

Thick C₆₀:ZnPc bulk heterojunction solar cells with improved performance by film deposition on heated substrates

Steffen Pfuetzner,^{a)} Jan Meiss, Annette Petrich, Moritz Riede, and Karl Leo
Institut für Angewandte Photophysik, Technische Universität Dresden, D-01062 Dresden, Germany

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We study the influence of different substrate temperatures during the deposition of the ZnPc:C₆₀ blend layer in bulk heterojunction organic solar cells. It is shown that substrate heating during evaporation leads to a significant improvement in the solar cell performance mainly due to an increase in photocurrent and fill factor (FF). This is attributed to improved morphology resulting in better charge carrier percolation pathways within the ZnPc:C₆₀ blend, leading to reduced transport losses. Using this method, blend layer thicknesses of 150 nm are possible without loss in FF, which requires a three-dimensional interpenetrating network without isolated clusters. When heating the substrate up to 110 °C, an efficiency of 2.56% is achieved compared to 1.59% for an identical device prepared at room temperature. © 2009 American Institute of Physics.

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Since the first copper phthalocyanine/perylene derivative-based flat heterojunction organic solar cell (OSC) by Tang,¹ this type of device has attracted considerable interest as a potential cost-efficient alternative to current silicon solar cells. However, a drawback of planar heterojunction OSC is that the blend layer thickness is usually limited by the exciton diffusion length L_D , i.e., the distance excitons move before recombination. Typical values are in the range of $L_D = 5\text{--}30$ nm.² This limitation can partially be overcome by the concept of bulk heterojunctions (BHJs),³ introducing layers consisting of an intimate mixture of donor and acceptor molecules, e.g., fullerene C₆₀:zinc phthalocyanine (ZnPc) combinations. Photogenerated excitons can usually be dissociated instantly into free charge carriers at the donor-acceptor interface. Thicker blend layers lead to better photon harvesting due to higher absorbance. A challenge associated with BHJ is that during film growth, isolated clusters of donor or acceptor molecules can form, which have no direct charge carrier percolation path toward the respective electrode. These clusters or dead ends act as recombination centers, reducing photocurrent and fill factor (FF). To achieve higher efficiencies, methods are necessary to influence the morphology and properties of the BHJ to increase the amount of percolation pathways and to reduce isolated clusters, trap sites, and (where applicable) grain boundaries.^{4,5}

In this letter, we introduce the controlled substrate heating during film deposition as a parameter to influence the layer morphology within a BHJ consisting of ZnPc:C₆₀, leading to operational OSC with thick blend layers of up to 150 nm. Despite the thick blend layer and thus an increased charge carrier recombination probability, reasonable FF of over 40% is achieved. Combined with an increased photocurrent, the solar cell efficiency is increased from 1.59% to 2.56% by controlled substrate heating.

The solar cells are fabricated in a custom-made multi-chamber ultrahigh vacuum evaporation system (BESTEC, Germany) at a base pressure of 10^{-8} mbar. As substrate, tin-doped indium oxide (ITO) coated glass (Thin Film De-

vices, USA) is used. The substrates are cleaned in ultrasonic baths with detergent, acetone, ethanol, and isopropanol prior to processing.

For sample heating during deposition, an additional glass substrate coated with ITO is put beneath the sample. The substrate temperature T_{sub} is changed by Ohmic heating of ITO and is monitored by a thermocouple glued with silver layer on the deposition side of the sample.

The OSC stack consists of ITO, followed by 5 nm of C₆₀ and a blend layer of 150 nm coevaporated C₆₀ and ZnPc (ratio 1:1). For the hole transport, a layer system of 5 nm *N,N'*-di[4-(2,2-diphenyl-ethen-1-yl)-phenyl]-*N,N'*-di(4-methylphenyl)phenylbenzidine (PV-TPD),⁶ 20 nm of PV-TPD doped with 3.2 wt % of a proprietary *p*-type dopant (Novaled AG, Dresden, Germany),⁷ and 10 nm of 4.4 wt % *p*-doped ZnPc is used. These layers are used as electron and exciton blocker to shift the maximum of the optical field within the solar cell and to ensure low energetic barriers for good hole extraction from ZnPc. Finally, a reflective Au back contact is deposited.

All organic materials had been purified at least twice by vacuum gradient sublimation to remove contaminations. The typical solar cell area is ≈ 6.4 mm² (measured individually using a light microscope). $J(V)$ characteristics are recorded using a source measurement unit 236 SMU (Keithley) under a sun simulator (Hoenle AG). All short-circuit current densities J_{SC} shown in this letter are normalized to 100 mW/cm² with respect to the calibrated Si reference. The reduction in the irradiation due to the additional ITO glass substrate with an average transmission of 85% in the spectral range of 350–900 nm takes into account photocurrent correction (see Fig. 1).

