Transverse charge transport in inkjet printed poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS)

Peter Wilson, Chunhong Lei, Constantina Lekakou, John F Watts

*Centre of Materials, Faculty of Engineering and Physical Sciences, University of Surrey,
Guildford GU2 7XH, UK*

Fax: +44 (0) 14 83 68 6291;

Tel: +44 (0) 14 83 68 96 22;

* E-mail: C.Lekakou@surrey.ac.uk

Abstract

Transverse (z) alignment of PEDOT grains was demonstrated in inkjet printed PEDOT:PSS. This explained the superior transverse charge conduction mode in inkjet printed PEDOT:PSS films, best fitted by the Efros-Shklovskii 1D-VRH (variable range hopping) model in this study compared with spin coated PEDOT:PSS films, which have demonstrated layers of generally in-plane aligned PEDOT:PSS grains. The findings of this study, regarding the microstructure of inkjet printed PEDOT:PSS films and their transverse charge transport model, justify measurements of the transverse conductivity of inkjet printed films in this study being 600 times higher than that of spin coated films. In addition, it was found that the addition of 5 wt% DMSO in the printing PEDOT:PSS ink lowers the workfunction by 3% approximately.

Keywords: Inkjet Printing. PEDOT:PSS. Transverse Conduction. Transverse conductivity. Charge transport model. Workfunction. Morphology.

1. Introduction

PEDOT:PSS (poly(3,4-ethylenedioxythiophene) polystyrene sulfonate) is a popular conductive polymer, used as a hole transport layer in organic photovoltaics (OPVs) and organic light emitting diodes (OLEDs) [1-6] given its high workfunction, reaching 5.2 eV, and high conductivity, reaching 130 S cm^{-1} in in-plane charge transport [7-9]. In all such applications, conduction takes place in the transverse, z, direction while the value of the workfunction of each conductive layer or active material is most important to maintain the continuous charge flow in the electron and hole transport, respectively. Due to the possible development of aligned or crystalline morphologies in polymeric materials and the conjugated character of the PEDOT polymer chain, conductivity may be anisotropic. Surface resistance values in $\text{ohm}/\square$ and in-plane conductivity values [8-9] do not represent transverse conductivity or indeed the mechanism of transverse conduction in PEDOT:PSS. Na et al [10] found that the ratio of the in-plane to transverse conductivities of spin coated PEDOT:PSS films varied from 60 to 10 for 0 to 3 % DMSO, reducing to 6 for 11% DMSO, which still amounted to a very low value of transverse conductivity of 0.02 S cm^{-1} . This low value of transverse conductivity of spin coated PEDOT:PSS, despite co-doping with a co-solvent such as DMSO and annealing, poses a major issue in the lowering of performance of optoelectronic devices with a PEDOT:PSS layer, despite the benefits of the workfunction of this layer in the driving potential of the hole transport. It is clear that processing methods of using a co-solvent and annealing, although improving the in-plane conductivity of PEDOT:PSS [8-10], do not raise sufficiently the transverse conductivity of PEDOT:PSS.

Nardes et al [11] investigated the mechanism of charge transport in in-plane and transverse conduction for spin coated PEDOT:PSS films. They concluded that the 3D Mott variable range hopping (M-VRH) model [12] applied for the in-plane (lateral) conduction and the nearest-neighbour hopping (nn-H) model [13-14] applied for the transverse conduction. Hence, while the hopping length decreases with temperature in

M-VRH charge transport, it is independent of temperature in nn-H charge transport. Addition of co-solvent, such as DMSO [8-10], ethylene glycol [15] or sorbitol [16], leads to the evolution of the in-plane conduction to 1D-M-VRH model of charge transport for both spin coated and inkjet printed [9] PEDOT:PSS films, which explains the higher in-plane conductivity of PEDOT:PSS with a co-solvent [4, 8-10, 15, 16-17]. However, the effect of inkjet printing on the transverse conductivity of PEDOT:PSS has not been investigated yet, although inkjet printing has yielded OPVs of high efficiency [18] and increase of the spin coating speed has improved conjugation and efficiency in PLEDs (polymer LEDs) [19].

