Direct Electrostatic Toner Marking with Novel Electric Field Induced Hole Injection Between PEDOT:PSS and Molecularly Doped Polymer Layers of Arylamine

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Abstract

PEDOT:PSS is the one of the most promising and widely used material for low cost large area flexible displays owing to their easy solution processing and nanoscale patternability. In this work, hole injection between PEDOT:PSS thin film and molecularly doped polymer layers of arylamine has been studied in a bilayer device configuration. The electrical properties of the bilayer device have been examined by studying the charge-discharge, I-V and Time of Flight (TOF) characteristics of the devices. The work function of the PEDOT:PSS and aryl amine has been estimated by electrochemical measurements. Results show that PEDOT:PSS are efficient hole injectors to arylamine owing to their favorable molecular energetics. The efficiency of hole injection also depends on the conductivity of PEDOT and the strength of the electric field. The interfacial contact behavior between PEDOT and arylamine studied by steady state IV measurements and TOF measurements suggests that for highly conductive PEDOT:PSS, the hole injection is limited by the hole mobility in the charge transport layer where as for higher resistive PEDOT:PSS, it is injection limited. Based on these results, a discharge mechanism has been proposed for the bilayer device. Initial printing experiments were done on a xerographic development housing, where toner development on the bilayer device was observed at the exit of the development nip. Results suggested that the negatively biased magnetic brush plays a dual role in the print process. It first discharges the bilayer device with its negative bias followed by toner development to the discharged area. The use of this novel electric field induced hole injection process for direct toner marking is discussed.

***Keywords**: PEDOT:PSS thin films, printing device, electrostatic latent image, electron transfer, hole injection*

Introduction

The basic steps in the xerographic (electrophotographic) process involve charge and image wise discharge of the photoconductor to create the electrostatic latent image, followed by development of the latent image with toner electrostatically and then image fixation with heat and pressure [1]. Xerography has become a multi-billion dollar industry and the technology is applying to almost all color laser printers ranging from low speed printers in home office to high speed color presses in print shop. It is interesting to note that, other than the image file input through the laser ROS, which is digital, the entire printing process is still in an analog mode. In this work, we report a study of a new electron transfer reaction from a molecularly doped layer of an aryl amine in polycarbonate to a thin film of PEDOT:PSS [2]. The net result of this electron transfer reaction is a hole injection from the PEDOT:PSS film to the arylamine charge transport layer. This hole injection process triggers the discharge of the bilayer device process. In addition, this hole injection process is shown to be sensitive to the applied electric field as well as the conductivity of the PEDOT:PSS film. The mechanism for the charge-discharge process of the bilayer is proposed. The use of the bilayer device to demonstrate direct toner marking in the xerographic printing process is discussed.

Experimental

Materials. PEDOT:PSS films of surface resistivity ranging from ~ 100 ohms/sq to ~ 5000 ohms/sq) on Mylar substrate were either purchased directly from Orgacon or alternatively the PEDOT:PSS ink was purchased from H.C.Starck/Orgacon and different thickness of PEDOT:PSS films were coated using an internal slot dye coater. Hole transporting molecule, TPD and the polycarbonate polymer binder PCZ200 were obtained from internal source (structures in Fig. 1). All coating solvents (methylene chloride, tetrahydrofuran and toluene) were analyzed reagent grade from Fischer and were used as received.

Devices. The bilayer devices studied in this work was fabricated by simply coating a solution containing TPD and PCZ200 in a mixed solvent of tetrahydrofuran and toluene (70:30 in ratio) over the PEDOT:PSS film (on Mylar) on a lab draw-down coater using a 3-5 mil draw bar. A typical coating solution consisted of ~ 14% of solid. The concentration of TPD in the charge transport layer (CTL) was at 40% by wt. The thickness of the CTL was typically ~ 20 μm and was controlled by the solid concentration of the coating solution as well as the wet gap of the draw bar. The resulting bilayer device was air dried for 0.5 hour followed by vacuum drying at 100^{o}C for 2 hours before electrical evaluation.

Measurements and Techniques. The surface resistivity of the PEDOT:PSS films were measured by a four probe point method using a Keithley 237 high voltage source. The charge-discharge characteristics of the bilayer device were performed on an in-house static scanner. Gold dot was evaporated on the CTL for the electrical contact. A schematic description of the apparatus is shown in Figure 1. Typically the bilayer devices were charged by the HV corona device and the surface potential were monitored using an electrostatic voltmeter (ESV). Since the bilayer device was "static" throughout the measurement, the charging and monitoring of the surface potential was controlled electronically through the electric circuit within the static scanner, typically there was a ~ 0.1 s delay between charging and monitoring.

