THIN FILM XRD TOTAL PATTERN FITTING APPLIED TO STUDY OF EVOLUTION OF MICROSTRUCTURE OF TiO₂ FILMS

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ABSTRACT

New XRD total pattern fitting software MStruct was used in study of crystallization and microstructure evolution of magnetron-deposited TiO₂ thin films and powders. It is an extension of the FOX program for structure determination from powder diffraction and it includes in particular the effects and corrections necessary for thin film analysis when parallel beam geometry and asymmetric detector scan at small angles of incidence are applied (corrections for refraction and absorption, residual stress, preferred orientation). The program also includes description of crystallite size broadening in terms of log-normal distribution, two models of strain (phenomenological and dislocation model) as well as the influence of stacking faults in the most common cubic and hexagonal structures. It was shown that during crystallization of amorphous TiO₂ films, tensile stresses are generated which cause anisotropic shifts of diffraction peaks and the consideration of the effect in terms of weighted Reuss-Voigt model improved the fits significantly: The determined stresses agree well with the values measured directly by stress analysis. The crystallite size determined was above 100 nm already from the very beginning of crystallization process in contrast to nanocrystalline films (5-10 nm) which were stable to much higher temperatures.

INTRODUCTION

Titanium dioxide films have many remarkable properties and can found applications in different areas for example as ultra thin film coatings, nanostructured membranes etc., in electrochemistry and electrocatalysis, in microoptics and electrooptics and in photocatalysis. The photocatalytic activity of TiO₂ (e.g. Sopyan et al., 1996, Byun et al., 2000, Negishi, 1998) can result in the decomposition of organic compounds on the TiO₂ surface. Irradiation by UV also leads to excellent hydrophilicity, significant drop of the contact angle between water and the TiO₂ surface. However, the properties are largely dependent on the phase composition and in particularly the structure and microstructure of the films. The films should not be amorphous as they often are after the deposition but rather nanocrystalline. Therefore, the crystallization, microstructure and its thermal stability are of particular interest. In previous studies, amorphous films of different thickness were annealed and it was found that they crystallize at approximately 250 °C and their crystallite size was then immediately above 100 nm (Kužel et al., 2007a). The films with the thickness below 400 nm crystallized at higher temperatures (350 °C). Tensile residual stresses have been found in crystallized films by the sin²ψ method. Studies of the deposited nanocrystalline films with different thickness and films prepared at different oxygen pressure were briefly described in (Kužel et al., 2007b and Kužel et al., 2008). It was found that rutile grows on the interface with the substrate and it is replaced by anatase with increasing distance from the substrate. Then detailed in-situ studies of crystallization of amorphous films were performed and it
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was found that the process can be well described by the modified Avrami equation (Nichtová et al., 2008). These studies also confirmed creation of tensile stresses during the crystallization.

In most cases, the films investigated were quite thin (tens or hundreds of nanometers) and conventional symmetric 0-2θ scans (Bragg-Brentano) were not very helpful. Instead, parallel beam geometry (with incident beam mirror and diffracted beam collimator) and 2θ scans at low angles of incidence were applied. However, this technique gives about three times worse resolution. Moreover, the peaks are broadened by strain and small crystallite size and are severely overlapped. In this case, the analysis of individual peaks or fitting of peak clusters can hardly be applied and the diffraction patterns should be evaluated by nowadays popular whole pattern fitting. There are several groups of programs available. The most famous are Rietveld type programs like Fullprof (Rodríguez-Carvajal, 1993) or GSAS (Larson and Von Dreele, 1994) or several commercial programs. They are mainly dedicated for crystal structure determination and they are also used for quantitative phase analysis. They also include phenomenological description of anisotropic line broadening and can be used for estimation of crystallite size and microstrain. The second group of programs (Scardi and Leoni, 2006, Ribárík et al., 2001) is concentrated on physically correct description of real structure parameters (different crystallite size distributions, dislocations, stacking faults) but usually does not include structural part of the refinement. Neither of the programs is suitable for the thin films investigated. The fitting procedure requires appropriate evaluation of 2θ scans taken for thin films at low angles of incidence. This should include appropriate absorption correction, refraction correction, consideration of residual stress and texture. For this case, only the program Maud (Lutterotti, 2004) having many options is available. However, this suffers from the lack of documentation and some models like dislocation broadening are not included either.