To find a correlation between substrate temperature T_{sub} and OSC performance, the temperature is varied during evaporation of the ZnPc:C₆₀ blend layers for different devices from ambient temperature to 130 °C. The characteristics of the complete devices are summarized in Table I. $J(V)$ curves under simulated sunlight and in the dark are shown for samples processed at room temperature and the optimal temperature T_{sub} of 110 °C in Fig. 2. The detailed dependence of the main OSC characteristics short-circuit current

^{a)}Electronic mail: steffen.pfuetzner@iapp.de.

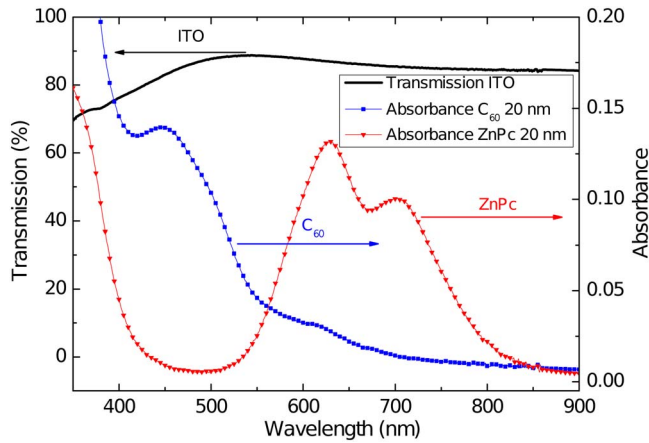


FIG. 1. (Color online) Transmission of the ITO coated substrate heater (continuous line) and absorbance of 20 nm thick C_{60} (filled squares) and ZnPc (filled upside-down triangles) layers in a spectral range from 350 to 900 nm.

density J_{SC} , FF, saturation defined as $[J(-1\text{ V})/J_{SC}]$, and efficiency η' (not corrected for spectral mismatch) on the substrate temperature is shown in Fig. 3.

Generally, the shape of the $J(V)$ curves hints at exciton recombination within the solar cell, which is expressed in the low FF, especially for lower substrate temperatures. It is observed that heating leads to improved lower saturation $[J(-1\text{ V})/J_{SC}]$, which changes from 1.6 at room temperature to <1.3 at temperatures of $>90^\circ\text{C}$. This suggests a higher parallel resistance R_p , indicating a better charge carrier separation and a better transport to the electrodes. At the same time, the dark currents in the forward bias indicate lower series resistances for higher T_{sub} . While FF and saturation are positively influenced by heating, the most decisive improvement that ultimately leads to the increased efficiency is J_{SC} . Starting with 8.10 mA/cm^2 at room temperature, the current reaches a maximum at $T_{sub}=110^\circ\text{C}$ with $J_{SC}=12.27\text{ mA/cm}^2$ before dropping to values around 11 mA/cm^2 for higher substrate temperatures. Combined with the higher FF, this increase in current of about 50% leads to an increase in η' of $>60\%$.

Absorption measurements of 20 nm blend ZnPc: C_{60} processed at room temperature and 110°C showed no enhancement in absorption for the heated layer compared to the unheated, which would explain the higher photocurrent in the OSC. Therefore, we attribute these observations to a change in the BHJ layer morphology: substrate heating increases the thermal energy of molecules evaporated onto the

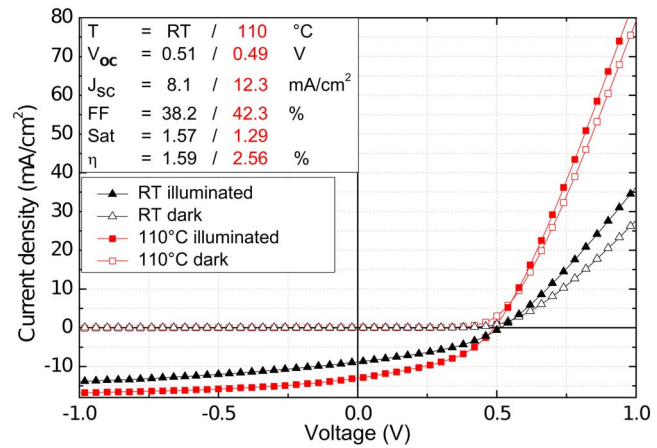


FIG. 2. (Color online) $J(V)$ characteristics of $[ITO/C_{60}(5\text{ nm})/C_{60}:ZnPc(30\text{ nm},1:1)/PV\text{-}TPD(5\text{ nm})/p\text{-}PV\text{-}TPD(40\text{ nm},4.4\text{ wt } \%) / p\text{-}ZnPc(10\text{ nm},3.2\text{ wt } \%) / Au]$ samples processed at room temperature and optimal temperature of $T_{sub}=110^\circ\text{C}$. Short-circuit current densities are normalized to 100 mW/cm^2 with respect to the Si reference.

