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# Effect of polyethylene oxide on camphor sulfonic acid doped polyaniline thin film field effect transistor with ionic liquid gating

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 Field effect transistors (FET) using camphor sulfonic acid (CSA) doped polyaniline (PANi) blended with several polyeniline

 Polyaniline
 polyethylene oxide (PEO) concentrations were investigated via ionic liquid gating. The pure PANi-CSA FET could not be turned "off" and had an on/off ratio of 2. Blending with 22 wt%-PEO retained a high "on" state throughput current and improved the mobility, while the on/off ratio increased by 10<sup>3</sup>. Superior film quality and PEO assisted electrostatic interactions with the PANi chains led to device parameter enhancement. For higher PEO concentrations the field effect was suppressed due to disorder. Analysis of the UV/Vis spectra polaron band peak area near 810 nm show an increase in the mobility with decrease in the peak area, consistent with the observed results. Enhanced device parameters, high throughput current and low operating voltages (± 2 V),

### 1. Introduction

Conducting polymers and their blends with non-conducting polymers play an important role in organic electronics. They are used in applications ranging from metallic interconnects [1], diodes [2], photovoltaics [3], field effect transistors (FET) [4], chemical sensors [5], solid state batteries [6,7], electromagnetic shielding [8] and rust prevention of metals [9] among others. Ease of chemical synthesis, good environmental stability and high conductivity has helped sustain interest in conducting polymers since its discovery in 1977 [10]. Among conducting polymers commercially available, polyaniline (PANi) has received the most attention. Depending on the oxidation level, PANi has three insulating forms [11]: 1) fully oxidized pernigranaline base, 2) fully reduced leucoemeraldine base and 3) half oxidized-half reduced emeraldine base (PANi-EB). Technologically, PANi-EB is more important as its conductivity can be reversibly tuned by 10 orders of magnitude via acid/base doping/de-doping [12]. The majority charge carriers in doped PANi are holes [13,14]. Using functionalized acids has made it possible to dope PANi-EB into the conducting form and dissolve it in organic solvents [15]. The ability to process PANi in the conducting form has consequently led to increased conductivity that is even metallic in some instances [16].

The high operating voltages required in conducting polymer blend based devices [17] are a serious drawback to their wide spread use in the electronics industry. Reducing the operating voltage (< 5 V) while maintaining high throughput "on" state current (>  $1\mu$ A) is crucial for successful implementation in practical devices. In this paper, camphor sulfonic acid (CSA) doped PANi thin film FET's were fabricated with the objective of reducing the operating voltages. Ionic liquid (IL) gating of the device revealed a field effect similar to that seen in a p-type semiconductor. This is the first report that uses an IL to tune the conductivity in doped PANi. The IL was used since it has a high specific capacitance which lowers the FET operating voltages ( $\pm 2V$ ) [18]. Blending PANi-CSA with non-conducting polyethylene oxide (PEO) improved the charge mobility and increased the on/off ratio by three orders of magnitude when used in a FET. Enhanced device parameters and low operating voltages, therefore, make PANi-CSA/PEO blends excellent candidates for use in low power consumption electronics, for eg. pixel displays. The blend material also has additional benefits, since it retains the mechanical properties of the insulating matrix.

#### 2. Experimental

#### 2.1. Polymer preparation

make PANi-CSA/PEO blends attractive materials for use in low power consumption electronics.