Therefore, we decided to develop own software allowing easy addition of models in terms of simple modules. Such a system exists for structure determination, Fox program (Favre-Nicolin and Cerny, 2002). This has been developed by Vincent Favre-Nicolin who also created flexible library of Crystal Objects which can be easily used for further programming (in C++). The system has been extended by features connected with Micro-Structure analysis by Z. Matěj, the extension is called MStruct (Matěj and Kužel, 2009), and it has been applied for several analysis (Kužel et al., 2008, Kužel et al., 2009). However, in these cases some important features in particular for thin films were missing and therefore a short description of new version and its application is described here.

**EXPERIMENTAL**

**Samples**

TiO\textsubscript{2} films were sputtered by dual magnetron equipped with two Ti(99.5) targets of 50 mm in diameter and supplied by a dc-pulsed Advanced Energy Pinnacle Plus+ 5kW power supply unit operating in bipolar asymmetric mode at repetition frequency \( f_r = 100\text{kHz} \) and duty cycle \( \tau/T = 0.5 \); here \( \tau \) and \( T \) are the length of pulse and the period of pulses. Films were deposited on unheated microscope glass slides \((26 \times 26 \times 1 \text{ mm}^3)\) and silicon (100) substrates \((26 \times 26 \times 1 \text{ mm}^3)\) at substrate to target distance \( d_{st} = 100 \text{ mm} \); total working pressure \( p_T = 0.9 \text{ Pa} \); average pulse discharge current \( I_{da1,2} = 3 \text{ A} \) and average pulse power density \( W_{da} \approx 55 \text{ W cm}^{-2} \). M aximum
substrate surface temperature during the deposition was lower than $T_{surf} \leq 160 \, ^\circ C$. Further details on dual magnetron system are given elsewhere (Baroch et al., 2005). For comparison nanocrystalline powders of TiO$_2$ were analysed too.

Different sets of amorphous and nanocrystalline samples were studied. Nanocrystalline TiO$_2$ films with different thickness $h = 100, 220, 515, 935, 2000$ nm were deposited on the glass and silicon substrates in the oxide mode of sputtering at oxygen partial pressure $p_{O2} = 0.15$ Pa and deposition rate $a_D = 9$ nm/min. The samples were annealed in the air in the temperature range 200-1000 $^\circ C$ with the step of 100 $^\circ C$ for 30 minutes at each temperature.

**Measurements**

The measurements were performed on Panalytical X'Pert MRD in parallel beam setup, 2$\theta$ scans with the angles of incidence 0.5-1.0$^\circ$ with parallel plate collimator placed in the diffracted beam and the Goebel mirror inserted in the primary beam. The use of small angles of incidence is necessary for the films studied because of their small thickness. Comparison of scans at different angles is shown on Fig. 1.

![Figure 1](image-url)

**Figure 1**: Part of the measured pattern for (a) 440 nm sample with an incidence angle $\omega = 1^\circ$, (b) 440 nm sample with an incidence angle $\omega = 0.5^\circ$ and (c) 200 nm sample with an incidence angle $\omega = 0.5^\circ$. Pictures (a-b) illustrate suppression of a “diffuse” background scattering from the silicon substrate by decreasing incidence angle $\omega$. For thinner samples e.g. (c) incidence angle $\omega = 0.5^\circ$ is still not small enough.

