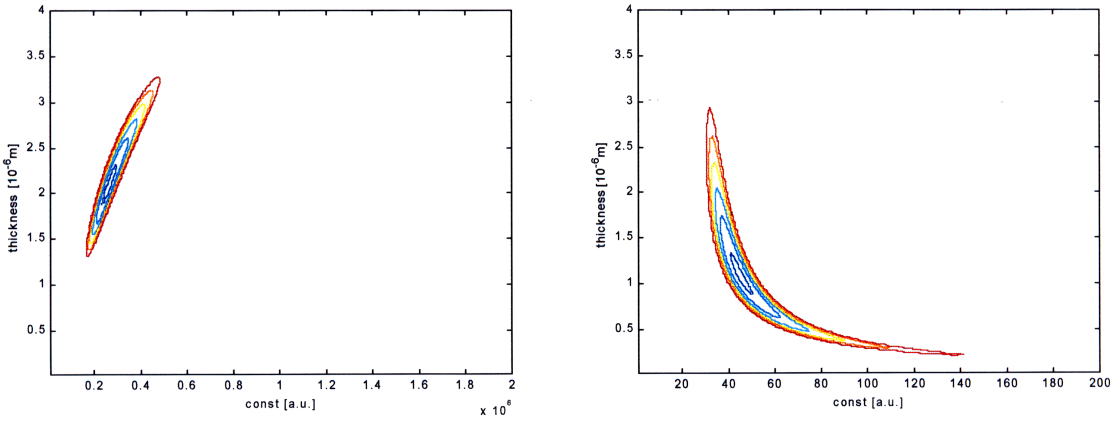

Figure 8 – Maps of residuals in the plane of fitted parameters *C* and t; a) WC(101), b) TiN (111).

The origin of such differences could be either experimental or physical, or they could be the consequence of the correlation between the fitted parameters *t* and *C*. It should be noted that any method based on intensity measurements depends strongly on the measurement accuracy. From this point of view, the stronger and well-separated reflections from the WC substrate are clearly much more convenient for the thickness determination in our case. The TiN thin-film reflection intensities are highest for small angles α because the irradiated volume is the highest as well, but instrumental effects can spoil the data in this angular region. The thin-film reflection intensities decrease with increasing α because of the gradual decrease of diffracting volume, and dependence of *I* versus α is almost linear for higher angles. On the other hand, the diffraction intensities from the substrate are the highest for $\alpha = \theta = \beta$ because the X-ray trajectory in the thin film is shortest in this symmetrical sample position. The reflection intensities of the substrate are thus less affected by instrumentation and by the decrease in irradiated area at this angular range. The effect of texture was found to be almost negligible in this particular case (see Table 2).

Physical effects that are independent of the angle of sample inclination can be neglected because they are included in the scale factor. This is true only for the methods based on the thin-film or substrate intensity data alone, not for the ratio of intensities from the two materials. A possible reason for the smaller thickness derived from the thin-film data than from the substrate data (t(TF) < t(SUB)) can be the presence of volume fractions of amorphous TiN in the thin film. These amorphous fragments do not diffract like crystalline TiN matrix but they do reduce the diffracted intensity from the substrate by absorption effects. Lateral inhomogeneity of the TiN film thickness, clearly seen on the optical micrograph, could also give rise to discrepancies between the X-ray diffraction and the optical microscopy results. The influence of the different radiation wavelengths used for texture analysis can be neglected as the small thickness of TiN thin film is fairly penetrable for both the Cu and Co X-rays. The texture data were treated as being independent of small changes in absorption in the TiN film during χ-tilting. This assumption was confirmed by additional calculations of the absorption effect, which is

practically negligible in comparison with the large absorption changes during the α-tilts. The reason for such a large difference is the relatively small change of the X-ray path in the texture measurements compared with the asymmetrical difraction at small angles as a function of the angle α.

Let now discuss the statistical effects. The fitted parameters *C* and *t* correlate more for the thin-film data than for the substrate data because the correlation of parameters is connected with statistical errors in the measured intensities, which are higher in the case of weak TiN reflections. Fig. 8 shows the maps of residuals in the plane of refined parameters. It can be clearly seen that the total minimum is much sharper for the substrate data than for the thin-film data.

The fluctuation in the thickness values from the ratio WC substrate/TiN thin-film reflection intensities (see Table 3) was expected because the errors in the four sets of experimental data had been added together. This fluctuation in the thickness values could also be due to the inaccuracy in the calculated parts of the scale factors. The efforts to compensate such errors by the additional (and artificial) free multiplicative factor *C* clearly failed.

5. Conclusions

Considering the results of our studies, we recommend using the substrate reflection for thin-film thickness measurement when the substrate reflections are sufficiently strong and only slightly influenced by grain size statistics and reasonably simple texture effects (small and systematic changes in reflection intensities during χ-scans). This technique is also preferable to the thin-film data because it has fewer problems due to unavoidable experimental effects at low incidence angles and to the correlation of fitted parameters. One of the advantages in using the intensity ratio is the absence of the correlation problem. Its drawback is the higher sensitivity to statistical errors in intensity measurements, to errors in texture correction determination and to possible inaccuracy in the calculation of the angularly independent part of the ratio of the scale factors. The tested methods are not routine techniques, but they could be used when microscopy is excluded, e.g., when the sample must not be destroyed or when information on the average thickness of the film is required instead of just the local information obtained by a microscope.

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