MICROSTRUCTURAL CHARACTERIZATION OF NANOCRYSTALLINE POWDERS AND THIN FILMS BY X-RAY POWDER DIFFRACTION

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Abstract

Possibilities of powder X-ray diffraction (XRD) for characterisation of nanocrystalline powders and thin polycrystalline films are briefly discussed. The method was used for study of crystallization and thermal stability of samples of titanium dioxide.

The most pronounced diffraction effect connected with nanocrystalline materials is huge broadening of diffraction peaks. Then the classical evaluation of XRD pattern based on the analysis of individual peaks becomes complicated because of severe peak overlapping and must be replaced by the so-called total pattern fitting or modelling. The model function should include all the necessary instrumental and physical parameters. A new software MStruct has been developed for the purpose and applied here for different samples of titanium dioxide. The model considers instrumental aberrations corresponding to the applied diffraction geometries (e.g. absorption, refraction) and mainly physical models of real microstructure such as crystallite size and distribution, dislocation densities and correlation, phenomenological microstrain, stacking faults, residual stress and preferred grain orientation. Corresponding parameters can be refined by optimisation algorithm.

The application of the method is demonstrated on the analysis of crystallites size distribution in nanocrystalline anatase powders and analysis of tensile residual stresses in the series of film samples of different thickness. The stresses appeared in the films during the crystallization and increase drastically with decreasing film thickness. The values obtained from XRD total pattern fitting agree well with the results of direct XRD stress measurements.

Thin films depth profiling revealed a gradient of phase composition with rutile grown on the interface and anatase on the top.

Keywords: XRD, titanium dioxide, nanocrystalline materials, thin films, size distribution, defects

1. INTRODUCTION

X-ray diffraction (XRD) is a widely used method for structural studies of materials on atomic scale up to the scale of few micrometres. XRD instrumentation and methods for investigation of size, shape and strain in epitaxial nanostructures [2] and polycrystalline bulk materials and thin films are continuously developing. Present methods of microstructure analysis by powder XRD, concerning mainly crystallite size distribution determination, defects density analysis, depth profiling and stress evaluation, are applied to the characterization of TiO₂ powders and thin films. This material has several remarkable properties such as photoactivity, hydrophilicity [3] and found many applications.
2. EXPERIMENTAL ARRANGEMENTS USED

Two coplanar diffraction geometrical arrangements are used in X-ray laboratories with conventional X-ray sources: (i) the symmetrical Bragg-Brentano geometry (Fig. 1.),

(ii) the parallel beam geometry (Fig. 2.).

![Fig. 1. Bragg-Brentano symmetric focusing diffraction geometry.](image1)

![Fig. 2. Parallel beam geometry with X-ray mirror producing X-ray beam with small divergence.](image2)

With the focusing symmetrical Bragg-Brentano geometry (Fig. 1) a position sensitive detector (PSD) can be used and hence either measurement time can be reduced by a factor of 10 - 100 or counting statistics can be significantly improved which makes detailed XRD line profile analysis possible. Effective diffracting sample depth depends on the material chemical composition and used X-ray radiation and usually achieves high value as 10 µm and hence the geometry is suitable for bulk solid samples and powders.

![Fig. 3. Schematic figure of a parallel beam experiment. X-ray beam impinges the sample surface at low incidence angle \( \omega \). The diffraction vector is inclined from the surface normal by angle \( \psi = \Theta - \omega \).](image3)

![Fig. 4. Penetration depth \( T_p \) for TiO\(_2\) (\( \rho = 3.92 \text{ g/cm}^3 \)) for various incidence angles \( \omega \) and the case of symmetrical scan in Bragg-Brentano geometry.](image4)
For thin films analysis the parallel beam geometry (Fig. 2.) is preferred in order to suppress substrate signal and improve surface sensitivity by increasing a length of X-ray path through the film (Fig. 3.). The penetration depth can be varied by changing the incidence angle $\omega$ of the X-ray beam to sample surface (Fig. 4.). At incidence angles close to the angle of total external reflection ($\omega_c = 0.28^\circ$ for TiO$_2$) the penetration depth decreases by orders of magnitude (Fig. 5.). However, the diffraction signal falls down equally and the laboratory measurements below the critical angle are difficult. With small incidence angle $\omega$ the sample irradiated area is rather large (Fig. 2), hence bigger samples (>∼ 1 cm length) are required, diffracted beam is wide, analyzing optics has to be used and PSD detector cannot be utilized. The resolution is usually three times worse than in the case of focusing Bragg-Brentano geometry. The experimental arrangement is suitable for studies of films with thickness of the order 10 - 1000 nm. The effect of decreasing the incidence angle $\omega$ is illustrated on Fig. 6. for a 440 nm magnetron deposited TiO$_2$ sample.

In recent time also experiments utilizing noncoplanar geometry and both small incidence and exit angles appeared [4].

