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Analysis of Mesoporous Iridium Oxide Thin Films by the Combined Methodical Approach SEM/EDS/STRATAGem

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Thin mesoporous films are versatile and attractive candidates for several energy applications like photovoltaics, electrolysis or batteries, due to the high surface area and ordered pore structure providing high activities. The performance of the porous films is affected by properties like size and shape of the mesopores (2-50 nm) as well as the crystallinity of the framework. The accurate determination of the complex morphology of thin mesoporous films requires new analytical approaches employing combination of data of different analytical methods. In this contribution we present the determination of thin mesoporous iridium oxide film properties by accurate evaluation with X-ray spectroscopy (EDS)/Electron Probe Microanalysis (EPMA) at SEM and countercheck the results with spectroscopic ellipsometry (SE).

Mesoporous iridium oxide films were prepared via dip-coating of a solution containing a triblock-copolymer as structure-directing agent and an iridium precursor in ethanol [1]. Deposited films were calcined in air at temperatures between 300 and 600 °C. Figure 1 shows SEM micrographs of a mesoporous IrO_2 film calcined at 375 °C. A top-view SEM image (Figure 1a) reveals the presence of a well-ordered mesopore structure. The average pore diameter is 16 nm (Figure 1b) and the periodic distance between pore centres amounts 24 nm. Based on cross-section SEM images (Figure 1c), a homogenous film with a thickness of 96 ± 6 nm has been observed.

For the determination of film porosity, EPMA can be used as part of a combined SEM/EDS/STRATAGem analysis [2]. The mass deposition (in μg cm^{-2}) of films was calculated with the analysis software STRATAGem via *k*-values measured with EDS [3]. The average density of coated films was obtained from the mass deposition and the film thickness as measured by the cross-section SEM. The porosity was calculated by dividing the average film density by the bulk (theoretical) density of the film material.

Figure 2a displays the *k*-values (circles) for Ir Lα and Si Kα from EDS spectra of films as measured at accelerating voltages of 15, 20, 25, and 30 kV by using a high-throughput SDD EDS detector. Pure bulk Ir and Si were measured as references and oxygen was quantified by stoichiometry. The curves present the fitting results from the STRATGem software, which are in a good agreement with the measured *k*-values. Film porosities were counterchecked by spectroscopic ellipsometry using the Bruggeman effective medium approximation (BEMA) [4]. Figure 2b demonstrates the good agreement of the results obtained by both analytical approaches/methods used, SEM/EDS/STRATAGem and SE.

In order to make the SEM/EDS/STRATAGem approach more time-efficient, a reduction of the number of accelerating voltages used has been considered. The accuracy and robustness of the STRATAGem approach has been proven as being accurate enough even when STRATAGem works with only one or two accelerating voltages [2,5].

The successful present analysis of the pure, mesoporous IrO_2 films as well earlier work on pure, porous TiO_2 films will be followed in a next step by the analysis of mixed mesoporous iridium oxide /titanium oxide films.

References:

