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## High work function materials for source/drain contacts in printed polymer thin film transistors

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Studies of materials for source-drain electrodes in ink-jet printed polymer-based thin film transistors (TFTs) are reported. Two systems are studied: a blend of Ag nanoparticles with poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) and an ethylene glycol-doped PEDOT:PSS solution (modified-PEDOT). The semiconductor used is the polythiophene derivative poly [5,5'-bis(3-dodecyl-2-thienyl)-2,2,2'-bithiophene]. PEDOT:Ag blends and modified-PEDOT yield TFTs with mobilities around  $10^{-2}$  and  $10^{-3}$   $\text{cm}^2/\text{V s}$ , respectively, subthreshold slopes around 1.6 V/decade and on-to-off current ratios of  $10^6$ – $10^7$ . Both systems show considerable improvement over printed TFTs with Ag nanoparticle source-drain electrodes. Results on film resistivity and morphology are discussed along with device characteristic analysis. © 2008 American Institute of Physics. [DOI: 10.1063/1.2857461]

The interest in reducing the cost of flat panel displays has led several groups to investigate the fabrication of fully printed thin film transistor (TFT) arrays as backplanes for displays.<sup>1–3</sup> Part of the challenge of fully printing polymer-based TFT arrays is finding suitable inks for the source and drain electrodes, which are in direct contact with the semiconducting polymer and require a high work function ink for good charge injection and minimal contact resistance at that interface. Several studies have investigated the effects of contact resistance of the source/drain electrodes on the performance of organic TFTs.<sup>4–9</sup> In addition to having high work function, the ink must be homogeneous, compatible with the printer nozzle, and highly conductive. Gold nanoparticle inks are good candidates, but lower cost alternatives are preferred. Silver is less expensive, but its low work function of 4.3 eV does not favor charge injection, leading to large contact resistance at the polymer/electrode interface.

Here, we consider blends of materials that are less expensive than Au while maintaining its good injection properties and high conductivity. We test poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) blended with Ag nanoparticles as well as PEDOT:PSS doped with an ethylene glycol-based solvent (modified PEDOT) as inks for printed source-drain electrodes of polymer-based TFTs. PEDOT:PSS, a polymeric solution of good conductivity and high work function, has been optimized for homogeneity and stability.<sup>10–12</sup> Homogeneous, stable Ag nanoparticle solutions can form highly conductive films with low annealing temperatures (125–150 °C). To test these solutions, we measured film resistivity ( $\rho$ ) and sheet resistivity ( $R_s$ ), studied film morphology, and ink-jet printed the solutions as source/drain contacts in TFTs.

PEDOT:PSS was obtained from H.C. Stark. Ag nanoparticles, 30–50 nm in size and dispersed in an ethylene glycol-based solvent, were purchased from Cabot. Good solvent compatibility allowed homogeneous mixing of PEDOT:PSS

and the Ag nanoparticle solution. Blends of these solutions were characterized in three ways: the ratio of solid weight of PEDOT to solid weight of Ag ( $w/w$ ), solution volume ratio ( $v/v$ ), and percentage solid volume of Ag (%sv). The modified-PEDOT solutions were characterized by the solution volume ratio of PEDOT:PSS and the dopant. For resistivity measurements, films were spun on  $\text{SiO}_2$ -coated substrates, annealed, and tested using the four-point probe technique. Film morphology was studied using a JEOL (Japan) JSM-7400F field emission scanning electron microscope (SEM).

TFTs were fabricated on a doped Si substrate, which served as the gate, coated with a 100 nm thermal  $\text{SiO}_2$  layer, which served as the gate dielectric (Fig. 1). Traditionally, the gate dielectric is treated with a monolayer of octyltrichlorosilane (OTS) before depositing the semiconducting polymer since this results in high mobility polymer films.<sup>14</sup> However, because solution wetting strongly depends on the surface

