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Correlating structure and function in small molecule organic solar cells by means of scanning probe and electron microscopy

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Von der Fakultät für Elektrotechnik, Informationstechnik, Physik der Technischen Universität Carolo-Wilhelmina zu Braunschweig

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Correlating structure and function in small molecule organic solar cells by means of scanning probe and electron microscopy.

In this work nanoscale properties in active layers of small molecule organic solar cells are studied regarding their impact on device performance. For this, the effect of variations in stack design and process conditions is examined both electrically and with high resolution imaging techniques. Two topics are addressed: (i) the visualization of charge extraction/injection properties of solar cell contacts and (ii) the tailoring of structural properties of co-evaporated material blends for bulk heterojunction (BHJ) organic solar cells.

(i) We study the impact of controlled contact manipulation on the internal electric potential distribution of fluorinated zincphtalocyanine $(F_4ZnPc)/fullerene (C_{60})$ organic solar cells under operating conditions. In a detailed analytical study using photoelectron spectroscopy and in-operando scanning Kelvin probe microscopy it is demonstrated that the electric field distribution of organic solar cells at the maximum power point depends in an overproportional manner on contact properties and ranges from bulk to contact dominated even for solar cells with decent device performance.

(ii) The morphology of co-evaporated active layer blends depends on both substrate and substrate temperature. Here we study the morphology of $F_4ZnPc:C_{60}$ blends with analytical transmission electron microscopy. For all substrates used is found that co-evaporation of the materials at elevated substrate temperature (100 °C) induces a distinct phase segregation of F_4ZnPc and C_{60} . However, only when using a C_{60} underlayer, as in inverted devices, also the crystallinity of the segregated C_{60} phase increases. There is only a slight increase in crystallinity when F_4ZnPc acts as an underlayer, as typically for non-inverted devices. Solar cell characterization reveals that the crystalline C_{60} domains are the main driving force for enhanced free charge carrier generation and higher power conversion efficiencies. With this we could provide a novel explanation why record efficiencies of small molecule organic solar cells are realized in inverted device architecture only.

Zusammenhang zwischen Struktur und Funktion organischer Solarzellen basierend auf kleinen Molekülen analysiert mit Rastersonden- und Elektronenmikroskopie.

Im Rahmen dieser Arbeit werden nanoskopische Eigenschaften von aktiven Schichten organischer Solarzellen hinsichtlich ihres Einflusses auf die Solarzellen-Funktion untersucht. Auswirkungen von Variationen bezüglich Bauteildesign und Prozessbedingungen werden sowohl elektrisch als auch mit hochauflösenden Mikroskopieverfahren analysiert. Zwei Themen werden dabei adressiert: (i) Die Abbildung von Ladungsextraktions- und injektionseigenschaften an Solarzellenkontakten sowie (ii) die Anpassung struktureller Eigenschaften in koverdampften Heteroschichten aus fluoriniertem Zinkphtalocyanin (F_4ZnPc) und Fulleren (C_{60}).

(i) Wir untersuchen den Einfluss einer kontrollierten Kontakt-Variation auf die Potentialverteilung organischer F_4ZnPc/C_{60} -Solarzellen im Betrieb. Mittels Photoelektronenspektroskopie und Rasterkelvinmikroskopie wird gezeigt, dass die elektrische Feldverteilung organischer Solarzellen betrieben am Arbeitspunkt in überproportionaler Abhängigkeit zu ihren Kontakteigenschaften steht. Die Feldverteilung kann dabei selbst für verschiedene Solarzellen mit respektablen Effizienzen zwischen einer reinen Kontaktlimitierung und einer Limitierung durch die aktive Schicht variieren.

(ii) Die Morphologie koverdampfter aktiver Heteroschichten, bestimmt sowohl durch die Wahl des Substrats als auch der Substrat-Temperatur, wird mittels analytischer Transmissions-Elektronenmikroskopie untersucht. Die Koverdampfung der Materialien bei einer Substrat-Temperatur von 100 °C führt bei allen verwendeten Substraten zu einer ausgeprägten Phasenseparation von F_4ZnPc und C_{60} . Dies geht jedoch nur im Falle eines C_{60} -Substrates, üblich in invertierter Bauteil-Architektur, mit einer erhöhten Kristallinität der C_{60} -Domänen in der aktiven Schicht einher. Wird wie bei nicht-invertierten Bauteilen ein F_4ZnPc -Substrat verwendet, ist kein analoger Anstieg in der Kristallinität zu verzeichnen. Mittels Charakterisierung von entsprechenden Solarzellen zeigen wir, dass die Kristallinität der C_{60} -Domänen die Haupttriebkraft für eine effizientere Erzeugung freier Ladungsträger und einer verbesserten Solarzellen-Effizienz darstellt. Wir können damit grundlegend neu erklären, warum Rekord-Effizienzen in organischen Solarzellen basierend auf kleinen Molekülen lediglich in invertierter Bauteil-Architektur erzielt werden.