substrate, which then can diffuse over a larger area before adsorption.⁸ It is estimated that the interaction energies between nearest neighbors are 0.87 eV ($CuPc-CuPc$),⁹ 1.5 eV ($C_{60}-C_{60}$),^{10,11} and 0.44 eV ($CuPc-C_{60}$),¹² respectively. Due to the similarity of CuPc and ZnPc in terms of molecular structure, optical properties, and energy levels, comparable properties are assumed for ZnPc. These high energies suggest a preferential aggregation of like molecules. Given enough thermal energy for diffusion, the formation of interconnected ZnPc and C_{60} networks occurs, resulting in less isolated clusters of, e.g., ZnPc in a C_{60} matrix or vice versa. This network allows for easier extraction of charge carriers generated from dissociated excitons and leads to less isolated recombination centers in the BHJ, increasing J_{SC} , FF, and R_p . There exists an optimum temperature, in the current case of 110°C , for maximum solar cell efficiency. For higher substrate temperatures, the short-circuit current decreases. This can be explained by the formations of too large clusters and therefore reduced charge carrier separating interfaces. At the same time, the transport properties are yet further improved

TABLE I. Solar cell characteristics. All J_{SC} are normalized to 100 mW/cm^2 .

Temperature T_{sub}	J_{SC} (mA/cm^2)	V_{oc} (V)	FF (%)	$J(-1\text{ V})/J_{SC}$	η' (%)
Room temperature	8.1	0.51	38.2	1.57	1.59
80°C	10.1	0.51	42.0	1.42	2.14
90°C	11.1	0.51	41.9	1.29	2.38
110°C	12.3	0.49	42.3	1.29	2.56
120°C	11.3	0.50	41.8	1.32	2.35
130°C	11.0	0.47	42.9	1.22	2.24

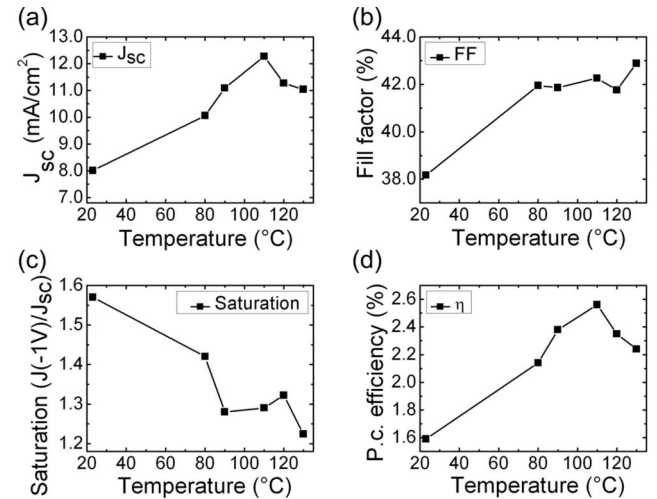


FIG. 3. (a) J_{SC} , (b) FF, (c) saturation, and (d) efficiency vs temperature. Short-circuit current densities are normalized to 100 mW/cm^2 with respect to the Si reference.

due to better developed percolation paths, which can be evidence by lower saturation and higher FF. Thus, for the substrate temperature of 110 °C an optimum between charge carrier separation and charge transport is found.⁶

In summary, we show that controlled *in situ* substrate heating during evaporation of ZnPc:C₆₀ can increase OSC performance by over 60%. The main factor here is the short-circuit current J_{SC} , which rises by over 50%, concurrent with a rising FF. It is illustrated that an optimum temperature is reached at $T_{sub}=110$ °C for a blend solar cell consisting of C₆₀:ZnPc with a ratio of 1:1. The observed effects are explained in terms of improved charge carrier percolation facilitated by an interconnected network within the BHJ due to higher interaction energies of like molecules. The decreasing performance for $T_{sub}>110$ °C is attributed to the reduced charge carrier separating interface due to too large clusters. Altogether, for OSC containing blend layers, *in situ* substrate heating is a promising method to influence layer morphology.

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