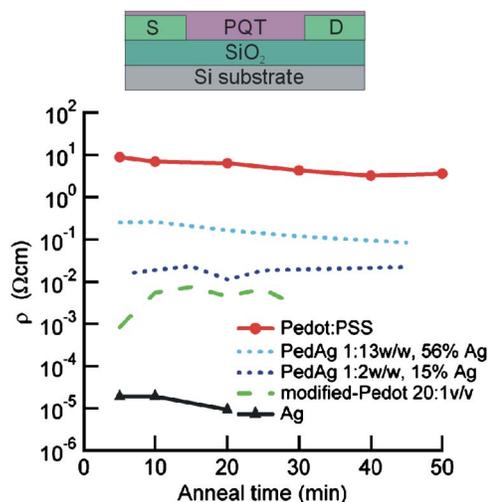


FIG. 1. (Color online) Top: TFT structure. Bottom: resistivity of spun cast films as a function of annealing time. The annealing temperature was 150 °C. PEDOT:Ag solutions were blended in a 1:1  $v/v$  ratio.

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tension of the ink,<sup>13</sup> it was necessary to apply different surface treatments before printing the PEDOT-Ag and modified-PEDOT solutions: these were OTS and O<sub>2</sub> plasma, respectively. Printing PEDOT:Ag single contact pads on OTS-treated substrates yielded uniform features with 105  $\mu\text{m}$  average width and 100 nm (500 nm) average thickness for the 1:2 *w/w* (1:13 *w/w*) blend, while printing on O<sub>2</sub> plasma-treated substrates yielded broad lines of 580  $\mu\text{m}$  average width and 25 nm (100 nm) thickness. Printed modified-PEDOT lines on O<sub>2</sub> plasma-treated substrates were approximately 180  $\mu\text{m}$  wide and 60 nm thick, while pervasive dewetting did not allow uniform printing of modified-Pedot on OTS-treated substrates. The source and drain electrodes were printed and annealed for 10–20 min at 150 °C. Subsequently, poly [5,5'-bis(3-dodecyl-2-thienyl)-22'-bithiophene] (PQT-12), provided by Xerox Research Center of Canada, was spin coated at 1500 rpm. The devices were then annealed at 120 °C for 1 h in a nitrogen atmosphere.

The resistivity of PEDOT:Ag and modified-PEDOT spin-cast films as a function of annealing time is shown in Fig. 1. All films were annealed at 150 °C; the film thickness averaged around 100 nm for all films except the PEDOT:Ag 1:13 *w/w* blend, which was around 500 nm thick. The resistivity  $\rho$  ( $R_S$ ) of PEDOT:PSS is approximately 10  $\Omega\text{ cm}$  ( $5 \times 10^5 \Omega/\text{sq}$ ) while the  $\rho$  ( $R_S$ ) of a Ag nanoparticle film annealed at 150 °C is around  $10^{-5} \Omega\text{ cm}$  (10  $\Omega/\text{sq}$ ), similar to the values for bulk Ag. As expected, the  $\rho$  ( $R_S$ ) of the PEDOT:Ag blends have intermediate values around  $10^{-1} \Omega\text{ cm}$  ( $5 \times 10^3 \Omega/\text{sq}$ ). Percolation theory predicts that for nonoverlapping regions, the minimum area (volume) for a percolation path to exist in a two-dimensional (three-dimensional) region is 45% (16%). We studied a series of films including ones prepared with 15%sv and 56%sv Ag, ensuring that the percolation theory thresholds are met. Interestingly, the data show that a larger amount of Ag nanoparticles in the blends increases film resistivity. This suggests that, although the Ag nanoparticles may be contributing to the conductivity of the PEDOT:Ag blends, other factors are affecting the film conductivity.

The ethylene glycol solution in which the Ag nanoparticles are dispersed may also contribute to the increase in conductivity of PEDOT:Ag blends. Solvents such as ethylene glycol may improve the conductivity of PEDOT:PSS films<sup>8,15–18</sup> and enhancements of several orders of magnitude have been observed. We doped PEDOT:PSS with the Ag nanoparticles' solvent in the ratios 20:1 *v/v* and 10:1 *v/v* (modified-PEDOT films). Figure 1 shows that the resistivity of modified-PEDOT 20:1 *v/v* ( $\rho=5 \times 10^{-3} \Omega\text{ cm}$ ;  $R_S=5 \times 10^2 \Omega/\text{sq}$ ) yields a four orders of magnitude enhancement over the conductivity of pure PEDOT:PSS. The solvent doping is very effective: the improvement on conductivity of PEDOT:PSS is more significant than when Ag nanoparticles are added to the solution.