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List of Abbreviations

AFM:	Atomic force microscopy		
SKPM:	Scanning Kelvin probe microscopy		
KP:	Kelvin probe		
FIB:	Focused ion beam		
TEM:	Transmission electron microscopy		
UPS:	Ultraviolet photoelectron spectroscopy		
XPS:	X-ray photoelectron spectroscopy		
UHV:	Ultra high vacuum		
OPV:	Organic photovoltaics		
OSC:	Organic semiconductor		
PCE:	Power conversion efficiency		
BHJ:	Bulk heterojunction		
F ₄ ZnPc:	Fluorinated zincphtalocyanine		
C ₆₀ :	Buckminster fullerene		
RT:	Room temperature		
HOMO:	Highest occupied molecular orbital		
LUMO:	Lowest unoccupied molecular orbital		
CT:	Charge transfer		

1 Introduction

The establishment of inorganic semiconductor technology is the most important technical milestone set in the 20th century. Inventions based on this technology comprise solar cells, light emitting diodes (LEDs) and especially field effect transistors (FETs). Information technology based on silicon FETs gave rise to a second industrial revolution, their cheap manufacturing costs lead to the introduction of logical elements in electronic devices of practically all scales.

However, fabrication and purification processes for these materials are often complex and energy consuming. Because of this, high efforts in terms of fundamental science as well as R&D are expended to establish organic electronics as a complementary technology to inorganic semiconductors. Organic electronics promises the fabrication of electronic devices on arbitrary substrates at large areas and in environmental friendly and cheap high-throughput processes at low temperatures.

Already in the early 20th century first electrical studies on anthracene crystals were performed [1,2]. In the 1960s electroluminescence in organic crystals was discovered [3,4], leading to the realization of the first organic LED (OLED) in 1970 [5]. Studies by Heeger, MacDiarmid and Shirakawa lead to the fundamental understanding of the electric properties of conjugated carbon bonds and expanded the tool kit of organic electronics [6]. Their research was awarded with the Nobel Prize in chemistry in 2000 [7]. In the mid 1980s first device applications based on organic semiconductors were realized that reached performances in the order of their inorganic counterparts [8–10]. Since then there is growing interest in the realization of organic electronic devices that compete or even outperform the established technologies. Today, many products based on OLEDs are launched in the markets successfully. The realization of true color contrast due to active color pixels and low energy consumption make OLED the technology of choice for displays in

mobile devices and high definition television screens. This is not (yet) the case for organic photovoltaics (OPV), although there is a steady increase in power conversion efficiency (PCE) to 13.2% for research cells and 7-8% in modules today [11] and a wide range of design options as tuning of color and transparency. The ease of applicability of integrated OPV on the one and the huge potential for tailoring the device properties by manipulation of the individual molecules on the other hand make OPV a both fascinating and promising technology. However, a deeper understanding of the fundamental processes present in organic material compounds is crucial on the road to highly efficient OPV.

Charge carrier generation and transport properties in OPV are a topic of ongoing research. The absence of long-range molecular order in the OPV systems necessitated the rethinking and -formulation of the terminology known from inorganic PV. In this process some properties of OPV devices were widely discussed but hardly accessed in experiments. Two of these properties are addressed in this work and correlated to OPV device performance, namely the electric potential distribution and the active layer morphology of OPV devices. This became possible by the application of state-of-the-art analytics with unprecedented lateral resolution to actual OPV devices.

In this thesis we apply scanning Kelvin probe microscopy (SKPM) to the cross sections of organic solar cells under working conditions to study their electric potential distribution on the nanoscale. After the first realization of such experiments at InnovationLab (iL) in 2012 and the characterization of different aspects in solution-processed OPV by Rebecca Saive [12,13], here we address the electric potential distribution in SKPM studies on vacuum processed OPV devices. The vacuum processing allows the preparation of highly defined OPV samples and the correlation of SKPM results with results from the complementary methods X-ray/ultraviolet photoelectron spectroscopy (XPS/UPS), infrared spectroscopy and scanning probe microscopy available at the integrated ultrahigh vacuum system at iL. Here we studied OPV devices with fluorinated zincphtalocvanine $(F_4ZnPc)/fullerene (C_{60})$ planar heterojunction active layers under working conditions with SKPM. We correlated results on solar cells with varied hole extracting contacts to device performance and findings from the above mentioned complementary methods and could demonstrate that the impact of the contact properties on the electric

potential distribution of OPV devices under working conditions is significantly stronger than expected from electrical and UPS studies on non-operating devices.

