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Oxygen K and titanium L_{23} XAS spectra of thin films applied as photoelectrodes for hydrogen generation

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Titanium dioxide thin films applied as photoelectrodes for hydrogen generation by water splitting suffer from incompatibility between the fundamental absorption (band gap of 3.0-3.4 eV) and the solar spectrum. Possible improvement in their performance is expected upon modification of the film stoichiometry. In order to study the electronic structure of modified thin films, X-ray absorption spectroscopy XAS with the use of synchrotron radiation was employed.

Thin films were deposited by rf reactive magnetron sputtering from Ti target in UHV system under flow controlled oxygen and argon gas mixture with intentionally varied $O_2/(Ar+O_2)$ ratio. X-ray diffraction XRD, X-ray reflectivity XRR, X-ray photoelectron spectroscopy XPS, and scanning electron microscopy SEM were used for films characterization. XAS measurements were performed at SOLARIS National Synchrotron Radiation Centre, Kraków, Poland. Spectral dependence of the absorption coefficient used for band gap analysis was based on the transmittance and reflectance measurements carried out by means of UV-VIS-NIR spectrophotometer. Current-voltage characteristics were collected under white light illumination in order to assess the performance of the photoanode material.

As the $O_2/(O_2+Ar)$ gas flow ratio changes, systematic evolution of thin films properties is observed. XRD results reveal that when the $O_2/(Ar+O_2)$ ratio falls within the range of 5-10%, lower oxides such as TiO, Ti_2O_3 and non-stoichiometric TiO_{2-x} rutile are formed. Upon further increase in this ratio, well-crystallized TiO_2 appears, with rutile dominating at $O_2/(Ar+O_2)$=15% and anatase at 30%. Changes in the phase composition are followed by variation in the electrical conductivity, grain size and band gap.

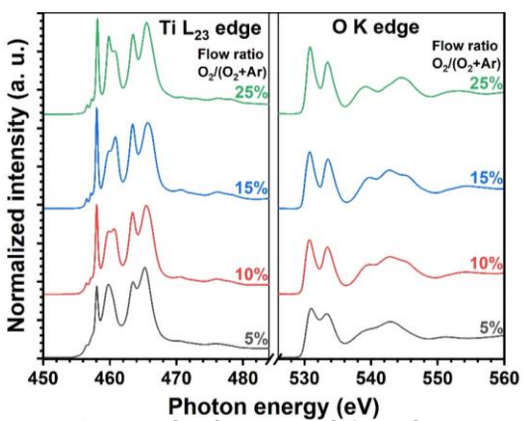

Figure 1. Normalized Ti L_{23} and O K edge X-ray absorption spectra for thin films sputtered at 5, 10, 15 and 25% of $O_2/(O_2+Ar)$ measured in TEY mode.

Titanium L_{23} and oxygen K spectra measured in Total Electron Yield TEY mode for thin films deposited at different flow ratio $O_2/(O_2+Ar)$ equal to 5, 10, 15 and 25% are shown in Figure 1. Crystal field splitting and relative bands occupancy, related to the crystal field strength, can be extracted from both the Ti L_{23} and the O K edges in agreement with the analysis presented recently in [1, 2]. The photocurrent *vs.* potential measurements confirm that crystallized, slightly substoichiometric films containing rutile or a mixture of anatase and rutile, i.e., deposited at $O_2/(O_2+Ar)$ flow ratio of 15-25%, perform quite well as photoanodes in the photoelectrochemical cells for water splitting. This observation requires careful analysis of the influence of the electronic structure, determined by XAS, on the photoelectrochemical properties of thin films.

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