Indeed, SEM studies confirm that the presence of PEDOT:PSS in the blend may be hindering the formation of a continuous nanoparticle network, which results in a film resistivity significantly higher than that of pristine Ag films. In Fig. 2, the morphology of Ag nanoparticle films is compared to that of PEDOT:Ag blends. The SEM micrographs of a PEDOT:Ag 1:2 *w/w* (1:1 *v/v* 15%sv Ag) film, a PEDOT:Ag 1:13 *w/w* (1:1 *v/v* 56%sv Ag) film, and of a pure

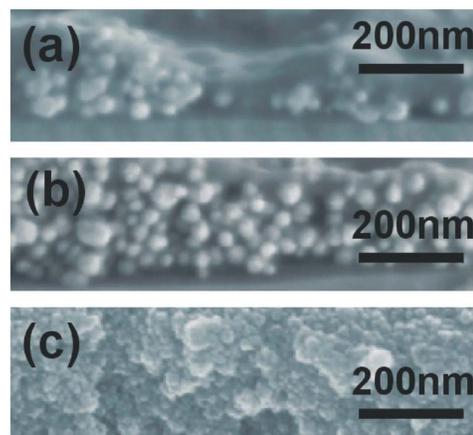


FIG. 2. (Color online) SEM images of (a) PEDOT:Ag 1:2 *w/w* 1:1 *v/v* 15%sv solid volume Ag film annealed for 45 min at 150 °C. (b) PEDOT:Ag 1:13 *w/w* 1:1 *v/v* 56%sv Ag film, annealed under same conditions as (a). (c) Pure Ag nanoparticle film annealed for 5 min at 150 °C. All films were spun on SiO<sub>2</sub> surfaces.

Ag nanoparticle film are displayed in Fig. 2. After 5 min of annealing at 150 °C, sintering of Ag nanoparticles is observed [Fig. 2(c)]. On the contrary, the PEDOT:Ag films show essentially no particle sintering even after extended annealing times (45 min). The nanoparticles are clearly visible in both blend concentrations. Arias *et al.*<sup>13</sup> have shown that the resistivity of a Ag nanoparticle film prepared as mentioned above is of the order of  $10^{-5} \Omega\text{ cm}$ , indicating that even a small extent of sintering reflects quite favorably on the conductivity of these films. We suggest that an affinity of PEDOT:PSS to the polymeric stabilizer of the Ag nanoparticles may be hindering the formation of a sintered nanoparticle network. This results in a film resistivity significantly higher than that of pristine Ag films and dominated by the resistance of PEDOT modified by the dopant. Furthermore, because the Ag nanoparticles are obstacles for the hopping charge carriers in the PEDOT, the blend has higher resistivity than the modified-PEDOT film.

TFTs with two types of contacts are compared. Typical, width (*W*) to length (*L*)-normalized current  $\times$  voltage (*IV*) characteristics for devices using Ag nanoparticles [mobilities around  $8 \times 10^{-3} \text{ cm}^2/\text{V s}$ , subthreshold slopes ( $S_{\text{subthreshold}}$ ) around 2.8 V/decade, on-to-off current ratios ( $I_{\text{on}}/I_{\text{off}}$ ) around  $10^6$ ,  $W=600 \mu\text{m}$ ,  $L=400 \mu\text{m}$ ], and PEDOT:Ag (1:2 *w/w*,  $W=100 \mu\text{m}$ ,  $L=100 \mu\text{m}$ , and 1:15 *w/w*,  $W=300 \mu\text{m}$ ,  $L=325 \mu\text{m}$ ) as source/drain contacts are displayed in Fig. 3(a). TFTs with PEDOT:Ag blend source/drain have mobilities of  $2.5 \times 10^{-2} \text{ cm}^2/\text{V s}$ ,  $S_{\text{subthreshold}}$  around 1.3 V/decade, and  $I_{\text{on}}/I_{\text{off}}$  around  $1 \times 10^7$ . Interestingly, the sample with barely enough Ag to form a percolation path behaves similarly to the sample with 59%sv Ag. The output curves, inset of Fig. 3(a), show that there is contact resistance at the electrode/polymer interface in PEDOT:Ag TFTs and Ag TFTs, suggesting that PEDOT:PSS is not solely defining the charge injection at the semiconductor/electrode interface, but rather that both PEDOT and Ag nanoparticles are present at the interface. Burgi *et al.*<sup>5</sup> have argued that, for small Schottky barriers at the interface as we expect for electrodes containing the high work function PEDOT:PSS, poor transport across an interfacial low-mobility region (due to polymer material defects) dominates the contact resistance. In this sense, roughness of the PEDOT:Ag printed lines or the

