

## SUMMARY

In this thesis, chemical spray deposition method was implemented and studied, as a low cost and user friendly approach for the deposition of Zr-doped TiO<sub>2</sub> thin film, which allows mixing of precursor solution prior to deposition. The physico-chemical properties of the CSP deposited Zr-doped TiO<sub>2</sub> films were investigated to study the effect of varying Zr dopant concentration on the properties of TiO<sub>2</sub> film. This research was carried out in the Laboratory of Thin film Chemical Technologies, Tallinn University of Technology. This work has also been presented at the 13<sup>th</sup> annual international conference of young scientist on energy issues (26 – 27 May 2016) in Lithuania and the paper is presented in appendix A of this thesis. The conclusions drawn from this research work was solely based on what was observed experimentally which was backed by other results from available literature on Zr-doped films prepared by other techniques.

1. A series of Zr-doped TiO<sub>2</sub> precursor solution was successfully prepared by varying the Zr/Ti mole ratio in the spray solution thus making it possible to investigate the effect of Zr dopant concentration on the sprayed films.
2. The SEM study revealed that uniform and compact Zr-doped TiO<sub>2</sub> films were deposited by CSP method. It was concluded that the presence of Zr in the spray solution influences the morphology of the film because the Zr-doped TiO<sub>2</sub> films have smaller grains of about 50 nm while, the undoped TiO<sub>2</sub> films have large grains of about 500 nm after annealing at 800 °C. The EDS compositional analysis revealed the presence of Zr atom in the deposited films. The Zr/Ti atomic ratio in the Zr-doped films increased from 0.014 to 0.13 corresponding to an increase in the Zr/Ti mole ratio in the spray solution from 5 mol% to 40 mol% respectively.
3. The XRD and Raman data revealed that the as-deposited Zr-doped TiO<sub>2</sub> films were amorphous while the undoped films are anatase crystalline. Zr-doped TiO<sub>2</sub> film became crystalline with anatase crystal structure after annealing at 500 °C. The mean crystallite size of the Zr-doped TiO<sub>2</sub> films is smaller compared to that of the undoped TiO<sub>2</sub> film, irrespective of the annealing temperature. The FWHM of the anatase phase at Raman band 141 cm<sup>-1</sup> increased from 14 to 22 cm<sup>-1</sup> as the concentration of zirconium in the spray solution increases from 0 to 20 mol%. A mixture of anatase and rutile phases was observed after annealing at 700 °C for undoped TiO<sub>2</sub> films and 800°C for the Zr-doped TiO<sub>2</sub> films. According to the Raman and XRD analysis, which complements each other, it was concluded that; an increase the amorphous-anatase-rutile phase transformation temperature, smaller crystallite size and larger FWHM values of the main Raman band with increasing concentration of zirconium in the spray solution indicate that zirconium ion was incorporated into the TiO<sub>2</sub> lattice thus creating lattice imperfections, evidences by the shift of the diffraction peaks to lower Bragg angles.
4. The as-deposited TiO<sub>2</sub> and Zr-TiO<sub>2</sub> films were optically transparent and the transparency increased with the doping concentration. The optical band gap of the as-deposited Zr-doped TiO<sub>2</sub> film was 3.2 eV, which is slightly higher than that of as-deposited undoped-TiO<sub>2</sub> with 3.14 eV. The changes in the optical properties of the deposited film are due to structural changes and annealing temperature.
5. The leakage current in the as-deposited TiO<sub>2</sub> was reduced by 2 orders of magnitude with Zr doping of TiO<sub>2</sub>. The reduction in the amount of leakage current was due to an increase in the energy barrier height of the doped films. The dielectric relaxation response at the oxide-electrode interface shifted to lower frequency from 72 kHz to 750 Hz as the Zirconium concentration in the sprayed solution was increased thus, influencing the dielectric properties of the Si/Zr-TiO<sub>2</sub>/Au structure.

Finally, based on improved amorphisation and reduction in leakage current of the as-deposited Zr-doped TiO<sub>2</sub> films when compared to undoped TiO<sub>2</sub> films, CSP is proposed as a suitable method for the deposition of Zr-doped TiO<sub>2</sub> films which can be used as dielectric layer in TFTs.