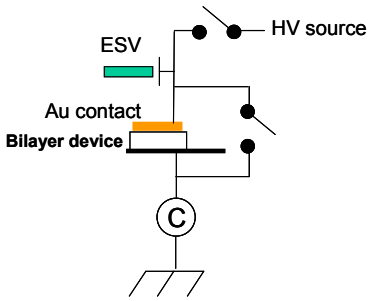


Fig. 1 A schematic of the "static" scanner.

Printing Experiment with the bilayer device: Print test was carried out for an inkjet patterned PEDOT:PSS bilayer device overcoated with a TPD CTL layer. The patterned bilayer device was pasted and grounded on photoreceptor drum by silver paste. The entire drum was placed in the print catridge and the print catridge was placed on a printing fixture. The toner marking experiments were carried out on a xerographic development unit. The bilayer device in this study consists of a PEDOT:PSS film (surface resistivity 350 ohms/sq) overcoated with a 18 µm CTL layer. The strip of the bilayer device was pasted on an organic photoconductor drum (OPC) and was grounded to the ground plane of the OPC drum with silver paste.

Results AND DISCUSSION

Device Configuration and Electrical Characterization

Figure 2 shows the configuration of the bilayer device and the materials used in this work. The device comprises a molecularly doped charge transport layer (CTL) made of hole transport molecule TPD in polycarbonate over a thin film of PEDOT:PSS on a Mylar substrate.

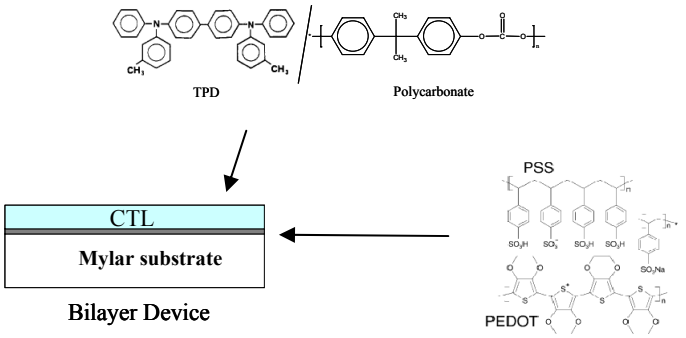


Fig. 2 Bilayer device: configuration and materials used.

The charge and discharge characteristic of the bilayer device was studied on an in-house static scanner (Fig. 1). Figure 3a shows the surface potential curves obtained from a typical PEDOT:PSS bilayer device. Figure 3b shows the surface potential curves from a controlled bilayer device where the PEDOT:PSS film is replaced by a Ti/Zr metal layer. By comparing with the control, the result indicates that the PEDOT:PSS bilayer device is charge capacitively. Unlike the control, the PEDOT:PSS bilayer device undergoes rapid discharge as soon as the electric field across the bilayer device is established.