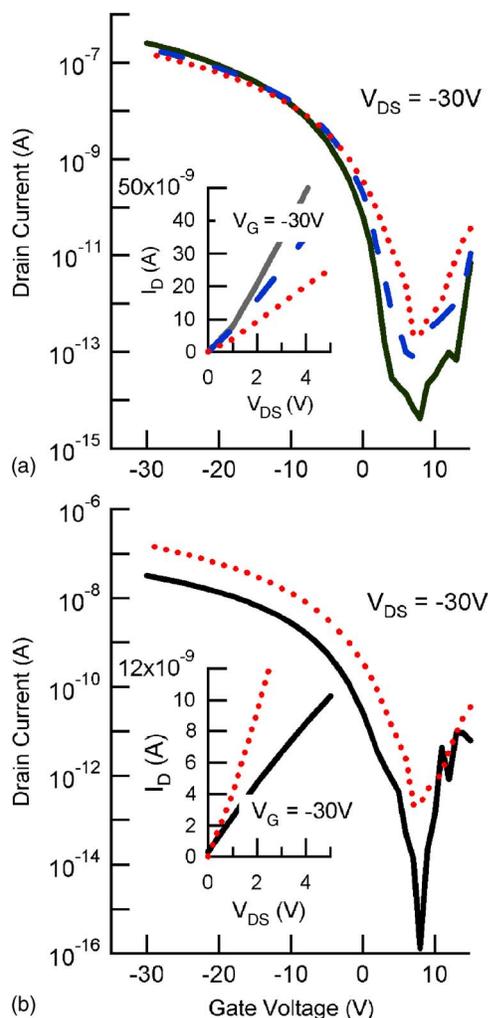


FIG. 3. (Color online) TFT characteristics of (a) printed Ag ink (dotted line) and PEDOT:Ag source/drain (PEDOT:Ag 1:2 w/w 1:1 v/v 15% solid volume Ag, solid line; PEDOT:Ag 1:13 w/w 1:1 v/v 56% solid volume Ag, dashed line). (b) Printed Ag ink (dotted line) and modified-PEDOT ink (solid line) source/drain. The modified-PEDOT solution used was 20:1 v/v.

presence of the polymeric stabilizer in the blends may create defects in the PQT film that lead to high contact resistance.

Figure 3(b) compares the transfer and output curves of Ag and modified-PEDOT source/drain TFTs, the latter showing mobilities of  $1.7 \times 10^{-3} \text{ cm}^2/\text{V s}$ ,  $S_{\text{subthresh}} = 1.8 \text{ V/decade}$ , and  $I_{\text{on}}/I_{\text{off}} = 2 \times 10^7$  ( $W = 250 \mu\text{m}$ ,  $L = 50 \mu\text{m}$ ). Because of the difference in dielectric surface treatments, the PEDOT:Ag samples had higher mobilities than the modified-Pedot TFTs. Ultimately, these TFTs will be fabricated using a polymer dielectric, so OTS surface treatment will not be needed to guarantee high mobilities. In this respect, using PEDOT:Ag blends or modified PEDOT for the contacts would be equally advantageous. The linear relationship between drain current and gate voltage at small voltages in modified-PEDOT TFTs indicates that there is minimal contact resistance. Adding high boiling point dopants to

PEDOT:PSS greatly improves the morphology of the contacts by reducing the coffee stain effect,<sup>8</sup> thus, forming contacts with a uniform edge. In this way, a modified-PEDOT contact has a small Schottky barrier and presumably a low defect concentration at the interface, resulting in low contact resistance. Furthermore, doping at the interface by the PSS could be enhancing charge injection.<sup>7</sup>

