1770
doi:10.1017/S1431927619009589
Microsc. Microanal. 25 (Suppl 2), 2019

Analysis of elemental composition and porosity of mesoporous iridium-titanium mixed oxide thin films for energy application by SEM/EDS

R. Sachse[1], V.-D. Hodoroaba[2], A. Hertwig[3], Leyla Kotil[1] and R. Kraehnert[1]

[1.] Technical University of Berlin, Berlin, Germany.
[2.] Federal Institute for Materials Research and Testing (BAM), Division 6.1, Berlin, Germany.
[3.] Federal Institute for Materials Research and Testing (BAM), Division 6.7, Berlin, Germany.

Porous materials play an important role in several fields of technology, especially for energy applications like photovoltaics, electrolysis or batteries. The activity of porous films is affected by properties like porosity, film thickness, chemical composition of the material as well as the crystallinity of the framework. The complex morphology of such porous films constitutes a challenge even for modern analytical techniques and requires new approaches employing the combination/complementation of data of different analytical methods. In this contribution we characterize thin mesoporous iridium-titanium mixed oxide film properties by Electron Probe Microanalysis (EPMA) with energy dispersive X-ray spectroscopy (EDS) at an SEM.

Mesoporous iridium oxide - titanium oxide (IrO_x-TiO_x) films were prepared via dip-coating of a solution containing a triblock-copolymer as structure-directing agent, an iridium precursor as well as a titanium precursor in ethanol. IrO_x-TiO_x films were synthesized with different amounts of iridium and calcined in air (Figure 1). The SEM micrographs in Figure 1 reveal for all films the achievement of a well-ordered mesopore structure and homogeneous films with thicknesses between 67 nm and 152 nm.

For the determination of film elemental composition and porosity, EPMA can be used as part of a combined SEM/EDS/STRATAGem analysis [1,2]. Elemental compositions (in wt%) and mass depositions (in µg cm^{-2}) of IrO_x-TiO_x films were calculated with the thin film analysis software STRATAGem via *k*-values measured with SEM/EDS [3]. Pure bulk Ir, TiO_2 and Si were measured as references. The average density of the films, $\rho_{film,meas.}$, was obtained from the mass deposition and the film thickness as measured by the cross-section SEM. The porosity *P* was then extracted from the measured average film density $\rho_{film,meas.}$ divided by a theoretical bulk density, ρ_{theo}. The latter is calculated from the weight fractions of IrO_x and TiO_x as determined with STRATAGem and the bulk mass densities of IrO_2 and TiO_2 (rutil) from literature (equation 1).

Figure 2a displays the *k*-values for Ir Lα, Ti Kα, O Kα 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. The curves present the fitting results from the STRATGem software, which are in fair agreement with the measured *k*-values. Figure 2b presents the correlation between the Ir mass fraction as measured with STRATAGem and the nominal Ir-loading.

The application of the SEM/EDS/STRATAGem approach for accurate porosity determination on pure mesoporous TiO_x films [1] and pure porous IrO_x films [4] has been recently demonstrated. The porosities of the series of pure IrO_x, TiO_x and mixed IrO_x-TiO_x films as determined in this study are shown in Figure 2c.

The contribution will assess in detail the advantages and limitations of the combined SEM/EDS/STRATAGem analysis for the morphology and porosity of thin metal oxide films. Moreover, the comparison with other measurement techniques and the combination of datasets from multiple measurements will be discussed.

References

$$P = 1 - \frac{\rho_{film,\,meas}}{\rho_{theo}}; with\ \frac{1}{\rho_{theo}} = \sum \frac{\omega_i}{\rho_i} \quad (1)$$

[1] E Ortel *et al.*, Anal. Chem. **88** (2016), p. 7083.
[2] V-D Hodoroaba *et al.*, Surf. Interface Anal. **44** (2012), p. 1459.
[3] Stratagem version 6.7, SAMx, 4, rue Galilée, 78280 Guyancourt, France.
[4] R Sachse *et al.*, Microscopy and Microanalysis **24** (2018), p. 762.
[5] The authors acknowledge funding from the European Metrology Programme for Innovation and Research (EMPIR) Project 16ENG03 Hybrid metrology for thin films in energy applications (HyMET).

