Abstract

Transition metal-oxide (TMOs) thin-films are commonly used in optoelectronic devices such as in photovoltaics and light emitting diodes, using both organic, inorganic and hybrid technologies. In such devices, TMOs typically act as an interfacial layer, where its functionality is to facilitate hole or electron extraction/injection from or to the active material under interest. The capability of TMOs to facilitate this functionality is very dependent on the work function of the layer, and therefore also the defect density within the film. In this direction, the ability to control the interfacial properties of metal-oxide thin films through surface defect engineering is vital to fine-tune their optoelectronic properties, and thus also their integration in novel optoelectronic devices.

In this work, MoOx thin-films with various different phases and compositions were prepared by direct-current reactive sputtering. The composition of the films was controlled mainly through the oxygen partial pressure during growth, and crystallization of the amorphous as-deposited films was obtained through ultra high vacuum annealing. The defect band of as-deposited MoOx films was studied by photoemission spectroscopy and optical absorption, and a very reliable method to extract the composition of the films by Rutherford Backscattering Spectrometry (RBS) was introduced. Importantly, it was demonstrated that very small changes in the oxygen partial pressure during growth leads to large modifications in both the optical and electrical properties of the films. Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM) were applied to assess the surface morphology and crystallography of the films. Changes in the electronic properties of the surface upon crystallization of the films were furthermore studied by probing the density of unoccupied and occupied states for different MoO_x compositions ($x\sim2.57$, $x\sim3.0$ and $x\sim3.16$) and different annealing temperatures.

Applications of the reactive sputtered MoOx thin-films in organic photovoltaic (OPV) devices based on the small molecules DBP and C70 are also covered in this work. The devices show interesting characteristics for very thin layers of the as-deposited MoOx films, displaying similar device efficiencies as those of *in situ* prepared MoOx thin-films formed from thermal evaporation. For the annealed MoOx films, the formation of a nearly stoichiometric phase ($Mo_{18}O_{52}$) after post annealing of superoxidized $MoO_{3.16}$ films, is demonstrated to present an enhanced thermal stability over thermally deposited MoOx thin-films, and based on the resulting device efficiencies and the high thermal stability, it is assumed that these could become potential candidates for the next generation metal-oxide based electrodes for PV applications. The results presented in this thesis could assist in the future developments and understanding of modified metal-oxide based functional interfaces for optoelectronic devices.