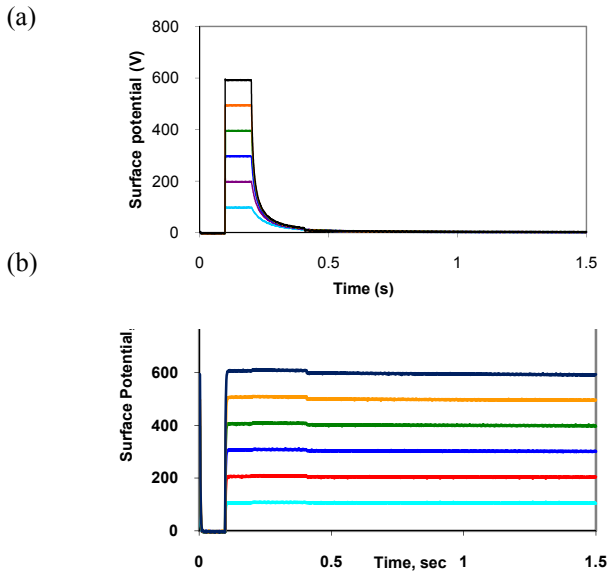


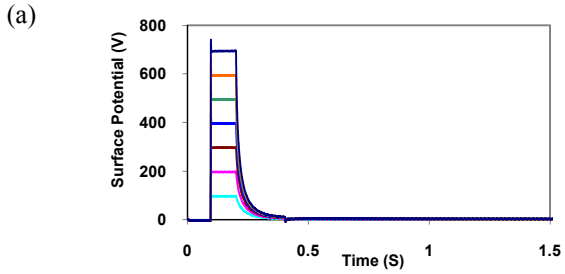
Fig. 3 (a) Typical charge – discharge curves for a PEDOT:PSS bilayer device, and (b) charge – discharge curves for a controlled bilayer device.

This implies the occurrence of a hole injection reaction from PEDOT:PSS film to the TPD CTL immediately after charging up the device. Subsequently electron transfer from the neighboring TPD molecule to the injected hole occurs.

A more detailed description of the charge-discharge process is described in the later section of the paper. It is important to note that very similar charge-discharge process is believed to occur in photoconductive devices in photoreceptors. The primary difference is that the charge-discharge process in photoreceptor is photogenerated where as in the present case it is a dark discharge process.

Effect of Surface Resistivity of PEDOT:PSS Films on Discharge Rate

The rate of the dark discharge was found to be sensitive to the conductivity of the PEDOT:PSS film for a common CTL (40% TDP in polycarbonate, ~ 18 µm thick). Figures 4a and 4b depict the discharge curves for two bilayer devices with PEDOT:PSS films of different surface resistivity. The result shows that the higher the conductivity of the PEDOT:PSS film, the faster the discharge rate and the more sensitive the device is.



(b)

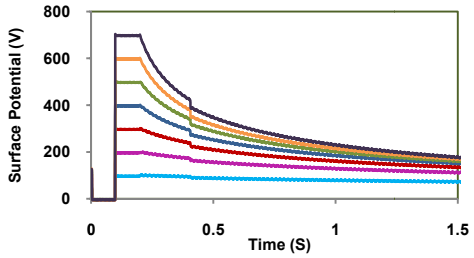


Fig. 4 Charge – discharge curves for bilayer devices with PEDOT:PSS films of different surface resistivity (a) 350 Ohm/Sq and (b) 4000 Ohm/Sq.

Effect of Electric Field on Discharge Rate

From the discharge curves in Figures 4a and 4b as well as similar plots obtained from bilayer devices of different PEDOT:PSS surface resistivity, one can analyze the initial discharge rates at different surface potential for these devices. Plots of the initial discharge rate (dV/dt) of these bilayer devices at different surface potentials are given in Figure 5.

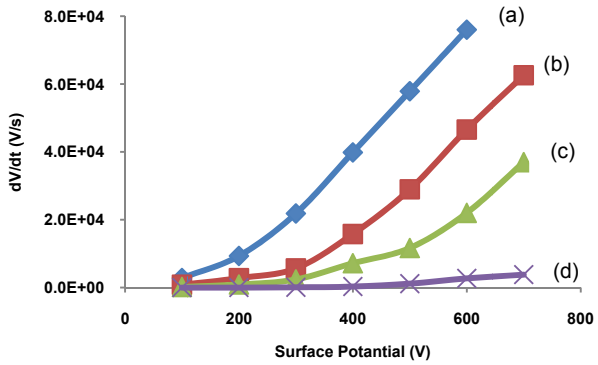


Fig. 5 Plot of initial discharge rate as a function of surface potential for bilayer devices with varying PEDOT:PSS surface resistivity (a) 350 ohms/sq(b) 1500 ohms/sq (c) 2250 ohms/sq (d) 4000 ohms/sq

The results indicate that (1) the discharge rate is highly sensitive to the surface resistivity of the PEDOT:PSS film, the higher the conductivity, the faster the discharge rate. (2) The discharge rate increases as the surface potential increases. Since the thickness of all these devices are held to be constant, ~ 18 µm, the result indicates that there is a strong electric field effect on the discharge rate, the higher the electric field across the device, the faster the discharge rate. Another important feature in Figure 5 is the apparent existence of a threshold electric field for the discharge rate. Specifically, dV/dt becomes negligible when the surface potential is < 200 V or when the electric field across the device is < ~ 10 V/µm.

The conclusions on the field and the threshold effects on dV/dt are substantiated by a second set of experiments where we vary the electrical field systematically by varying the CTL thickness.

