

Tailoring reactively sputtered ultrathin nickel oxide films for solar water splitting devices

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Nickel oxide is a promising photo-catalytic material for the oxygen evolution reaction (OER). It offers a wide band-gap, has a good corrosion resistance when polarised anodically in alkaline media, and upon p-doping obtains a low work function facilitating hole transfer to the water oxidation redox reaction. However, in practice, it is difficult to obtain a perfect crystal having the ideal properties to absorb the light and to convert it into electrochemical energy. The challenge is therefore to produce NiO thin films with a minimum of defects, both at the grain boundaries and in the "bulk" of the usually highly-textured and nano-sized grains. The current presentation will discuss some of our recent insights regarding ultrathin photo-catalytic nickel oxide thin films, deposited by reactive magnetron sputtering on Al₂O₃ passivated photo-active silicon substrates.

As to the deposition process itself, in-situ internal stress measurements have been performed in real-time during room temperature reactive sputtering with various amounts of oxygen (5-23%). From the high-resolution stress data obtained, which can be taken as indicative for the amount of defect incorporation during film growth, it was possible to clearly resolve two characteristic deposition regimes. As a result, the NiO film can be considered as being composed of two distinct sublayers : a first layer, responsible for charge transfer to the photo-active substrate, was characterized by a high degree of compressive internal stress, ranging from about -1,6 GPa at the lowest upto 2,3 GPa at the highest oxygen flow. The second outermost layer, providing electro-catalytic properties to the OER, was deposited almost stress-free. Moreover, the transition thickness between both sublayers was found to depend on the oxygen flow during reactive sputtering, decreasing from 34 nm at 5% down to 19 nm at 23% of oxygen.

A number of ex-situ characterizations were then carried out, including resistivity measurements, microstructural characterisations (XRD, SEM, TEM) and cyclic voltammetry, the latter both in the dark and under simulated solar illumination, with the objective to link the internal stress and hence defect levels in the different films to their electro- and photo-catalytic performance for the OER. Our initial results already provide convincing evidence for a remarkable difference in behaviour of each of the 2 sub-layers identified earlier, thus helping to determine the optimal NiO film thickness for water splitting devices.