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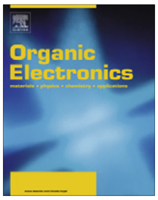

The fabrication and characterization of poly(4-vinylpyridine)-based thin film transistors exhibiting enhanced ion modulation

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ABSTRACT

Lithium perchlorate-doped hygroscopic poly(4-vinylpyridine)-based organic thin film transistors have been fabricated and characterized. More than one mechanism of current modulation is observed in these devices with the observed mechanism depending upon both the amount of added dopant and the operating voltage. At low gate voltages (0 to −0.8 V) the current modulation mechanism is dominated by ions intrinsic to the dielectric layer (due to its hygroscopic nature), while at higher gate voltages (−1 to −2 V) the device behavior is governed by the movement of the dopant ions. Most importantly, through careful control of dopant concentration, we show that it is now possible to fabricate all-solution processed devices with significantly enhanced current modulation. In particular, we demonstrate that current modulation ratios in excess of 10^5 are possible with this device architecture.

1. Introduction

The development of organic thin film transistors (OTFTs) has grown rapidly in recent years, motivated primarily by the unique physical properties of polymer devices, including their flexibility and ability to be fabricated using low-cost solution-based techniques [1]. Conventional organic field-effect transistors (OFETs) typically require gate voltages (V_G) in the order of tens of volts in order to operate due to the limited charge carrier mobility of the conductive polymeric materials [2]. However, many applications for organic transistors require low voltage operation and, as such, much recent effort has been focussed on the development of OTFTs with lower operating voltages [3].

Low voltage OTFT operation often involves altering the properties of the dielectric layer, by increasing the specific capacitance of the material (by decreasing dielectric layer thickness or increasing the permittivity of the dielectric material) or changing the mechanism of device operation. One approach which has been introduced is utilizing polymer electrolytes in which ions are added to induce a high charge density electrolyte double layer and thus enhanced drain currents (I_D) can be obtained in the order of several milliamps [4–6]. When these devices are operated in an inert environment, moisture-induced electrochemical doping can be avoided. When devices are characterized in air, both electrostatic double layer formation and electrochemical doping modulate the drain current at different operation gate voltages [7]. Another approach which has been reported involves using ion-conducting polyelectrolytes such as Nafion or poly(styrenesulfonic acid) (PSS:H) as the dielectric [8–10]. Although these types of devices can show good transistor characteristics, their off current (I_{OFF}) can be susceptible to increases at high relative humidity (RH) levels, making their performance variable under ambient conditions.

An early approach reported by Sandberg et al. uses poly(3-hexyl-thiophene) (P3HT)/poly(4-vinylphenol) (PVP)/poly (3,4-ethylenedioxythiophene): poly (styrene sulfonate) (PEDOT:PSS) as the semiconducting layer/dielectric layer/gate electrode, respectively [11–13]. The PVP dielectric is a highly hygroscopic material and moisture adsorbed by it plays a central role in modulating I_D under low V_G

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values. The current modulation mechanism in these devices is chemical doping of the semiconducting channel stemming from ion diffusion at the dielectric-semiconductor interface [11]. These devices have maximum output currents (I_{ON}) of a few microamps, which is comparable to, or even higher than, many conventional OFETs. However, the current modulation ratios (I_{ON}/I_{OFF}) of hygroscopic insulator transistors depend highly on the RH level of where they are measured because of the large I_{OFF} associated with increased RH levels [8,14].

Devices of this type were fabricated in our laboratory and performed similarly to those reported by Sandberg et al. [13]. In these transistors, the combination of V_D and V_G controls the location of ions at the semiconductor/insulator interface layer. For a given negative V_G, anions migrate to this interface and induce an increase in conductance in the P3HT layer. The effect on I_D of increasing V_D is balanced by an increased fraction of low conductance P3HT in the channel (induced by the movement of ions along the interface) which leads to a saturation of I_D, effectively resembling a conventional field-effect transistor mechanism. I_{ON}/I_{OFF} ratios of between 10 and 100 were observed – this lower than expected value can be attributed to a high relative humidity causing an increase in I_{OFF} (the RH has been consistently recorded as 50 ± 10% in the laboratory in which these devices were characterized). Another possible cause of high I_{OFF} in these devices is the contribution of the acidic PEDOT:PSS suspension which is drop-cast as a gate electrode [15]. Protons from the PEDOT:PSS likely diffuse across the PVP layer and further dope the P3HT layer.

