

5 Summary

In this work, organic solar cells consisting of Zinc Phthalocyanine (ZnPc), Fullerene (C₆₀) and Bathocuproine (BCP), with an overall thickness of about 70 nm, were studied. In this layer system, interface processes dominate over their bulk properties. The most challenging interfaces in these cells are between inorganic electrodes and organic photoactive layers, where an ohmic contact is difficult to achieve. In the present dissertation, a comprehensive study of the Indium-Tin Oxide (ITO)-organics interface was carried out. The main topic of this work is to improve the contact resistance by chemical passivation of ITO surface and enhance charge carrier transport through this interface.

The surface of the ITO electrode, as the main focus of the current dissertation, was thoroughly examined, before any modifications were undertaken. To establish an understanding of the commercial ITO substrates, a comparison between different ITO types, offered by the industry was made. On the basis of optical transmission, electrical resistance and surface homogeneity, 5 ohm ITO was chosen as a solar cell substrate.

Annealing of the ITO electrode and measuring its resistance in situ, showed that up to 250°C this TCO can be reversibly heated and cooled. Irreversible change in resistance appears to happen above this temperature. The work function of ITO, as an important parameter and a reference value, was measured using X-ray Photoelectron Spectroscopy (XPS) and Kelvin Probe Force Microscope (KPFM). The resultant values were in good agreement: 4,2±0,1 and 4,3±0,2 eV, respectively.

The chemical stability of the active layer materials, under air and UV irradiance was examined using Fourier-Transform Infrared Spectroscopy (FTIR) spectroscopy. No significant change in substance IR absorption spectrum, before and after air/UV treatment, was observed. The initial purity of the material 99%, rest unchanged.

An optical study of the solar cell was made, with a computer simulation. For this, layer thickness, refraction index (**n**) and extinction coefficient (**k**) for each cell material were supplied to a computer program. **n** and **k** were calculated from spectroscopic measurements of material reflection and transmission in the visible region. The optical cell simulation yielded the sun light intensity distribution in the solar cell, depending on the material properties. The simulation showed that the good absorption properties of ZnPc and C₆₀ are not fully utilized. The intensity distribution of the wavelengths, beneficial for the two materials (570-720 nm for ZnPc, 420-520 nm for C₆₀), is very wide, thus no wavelength is absorbed completely by the narrow layers. This is an indication of the big potential of these solar cells, if geometry can be modified. In addition, the optical simulation demonstrates, that wavelengths around the sun energy

spectrum maximum (≈ 540 nm) are very weakly absorbed, thus broadening the potential of these cells to better absorption through additional absorber dye mixing or extending the current absorption with chemical modifications.

The optical simulation of the solar cell emphasized on the importance of precise layer thickness. As a standard, calibration of the deposition controllers is done with profilometer, despite its 10% error. The calibration was revised with X-ray reflection and Ellipsometry. X-ray reflection showed for ZnPc 20% and for C₆₀ 7% higher thicknesses, than measured with the deposition controllers. Ellipsometry confirmed for ZnPc and C₆₀ a thickness with 14%, respectively 17% higher, than by the measurements of the deposition controllers. The structure of the ZnPc film was determined with a fit of the x-ray reflection data and two different molecule orientations were found. Ellipsometry proved BCP and C₆₀ to have too high roughness for x-ray analysis.

As the main highlight of the present work, the chemical modification of the ITO surface with monomolecular layer, has the objectives to adjust its conduction band to the valence band (HOMO) of ZnPc and improve the electrical conductivity through this interface. Two general approaches were examined.

Introducing an aromatic passivation on the ITO surface, consisting of covalently bound 8-Hydroxyquinoline, yielded a solar cell with 1,3% efficiency (η), compared to 0,8% for untreated ITO. The cell parameter, contributing mostly for this improvement, is the increased short circuit current (J_{sc}) $5,5 \cdot 10^{-3} \text{ A/cm}^2$. The corresponding value for J_{sc} of untreated ITO cell is $4,56 \cdot 10^{-3} \text{ A/cm}^2$. Comparison showed also, that the fitted serial resistance (R_s) of the passivated cell $15,19 \pm 0,28 \text{ } \Omega \cdot \text{cm}^2$ is roughly four times less than the one for non-passivated ITO cell $63,25 \pm 0,76 \text{ } \Omega \cdot \text{cm}^2$. Most likely, the serial resistance is influenced by improved contact resistance, at this interface. Since conductivity between ITO and ZnPc is improved with an aromatic termination of the ITO surface, it is concluded that an aromatic ITO passivation is helpful for the cell performance.