3. NANOCRYSTALLINE MATERIALS AND POWDER XRD

Any deviation of a real crystal from an infinite periodic object represents a defect from diffraction point of view. Such defects affect width, shape, position and intensity of diffraction lines.

3.1 Size and deformation broadening

Very small crystallites size is an apparent property of the nanocrystalline materials and causes strong broadening of diffraction peaks. Small objects in real space have simply large pictures in the reciprocal space. This is the idea of the well known Scherrer formula connecting average crystal dimension $D$ and peak width $FWHM$ in reciprocal space units ($1/d$) [1]:

**Fig. 5.** Dependence of the penetration depth $T_p$ for TiO$_2$ anatase 101 reflection on the incidence angle $\omega$ close to the critical angle of total external reflection (0.28°).

**Fig. 6.** Details of powder patterns of TiO$_2$ 440 nm thick film sample for incidence angle (a) $\omega = 1^\circ$ and (b) $\omega = 0.5^\circ$. Suppression of background “diffuse” scattering from Si substrate with smaller incidence angle $\omega$ is visible.
The Scherrer equation (1) is often used to determine crystallites size simply from a measured width of one diffraction line. However, such evaluation is completely neglecting the other sources of broadening, mainly instrumental effects and presence of defects in the crystal. At least measured peak width should be compared with the known or expected instrumental resolution and deconvolution should be applied. It is also necessary to investigate widths of multiple diffraction lines in order to reveal the presence of various defects in the material. Broadening caused by lattice parameter variation connected with strain fields around defects is increasing with the length of the diffraction vector $1/d = 2\sin \theta$. This is approximately expressed by the Williamson-Hall plot [1]:

$$FWHM(1/d) = \frac{0.94}{D} + \frac{4e \sin(\theta)}{\lambda},$$  \hspace{1cm} (2)

where $e$ is so called microstrain, characterizing a mean value of relative lattice parameter variations inside crystallites. Such dependence is shown on Fig. 7. for nanocrystalline anatase powder.

Various defects (dislocations, stacking-faults) have characteristic influence on the width and position of different hkl diffraction lines and hence they can be often distinguished. In many cases, these effects are well known [5]. Then XRD can be used for determination of the type and density of such defects.

**Fig. 7.** Williamson-Hall plot of two nanocrystalline anatase powders. Crystallites size was determined to be approximately (a) 16 nm and (b) 8 nm. Width of instrumental function is plotted for comparison (c).

**Fig. 8.** Calculated dependences of 101 anatase reflection intensity on the incidence angle $\omega$ for different film thicknesses.

### 3.2 Modelling of broadening effects (Total Pattern Fitting - TPF)

Equations (1) and (2) represent very simple approximations of relations between diffraction lines width and parameters characterising material microstructure. Nowadays less approximate methods are preferred [6-7]. Related effects are usually modelled in the real space and with the aid of the Fourier transform diffraction profiles are calculated directly. The simulated or known instrumental function is included inherently by
convolution with physical profiles. The other effects affecting peaks positions (residual stresses, instrumental aberrations) and intensities (texture) are also taken into account. The whole diffraction pattern is calculated and compared with measured data.

The measured powder diffraction pattern is a projection of the Fourier transformation of the object into the direction of the diffraction vector. E.g. diffraction profile of a crystallite defined by its shape function $\Omega_c(r)$ (one inside the crystal, zero elsewhere) can be simply calculated as:

$$I(q) = \int d^2 q \int d^3 q \Omega_c(r) e^{iqr},$$

where $q$ is the diffraction vector deviation from the given diffraction point in the reciprocal space and $q_{||}$ is its projection in the direction of measurement in the reciprocal space. In a similar way also profiles corresponding to various defects as dislocations, stacking faults or more simple phenomenological microstrain effects can be calculated from appropriate models. The whole powder pattern is calculated and models parameters (crystallite size distribution, dislocation density, stacking faults probabilities etc.) are refined from measured data using the least square algorithm.

For very small crystallites ($\sim 5$ nm) the classical crystallographical approach of considering diffraction pattern as a sum of diffraction peaks is no more correct. In this case the powder pattern can be calculated from the atom positions and their distances $r_{ij}$ according to the Debye scattering equation [1, 8]:

$$I = \sum_m \sum_n f_m f_n \frac{\sin(k r_{mn})}{k r_{mn}},$$

where $f_n$ are atomic scattering factor at n-atom sites and $k = 4\pi/\lambda \sin \Theta$. The formula contains a double summation over all atoms in the 3D crystal and hence its evaluation is computationally difficult.

### 3.3 Other effects (film thickness, depth profiling, residual stress)

Many other aspects of real materials microstructure do not influence peak width and shape, but affects strongly intensities and positions of diffraction peaks. Preferred grain orientation is often the most pronounced effect affecting the intensities. In the case of thin films the absorption effect should also be accounted. The effective penetration depth is the essential parameter for the absorption correction. As it was shown on Figs. 4, 5 the penetration depth can be varied by the incidence angle $\omega$ and from such a measurement the film thickness can be determined (Fig. 8.).