A key challenge then, is to improve the low current modulation ratio that results from the high I_{OFF} at a relative high humid environment. In this paper, we show that by changing the hygroscopic polymer and subsequently doping the dielectric layer we are able to fabricate OTFT devices with greatly reduced I_{OFF} and significantly enhanced current modulation. Furthermore, we show that at low V_G the current modulation mechanism is dominated by the movement of ions associated with the hygroscopic nature of the dielectric whereas at high V_G it is governed by the movement and diffusion of the dopant ions. Consequently, we demonstrate that by using lithium perchlorate ($LiClO_4$)-doped poly(4-vinylpyridine) (PVPy) as the dielectric, an all solution-processible, low operating voltage transistor can be fabricated with greatly enhanced transistor performance parameters.

2. Material and methods

All devices were fabricated on glass substrates with pre-patterned indium-tin-oxide (ITO) source and drain electrodes. The channel length and width is 20 μm and 3 mm, respectively. P3HT was purchased from Rieke Metals and dissolved in chloroform at a concentration of 20 mg/mL. A 100 nm thick P3HT layer was spin-coated (60 s at 2000 rpm) onto the substrate as measured by a KLA Tencor profilometer. Dielectric materials PVP and PVPy (Aldrich) and dissolved in ethanol at a concentration of 80 mg/mL. $LiClO_4$ (Aldrich) was dissolved in the PVPy solution in various concentrations. The dielectric layers were spin-coated (60 s at 2000 rpm) to a thickness of approximately 500 nm. The P3HT/PVP or P3HT/PVPy two-layer structures were annealed at 85 °C in air to remove any remaining solvents. Lastly, PEDOT:PSS (Aldrich, pH 1–2) was drop-cast on the top of gate dielectric layer and dried on a hot plate at 40 °C in air. Two Keithley 2400 source meters were used for the device characterization. All output characteristic measurements have been conducted at a scan rate 0.1 V/s. All fabricated devices were measured in air immediately after drying the PEDOT:PSS layer. The RH has been consistently recorded as 50 ± 10% in the laboratory in which these devices were characterized.

3. Results and discussion

One approach for reducing the inherently high I_{OFF} in PVP-based OTFTs is to decrease the number of mobile protons in the dielectric layer by replacing the acidic PVP with a hygroscopic polymer which is basic in nature. PVPy is another polyvinyl aromatic polymer where the phenol group has been replaced by a pyridine moiety. As shown in Fig. 1, whereas PVP is weakly acidic (and therefore acts as a proton source), PVPy is weakly basic and acts as a proton acceptor [16]. Fig. 2 shows the difference in I_{OFF} and I_G in the off state for PVP- and PVPy-based devices. There is a clear reduction in I_{OFF} in the PVPy case indicating that the attempt to reduce the inherent doping level of the P3HT layer has been successful, and that this can be attributed to the PVPy being more effective in blocking current contributions from the gate and/or doping of P3HT due to diffusion of protons from the PEDOT:PSS suspension.

Fig. 3(a) shows the output characteristics of a transistor employing PVPy as the dielectric layer. Again, FET-like drain current modulation is exhibited and the output characteristic is very similar to that of the PVP-based device. However, the I_D measured for PVPy-based transistors are generally one order of magnitude lower than those for the corresponding PVP-based devices confirming that there are fewer mobile protons. Nevertheless, the current modulation ratio of the PVPy-based transistors is between 10 and 100, as shown in Fig. 3(b), which is comparable to that observed for the PVP-based devices at a high humidity level. This close agreement in results implies that the benefits of reducing I_{OFF} have been largely offset by an associated reduction in I_{ON}. Fig. 3(b) shows that the transfer characteristic of the PVPy-based device is highly reversible

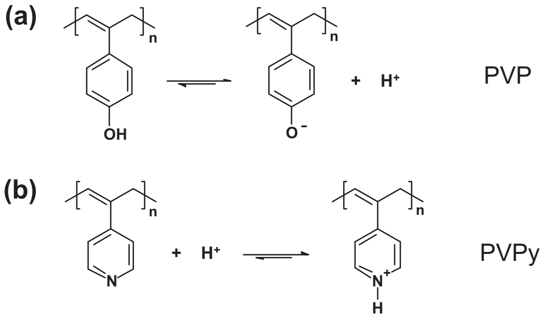

Fig. 1. The molecular structure of (a) PVP and (b) PVPy.