Workfunction of PEDOT:PSS has been measured for spin-coated films. It has been found [20] that raising the annealing temperature above 130 °C lowers the workfunction of spin coated PEDOT:PSS from 5.2 eV (for 120 min annealing at 130 °C) to 4.5 eV for 120 min annealing at 220 °C. On the other hand, UV treatment increases the workfunction [21]. Addition of a co-solvent reduced the workfunction of spin coated PEDOT:PSS [22], while doping of PEDOT:PSS with Cl⁻ ions to 33 at.% increased the workfunction to 5.4 eV [23].

Hence, the aim of this study has been to determine the properties of inkjet printed PEDOT:PSS which control the transverse charge transport in optoelectronic devices, investigate the mechanism of transverse charge transport in inkjet printed PEDOT:PSS and analyse the morphology of the printed films to explain the findings for electronic transport. The workfunction of inkjet printed PEDOT:PSS was also measured.

Through temperature and field dependant conduction analysis, many authors have noted the tendency for PEDOT:PSS to exhibit in-plane conduction via Mott's variable range hopping (M-VRH) in d dimensions [12-14], given by the equation:

$$\sigma_{M-VRH} = \sigma_0 \exp \left[- \left(\frac{T_0}{T} \right)^\gamma \right] \quad (1)$$

where σ and σ_0 represent the conductivity at a temperature T and a characteristic temperature T_0 , respectively, where T_0 can be interpreted as the temperature of disorder induced effective energy separation between localized states, $\gamma = \frac{1}{1+d}$ where d is the hopping dimensionality. Nardes *et al* [11, 16, 22, 24] investigated the conduction mechanisms of spin cast PEDOT:PSS in both in-plane and transverse directions. Their work demonstrated how the action of solvent evaporation in spin coating leads to charge conduction anisotropy generating a disparity between in-plane and transverse conduction models, 3D M-VRH and nearest-neighbour hopping, respectively. Indeed, a number of groups have theorised that the action of spin coating essentially ‘freezes’ the morphology in a non-thermodynamically favoured state [24, 25] whilst others have stipulated that the intense centripetal forces might generate a radially aligned morphology in the in-plane direction [26]. Hence, the fast drying process in spin coating freezes this type of morphology, creating an anisotropy between in-plane flattened PEDOT grains and their transverse, z-direction.

For the nearest neighbour hopping (nn-H) model of electron transport, the conductivity is given by the following relation [11], as a function of temperature, T , and field, F , for moderate fields:

$$\sigma_{nn-H} = \sigma_0 \left(1 + \frac{1}{6} \left(\frac{eFL}{k_B T} \right)^2 \right) \quad (2)$$

where L is the hopping length (independent of T in the nn-H model) and k_B is the Boltzmann’s constant. Both M-VRH and nn-H models have been investigated for the mechanism of the transverse electron transport in inkjet printed PEDOT:PSS in this study.

2. Experimental part

Conductive grade PEDOT:PSS (1.3 wt% in water, $\sigma = 1\text{S/cm}$ as specified by the supplier) was purchased from Sigma Aldrich. Our XPS studies (reported in [8]) of the surface of

inkjet printed samples with this PEDOT:PSS emulsion yielded PEDOT to PSS ratio at the printed surface varying from 0.4 to 0.5 for different concentrations of conductivity enhancing co-solvent (DMSO) in the range of 0 to 5 wt%, respectively. Samples were prepared by inkjet printing with the inkjet printing system incorporating an MJ-ATP injector from MicroFab with a JetDrive III control server. The substrate was motioned via a two axis CNC controlled stage feeding back to the JetDrive controller, substrate temperature was maintained to within 0.1 K via a Novus RRR temperature controller, a Pt temperature probe and a heating pad. The printed samples used for the transverse conduction measurements and AFM were inkjet printed onto a 100 nm Au electrode, itself evaporated onto a cleaned glass substrate; a second 100 nm Au electrode was evaporated on top of the PEDOT:PSS film with the overlap forming the working area. The height of the layer was measured using a Veeco Dektak 8 stylus profilometer. Optical microscopy defined the working area as 2 mm² and profilometry measured a film thickness of approximately 200 nm. Samples for the in-plane conduction measurements were generated by printing PEDOT:PSS on a cleaned glass slide in a cross-bar format for Hall probe analysis.