The concept of the active layer morphology comprises all aspects regarding the composition of OPV active layers, namely the spatial distribution of different material components as well as their structural appearance in terms of short- and long-range ordering. Here, we access the active layer morphology with studies based on analytical transmission electron microscopy (TEM). In vacuum processed small molecule OPV, substrate heating during the application of the active layers is a popular method to control the active layer morphology due to enhancing the diffusivity of the molecules by supplying additional thermal energy. However, the specific impact of substrate heating on the active layer morphology as well as on the device performance is still a matter of debate. Some publications report on a clear improvement [14-18], others on no change [19, 20] or even on a decrease [21, 22] in device efficiency due to substrate heating. Here, we demonstrate the effect of substrate heating exemplary on OPV devices with intermixed active layer blends of the wellknown material system $F_4 ZnPc/C_{60}$. For this, we process devices as well as TEM samples mimicking devices in different solar cell architectures and on different substrate temperatures. Via the correlation of results from analytical TEM and electrical measurements we identified enhanced fullerene crystallinity induced by substrate heating as the crucial parameter for the improvement of device efficiency. This fullerene ordering depends critically on the sequence of active layer application, i.e. on whether the devices are realized in inverted or non-inverted architecture.

This work was performed in cooperation of the Technische Universität Braunschweig (sample preparation, electrical characterization and SKPM studies) and Universität Heidelberg (TEM studies) consolidated at the InnovationLab Heidelberg GmbH. The main research activities are conducted at the InnovationLab GmbH, which is a joint transfer platform allowing to merge substantial competences such as synthesis, simulation, analytics, device physics and printing of organic electronics.

1 Introduction

Outline

In the following, a brief introduction in the fundamentals of organic semiconductors with the main focus on organic solar cells is given. In chapter 3 the analytical methods and the process technologies used in this thesis are introduced. In chapter 4 a detailed study on the electric potential distribution within organic solar cell devices is presented. SKPM studies are correlated with XPS/UPS and KP measurements as well as with results from simulations. At the end of the chapter the limits and prospects of SKPM studies on operating organic electronic devices are discussed. In the following chapter 5 we present results on the structure-function relationship of both planar and intermixed bulk heterojunctions. For this, OPV device performance is related to morphology and topography of the active layers of the cells. The importance of fullerene crystallinity is discussed in the light of our findings and latest literature reports. Finally, in chapter 6 the results of this thesis are reflected and a brief outlook on potential future research topics is given.

2 Fundamentals

In this chapter we give a short review on the basic theoretical concepts used in this work. Features of charge transport in organic solids are discussed. We comment on the strong polarization effects in organic solids, which lead to a distinct dependence of semiconductor band gaps from their environment. The fundamentals of organic solar cells are discussed in the framework of general solar cell theory.

2.1 Charge transport in organic semiconductors

When describing charge transport in organic semiconductors weak intermolecular bonds and high polarizability necessitate some modifications to traditional models applied in semiconductor research. Here, we address bulk phenomena as density of states and the theory of hopping charge transport in organic solids before we discuss how polarization effects give rise to a more detailed definition of the semiconductor band gap.

The physics discussed here is based on "Organic molecular solids" from Marcus Schwörer and Hans Christoph Wolf [23].

In organic semiconductors (OSCs), opposite to inorganic semiconductors as silicon or GaAs, some of the properties usually related to semiconductors such as optical band gaps are not induced via crystal formation, but are present already in the individual molecules. Strong intramolecular bonds lead to a splitting of the valence orbitals creating an energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in the individual molecular unit. There are organic solids that exhibit distinct crystallinity and long-range band transport (realized in transistors [24,25] and solar cells [18]), but the overmost systems discussed here are strongly influenced by their disordered nature. The weak van der Waals

2 Fundamentals

bonds imply that there is only weak overlap of the electron wavefunctions on the intermolecular scale, leading to low intrinsic charge carrier densities $n_{\rm intr}$ and poor electric polarizability/screening capabilities in these materials (relative permittivity $\varepsilon_{\rm r} \approx 3-4$ in most organic materials).