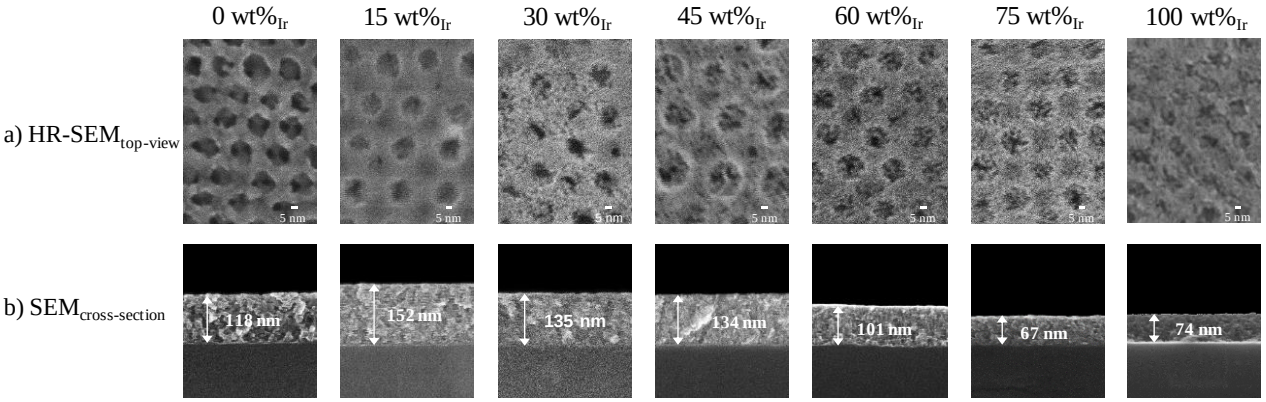

Figure 1. SEM micrographs of a mesoporous IrO_x-TiO_x films with different amount of Ir, calcined in air. a) top-view HR-SEM images and b) cross-section SEM micrographs of the films.

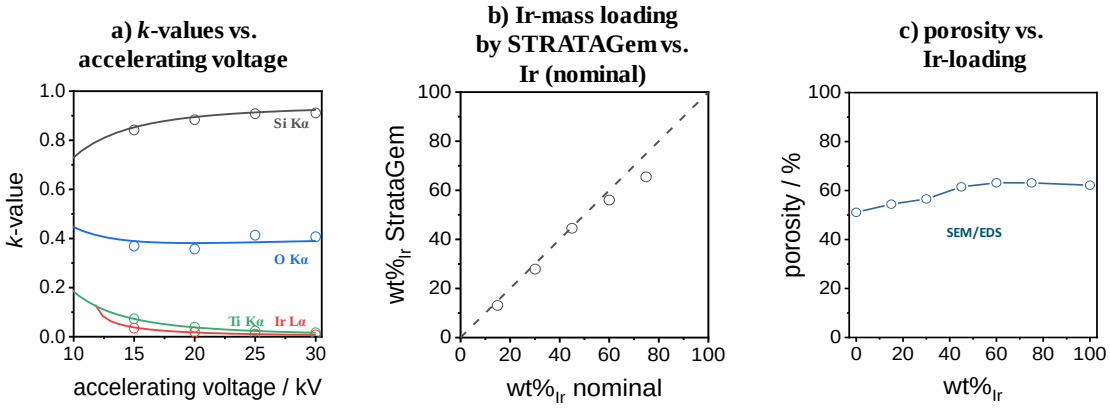

Figure 2. Results of SEM/EDS/STRATAGem analysis of mesoporous IrO_x, TiO_x and IrO_x-TiO_x films. a) *k*-values *vs* accelerating voltage of the 30wt%Ir IrO_x-TiO_x film. Open dots represent the measured values for Ir Lα (red), Ti Kα (green), O Kα (blue) as well as Si Kα (black) and the curves indicate the STRATAGem fit. b) Ir-mass loadings from STRATAGem *vs* the nominal Ir-loading. c) film porosities determined from the EPMA approach for the complete set of IrO_x-TiO_x films.

https://doi.org/10.1017/S1431927619009589 Published online by Cambridge University Press