Spin coated PEDOT:PSS samples were prepared as reference samples by spin coating a constant volume of 3.8 ml at 3000 rpm for 30 s. The in-plane and transverse conductivities of the spin coated sample were measured at room temperature.

For the in-plane conduction, Hall probe measurements were conducted using an Accent HL5500 Hall System with cryogenic chamber held at vacuum. Target voltage of the scan was limited to 20 mV with magnetic field strength maintained at 0.328 Tesla. Contact resistance and IV measurements ensured ohmic contacts between sample and probe with each sample being the result of averaging up to 9 identical specimens. Sheet resistance was measured and bulk resistance was determined using the film thickness which was averaged by profiling the sample on a Veeco Instruments Dektak 8 stylus profilometer. Misalignment and correction factors were rectified by cycling the analysis between

contacts.

Transverse conductivity measurements were conducted using an Oxford Instruments Compact Liquid Nitrogen cryostat with a HP 4140B pA Meter / Voltage Source with results recorded by a hand-coded LABView interface. The sample was contained in argon transfer gas with temperature maintained between 100 K and 300 K by an Oxford Instruments DTC-2 temperature controller. Voltage was recorded in 0.1 V steps between -1 V and 1 V resulting in potential gradients of the order of $5 \times 10^4 \text{ V cm}^{-1}$.

All TM-AFM analysis of film cross-sections was carried out using a VEECO (Digital Instruments) Nanoscope IIIa 'Multimode' atomic force microscope. Each sample was analysed in tapping mode using silicon cantilevers with an average resonant frequency of the order of 270 kHz.

Workfunction was determined in scanning Kelvin probe force microscopy (SKPFM) performed on a VEECO (Digital Instruments) NanoScope III 'multimode' AFM in lift-mode. Each sample was analysed in a double-pass method where the surface topography was recorded before a second pass measures the workfunction. Each sample was grounded through the piezo scanner with the tip held at an ac amplitude of 5-6V. The second pass was performed at a distance of approximately 10 nm. Each sample was referenced to a gold target, sputter-coated on top over a metallic grid. The gold reference also served to ground the sample and ensure no charge build up could occur. All SKPFM was performed in a nitrogen atmosphere using the environmental hood to ensure minimal moisture build-up over the course of a scan.

3. Results

3.1 Measurements of PEDOT:PSS properties for transverse charge transport in optoelectronic devices

The values of transverse (z-direction) and in-plane conductivity of inkjet printed PEDOT:PSS were measured (at room temperature) as $\sigma_{\perp} = 0.018 \text{ S cm}^{-1}$ and $\sigma_{\parallel} = 0.014 \text{ S cm}^{-1}$, respectively, demonstrating a little higher transverse conductivity than in-plane conductivity. In contrast, the in-plane and transverse conductivity of the spin coated PEDOT:PSS was measured as $\sigma_{\parallel} = 0.01 \text{ S cm}^{-1}$ and $\sigma_{\perp} = 3 \times 10^{-5} \text{ S cm}^{-1}$, demonstrating about 300 times higher conductivity in-plane than in the transverse direction, in qualitative agreement with Nardes et al's data [11] for spin coated PEDOT:PSS ($\sigma_{\perp} = 2 \times 10^{-6} \text{ S cm}^{-1}$ and $\sigma_{\parallel} = 9 \times 10^{-4} \text{ S cm}^{-1}$ [11]). Adding even 1 wt% DMSO in the printing ink, raised the transverse conductivity of the inkjet printed film so much that also given its small thickness, 200 nm, no transverse resistance of the PEDOT:PSS film could be measured, as it was so low comparable to the resistance of the connecting copper wires.