Figure 2.1: a) Energetic position of (i) isolated molecules in the gas phase (G) and condensed molecules in a (ii) crystalline and (iii) disordered solid (S). The polarization of the environment leads to an energy level shift $P_{HOMO, LUMO}$ of the condensed molecules. In the perfect crystal the polarization of the surrounding is identical for every molecule (constant $P_{HOMO, LUMO}$), in the disordered solid it varies slightly from molecule to molecule (varying $P_{HOMO, LUMO}$), leading to a Gaussian DOS. b) Hopping transport in a disordered solid. If an electric field is applied, a net current flows.

2.1.1 Hopping transport

The weak van der Waals bonding implies that no long-range order is established and that the polarization environment for all individual molecules is slightly different, leading to differing polarization modifications for all individual molecules. This gives rise to a Gaussian distributed density of states (DOS) in the organic solid, depicted in figure 2.1. The absence of long-range electron coupling implies that the charge carriers are localized on single molecules and propagate in the solid via hopping: charge carriers have to overcome certain energy barriers when moving between neighboring molecules, as depicted in figure 2.1.

Temperature dependence of the mobility

Because of the low screening in organic solids, an additional charge carrier alters the energy levels of the hosting molecule significantly. The molecule as well as its surrounding relaxes, the charge carrier becomes localized. Because of this, the mobility edges of the charge carriers are not given by the maxima of the Gaussian DOS, but are lowered (elevated) by the energy barrier Δ with respect to the LUMO (HOMO) maximum for electrons (holes)¹. This energy barrier has to be overcome, implying that the mobility of the charge carriers in these solids is temperature-activated: $\mu \sim \exp\left(-\frac{\Delta}{k_{\rm B}T}\right)$. The barrier is given by $\Delta = \frac{\sigma^2}{k_{\rm B}T}$ with the variance σ^2 of the Gaussian distribution. This yields for the temperature dependence of the charge carrier mobility in disordered solids:

$$\mu \sim e^{-\left(\frac{\sigma}{k_{\rm B}T}\right)^2}.\tag{2.1}$$

Field dependence of the mobility- the Poole-Frenkel effect

Another feature of disordered solids is the electric field dependence of the charge carrier mobility, described by the Poole-Frenkel effect. As discussed above the mobile charge carriers that propagate by hopping in the solid are trapped at their hosting molecule by the (average) energy barrier Δ (plus a possible additional energy barrier to the neighboring molecule). If an electric field is present in the solid, this barrier is lowered in direction of the

¹We remark here that it is this localization which causes the hopping transport, *not* (only) the Gaussian DOS. Even in a weakly interacting perfect crystal this strong localization would induce hopping transport.

field. Assuming an image charge accounting for the polarization, the field dependence of the hopping mobility is given by

$$\mu = \mu_0 \cdot \exp\left[\frac{\mathrm{e}^{3/2}}{2k_\mathrm{B}T}\sqrt{\frac{F}{\pi\varepsilon_0\varepsilon_r}}\right],\tag{2.2}$$

with the zero-field mobility μ_0 , the elementary charge e and the applied electric field F.

In the very thin organic electronic devices the exponential Poole-Frenkel factor has a strong impact on the charge carrier mobilities under device operation. For a device with an active organic layer of 100 nm the mobility increases with respect to its zero-field mobility by a factor of 6/13/38/310 if a bias voltage of 0.5 V/1 V/2 V/5 V is applied (assuming a constant electric field).

The Poole-Frenkel effect was published in 1938 [26] to describe conductivity in insulators under high electric fields and is thus not restricted to organic semiconductors. However, because of the very thin active layers (corresponding to high electric fields) present in organic electronic devices here the impact of the Poole-Frenkel effect is very prominent.

Space charge limited currents- the Child law

Organic solids are characterized by very low intrinsic charge carrier densities $n_{\rm intr}$. Therefore in organic electronic devices under operation typically the charge carrier density in the organic active layer is governed by charge carriers injected from high quality contacts rather than by the intrinsic charge carriers, i.e. $n_{\rm intr} \ll n_{\rm inj}$. In this situation the charge neutrality in the device is canceled and the injected charge carriers create an additional, local electric field that has to be considered in the drift-diffusion equations. Assuming field-independent mobility μ , the Child law is obtained:

$$j = \frac{9}{8} \epsilon_{\rm r} \epsilon_0 \mu \frac{V^2}{d^3},\tag{2.3}$$

with the applied voltage V and the thickness of the active layer d. The Child law was proposed in 1911 [27] to describe charge transport in