In addition to these 2$\theta$ scans with small constant incidence angle, X-ray reflectivity curves were measured for all the samples and measurements of residual stresses were carried out by using a polycapillary and Eulerian cradle by the sin$^2\psi$ method for several different peaks.
TOTAL PATTERN FITTING – MStruct PROGRAM

The program has been written as an extension of the FOX system and applied to several problems. It can be downloaded from xray.cz/mstruct. It comprises several groups of parameters.

Peak positions

Peak positions are determined by variable lattice parameters and zero shift error. Specimen displacement error is not considered for parallel beam geometry but included for symmetrical 0-2θ scans. For low angles of incidence close to the angle of total reflection which are required for very thin films, in particular below 1°, the refraction correction must be included (Toney and Brennan, 1989, Noma et al., 1999, Colombi et al., 2006). It can be calculated according to the relation

\[ \Delta 2\Theta = \alpha - \frac{1}{\sqrt{2}} \sqrt{(\alpha^2 - 2\delta) + \sqrt{(\alpha^2 - 2\delta)^2 + 4\beta^2}} \quad , \]

where \( \alpha \) is angle of incidence, \( \delta \) and \( \beta \) are real and imaginary parts of refraction index \( n \), respectively \( (n = 1 - \delta - i\beta \sim 1 + \chi_0/2) \) (Toney & Brennan, 1989; Noma et al., 1999). The refraction index \( n \) is connected with an electron and hence also with an absolute density of the film. The effect on the peak shift of anatase for different angles of incidence can be seen on Fig. 2 and for low angles it is quite significant. For anatase, \( \chi_0 = -2.30 \times 10^{-5} - i 1.16 \times 10^{-6} \) and the peak shifts (in °2θ) for three different angles of incidence 0.27°, 0.5° and 1.0° are 0.25°, 0.09° and 0.04°, re-

**Figure 2:** Experimental diffraction peak (anatase, 101) positions (dots) of the 800 nm thick sample in dependence on the angle of incidence \( \omega \). The maximum corresponds to the angle of total reflection. The fitted curve corresponds to the formula (1) and absolute TiO₂ density 3.25 g/cm³.

**Figure 3:** Part of the measured pattern of the 440 nm (64-6) sample: (o) data, (blue line) calculated pattern, (green lines) 219, 1 1 10, 228, 413, 404 and 332 anatase reflections.
spectively as it is also seen from the Fig. 2. When the peak profiles are measured and evaluated for different angles of incidence, then formula (1) can also be used for fitting of film densities and instrumental peak shifts. The curve is shown on Fig. 2 for sample 800 nm thick and peak 101 of anatase.

As follows from the formula, in total pattern fitting the shifts due to the refraction have the same effect as a zero-shift error, i.e. they are independent of \( \theta \). Modelling of the refraction effect only by the \( \theta \) zero-shift correction can result in unrealistic high values of the zero-shift error (e.g. 0.1°). This can be significantly improved if the refraction correction is included. Moreover with the refraction correction it is not necessary to refine zero-shift error if different or multiple incidence angles are used for the same sample. And for samples consisting of multiple layers of different electron densities the zero-shift error cannot account for the refraction effect properly. These three points make the refraction correction useful.

The positions can also be influenced by stacking faults or residual stresses (see below). How important task is the \( \theta \) zero-shift error determination, it can be illustrated by a numerical test on the powder stress-free silicon standard data measured under the same conditions as studied TiO\(_2\) samples. This shows that the zero-shift error of the order of 0.01° implies a deviation of about 50 MPa in the residual stress analysis.