Proposed Discharge Mechanism

The results in Figures 4 and 5 clearly suggest that the discharge rate of the PEDOT:PSS bilayer device is very sensitive to the electric field. There also appears to be a threshold field to trigger the discharge process. We hypothesize that, under the influence of the electrical field, "bounded" electron-hole (e-h) pairs are generated in the bilayer device. At fields weaker than the threshold field, the e-h pairs recombine and no discharge occurs. On the other hand, when the field across the bilayer device is higher than the threshold field, the e-h pairs dissociate. This is followed by an electron transfer from the arylamine CTL to the PEDOT:PSS film. In other words, hole injection from the PEDOT:PSS film to the CTL results. The injected holes then migrate across the CTL, discharging the bilayer device. This hypothesis is supported by the observation that the discharge process is facilitated when the conductivity of the PEDOT:PSS film is high. Presumably, the bounded e-h pair can also dissociate under weak field when the PEDOT:PSS film is conductive. The mechanistic picture of the e-h pair generation and dissociation is summarized in Figure 6.

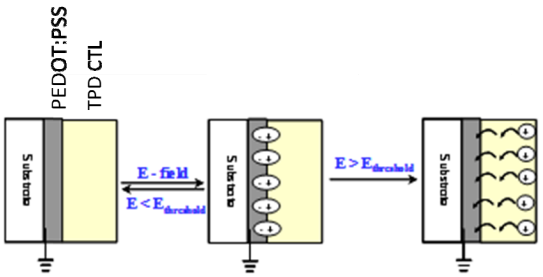


Fig. 6 Proposed discharge mechanism for the PEDOT:PSS bilayer device.

This proposed mechanism is supported by the favorable molecular energetic of PEDOT:PSS (5.1 eV) and aryl amine (5 eV) films obtained from electrochemical measurements.

The discharge mechanism is further supported by the interfacial contact behavior between PEDOT:PSS and aryl amine film studied by steady state IV measurements and Time of Flight (TOF) drift mobility data. Figure 8 shows the plot of steady state current density measured from two different PEDOT:PSS bilayer devices as a function of electric field. Independently, we also measured the TOF drift mobility data of the CTL alone and the current density of CTL can be calculated from the drift mobility from equation 1 [3].

$$JTOF = 9/8 \in \in o\mu E2/L \qquad (1)$$

Here $\in$ is the relative dielectric constant μ is the drift mobility, E is the effective field and L is the film thickness.

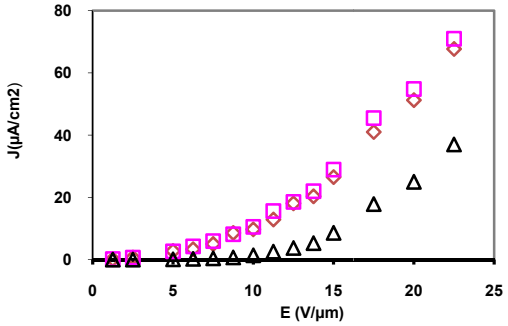
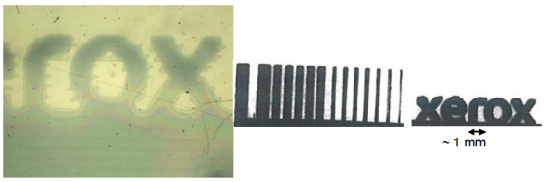


Fig. 7: Plot of steady state current density as a function of electric field for a CTL layer consisting of 40% aryl amine in polycarbonate(◊) and PEDOT:PSS bilayer devices with surface resistivity of (□) 350 ohms/sq and (Δ) 1500 ohms/sq.

The calculated current density of CTL calculated from the drift mobility data is included in figure 7. The results indicate that the field effect of the CTL coincides with that of PEDOT:PSS bilayer devices prepared from PEDOT:PSS film with surface resistivity of 350 ohms/sq. The comparable current density between the two devices indicate that the discharge of this particular bilayer device is limited by the hole mobility of CTL. In other words, the hole injection efficiency of the above PEDOT:PSS bilayer device is close to unity. On the other hand PEDOT:PSS bilayer device prepared from more resistive films (surface resistivity 1500 ohms/sq) the field effect on current density is lower than that of CTL alone. This indicates that the discharge process is injection limited for more resistive films.