PANi was synthesized using the oxidative polymerization of aniline in acidic media [12,19]. In this work, PANi-EB was doped with CSA and blended with PEO at four different concentrations. For each

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concentration the following steps were performed: 100 mg of PANi-EB was mixed with 129 mg of CSA using a mortar and pestle, and then dissolved *via* magnetic stirring in 10 ml of chloroform (CHCl<sub>3</sub>) for 6 h to yield a dark green solution. The solution was filtered, and the undissolved solid particles dried and weighed. Based on the undissolved polymer mass and the initial mass, the amount of dissolved polymer in solution was determined and PEO (MW 900,000- Sigma Aldrich) was added to it at pre-selected concentrations (wt%) and dissolved *via* magnetic stirring for an additional 2 h to yield a homogenous dark green solution. The following blend solutions in CHCl<sub>3</sub> were prepared: 0 wt% (i.e. pure PANi-CSA), 6 wt%, 22 wt% and 33 wt%. The percolation threshold for PANi-CSA in blends with PEO was found to be just 4% [20], where the 4% refers to the volume fraction of PANi-CSA in the blend with PEO. Thus, in all of the blends studied here, the PANi-CSA was above the percolation threshold.

### 2.2. Ionic liquid gel preparation

The IL used in this work was prepared by dissolving 9 wt% of 1ethyl-3-methylimidazolium bis (trifluromethylsulfonyl) amide –  $(EMI)^+(TFSA)^-$  (0.135 g) and 1 wt% of poly(styrene-b-methyl methacrylate-b-styrene) triblock copolymer-SMS-15-81-15 (0.015 g) in 90 wt % of methylene chloride (1.35 g) to form a clear solution [18,21]. The anion was bis (trifluromethylsulfonyl) amide (TFSA<sup>-</sup>), while the cation was 1-ethyl-3-methylimidazolium (EMI<sup>+</sup>). In order to increase its viscosity prior to use *via* solvent evaporation, the IL was placed in an oven at 70 °C for several hours.

## 2.3. Device (FET) fabrication

Pre-patterned and doped  $\mathrm{Si}^+/\mathrm{SiO}_2$  substrates were cleaned with acetone and then with an O2 plasma etch prior to use. The pre-patterned electrodes consisted of four parallel and closely spaced gold fingers. Each gold finger was connected to a large gold contact pad at one end for hard wiring an external contact. Two adjacent fingers eventually became the source (S) and drain (D) terminals of the device. The distance (L) between S/D was the channel length and W was the channel width represented by the length of the gold finger. The substrates were then spun-coated (4000 rpm/45 s) with the desired PANi-CSA/PEO solution and placed in an oven at 70 °C overnight to remove trace amounts of the solvent. Once dry, the polymer was carefully scratched off, leaving a film that only covered the four gold fingers. An IL drop was then carefully placed over the polymer film to finish the fabrication process. A gold wire inserted into the IL served as the gate (G) electrode of the device. Thin glass microscope cover-slips were also spin coated with each solution and dried, to be later characterized via UV/Vis spectroscopy. Devices were fabricated from each of the four solutions following the same steps discussed above.

Fig. 1(a)–(d) show the top view optical microscope images of four devices prepared from each of the four solutions mentioned above, before placing the IL. For 0 wt% PEO and 6 wt% PEO, the film was not uniform as seen in Fig. 1(a) and (b). This could be due to the hydrophilic substrate and hydrophobic solution incompatibility during the spinning process. The device with 22 wt% PEO was the most uniform (Fig. 1(c)), while for 33 wt% PEO, the polymer film appeared to phase segregate (Fig. 1(d)), with polymer particles adhering to the edge of the substrate. Fig. 1(e) shows a magnified view of Fig. 1(a) after an IL drop was placed over the region containing the S/D electrodes that are clearly visible in this image. Fig. 1(f) represents the schematic circuit diagram of the complete device with external connections. The source (S) was the common grounded terminal of the FET.  $V_{DS}$  and  $V_{GS}$  represent the drain-source and gate-source voltages. Each device was hard wired with gold wire and silver epoxy, and placed in a closed chamber under vacuum of  $10^{-2}$  Torr during the measurements.

