

Thermal stability and crystallization of amorphous and nanocrystalline TiO₂ thin films and powders studied by XRD

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Different TiO₂ samples – magnetron deposited amorphous and nanocrystalline thin films and powders – were annealed both off-situ and in-situ in XRD high-temperature chamber and their microstructure evolution with temperature and time was studied.

Coplanar XRD grazing incidence measurements (2θ scans) in parallel beam setup with a mirror were evaluated by both the profile fitting of peak clusters and total pattern fitting. Residual stresses and X-ray reflectivity curves were studied as well. Because of severe peak overlap the whole pattern evaluation was preferred in most cases. Since some features necessary for the analysis of thin films in the above geometry (appropriate corrections, influence of texture and stress) are missing in the common Rietveld type programs, we have extended flexible modular system of Crystal Objects and Fox program (developed by V. Favre-Nicolin) for studies of real structure. Applied model include the following features. Variable peak positions determined by variable lattice parameters and zero shift error, possibly also by residual stress. Peak intensities calculated by the ObjCryst library from a known crystal structure model. They can be modified by absorption and the texture correction obtained from the known model of ODF after numerical integration over all crystallites with diffracting $\{hkl\}$ planes perpendicular to direction of the measured diffraction vector, or they can be varied independently. Peak profiles are given by numerical convolution of the known instrumental function described by the pseudo-Voigt function and physical profiles including several free parameters (models). The size broadening is described by the model of log-normal distribution of spherical crystallites, the strain broadening either by phenomenological microstrain or dislocation model. Stacking faults can be included too. Individual layers in the system are characterized by their thickness and linear absorption coefficient.

It was shown that crystallization of amorphous films could be well described by the Avrami equation and strong dependence of the process and consequently the parameters of the equation on the film thickness was found indicating significantly slower crystallization of very thin films. Fast crystallization occurred in the range 220–300 °C when relatively large crystallites (> 100 nm) grew quickly. By contrast as-deposited nanocrystalline films (crystallite size ~ 5 nm) showed the fine microstructure stable to higher temperatures (500 °C) before the strain relaxation and crystallite growth.