

Abstract

In this work, organic solar cells (OSCs), primarily based on a bulk-heterojunction (BHJ) blend of the hole conducting polymer poly(3-hexylthiophene) (P3HT) and the fullerene [6,6]-phenyl-C₆₁ butyric acid methyl ester (PCBM) were examined. This particular donor:acceptor system is at present the benchmark system in OSC research since synthesis and processability of the individual components are straightforward and photovoltaic performances are almost practicable. The thesis can be divided into three parts. The first reports on manipulating the work function of the hole-collecting contact. Poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrene-sulfonate) (PSS⁻) is commonly used as electrode modification in solution processed OSCs. The work function of the commercially available ready-to-use product is poorly suited for electrochemical manipulation, most probably due to the size of the polymeric anion. In-situ PEDOT (IS-PEDOT) films with a monomeric anion were synthesized by polymerization of EDOT on the substrate itself. The thin, transparent films were easily accessible for subsequent work function adjustment. IS-PEDOT films as hole-collecting electrode modification with variable work function in P3HT:PCBM BHJ solar cells resulted in distinct operation modes, e. g. inverted characteristics. In addition, the work functions of several other available hole injection layers (HILs) were determined and the effect of UV-ozone treatment examined.

The second part is dedicated to explore the influence of the active layer morphology on the energy levels of the individual components. Molecular orbital (MO) energies of the pristine materials determined via cyclic voltammetry (CV) in solution or photo-electron spectroscopy (UPS) are suited for rough predictions about the open-circuit voltage (V_{OC}), but fail to explain V_{OC} variations occurring within a given system. Furthermore, V_{OC} deviations from CV (UPS) predictions occur frequently in the literature. P3HT:PCBM films with a wide range of different morphology states were fabricated using commonly used morphology influencing methods. The degree of aggregated:amorphous P3HT was estimated using UV/Vis absorption spectroscopy. Surface information obtained using atomic force microscopy (AFM) and scanning electron

microscopy (SEM) turned out to be of limited use describing the relevant morphology inside the bulk, especially in annealed devices. *Kelvin* probe measurements of the blend films revealed that increasing P3HT aggregation raises the highest occupied molecular orbital (HOMO) level until a thermodynamic equilibrium is reached. This behaviour was furthermore found to be independent from the type of fullerene and attributed to increasing HOMO-HOMO interactions. Considering the built-in voltage V^* , the relative positions of the lowest unoccupied molecular orbitals (LUMOs) of several fullerene derivatives within the P3HT:fullerene blend were estimated. Consequently, LUMO level variations were assigned to LUMO-LUMO interactions which are promoted upon distinct formation of fullerene agglomerates. In contrast to the HOMO level of P3HT, the fullerene LUMO level do not converge to a given value. Several explanations were given whereby the exact origin has to be investigated further. In addition, distinctive formation of PCBM agglomerates was found to reduce the photocurrent using spatially resolved laser beam induced current measurements (LBIC) and reflected optical microscopy (ROM).

The third part of this thesis reports on monochromatic photocurrent measurements as a function of the angle of the incident light. A setup was established considering several points based on fundamental principles in optics. Experimental photocurrents were compared with results of optical modeling of the active layer absorption. In this context, the optical constants of the individual layers in the solar cell stack were determined. Both, PEDOT and P3HT:PCBM films turned out to be birefringent. Deviations between experiment and simulation were assigned to be originated in the facts that the used transfer-matrix model deals with isotropic films and neglects surface roughness. In addition, the concept of enhanced light incoupling in active layers featuring an implemented holographic grating was successful. Thereby, an increase of the absorption path length was most pronounced for the weaker absorption wavelengths. With certain illumination wavelengths and certain angles of incident light, grating diffraction and light incoupling into waveguided modes resulted in photocurrent improvement factors of up to 3.1 compared to flat reference devices. Direct structuring of the active layer and shifting the angles of maximum light incoupling to values near zero (perpendicular illumination) are in the focus of further investigations.