In this work, we have presented the use of high work function materials as the source and drain electrodes in inkjet printed TFTs. TFTs fabricated with PEDOT:Ag blends and modified-PEDOT source/drain electrodes showed high mobilities, low  $S_{\text{subthresh}}$ , and high  $I_{\text{on}}/I_{\text{off}}$ . While modified-PEDOT TFTs have lower contact resistance and lower cost than PEDOT:Ag TFTs, the contacts in the latter were more robust, even after relatively small additions of Ag nanoparticles to the PEDOT solution, and the corresponding TFTs showed higher mobilities ( $2.5 \times 10^{-2} \text{ cm}^2/\text{V s}$ ). Further development of the Ag nanoparticle coating will allow achievement of higher conductivities for the blends.

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<sup>1</sup>H. Sirringhaus, T. Kawase, R. H. Friend, T. Shimoda, M. Inbasekaran, W. Wu, and E. P. Woo, *Science* **290**, 2123 (2000).

<sup>2</sup>A. C. Arias, S. E. Ready, R. Lujan, W. S. Wong, K. E. Paul, A. Salleo, M. L. Chabinyc, R. Apte, R. A. Street, Y. Wu, P. Liu, and B. Ong., *Appl. Phys. Lett.* **85**, 3304 (2004).

<sup>3</sup>T. Kawase, T. Shimoda, C. Newsome, H. Sirringhaus, and R. H. Friend, *Thin Solid Films* **438**, 279 (2003).

<sup>4</sup>R. A. Street and A. Salleo, *Appl. Phys. Lett.* **81**, 2887 (2002).

<sup>5</sup>L. Burgi, T. J. Richards, R. H. Friend, and H. Sirringhaus, *J. Appl. Phys.* **94**, 6129 (2003).

<sup>6</sup>T. Li, P. P. Ruden, I. H. Campbell, and D. L. Smith, *J. Appl. Phys.* **93**, 4017 (2003).

<sup>7</sup>J. Z. Wang, J. F. Chang, and H. Sirringhaus, *Appl. Phys. Lett.* **87**, 083503 (2005).

<sup>8</sup>J. A. Lim, J. H. Cho, Y. D. Park, D. H. Kim, M. Hwang, and K. Cho, *Appl. Phys. Lett.* **88**, 082102 (2006).

<sup>9</sup>P. V. Pesavento, K. P. Puntambekar, C. D. Frisbie, J. C. McKeen, and P. P. Ruden, *J. Appl. Phys.* **99**, 094504 (2006).

<sup>10</sup>B. C. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, and J. R. Reynolds, *Adv. Mater. (Weinheim, Ger.)* **12**, 481 (2000).

<sup>11</sup>G. Greczynski, T. Kugler, M. Keil, W. Osikowicz, M. Fahlman, and W. R. Salaneck, *J. Electron Spectrosc. Relat. Phenom.* **121**, 1 (2001).

<sup>12</sup>C. Ionescu-Zanetti, A. Mechler, S. A. Carter, and R. Lal, *Adv. Mater. (Weinheim, Ger.)* **16**, 385 (2004).

<sup>13</sup>A. C. Arias, J. Daniel, B. Krusor, S. Ready, V. Sholin, and R. A. Street, *J. Soc. Inf. Disp.* **15**, 485 (2007).

<sup>14</sup>A. Salleo, M. Chabinyc, M. S. Yang, and R. A. Street, *Appl. Phys. Lett.* **81**, 4383 (2002).

<sup>15</sup>S. Ghosh, J. Rasmusson, and O. Inganäs, *Adv. Mater. (Weinheim, Ger.)* **10**, 1097 (1998).

<sup>16</sup>W. H. Kim, G. P. Kushto, and Z. H. Kafafi, *J. Polym. Sci., Part B: Polym. Phys.* **41**, 2522 (2003).

<sup>17</sup>S. K. M. Jönsson, J. Birgeron, X. Crispin, G. Greczynski, W. Osikowicz, A. W. D. van der Gon, W. R. Salaneck, and M. Fahlman, *Synth. Met.* **139**, 1 (2003).

<sup>18</sup>J. Ouyang, C.-W. Chu, F.-C. Chen, Q. Xu, and Y. Yang, *Adv. Funct. Mater.* **15**, 203 (2005).