Crystallization behavior of TiO$_2$ thin films

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Thin films of titanium dioxide (TiO$_2$) have attracted considerable attention in the past few years, since nanocrystalline TiO$_2$ shows outstanding properties and has widespread application potential. The possible applications range from solar cells and energy conversion systems, gas and UV-sensors, battery systems to photocatalysis and self-cleaning surfaces. All these applications rely on the semiconducting property of the TiO$_2$, which is only found in crystalline TiO$_2$. Crystalline TiO$_2$ has three natural crystalline modifications (named anatase, rutile and brookit), which differ in their semiconducting characteristics [1]. Consequently, usually a defined crystalline state is desired for a particular application. For example, anatase TiO$_2$ has a higher electric conductivity as compared to rutile TiO$_2$ and is therefore preferred in solar cell and electronic applications.

Among many different techniques, a common method to prepare nanostructured TiO$_2$ is a sol-gel process. The obtained TiO$_2$ is usually in an amorphous state and has to be transferred to a crystalline phase by applying a post-production heat treatment. This heat treatment determines the degree of crystallinity as well as the crystalline modification, and is therefore of outmost importance for the preparation of TiO$_2$ with well defined properties. In this experiment, we prepared a TiO$_2$ film with a functional hierarchical structure [2] and investigated the development of the crystalline structure with grazing incidence wide-angle X-ray scattering (GIWAXS).

The films were prepared by a sol-gel process with the diblock copolymer poly(dimethyl siloxane)-block-methyl methacrylate poly(ethylene oxide) [PDMS-b-MA(PEO)] as structure directing agent [2]. To transfer the TiO$_2$ to a crystalline modification, the films were annealed for 4 h at 450 °C, 600 °C, 750 °C or 1000 °C, respectively. GIWAXS measurements were carried out at the HASYLAB beamline BW2 at a wavelength of 1.38 Å and an incidence angle of 0.25°. The scattering signal was probed with a scintillation counter along the plane of the film.

![Figure 1: GIWAXS spectra of TiO$_2$ thin films annealed at different temperatures between 450 °C and 1000°C. All films are in the anatase phase and the crystallinity increases with the annealing temperature.](image)
Figure 1 shows the development of the crystallinity of the TiO$_2$ with annealing temperature. At a temperature of 450 °C, a completely amorphous film is obtained and no diffraction peaks are observed. With increasing temperature diffraction peaks develop, indicating a transition of the amorphous TiO$_2$ to a crystalline phase. The intensity of the peaks increases as the temperature increases, and at a temperature of 1000 °C a well-developed diffraction spectrum is observed. Thus, only at very high temperatures a considerable amount of TiO$_2$ can undergo the transition to crystallinity and form a crystalline structure. This is an unexpected result, since TiO$_2$ is known to convert to a crystalline state already at temperatures below 400 °C [3]. In addition, at temperatures of about 600-750 °C typically a phase transition occurs in nanocrystalline TiO$_2$ from anatase to rutile [4]. However, in the investigated samples, no change in the diffraction spectrum is obvious and all diffraction peaks observed at 1000 °C originate from the anatase phase.

A possible explanation for this behavior might be found in the presence of dopants or impurities in the TiO$_2$. It is well-known that by doping or blending TiO$_2$ with other materials such as fluorine, yttrium or secondary oxides the crystalline growth and the phase transition from anatase to rutile can be inhibited and high-temperature stable, anatase films obtained [5,6]. In our case, such effect might arise from the PDMS block in the PDMS-b-MA(PEO) block copolymer used in the sol-gel process. During calcination, the PDMS is converted to silica, which forms a blend with the TiO$_2$ and inhibits its crystalline growth. However, further investigations are needed to corroborate this theory.

In conclusion, we have prepared TiO$_2$ thin films with exceptional thermal stability. Crystallisation starts at a temperatures above 450 °C and the anatase phase does not convert to rutile up to 1000 °C. An application potential for this films arises in the field of catalysis, where porous anatase structures with high thermal stability are needed for in-situ gas catalysis during high-temperature processes.

References