A Keithley electrometer model 6517B supplied  $V_{\rm DS}$  and recorded the drain-source current ( $I_{\rm DS}$ ). Another Keithley source meter model 2400

supplied V<sub>GS</sub>. V<sub>DS</sub> was swept in steps of 10 mV at a rate of 20 mV/s in all of the measurements. Capacitance measurements were performed in air using an Agilent Technologies 4294A impedance analyzer and a HP 16453A modified dielectric test fixture. The film thickness was measured with a D-500 KLA-Tencor profilometer. UV/Vis spectroscopy was carried out using an Agilent 8453 spectrophotometer. Spectral deconvolution to determine the area were performed by first running a linear baseline correction followed by a non-linear regression using the following function:  $Y_{fit} = Y_0 + (2/\pi)^{1/2} \Sigma (A_i/w_i) \exp[-2(X-X_{max, i})^2/w_i]$ , where  $Y_0$  is an offset,  $A_i$ ,  $w_i$ , and  $X_{max,i}$  are the peak area, peak width, and peak position maximum, respectively, for peaks 1 or 2 in the long wavelength region. The total peak area is the sum of the corresponding areas of peak 1 and 2. The best fitting was defined by the correlation coefficient, residuals, and the statistical parameters of the fitting variables. All fittings were run using a combination of the Solver add-in in MS-Office 2016 and the SolvStat macro.

#### 3. Results and discussion

The PANi-CSA/PEO thin films with various PEO concentrations under study were characterized by UV-Vis spectroscopy. Fig. 2 shows the UV-Vis absorption spectra of the different films. Three absorption peaks were observed for all cases. The 350 nm wavelength peak represents  $\pi$ - $\pi$ \* transitions in the benzenoid/quinoid rings, at 436 nm, which represents the protonation (doping) on the nitrogen of imine (low wavelength polaron band, i.e. polaron-  $\pi^*$  transition). The peak in the 800 nm region reflects the excitation formation in the quinoid rings ( $\pi$ -polaron transition) [22]. These results are consistent with previous studies [23]. Two isobestic points at 450 nm and 700 nm are seen in Fig. 2 for the PEO containing films. Optical absorption spectroscopy on polyaniline reveal that isobestic points in the UV/VIS spectra indicate changes in the base form of polyaniline [24]. In Fig. 2, the isobestic points could be due to slight changes in the oxidation state in PANi-CSA via interactions with PEO. The net effect is to shift the electrical properties of the film away from the highly conducting form toward the semiconducting regime as will be demonstrated later. The presence of a localized polaron band around 810 nm with no significant near-infrared absorption, indicates a "compact coil" conformation of the PANi chains [23]. A slight red shift in the high wavelength peak as the PEO wt% was increased (810 nm for 0 wt% to 820 nm for 33 wt%) suggest a charge confining effect due to increased entanglement of the PANi chains with PEO. This effect is opposite to that reported in [23] where a blue shift is recorded as the PEO concentration in increased. This is due to de-aggregation of the PANi-CSA and PEO in reference 23, as their films were prepared after a period 24 h. of stirring. Our films were prepared after 2 h. of stirring which preclude de-segregation of the two components. Indeed, the polaron band absorption area changed with PEO concentration, and was an indication of changes in the interactions between PANi and PEO chains.

Prior to device testing, the IL was dielectrically characterized separately using an impedance analyzer. Fig. 3(a) shows the specific capacitance (C<sub>i</sub>) of the IL as a function of frequency in the range 40 Hz - 1 MHz using the dielectric test fixture shown in the inset. The space between the capacitor plates was filled with the IL via capillary action. At low frequencies, Ci was relatively constant and decreased at higher frequencies, since the heavy ions in the IL were not able to follow the exciting electric field. C<sub>i</sub> at low frequencies approached 30µF/cm<sup>2</sup> and was relatively high. For comparison, the specific capacitance of a 150 nm thick SiO<sub>2</sub> layer was ~20 nF/cm<sup>2</sup> [25]. A large specific capacitance implies a small voltage drop across the IL and the applied voltage appears directly at the IL/polymer interface. This explains why a low gate voltage generated large electric fields to observe the field effect in our devices. Fig. 3(b) shows the dependence of the IL specific capacitance with a DC bias superimposed on the 500 mV exciting AC frequency in a metal-insulator-p-type semiconductor (MIS) test structure. A schematic of this device is seen in the inset to this