**Peak intensities**

Peak intensities are calculated by the ObjCryst library from a known atomic structure. The structural parameters can be varied only if necessary. However, they are used as constraints for the peak positions and intensities. The effects of absorption in the thin film and a texture correction (see below) can be included. The model of the absorption correction for our TiO\(_2\) samples consists of a simple anatase and rutile layered structure on the Si or glass substrate. Individual layers are characterized with their thickness \((T_i)\) and linear absorption coefficient \((\mu_i = 2\pi/\lambda \times |\chi_{0,im,i}|)\). In general, multilayer systems can be modeled. The intensity correction for diffraction from one layer if the refraction effects are neglected can be calculated from a length of path of the incident and diffracted beam through the film by a well known formula (Simek et al., 2006):

\[
I_i = \frac{T_i}{\sin(\omega)} [1 - \exp(-T_i / T_i^\text{p})] .
\]

\(T_i^\text{p}\) is the so-called penetration depth for a given layer and

\[
1/T_i^\text{p} = \mu_i [1/\sin(\omega) + 1/\sin(2\theta - \omega)] ,
\]

where \( \omega \) is the angle of incidence. Equation (2) includes also a \( 1/\sin(\omega) \) term accounting for an irradiated sample length. If the diffracting layer is buried under a series of other layers, the absorption in these layers should be also corrected by corresponding exponential terms.

If the refraction effects cannot be neglected then an additional term for a Fresnel transmission coefficient of the layers interfaces should be included (Noma et al., 1999; Colombi et al., 2007) and the absorption of the incident beam in the layer should be treated more precisely to account
for a finite but steep decrease of the effective diffracting depth close to the angle of total external reflection. If the interference effects in the case of general multilayer structure take place the problem becomes complex (Fewster et al., 2005).

**Texture**

In general, the texture correction can be obtained from a known model ODF after appropriate integration over all crystallites with diffracting \{hkl\} planes perpendicular to direction of the measured diffraction vector. This is, of course, different for asymmetric scans than for conventional Bragg-Brentano geometry. At present a simple numerical integration algorithm for this task is implemented in the system. Principally any type of the ODF function can be supplied to the algorithm and used for texture correction, but only a simple model using Gaussian distributions of crystallites and possible inclinations of texture with respect to the sample normal is included now and available for the refinement.

There is only a weak texture in the TiO₂ films obtained by crystallization of amorphous films. The texture in the as-deposited nanocrystalline films investigated is quite complex, not of fibre type, because of deposition geometry not having axial symmetry (dual magnetron). Moreover, the pole figures of samples, where both rutile and anatase phases are still nanocrystalline are hard to measure, hence it is difficult to find out an appropriate model ODF function.

For such cases, if the texture is unknown or difficult to describe, the peak intensities can be varied also independently by multiplication of intensities of individual peaks by refineable factors. This is called an “Arbitrary texture” in the Maud (Lutterotti et al., 2004). Of course, this can lead to more correlation in fitting, it introduces a need for more interactive work of the user and should be used only if inevitable.

This way was used for the fitting of diffraction patterns of studied samples. The patterns were in the first step refined with intensities completely constrained by the atomic structure model and in the second step few peaks or clusters of peaks were let to refine their individual intensity correction factors.

**Line profiles**

*Instrumental function, instrumental corrections, instrumental parameters*

Peak profiles are given by the numerical convolution of the known instrumental function and physical profiles including several free parameters (Scardi and Leoni, 2002). The instrumental function is described by the pseudo-Voigt (pV) function. 2θ angular dependence of its parameters (FWHM, pV mixing parameter \(\eta\) and asymmetry \(A\)) are given by the commonly used relations:

\[
\text{FWHM (rad)}^2 = W + V \tan(\theta) + U \tan^2(\theta) ,
\]

\[
\eta = \eta_0 + \eta_1 2\theta (\text{rad}) ,
\]

\[
A = A_0 + A_1 / \sin(2\theta) + A_2 / \sin^2(2\theta) .
\]
The parameters $U$, $V$, $W$, $\eta_0$, $\eta_1$, $A_0$, $A_1$, $A_2$ are determined by the fitting of standard diffraction pattern (LaB$_6$) measured on the same instrumental arrangement as the one used for measurement of the samples investigated.

