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Thin Film Porosity Determined by X-Rays at SEM

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Various applications such as automotive catalysts, photocatalysis and sensors rely on thin coatings with high active surface area. The development of new and improved coatings requires in-depth understanding of the film morphology and texture. Especially the film porosity is a key parameter to identify structure-property relationships in applications. However, an accurate porosity determination of thin porous coatings is a challenging. In this contribution we present and discuss a new approach for determining the porosity of films by x-rays at SEM.

The mass coverage of layers can be calculated by the film analysis software STRATAGem [1] from EDX determined *k*-values (the ratio of normalized intensity between unknown sample and standard) based on the well known Pouchou and Pichoir approach.[2] The high accuracy of STRATAGem results has been proven for various layered materials.[3-5] We present an approach for determination of the porosity by a combined SEM/EDX/STRATAGem analysis. From the STRATAGem-derived mass coverage and the coating thickness as determined by cross-section SEM micrographs, the average density of the film can be obtained. In a second step, the porosity can be calculated from the measured porous film density and the literature value for the pore walls bulk density. The complete approach is sketched in Figure 1.

The general procedure to determine the porosity is demonstrated on thin mesoporous TiO_2 films on Si wafer substrates. The TiO_2 films were synthesized by a template-assisted synthesis route, which provides a scalable model system with tunable porosity, see Figure 2.[6] EDX spectra of these films were measured at beam voltages of 7, 10, 15, 20, and 30 kV by using a high-throughput SDD EDS detector which enables a time-efficient analysis. Polished bulk of pure Ti and Si served as standard references. Oxygen was quantified by stoichiometry as well as by using a pure SiO_2 reference. The resulting *k*-values were verified by WDX analysis. The calculated mass coverage was independently validated by weighing and by ICP-OES of dissolved coatings. To determine the film thickness, the TiO_2 films were cleaved and the resulting cross-section was imaged with a SEM.

The measured *k*-values for Ti Kα and Si Kα in dependence on the beam voltage and the corresponding fitted curves calculated by STRATAGem are shown in Figure 3a for a porous 180 nm thick TiO_2 film. Figure 3b visualizes the resulting mass coverage values for all beam voltages. The scattering of the individual mass coverage values at different voltages reflects the robustness of the model.
An excellent agreement was obtained between the mass coverage calculated by STRATAGem and the mass coverage determined by weighing and ICP-OES of the same film. The increasing porosity of the thin TiO_2 films illustrated in Figure 2 could be calculated quantitatively by the new approach. The validation and traceability of the porosity results will be discussed. These combined SEM/EDX/STRATAGem analyses demonstrate a unique tool for non-destructive examination of the porosity of thin porous films.

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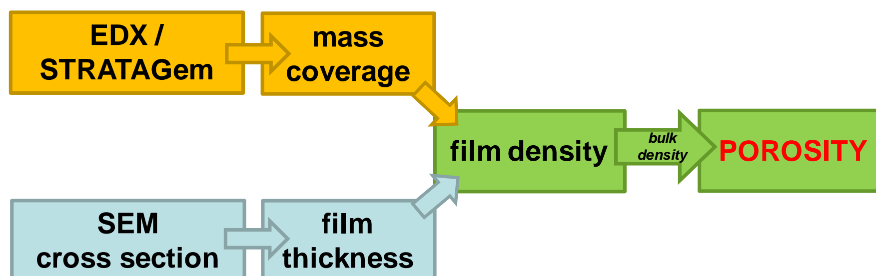

Figure 1. Illustration of the approach for the determination of the porosity of thin films by EDX/SEM analysis.

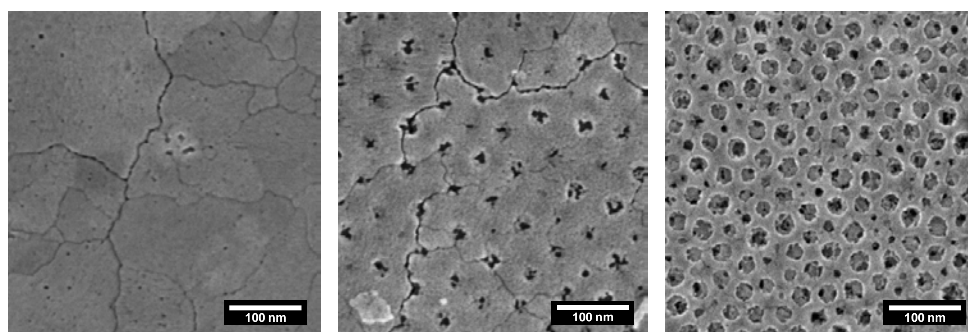

Figure 2. Top-view SEM micrographs of TiO_2 films synthesized with increased amount of a mesopore template, which results in an increase of the void fraction, i.e. film porosity (from left to right).

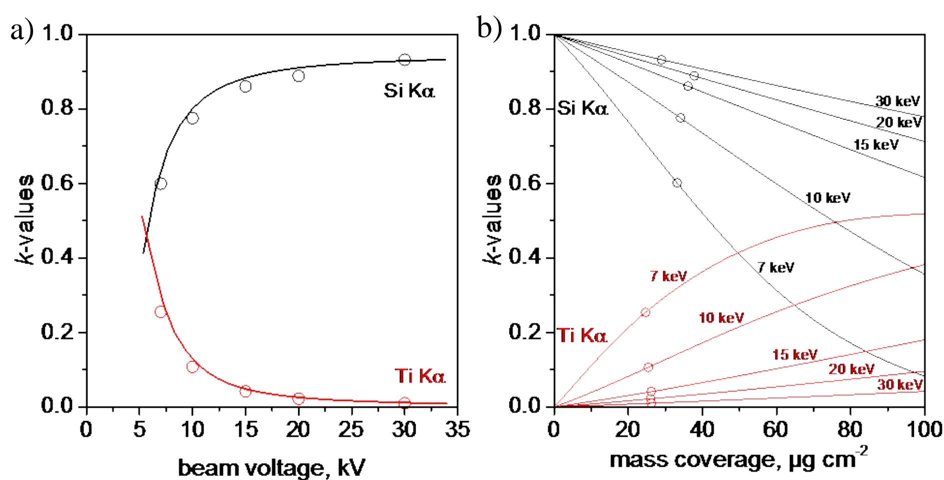

Figure 3. a) *k*-values versus beam voltage for Ti Kα (red) and Si Kα (black); the markers represent the measured values, the curves are fitted to the *k*-values. b) *k*-values of Ti Kα and Si Kα versus calculated mass coverage at each beam voltage.

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