**Fig. 1.** Top view optical microscope image of pre-patterned electrodes on  $\text{Si}^+/\text{SiO}_2$  substrates spin coated with PANi-CSA/PEO thin films. The electrode pattern consists of 4 "fingers" each connected to a contact pad as seen in (e). The polymer films contained the following wt% of PEO: (a) 0% (b) 6% (c) 22% (d) 33%. These images were taken prior to placing the ionic liquid (IL) over the polymer film. (e) Magnified image of the device seen in (a) after a drop of the IL had been placed to cover the entire polymer film between the fingers. Two adjacent fingers, S and D represent the source and drain electrodes of the device. The electrode separation (channel length) was 10 µm in all devices. The channel width was 425 µm in (a) and (d) and 850 µm in (b) and (c). A gold wire inserted into the IL served as the gate electrode (G). (f) Cross sectional schematic diagram showing the device parts and the electrical connections used to characterize it.



**Fig. 2.** UV/Vis absorption spectra of spin coated thin films of PANi-CSA blended with PEO for different PEO wt%.

Figure. The MIS structure mimics the devices studied since doped PANi is a hole conductor and helps interpret the data in the next section. As seen in Fig. 3(b), at a pre-selected frequency  $C_i$  increases as the DC bias was made more negative. This indicates hole accumulation in the *p*-Si at the interface with the IL. A positive DC bias on the other hand depletes holes in *p*-Si reducing the capacitance. Overall,  $C_i$  was reduced for higher frequencies and was relatively constant for large negative DC voltage similar to previous reports [25]. A constant capacitance at





**Fig. 4.**  $I_{DS}$  vs.  $V_{DS}$  of the thin film device with 0 wt% PEO before (blue) and after (red) placing the ionic liquid over the polymer film. No voltage was applied to the IL. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

negative bias suggests charge injection into the *p*-semiconductor with no chemical reaction at the semiconductor/IL interface [26].

Fig. 4 shows the I<sub>DS</sub> vs. V<sub>DS</sub> curves of the 0 wt% PEO (pure PANi-CSA) thin film FET before and after the IL was drop cast over it. Prior to covering the film with the IL, the curve was Ohmic over the entire voltage range ( $\pm 1$  V) and the channel conductivity ( $\sigma = \frac{G + L}{W + t}$ ) was calculated to be 2.9 × 10<sup>-3</sup> S/cm, where G is the channel conductance.

> **Fig. 3. (a)** Ionic liquid specific capacitance vs. frequency. Inset: Image of the actual dielectric test fixture that consists of two parallel gold coated cylinders with separation control, and the schematic diagram. The cylinder separation was ~100µm. **(b)** Specific capacitance of the ionic liquid/p-Si configuration as seen in the inset as a function of DC bias voltage superimposed on a 0.5 V AC excitation signal.

#### Table 1

Tabulated values of the various parameters extracted from the data taken on the devices containing different PEO wt%. L, W and t represent the channel length, width and film thickness respectively.  $\sigma$  is the channel conductivity, calculated with  $V_{GS} = 0$  V.  $I_{on}$  and  $I_{off}$  represent the current ( $I_{DS}$ ) measured at  $V_{DS} = -1$  V for  $V_{GS}$ : -2 V and +2 V respectively.  $\mu$  is the hole mobility,  $V_{TH}$  is the threshold voltage and SS is the sub-threshold swing.

