UV induced photochromism in Fe-doped SrTiO₃ caused by oxygen stoichiometry changes

Alexander Viernstein⁽ᵃ⁾*, Markus Kubicek⁽ᵃ⁾, Maximilian Morgenbesser⁽ᵃ⁾, Gregor Walch⁽ᵃ⁾, Jürgen Fleig⁽ᵃ⁾

⁽ᵃ⁾ TU Wien, Institute of Chemical Technologies and Analytics, Getreidemarkt 9 164/EC, 1060 Vienna, Austria
*alexander.viernstein@tuwien.ac.at

In the last decades Fe-doped SrTiO₃ (Fe:STO) has become one of the best investigated mixed conducting materials. Nevertheless, the effect of UV irradiation at elevated temperatures on the material’s composition, more precisely on its oxygen content, has hardly been examined so far. UV illumination in oxygen causes an enhanced oxygen incorporation rate [1] and therefore a decreased oxygen vacancy concentration of SrTiO₃ [2]. Consequently, Fe³⁺ in Fe:STO is oxidized to Fe⁴⁺ to preserve charge neutrality (more exactly, the charge of the electron hole is not simply trapped at the Fe, but also distributed at the surrounding O-atoms due to the covalent nature of the bonds). This oxidation may also cause color changes in Fe:STO.

In this contribution, it is shown that the color of UV illuminated Fe:STO indeed changes from transparent/brownish to black. This was investigated by in-situ UV/VIS measurements at ca. 440 °C (Figure 1) and can be attributed to an increasing “Fe⁴⁺” concentration caused by oxygen chemical diffusion into Fe:STO and thus a change of the oxygen stoichiometry in the entire sample. The photochromic blackening is irreversible at room temperature but the initial state can be restored by annealing the Fe:STO samples at 700 °C for more than 12 h [3].

Furthermore, UV irradiation enhances the electron hole conductivity by almost a factor of ten, as shown by van der Pauw measurements and in-plane electrochemical impedance spectroscopy. Existing bulk defect chemical models are used to estimate the corresponding increase of the oxygen chemical potential by UV illumination and suggest a nominal p(O₂) to more than 10⁹ Pa in Fe:STO after UV-treatment. Hence, UV light can be used to tune the color, but also electrical properties of Fe:STO by directly impacting the bulk defect concentrations.

References