With regards to the determination of workfunction via SKPFM studies, the AFM tip potential was required and was determined with reference to Au. For this purpose, an initial SKPFM study involved a PEDOT:PSS inkjet printed sample (with 5 %_{wt} DMSO), sputter-coated with a gold layer on either side to be used as a reference material in an attempt to calibrate the SKPFM tip. Assuming a nominal workfunction of 5.1 eV for the gold layers (freshly evaporated under UHV [27]), which exhibited a large peak on the SKPFM micrograph at 0.21 V, the AFM tip potential can be calibrated at 5.31 eV, which is consistent with the tip being made from a Pt/Ir alloy (according to information from the manufacturer), whose workfunction is expected to be higher than that of Au. Although Au was used as a reference, it has been reported that physisorption of surface adsorbates, especially polar adsorbates, may reduce the gold workfunction by up to 0.4 eV in ambient [28]. For these reasons, it may not be possible to determine accurate workfunction values for the PEDOT:PSS in this study and, hence, it is prudent to dwell on the workfunction change of PEDOT:PSS in the presence of DMSO, rather than the absolute workfunction value.

Figures 1 and 2 present the SKPFM maps and potential distribution for the inkjet printed

films, leading to an estimated workfunction of 5.27 eV for pristine PEDOT:PSS and 5.12 eV for PEDOT:PSS with 5 wt% DMSO in the printing ink. It can be also observed that the pristine PEDOT:PSS film has a narrow potential distribution of approximately ± 0.01 V whereas the addition of 5 wt% DMSO in the printing ink widens the potential distribution to ± 0.1 V, indicating a large inhomogeneity in the potential map in the latter case due to phase segregation in the coarsening of PEDOT grains upon the addition of DMSO [8,9]. Hence, the addition of 5 wt% DMSO in the printing ink brings a decrease of 150 meV in the workfunction of the printed PEDOT:PSS film. Similar decrease in the workfunction of PEDOT:PSS was reported in previous studies, due to the addition of a co-solvent: 120 meV by adding 8 wt% glycerol [29] and 300 meV by adding 10 wt% Sorbitol [19, 30].

Figure 1. Scanning Kelvin probe force microscopy map (500 nm x 120 nm) and potential distribution for inkjet printed PEDOT:PSS with 0 wt% DMSO (AFM tip potential calibrated at 5.31 eV). Workfunction of inkjet printed PEDOT:PSS = 5.27 eV.

Figure 2. Scanning Kelvin probe force microscopy map (500 nm x 120 nm) and potential distribution for inkjet printed PEDOT:PSS with 5 wt% DMSO in the printing ink (AFM tip potential calibrated at 5.31 eV). Workfunction of inkjet printed PEDOT:PSS (with 5 wt%

$$\text{DMSO}) = 5.12 \text{ eV.}$$

3.2 Transverse conductivity as a function of temperature and charge transport model

Temperature dependence conduction experiments were performed in vacuum between 100 and 300 K, in steps of 10 K, for both in-plane and transverse conduction in inkjet printed PEDOT:PSS films. The M-VRH model in d dimensions provided the best fit for low field runs for both in-plane and transverse conductivity. Equation (1) was fitted for various values of the γ exponent and the correlation coefficient χ^2 was plotted as a function of the tried values of γ : the plot is displayed in Figure 3 for both the in-plane and transverse charge transport. The maximum value of χ^2 occurred at $\gamma = 0.25$ for the in-plane conductivity ($d = 3$) and $\gamma = 0.5$ for the transverse conductivity ($d = 1$). Figure 4 then shows the best fit lines in each case, according to equation (1), and Table 1 presents the values of the parameters of the M-VRH model determined from the best fit lines.

Figure 3. Value of the correlation coefficient, χ^2 , of the linear best fit of the experimental data of the graph of temperature dependence of conductivity modelled against M-VRH exponent γ , for the in-plane and transverse conductivity of inkjet printed PEDOT:PSS films.

Figure 4. M-VRH model: Temperature dependence of conduction for (a) in-plane conductivity fit to temperature exponent $\gamma = 0.25$ and (b) transverse conductivity fit to temperature exponent $\gamma = 0.5$ for inkjet printed PEDOT:PSS film.

