

## Abstract

Since the early 2000's, industrial and academic research interests in Atomic Layer Deposition continue to grow. Its versatility arises from the controlled growth of ultrathin and well defined material thin films on a large variety of substrates. ALD started to gain attention in the semiconductor industry, but is now demanded by a vast area of research purposes, including biotechnological and sensor applications like diffusion barriers and gas sensing materials. Current research efforts also focus on the implementation of ALD in fabrication of solar cells and photoelectrodes for sustainable energy production. However, this very elaborate technique is strongly limited to a few materials, since the number of suitable precursors is still very low.

In the first part of this thesis, a new ligand system for the self-limiting growth of conformal cobalt, nickel and copper thin films from air-stable and volatile precursors is introduced. Tridentate enaminone ligands for cobalt and nickel complexation, as well as bidentate heteroarylalkenolate ligands for copper are designed to fit the requirements of molecular stability and reactivity towards functional groups of the substrate surface. The vapor phase behavior during the reactor pulse as well as the mechanism of ligand dissociation after reaction with hydrogen radicals is investigated. It was found, that modification of the enaminone ligand-chain leads to structural isomerism, resulting in a lower crystal packing and enhanced volatility. The molecular stability allows direct spectroscopic analysis of the chemisorption behavior towards surface functional groups. However, the ligand-oxygen leads to hydroxylation of the metal atom upon hydrogen radical exposure to the chemisorbed precursor. By applying an immediate hydrogen radical treatment, the reduction of the layer to the metallic and even the hydridic state was achieved. The new precursor concept enabled homogenous film growth on complex structured substrates.

For the second part of this work, TiO<sub>2</sub> thin films have been deposited as photoanode materials for solar water splitting application. A well-defined modification of the defect structure in a reproducible manner was used to describe the specific effect on the water splitting properties. The particular impact of doping ALD-TiO<sub>2</sub> with hydrogen and nitrogen atoms was investigated by a combined approach of spectroscopic analysis and computational calculations. Morphological studies revealed a direct correlation between deposition temperature and the grain structure. Post-annealing plasma treatment with hydrogen or nitrogen plasma leads to partial reduction of titania. Upon plasma treatment, the grain structure affects the recrystallization process, which itself is affected by the deposition temperature. Particular

defect structures have been generated by using different plasma gas compositions, including oxygen vacancies as well as hydrogen/nitrogen doping. A combined spectroscopic and computational study revealed the specific impact of the dopant atoms on the water splitting properties of TiO<sub>2</sub>.