The positions of diffraction lines can be affected by the residual stress arising in thin films for example due to different thermal expansion coefficients of the film and substrate. Diffraction can study interplanar distances of diffracting planes inclined by an asymmetry angle $\psi$ from the sample surface (Fig. 9.). If the tensile stress is applied to the sample (Fig. 9.) the interplanar distances of crystallites with diffraction planes perpendicular to the surface (parallel to the applied tensile stress) are increasing while the interplanar distances of planes parallel to the surface (perpendicular to applied tensile stress) are decreasing. The influence of the applied stress on the diffraction lines positions can be well described by material elastic constants, grain interaction model and geometrical considerations. The stress-induced shift can be included in the microstructure model and values of the stress can be evaluated from the measured data.
Fig. 9. Schematic figure showing the principle of residual stress determination from diffraction measurements. Stress in the film affects diffraction planes differently in dependence on their orientation relatively to the film surface. From difference of the interplanar deformations of differently oriented grains the residual stress is evaluated.

4. PREVIEW OF SOME EXPERIMENTAL RESULTS

The above described effects are illustrated on the TiO₂ nanocrystalline powder and thin films samples. Measured XRD patterns were fitted by the model function including the effects described above and using our own new software MStruct.

4.1 Size distribution determination

Fig. 10. (a) Measured powder diffraction patterns of two TiO₂ powder samples. One sample was annealed at 300 °C, the second at 380 °C. The crystallites size distributions (b) determined by the total pattern fitting are different. The refined parameters of the assumed lognormal distribution were: median of crystallites diameter $d = 4.2$ nm and the $\sigma$ parameter $\sigma = 0.39$ for the sample annealed at 300 °C and $M = 6.2$ nm, $\sigma = 0.43$ for the sample annealed at 380 °C.
XRD powder patterns of nanocrystalline TiO$_2$ powder samples prepared by sol-gel method and annealed at different temperatures were measured in the focusing Bragg-Brentano geometry with a PSD detector. Crystallites of spherical shape with a log-normal distribution of the crystallites diameter $D$ were assumed. In addition phenomenological microstrain effect ($e$) and known (measured on LaB$_6$ standard) instrumental function were included in the model [9]. The median of the size distribution $M$ and the dispersion parameter $\sigma$ were refined for two different samples (Fig. 10.).

4.2 Depth profiling

Magnetron sputtered nanocrystalline TiO$_2$ samples on silicon substrates were measured in the parallel beam geometry with different angles of incidence $\omega$ (Fig. 11.). For lower incidence angles only anatase 101 reflection could be observed, while for higher angles rutile 110 reflection appeared. This indicates that there is only anatase close to vicinity of the sample surface and that there is a mixture of rutile and anatase or pure rutile deeper in the film close to the substrate [10].

![Fig. 11. Part of powder patterns of nanocrystalline magnetron sputtered thin film sample. Two reflections are visible: 101 anatase reflection ($2\Theta \sim 25.3^\circ$) and rutile 110 reflection ($2\Theta \sim 27.5^\circ$). For small incidence angles ($\omega$) negligible rutile signal was observed. Penetration depths $T_p$ are printed to imagine the depth scale.](image)

![Fig. 12. Results of the residual stress measurements in the series of TiO$_2$ films of different thicknesses. Films were amorphous after deposition and crystallised after annealing. (●) are values obtained from direct XRD stress measurements and (▲) are values obtained from the total pattern fitting of powder patterns measured in the parallel beam geometry (Fig. 2.).](image)

4.3 Residual stress determination

A series of TiO$_2$ thin film samples of different thicknesses ($40 \sim 800$ nm) was studied. The samples were amorphous as deposited by magnetron sputtering and they were annealed in-situ in the high temperature chamber to study the crystallisation process [11]. The films crystallised directly into large grains ($D \sim 300$ nm) for thicker samples and grains of dimensions comparable with film thickness for thinner samples. Therefore, it was shown that unlike powders, it is not possible to prepare nanocrystalline thin films in this way. By contrast, as-deposited nanocrystalline films are quite stable with temperature and crystallites
begin to grow only above about 500 °C [12]. Quite pronounced tensile residual stress evolved during the crystallization. The measured powder patterns were analysed by the total pattern fitting as well as direct XRD residual stress measurements were done. The dependence of tensile residual stress on the film thickness is depicted on Fig. 12.

5. SUMMARY
Possibilities of XRD characterization of nanocrystalline powders and thin films were demonstrated on (i) crystallites size distribution determination in nanocrystalline anatase powders, (ii) depth profiling of TiO₂ thin films and (iii) residual stress evaluation in the series of anatase thin films samples. Methods of modelling and fitting XRD data in a complex way, such as the total patterning fitting, based on physically relevant microstructure models, can improve reliability of determined microstructure parameters, help with their interpretation and understanding their relation with other properties of studied material.

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