[1] E Ortel *et al*, *Chem Mater* **23** (2011), p. 3201.
[2] E Ortel *et al*, *Anal Chem* **88** (2016), p. 7083.
[3] Stratagem version 2.6, SAMx, 4, rue Galilée, 78280 Guyancourt, France.
[4] D-M Rosu *et al*, *Appl Surf Sci* **421** (2017), p. 487.
[5] V-D Hodoroaba *et al*, *Surf Interface Anal* **44** (2012), p. 1459.
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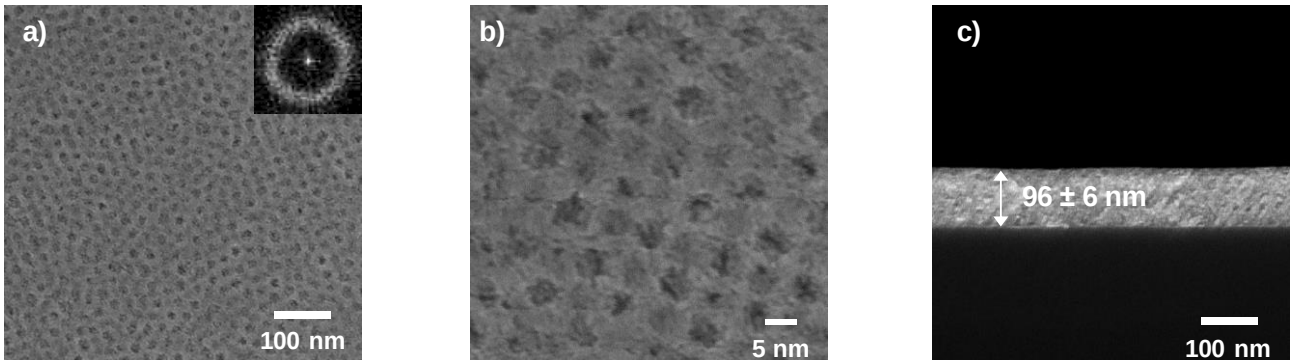

Figure 1. SEM micrographs of a mesoporous IrO_2 film calcined at 375 °C in air. a) top-view SEM image with a FFT inset. b) top-view SEM image at higher magnification, and c) cross-section SEM image of the film.

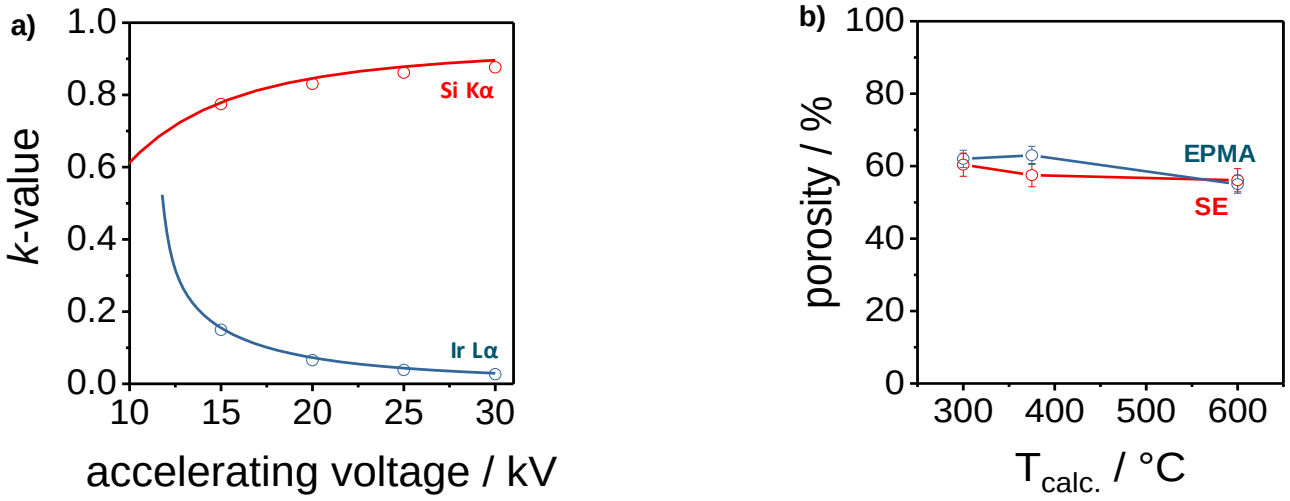

Figure 2. Results of SEM/EDS/STRATAGem analysis (a) and comparison of porosity of IrO_2 films calcined at the given temperature with SE (b). a) *k*-values *vs* accelerating voltage. Open dots represent the measured values for Si Kα (red) and Ir Lα (blue) and the curves indicate the STRATAGem fit. b) film porosity determined from the EPMA approach (blue) and SE (red) *vs* calcination temperature.

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