**Size, strain, lattice defects**

Physical effects can be conveniently modelled in real space (Fourier coefficients). The size broadening effect is described by the model function for log-normally distributed spherical crystallites like in (Scardi and Leoni, 2002; Ribárik et al, 2003) with two refineable parameters – median of crystallite size and variance of the distribution or alternatively by distribution histogram like in (Scardi and Leoni, 2006). Similarly to these programs the strain broadening is described by the dislocation model including three parameters – dislocation density, dislocation-correlation parameter (cut-off radius) and fraction of the edge dislocations assuming that possible dislocation types and consequently the contrast factors are known. Recently, the influence of stacking faults (Scardi and Leoni, 1999, 2002; Velterop et al, 2000; Balogh et al, 2006) in the f.c.c. has also been included. The dislocation broadening was used mainly for the evaluation of metals after severe plastic deformation (Kužel et al, 2009). However, since the type of crystal defects in TiO$_2$ crystalline phases that are related to the microstrain are not known and could not be simply observed, the phenomenological microstrain broadening function was used. The peak broadening dependent on the diffraction vector magnitude is modelled by the pV function. Its FWHM dependence with diffraction angle $2\theta$ is given by the Cagliotti polynomial with only the quadratic term $U$ nonzero. This means that the FWHM in the reciprocal space units is linearly increasing with the diffraction vector magnitude. The shape factor $\eta$ of the pV-function common for all the $2\theta_{hkl}$ diffraction peaks of a particular phase can also be refined. The relation for FWHM can be converted into the integral breadth $\beta$ and by using the formulas from (Wilson, 1949; Scardi and Leoni, 1999) one parameter - microstrain $e$ is determined:

$$FWHM\left(2\theta [\text{rad}]\right)^2 = U \tan^2(\theta) ; \beta(2\theta [\text{rad}]) = 4e \tan(\theta) ; 4e = \left(\frac{1-\eta}{\varphi_G} + \frac{\eta}{\varphi_C}\right) \sqrt{U},$$

where $\varphi_G = 2(\ln(2)/\pi)^{1/2}$, $\varphi_C = 2/\pi$ are the well known Gaussian and Lorentzian shape parameters.

**Residual stress**

In previous work (e.g. Kužel et al (2008)), the effect of residual stress was not included in the total pattern fitting algorithm. The stress can cause shift of peaks which is varying, in $2\theta$ scans, with $2\theta$ according to the sign and magnitude of the stress. However, it can also result in a significant anisotropy of these shifts in case of elastic anisotropy. Tensile residual stresses in the as-deposited amorphous films were found in (Kužel et al 2007a) together with a systematic anisotropy in peak shifts. It was not possible to explain the anisotropy with the aid of elastic constants for rutile phase of TiO$_2$ and the constants were not available for anatase. The calculated elastic constants appeared recently (Iuga et al, 2007), though and MStruct has been extended for the effect of residual stress as well. Putting more constraints on peak positions and/or intensities in total pattern fitting of TiO$_2$ films with severe peak overlap as can be seen on a typical segment of diffraction pattern on Fig. 3 is absolutely necessary.
The effect of residual stress in the current version of MStruct is included for a simple symmetric-biaxial stress \( \sigma \) in the plane of sample surface \((\sigma_{11} = \sigma_{22} = \sigma, \text{ all other } \sigma_{ij} \text{ components are zero})\) with linear \( \sin^{2}\psi \) dependence of interplanar spacing \( d \):

\[
\varepsilon_{\psi}^{hkl} = \frac{1}{2} s_{2}^{hkl} \sigma \cdot \sin^{2}\psi + 2 s_{1}^{hkl} \sigma \quad (7)
\]