Creation of a surface dipole, by dipping ITO in acidic solutions, increased its work function from $4,2 \pm 0,2$ eV for untreated ITO to $4,8 \pm 0,1$ eV for H₃PO₄ passivated and $4,8 \pm 0,1$ eV for HIO₄ passivated ITO. This had positive influence on the solar cell parameters. Improved were mainly the fill factor (FF) and J_{sc} which for H₃PO₄ passivated ITO were: FF 0,54%, I_{sc} $6 \cdot 10^{-3} \text{ A/cm}^2$ and for HIO₄ FF 0,54%, I_{sc} $5,28 \cdot 10^{-3} \text{ A/cm}^2$. The cell parameter improvement contributed to the efficiency (η) the following way: $\eta_{\text{H}_3\text{PO}_4}$ 1,72%, η_{HIO_4} 1,5%. Both acid passivations brought the R_s of the solar cells to very lower values, $3,06 \pm 0,0025 \text{ } \Omega \cdot \text{cm}^2$ for H₃PO₄ and $2,82 \pm 0,039 \text{ } \Omega \cdot \text{cm}^2$ for HIO₄, thus improving the contact resistance of the ITO-ZnPc interface and charge carrier transport from the organic layer to the TCO electrode. XPS proved that phosphoric acid creates very stable (up to $\approx 300^\circ\text{C}$) adsorption species on ITO surface.

A surface dipole in the opposite direction, created with an alkaline treatment of ITO (NH_3 solution), ruined the solar cell, which showed no photocurrent at all.

From all tested ITO surface chemical modifications, organic and acid passivations had the biggest contribution to solar cell performance.

To combine both requirements contributing to cell performance, aromatic passivation and anionic (acid) surface dipole, a new chemical passivation for ITO was designed, namely Zincphthalocyaninetetraphosphonic acid (ZnPc4P). This concept of combining organic and acid in one substance for TCO passivation was never reported before. ZnPc4P was never used for a TCO passivation in organic solar cells up to the present. It is a water soluble, aromatic acid molecule, even from the phthalocyanine class. It has four $-\text{PO}_3\text{H}_2$ groups, covalently bound to the benzene rings of the four benzopyrrole rests. The acid groups were chosen by the high stability of adsorbed phosphate species on ITO, proven by XPS studies. ZnPc4P retained this property, so that after passivating ITO with it, the blue coloration could not be removed by washing with water. This passivation created a surface dipole, which pushed the ITO work function to the highest value of 5,2 eV, comparable to that of PEDOT:PSS. Solar cells, made on ITO passivated with ZnPc4P, had the highest FF ever observed by us: 57%. The open circuit voltage (V_{oc}) is at the upper limit, which this cell concept ever showed 0,54V. J_{sc} with a value of $4,2 \cdot 10^{-3} \text{ A/cm}^2$ was not significantly improved. The fitted R_s of the cell $2,55 \pm 0,1 \Omega \cdot \text{cm}^2$ is the lowest ever measured by us and is attributed to an improved contact resistance on the ITO-ZnPc interface. R_p of $1351 \pm 62 \Omega \cdot \text{cm}^2$ is almost the double, compared to other passivations, and stands for extremely low recombination of charge carriers and lack of leakage currents. Although the power conversion efficiency is 1,3%, the influence of this new treatment on the cell parameters proves the potential of the cell concept.

In order to obtain a better understanding of V_{oc} , a counter-electrode study was made, where instead of the standard aluminum, Ca and Mg as materials with different work function were used. It showed that V_{oc} is in linear dependence of the back-electrode work function in these solar cells. This was attributed to the creation of an energetic barrier hindering electron transport from the bulk to the contact.

It can be summarized, that in the present dissertation the charge transport through the interface ITO-organics in ZnPc/ C_{60} organic solar cells was studied and optimized. Using a self designed chemical passivation, the work function of ITO electrode was adjusted for optimal charge transport. It is shown that driving the TCO work function to higher values exhausts its contribution to cell improvement, so different ways of optimization have to be sought. In this work it was shown that mono-molecular layers can be used as buffers in solar cells and thus they can be made thinner and economical in production through buffer layer substitution.