Table 1. M-VRH parameter values for in-plane and transverse charge transport in inkjet printed PEDOT:PSS films

Conduction	γ	T_0 [K]	σ_0 [S cm ⁻¹]	σ_{rt} [S cm ⁻¹]
In-Plane	0.25	516793	0.1	0.014
Transverse	0.5	1039	0.11	0.018

The next stage was to also investigate the applicability of the nn-H charge transport model in the transverse conduction direction, as this model was found to be best for the transverse conduction in spin coated PEDOT:PSS films [11, 24]. In order to assess the hopping distance, L , transverse conductivity measurements were performed under variable field and variable temperature conditions. In this case, the general solution for the current, I , is given by:

$$I_{nn-H} = I_0 \exp \left[- \left(\frac{T_0}{T} \right)^\gamma \left(1 - A \frac{(eFL)^\alpha}{(k_B T)^{\alpha'}} + B \left(\frac{eFL}{k_B T} \right)^\beta \right) \right] \quad (3)$$

where e is the electric charge, and A , B , α , α' and β are constants with A and B being positive. Equation (3) can be interpreted as the action of two parts, the first term,

$A(eFL)^{\alpha}/(k_B T)^{\alpha'}$, expresses the increased probability of a hop as the field increases whereas the second term, $B[(eFL)/(k_B T)]^{\beta}$, was formulated by Bottger et al [31-34] to include the possibility of hops against the electric field. As discussed by Ladieu et al [35], in the presence of a high electric field which satisfies $(eFL)/(k_B T) \gg 1$, no reverse hops occur so that equation (3) can be approximated by the relation:

$$\sigma(F, T) = \sigma_0(0, T) \exp\left(c \frac{eFL_{\perp}}{k_B T}\right) \quad (4)$$

with c being a constant, approximated by $c=1/6$ [11]. At moderate fields, $(eFL)/(k_B T) < 1$, the process becomes much more complicated where Nardes et al [11] approximated equation (3) with relation (2). If the nn-H model is applicable [11, 16, 17], the hopping length, L , is independent of temperature.

Figure 5 presents the plot of the experimental data of transverse z-conductivity of inkjet printed PEDOT:PSS as a function of the field strength, F , and different temperatures for variable field F -variable temperature T experiments. In general, exponential type conductivity curves are observed as a function of F/T at different temperature levels to incorporate the term $\sigma_0(0, T)$. In this case, the data fit relation (4) for $F > 1.2$ mV/nm, across the range of moderate and high fields, hence the probability of a reverse hop is dramatically low not just for the high fields but also for moderate fields, which gives the first indication that the nn-H model does not apply in the transverse conduction through inkjet printed PEDOT:PSS films.

Figure 5. Transverse z- conductivity of inkjet printed PEDOT:PSS films as a function of a variable field at incremental temperatures.

Under these circumstances, using the best fit lines of experimental data according to relation (4) at different temperatures [11, 36], the hopping distance, $L_{\perp}$, in transverse z-conduction was determined as a function of temperature and is presented in Figure 6 (normalized against $L_{\perp}$ at 300 K). It can be seen that the effective hopping distance in transverse conduction in inkjet printed PEDOT:PSS films is temperature dependent, indicating that transverse charge transport occurs according to the M-VRH model rather than the nn-H model [11, 37]. Figure 6 also presents the 1D VRH line ($L_{\perp} \propto T^{-0.5}$) fitted to the experimental data.

Figure 6. Data of variable electric field / variable temperature derived hopping length, $L_{\perp}$ (normalized), as a function of temperature for the transverse conduction in inkjet printed PEDOT:PSS. The line is the predicted normalised $L_{\perp}$ versus T fit according to the 1D VRH model ($L_{\perp} \propto T^{-0.5}$).