where the strain \( \varepsilon_{\psi}^{hkl} = (d^{hkl} - d_{0}^{hkl})/d_{0}^{hkl} \) is given as a relative change of interplanar spacing \( d \) measured at inclinations \( \psi \). In the case of the 2\( \Theta \) scan with and incidence angle \( \omega \) the inclination angle \( \psi \) can be written as \( \psi = \Theta - \omega \). Each \( hkl \) reflection in the powder pattern than measures an interplanar distance \( d^{hkl} \) of \( hkl \) lattice planes which normal is inclined by an angle \( \psi^{hkl} = \Theta^{hkl} - \omega \) to the sample surface normal. From the model the stress free lattice parameters (stress free interplanar distance \( d_{0}^{hkl} \)) can be calculated. By combining the information from multiple \( hkl \) reflections lattice the residual stress parameters can be determined from a single powder pattern.

The X-ray elastic constants \((s_{1}^{hkl}, s_{2}^{hkl})\) (XEC) are calculated in two extreme models of grain interactions – Reuss and Voigt. In the case of lower symmetry (tetragonal for anatase) they can be conveniently calculated according to (Popa (2000); also Popa and Balzar, 2001; Behnken and Hauk, 1986). Then two refineable parameters appear – residual stress and fraction of Voigt-Reuss models.

The extended program MStruct has been used for the evaluation of the sets of amorphous magnetron deposited thin films with different thickness that were annealed and the crystallization studied in-situ in XRD high temperature chamber (Kužel et al., 2008). During the crystallization tensile residual stresses were generated. The films were then studied at room temperature with both parallel beam 2\( \Theta \) scans and total pattern fitting including the effect of residual stress and direct stress measurement by \( \sin^{2}\psi \) method on several peaks.

**EXPERIMENTAL RESULTS**

Size and microstrain parameters for films of different thicknesses reveal no systematic dependence. Microstrain in all samples was found to be about \( \varepsilon \sim 0.2\% \). Crystallites size for thicker samples reached approximately 150 nm exceeding the XRD sensitivity limit (considering resolution \( \Delta2\Theta \sim 0.3^\circ \)). For thinner samples refinement gave crystallite size values slightly bigger than the film thickness. It is assumed that crystallite size is approximately equal to 200 nm. For thinner samples the crystallites size is limited at least in one dimension by the finite film thickness and slightly higher determined values of crystallite size could be caused by measurement of inclined planes in asymmetric diffraction.

Correction for a refraction effect was included into the model. From the fits of measured X-ray reflectivities, the densities \( \rho \) of TiO\(_2\) films were obtained as 3.73 g/cm\(^3\) for all the samples. This density was later used for calculation of proper refraction index \( n \) and refraction correction according Eq. (1) \((\Delta2\Theta \sim 0.08^\circ \text{ for incidence angle } \omega = 0.5^\circ)\). With this correction the 2\( \Theta \) zero-shift could be reduced to realistic values \( \pm 0.01^\circ \) and was set to zero for all samples. Moreover it was worthless to compensate the zero-shift error in any other way, if a different incidence angle was used or the measurements for multiple incidence angles were performed (e.g. as in the Fig. 1 a-b).
The effect of including the peak position correction due to the residual stress is illustrated on Figs. 4-5 and in the Table 1. Measured and calculated diffraction patterns (a-b) and their difference curves (c) for the case, when residual stress was not included in the model and only lattice parameters were refined and when the residual stress effect was assumed, are depicted on Fig. 4 for a sample of thickness 300 nm (64-5). Details of the 2\(\Theta\) high angle anatase reflections are shown on Fig. 5. Shifts of diffraction lines are apparent especially for soft anatase directions - 219 and 1 1 10. The Reuss-Voigt weight ratio in the stress model was fixed at average value determined from the direct stress measurement (0.3). Residual stress values in the films obtained by the total pattern fitting are presented in the Table. 1 together with \(R_{wp}\) factors for both the case of stress omission and the case of stress inclusion in the fitting. Consideration of the residual stress leads to improvement of the \(R_{wp}\) factor (in average about 2.5%).

