

# Abstract

Organic photovoltaics (OPV) have attracted a lot of attention during the last couple of decades, due to them having several advantageous properties such as light-weight, abundant and non-toxic materials, mechanical flexibility, semi-transparency, low energy pay back times and low cost manufacturing, which favours them over conventional Si-based PV, when it comes to price, pay-back times, accessibility, production speed, environmental impact and ease of installation. Currently, some OPV devices have reached power conversion efficiency (PCE) values that exceed 19%, which is getting close to Si-based PV, however OPV are still challenged by shorter lifetimes and poor long-term stability, which makes it hard for them to compete with their Si-based counterparts. In order for large scale commercialization of OPV with significant PV market share to become a reality, it is crucial to improve the device performance and stability of OPV. This can be achieved by device engineering and by introducing new efficient and stable materials (thin-films), but to do that, we need a deeper understanding of the structure and optoelectronic properties of such materials. In addition, it is also important to understand the energy level alignment and electronic interactions at the interfaces between materials in an OPV device. The structure, crystallinity, composition and electronic structure of thin-films can be studied using X-ray based characterization techniques, since X-rays have wavelengths comparable to inter-atomic distances and photon energies comparable to energy differences between electronic levels in materials. In this thesis, three X-rays based characterization techniques; X-ray photoelectron spectroscopy (XPS), Near-edge X-ray absorption Fine Structure (NEXAFS) and X-ray scattering (XRD) have been used to study functional materials, namely metal oxide and organic thin films for OPV applications. This includes their interfaces and their electronic interactions at their interfaces, to gain a deeper insight of the structure and properties of these thin-films, and their interfaces and thereby to unveil their contribution to the performance and stability of OPV.

A former study from our group has shown that using the organic molecule, 4P-NPD, as an exciton blocking layer (EBL) in DBP:C<sub>70</sub> based OPV devices resulted in an improvement of the PCE of up to 24% compared to reference devices. This PCE enhancement was only observed when ultra-thin 4P-NPD layers of maximum 1 nm were used, however when the thickness of 4P-NPD was increased, the resulting devices performed worse than reference devices, which suggests that the interface plays an important part in the process. The 4P-NPD EBL was implemented between the DBP donor and the MoO<sub>x</sub> hole transport layer (HTL). In order to understand, why only ultra-thin 4P-NPD layers improve device performance, while thicker layers result in diminished device performance, we studied the in-situ prepared DBP/4P-NPD and 4P-NPD/MoO<sub>x</sub> interfaces using synchrotron based XPS and NEXAFS. We observe a small HOMO off-set at the DBP/4P-NPD interface, which enables hole transport between the two materials, however for thicker layers, this HOMO off-set increases and creates a hole extraction barrier. We also observe an upwards shift of all the electronic levels of 4P-NPD at the 4P-NP/MoO<sub>x</sub> interface, which results in a large LUMO off-set between DBP and 4P-NPD that blocks electrons and thereby makes the interface hole-selective. Additionally, an upwards shift of the 4P-NPD HOMO level removes any extraction barrier towards DBP. After increasing the 4P-NPD thickness, the electronic levels of 4P-NPD relax to their initial positions, which results in a small LUMO off-set that does not block electrons and the recovery of a HOMO extraction barrier. These findings explain why only ultra-thin layers of 4P-NPD improve the device performance.

In another study, we show that using sputter deposited TiO<sub>x</sub> films, deposited at 150°C and cooled in the presence of oxygen, as electron transport layers (ETLs) in PBDB-T:ITIC based OPV devices, results

in a significant improvement of the long-term device stability compared to conventionally used solution processed ZnO ETLs. The devices with the sputtered  $\text{TiO}_x$  ETLs saturated at 60% of their initial PCE after 14 days of degradation, while the devices with ZnO saturated at 35% of their initial PCE after 14 days of degradation. Optical spectroscopy showed that this improved stability results from a reduced UV-induced photo-catalytic degradation of the ITIC acceptor by the sputtered  $\text{TiO}_x$  compared to ZnO. This is a surprising finding, since  $\text{TiO}_x$  is also known to have a strong photo-catalytic activity. To understand the mechanisms behind the decreased photo-catalytic degradation of ITIC by the sputtered  $\text{TiO}_x$ , we studied the defect states and electronic state interplay at the semi in-situ prepared sputtered  $\text{TiO}_x$ /ITIC interface using synchrotron based XPS, NEXAFS and resonant photoemission spectroscopy (RESPES). These results were compared to similar measurements on an anatase  $\text{TiO}_x$  single crystal, since anatase  $\text{TiO}_x$  is known to have a strong photo-catalytic activity and therefore acts as a good reference for our sputtered oxide. We observe a defect feature in the valence band of both sputtered and anatase  $\text{TiO}_x$ , which is related to oxygen vacancies. RESPES measurements showed, that all the oxygen vacancies in the anatase crystal lie in the sub-surface region, while the sputtered  $\text{TiO}_x$  has both surface and sub-surface vacancies, however the surface vacancies strongly dominate. This major difference could explain the reduced photo-catalytic activity of the sputtered  $\text{TiO}_x$ , since surface oxygen vacancies can be quenched by surface adsorbates, which prevents them from participating in the photo-catalysis process.

In another stability study of PBDB-T:ITIC devices, we replaced conventional thermally deposited  $\text{MoO}_x$  HTLs with crystalline sputter deposited  $\text{MoO}_x$  films. Seven different sputtered  $\text{MoO}_x$  films were tested, post-annealed in vacuum at 200°C and 350°C with different heating rates. Stability testing showed, that all the devices with the 200°C annealed films had an improved long-term stability compared to devices with thermally deposited  $\text{MoO}_x$ . The heating rate did affect device stability and the champion devices, which saturated at 47% of their initial PCE after 215 h of degradation, were the devices with the 200°C annealed sputtered  $\text{MoO}_x$  annealed with a heating rate of 45 K/min. In comparison, the devices with the thermal  $\text{MoO}_x$  saturated at 25% of their initial PCE after 215 h of degradation. The 350°C annealed films resulted in poor long-term device stability comparable to thermal  $\text{MoO}_x$ , which can be explained by a larger concentration of adsorbed OH defects and a larger surface roughness.

The degradation behaviour of the PM6 polymer donor and the Y7 NFA was studied using synchrotron based XPS. PM6 was degraded in-situ by X-rays and light/heat in vacuum, while Y7 was degraded in-situ by X-rays in vacuum. Degradation of PM6 by X-rays showed evidence of polymerization, while degradation of PM6 by light and heat in show evidence of bonds being broken. Degradation of Y7 by X-rays resulted in large shifts of the C1s core level and HOMO on-set towards lower binding energies. The shifts observed in the Y7 core levels and HOMO on-set after degradation by X-rays are larger than the shifts observed for PM6 after degradation by X-rays, which suggests that Y7 is more sensitive to X-rays than PM6.