3.3 Morphology of cross-sections of the inkjet printed PEDOT:PSS films

PEDOT:PSS lines were printed at a substrate temperature of 300 and 313 K exhibiting flat profile and raised edge profile (Figure 7), respectively, as expected for heated substrates [38]. A PEDOT:PSS line was printed at a substrate temperature of 303 K and a sample was sliced from the position indicated in Figure 7. PEDOT:PSS samples were also prepared by spin coating and transverse sections along the radial direction were cleaved. For both

inkjet printed and spin coated PEDOT:PSS samples on glass slide substrate, each sample was submerged in liquid nitrogen for 25 minutes before cleaving. The transverse cross-section samples were examined under atomic force microscopy (AFM) and Figure 8 presents the AFM micrographs of the transverse cross-section for a typical spin coated and a printed PEDOT:PSS sample. The typical AFM topography of PEDOT:PSS surfaces or cross-sections displays elevated PEDOT grains surrounded by a PSS matrix shell [8, 24]. Figure 8(a) presents the AFM cross-section topography of the spin coated PEDOT:PSS where circular PEDOT grain cross-sections can be seen with a topography height of 10-14 nm; these PEDOT grains seem to form grain clusters elongated and aligned in the radial direction of the spin coated samples (horizontal direction on the page), which agrees with similar findings in the literature for spin coated PEDOT:PSS [11, 24]. On the other hand, the cross-section AFM phase map of the printed PEDOT:PSS in Figure 8(b) demonstrates clearly strings of PEDOT grains aligned in the transverse z-direction of the printed film (vertical direction on the page), in contrast with the in-plane aligned PEDOT grain structures in the transverse cross-sections of spin coated PEDOT:PSS in this study and in literature [11, 24].

Figure 7. Profiles of inkjet printed lines of PEDOT:PSS at substrate temperature of (a) 300 K (width of printed line = 125 μm , maximum height of printed line profile = 140 nm) and (b) 313 K (width of printed line = 140 μm , maximum height of printed line profile = 140 nm). The position of cross-section sample examined under AFM in Figure 8(b) is indicated.

Figure 8. AFM micrographs of transverse cross-section of cryogenically cleaved PEDOT:PSS. (a) Spin coated – AFM topography map, with image at the top illustrating a diagram of perceived pie-clusters of PEDOT grains radially aligned (horizontal direction on the page) and (b) printed at a substrate temperature of 303 K - AFM phase map - demonstrating transverse PEDOT grain alignment (vertical direction).

4. Discussion

It is clear that the inkjet printed PEDOT:PSS has good transverse z-conductivity in comparison to the 600 times lower transverse conductivity of spin coated PEDOT:PSS in our study (and also in [11] for spin coated PEDOT:PSS). This is justified by the 1D-M-VRH charge transport identified in this study for the transverse z-conduction in inkjet printed PEDOT:PSS films, compared to nn-H type of charge transport modelled [11] for the transverse z-conduction in spin coated PEDOT:PSS. We believe that the key reason for these phenomena is the effect of the processing conditions in the inkjet printing to

create a morphology of transversely aligned and elongated structures of PEDOT grains.

Spin coating under high speeds generates radial in-plane alignment of flat PEDOT grain structures under the effect of centrifugal forces, which “freezes” under the quick evaporation of solvent [11]. This leaves layers of in-plane elongated and aligned PEDOT grain clusters or structures as is illustrated in Figure 9. Flow in inkjet printed drops and lines is much more complicated. First of all, the jetted droplet impacts the substrate changing flow direction outwards. Solvent evaporation is expected to occur faster at the drop edges (or line edges), generating convective solvent flow [39-40] towards the edges and sustaining a relatively slow evaporation rate. Under such circumstances the circulating convective flow occurring for printed flat or elliptical top surface profiles (Figure 10(a)) creates columns of transversely elongated and aligned structures or strings of PEDOT grains that enhance transverse z-conductivity. On the other hand, the top layer has the possibility to create domains of flat PEDOT grain structures, also enhancing in-plane conductivity. In the case, of highly heated substrate, surface tension gradients lead to “Marangoni” flow and the “coffee cup ring” effect [38-46], as is presented in Figure 10(b), which also leads to columns of transversely aligned PEDOT grains.