Print test and Direct Toner marking with PEDOT:PSS bilayer devices:

Figure 8 shows the print test with inkjet patterned PEDOT:PSS bilayer devices. This shows that the patterns can be printed normally using toner implying the successful demonstration of the novel electric field induced hole injection process in the xerographic printing process.



(a) (b)

Fig. 8: PEDOT:PSS film patterned with the Dimatix inkjet printer (b) lines and text printed in the xerographic fixture using PEDOT:PSS/CTL bilayer device.

Our next step was to carry out the printing experiment on the PEDOT:PSS bilayer devices using a xerographic development fixture without using the ROS and charger. The PEDOT:PSS bilayer device grounded to the drum was rotated through the development nip at a speed of 264 mm/sec. Figure 9 shows the cyan toner development before and after it passed through the development nip. This indicates that the toner can be directly printed into the imaging drum thus reducing both the number of components and steps in the xerographic process.

(a) (b)

Fig. 9: (a) Photograph of the PEDOT:PSS bilayer device grounded to the OPC drum (b) development of the toner patch on the PEDOT :PSS bilayer device

Based on our mechanistic understanding, we hypothesize that the toner printing process still occurs in 2-step, namely electric field induced hole injection of the imaging member to create a surface voltage contrast followed by toner development. This 2-step process is accomplished within the development nip, resulting in direct toner printing without laser, ROS, charge and PR. A schematic summary of the hardware and the print process is given in Fig. 10.

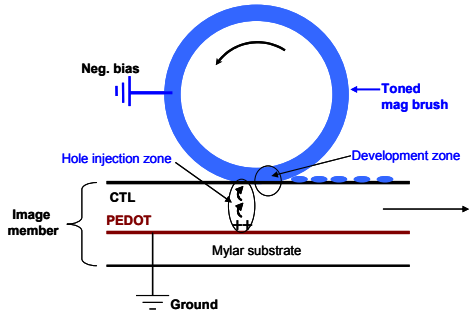


Fig. 10 Schematic illustration of the hardware and print process.

This was further supported by comparing the Development Mass per unit Area (DMA) of the toner on PEDOT/TPD bilayer device with and without charger as a function of the development potential (Vdev). Figure 1 shows the plot of DMA vs. Vdev with and without charger. In the first case, the charger provides the negative bias followed by hole injection from the bilayer device resulting in the discharge of the device. Then the toner development occurs in the discharge areas

by a toned mag brush. In the second case, as described above mag brush plays a dual role, it provides the required electric field for the hole injection process followed by the development of the toner onto the electrostatic image resulted by hole injection process. It can be seen that the DMA of toner with and without charger are quite similar further confirming our hypothesis.

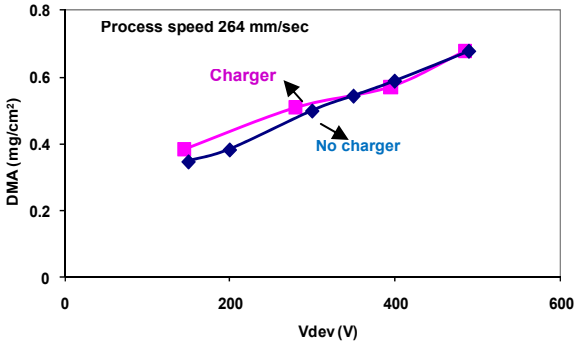


Fig. 11: Plot of Development mass of toner vs. Development potential (Vdev) with and without charger.

Concluding Remarks

In this work, we report a novel electric field induced electron transfer reaction between an arylamine hole transport molecule, TPD, and PEDOT:PSS thin film in bilayer device. Evidence is

provided that bounded e-h pairs are formed under the influence of an electric field. At field strength lower than the threshold field, the e-h pairs recombine . On the other hand, at higher electric fields, the e-h pairs dissociate, and this is followed by a hole injection reaction and a series of isoenergetic electron transfer across the CTL, leading to total discharge of the bilayer device. This hypothesis is supported by the interfacial contact behavior between PEDOT:PSS and CTL layer. We were also able to demonstrate direct toner marking using this novel electric field induced hole injection process. This simplifies the xerographic marking process by reducing the number of components and steps. We suggest that, we should be able to digitize the xerographic process when we couple the discharge process of the present bilayer device with an addressable TFT backplane.

Acknowledgements

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References

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