Significance of the residual stress inclusion into the model can be confirmed by an F-test of \(\chi^2\) or \(R_{wp}^2\) factors. Two questions were tested: A) if the \(R_{wp}\) values differ significantly (weighted residual fit patterns have significantly different variances) and B) if the addition of the stress parameter improves \(R_{wp}\) factors significantly? Typical analysed 2\(\Theta\) scan consisted of 2500 data points, 30 parameters were refined, average \(R_{exp}\) was about 12% and obtained \(R_{wp}\) was about 18%. In the case A) two \(\chi^2\) variances with almost the same number of degrees of freedom (dof) are compared. In the case B) of the nested model test a \(\chi^2\) variance with a single dof is compared with a \(\chi^2\) variance with approx. 2500 dof. This gives for significance level \(\alpha = 1\%\) minimal required absolute difference of \(R_{wp}\) factors: A) \(\Delta R_{wpA} \sim 1\%\) and B) \(\Delta R_{wpB} \sim 0.02\%.\) The limit in the case B) is unrealistically small and this type of a statistical test for nested models is not useful for analysed data. The limit A) gives some reasonable scale. Improvement of \(R_{wp}\) values with inclusion of the residual stress is better than the required \(\Delta R_{wpA}\) limit for all samples (Table 1.). The worst result was reached for the sample no. 2.

The results can be compared with the models calculated under different assumptions. No residual stress was assumed and zero-shift-error (2\(\Theta_0\)) was refined instead. Improvement of the \(R_{wp}\) factors was about 1% and 2\(\Theta_0\) changed about 0.04° in average. Much less improvement of the \(R_{wp}\) factors was reached by an additional refinement of the zero-shift in the original model with non-zero stress giving only 0.1% absolute improvement of \(R_{wp}\) factors and 2\(\Theta_0\) about -0.01° in average. Moreover this additional inclusion of the zero-shift affected negatively the overall stability of the fit and accuracy of the refined parameters for some samples (no. 2 and 5). Because of this correlation of the zero-shift error parametr with other parameters (stress value, lattice parameters) and relatively small significance of the fit improvement, the zero-shift error 2\(\Theta_0\) was fixed to zero, and only 2\(\Theta\) refraction correction (1) was used for the final residual stress evaluation.

The results of the direct stress measurement by sin\(^2\)\(\psi\) method and evaluation by the total pattern fitting are in good agreement, as it can be seen on Fig. 6, where strong dependence of residual stress on film thickness is depicted.
Figure 4: (a) Comparison of the measured (red points) and calculated (blue line) diffraction pattern of the 300 nm thick film sample (64-5). (b) Details of selected parts of the above plot in the case the residual stress in the film is included (blue) and in the case no residual stress is assumed and only lattice parameters are refined (black), (c) difference plots for the two cases in above plots.

Figure 5: Details of the measured (red points) and calculated (blue line) diffraction pattern of the 300 nm thick film sample (64-5) in the case (a) stress is neglected, (b) residual stress is included.
A new program for XRD total pattern fitting was developed and applied for studies of TiO\(_2\) thin films, in particular, for the investigation of crystallization and thickness dependence of microstructural parameters. It was shown that the application of the refraction correction to the diffraction lines positions can make a 2\(\Theta\) zero-shift value (1) physically realistic, (2) independent of the incidence angle and (3) it is correct generally also in the case of multi-layers with different electron density. It was also shown that including the simple residual stress effect in the microstructural model improves fits of the studied TiO\(_2\) films significantly and that even though the residual stress values determined by the total pattern fitting are influenced strongly by various systematic errors (mainly by the 2\(\Theta\) zero-shift error), they are in good agreement with the results of direct stress measurement. The total pattern fitting in the case of studied TiO\(_2\) thin films is sensitive to residual stresses of about 200 MPa, with an evaluation error of about 100 MPa. It can reveal such stresses and it can be used for their investigation in correlation with some other parameters.

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