Figure 9. Diagram of a spin coated drop or spin coated line cross-section under solvent evaporation, showing the direction of the centrifugal forces and flow stresses. Elliptical pies represent PEDOT grain structures, with these structures elongated and aligned along the flow.

Figure 10. Diagram of printed drop or printed line cross-section under solvent evaporation: (a) elliptical top surface profile with convective flow; (b) “coffee ring” surface profile with “Marangoni” flow. Elliptical pies represent PEDOT grain structures elongated and aligned along the flow.

At a substrate temperature of 303 K, inkjet printing using the printing system in this study generates a flat top surface profile, as is presented in Figure 7(a) [38], with expected convective circulating flow as illustrated in Figure 10(a). The AFM micrograph of the transverse cross-section of the printed PEDOT line confirmed the existence of transverse grain alignment in Figure 8(b). This justifies the 1D-M-VRH charge transport model in the transverse direction, where conduction is carried out by the transversely aligned PEDOT grains. On the other hand, 3D-M-VRH charge transport has been determined for the in-plane conduction with 500 times higher value for T_0 in the in-plane direction than in the transverse direction. In this case, given that the transversely aligned PEDOT grain columns are only a portion of the total morphology, in-plane flattened PEDOT grain clusters also existing in inkjet printed films, the transverse z-conductivity is a little higher only than the in-plane conductivity for the inkjet printed PEDOT:PSS films.

Addition of DMSO and other co-solvents has been reported to increase the in-plane conductivity of both inkjet printed [8,9] and spin coated PEDOT:PSS [15, 19, 47-50] by acquiring a morphology of more coarsened PEDOT grains and reduction of the charge hopping distance [9], while 1D-M-VRH charge transport also applies to in-plane conduction. As transverse conduction is already controlled by 1D-M-VRH charge transport

in inkjet printed PEDOT:PSS films without any co-solvents in this study, further coarsening of PEDOT grains aligned in the transverse direction is expected by adding DMSO up to 5 wt% in the printing ink [9], which is expected to further raise the transverse conductivity of inkjet printed PEDOT:PSS above the values of the transverse conductivity of spin coated PEDOT:PSS with a co-solvent, where the latter totally lacks any transverse PEDOT grain alignment.

5. Conclusions

The major contribution of this study was to prove and explain the advantage of inkjet printing in achieving very good transverse conductivity in PEDOT:PSS compared to spin coating. This is explained by the observed morphology of transversely aligned PEDOT grain strings in printed PEDOT:PSS which was attributed to convective flow and/or “Marangoni” flow during the drying of printed drops in contrast to only in-plane aligned, elongated PEDOT grain structures in spin coated PEDOT:PSS: the in-plane alignment explains the very low ratio of transverse to in-plane conductivity in spin coated films, 0.003-0.17 for 0-11 wt% DMSO respectively, in this study (0 % DMSO) and in the literature [10]. The presence of transverse grain alignment explains the 1.3:1 ratio of transverse to in-plane conductivity in inkjet printed PEDOT:PSS films for 0 % DMSO in this study. Furthermore, investigations of the charge transport mechanism and model revealed that the data of conductivity at different temperatures can be best fitted with the 1D Mott VRH model for transverse conduction in inkjet printed PEDOT:PSS films compared to the nn-H model best fitted for the transverse conduction in spin coated PEDOT:PSS films [11]. The proven dependence (decrease) of hopping length on temperature in transverse charge transport invalidates the nn-H model for the transverse conduction in inkjet printed PEDOT:PSS. Hence, the film morphology and the elucidation of the transverse charge transport mechanism in inkjet printed PEDOT:PSS as 1D Mott VRH model justify the much higher transverse conductivity of inkjet printed PEDOT:PSS compared to that of spin coated PEDOT:PSS. This means that inkjet printing or other printing techniques are advantageous in the processing of PEDOT:PSS for OPVs, OLEDs

and generally optoelectronic applications with predominantly transverse charge transport.

The workfunction of inkjet printed PEDOT:PSS films was measured by SKPFM and was found to decrease from 5.27 eV to 5.12 eV for 0 and 5 wt% DMSO added in the printing ink, respectively.

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