% PEO	L (µm)	W (µm)	t (nm)	σ (S/cm)		$I_{\rm on}/I_{\rm off}$	μ (cm <sup>2</sup> /V-s)	V <sub>TH</sub> (V)	SS (V/dec)
				No IL	IL				
0	10	425	35	$2.9  imes 10^{-3}$	$1.3  imes 10^{-2}$	2	$1.8 \times 10^{-4}$	1.8	3.7
6	10	850	35	$3.5  imes 10^{-3}$	$2.8  imes 10^{-2}$	2	$1.4 \times 10^{-4}$	1.7	5.5
22	10	850	50	$2.4  imes 10^{-4}$	$7.1 \times 10^{-3}$	2300	$5.4 \times 10^{-4}$	-0.6	0.9
33	10	425	90	$3.1  imes 10^{-4}$	$4.2 \times 10^{-3}$	1	-	-	-

This was lower than reported values and was due to the "tight coil" conformation of the PANi chains [23] but it does not affect the results presented here. It is important however to note that once in contact with the IL (and  $V_{GS} = 0 V$ ), the channel conductivity increased to  $1.3 \times 10^{-2}$  S/cm. The curve in this instance is Ohmic at low applied voltages ( $V_{DS} < 0.5 V$ ) but then tends to saturate at higher values  $(V_{DS} > 0.5 \text{ V})$ . The saturation effect suggest a pinch-off in the channel that limits the current flow and a behavior similar to that of a semiconductor. The increase in the channel conductivity can be attributed to an increase in the polymer work function. This in turn reduces the energy level mismatch between the Au electrode and PEDOT-PSS, making hole injection into the channel, and removal of holes from the channel easier [27]. The increase in conductivity can also be attributed to IL induced doping [20]. Table 1 gives conductivity values of the blend films before and after contact with the IL for each of the samples studied here. In all the FET's studied, contact with the IL increased the channel conductivity regardless of PEO concentration. It is interesting to note that the largest fractional change in the conductivity was for the 22 wt% PEO-FET.

Fig. 5 shows the variation of  $I_{DS}$  versus  $V_{DS}$  as  $V_{GS}$  was changed from + 2 V to -2 V in steps of 0.2 V for the FET with 0 wt% PEO. Since holes are the majority charge carriers in doped PANi, electrical characterization of the device was carried out in the third quadrant of the I–V plot [28]. Four significant features of this plot were the following: (*i*) a non-negligible channel current when the gate voltage was 0 V, (*ii*) a super linear I–V curve at low  $V_{DS}$  (see also Fig. 4 – red curve) for all gate voltages (*iii*) the currents increase(decrease) when the gate voltage was made more negative(positive) with respect to the common source



**Fig. 5.** Drain-source current (I<sub>DS</sub>) vs. drain-source voltage (V<sub>DS</sub>) for the 0 wt% PEO device as a function of gate-source voltage (V<sub>GS</sub>). The gate voltage was varied from +2 V to -2 V in steps of 0.2 V. Inset:  $\sqrt{I_{DS}}$  vs.  $V_{GS}$  for V<sub>DS</sub> = -1 V. The slope of the line shown was used to calculate the hole mobility and the threshold voltage (V<sub>TH</sub>).

terminal, (*iv*) the currents tend to saturate at higher V<sub>DS</sub> values for each applied gate voltage. Since doped polyaniline is a conducing polymer, it was reasonable to expect the device to be in the normally "on" state with high current (at V<sub>DS</sub> = -1 V) in the absence of a gate voltage. The super-linear variation in I<sub>DS</sub> for V<sub>DS</sub> < 0.1 V indicates that Schottky barriers at the metal/polymer interface are negligible and the contact resistance was relatively insignificant. This results in efficient hole injection into the HOMO band of the polymer from the source electrode (likely via tunneling). The increase in the channel current with increasing negative gate voltage shows that the majority charge carriers are indeed holes and the current saturation at higher values of V<sub>DS</sub> show that the device operates as a *p*-type FET. The operating mechanism will be discussed later.

In order to analyze the data and extract device parameters, the standard FET equation for the  $I_{DS}$  vs.  $V_{DS}$  curve in the saturation regime was used [29]:

$$I_{DS} = \frac{\mu W C_i}{2L} (V_{GS} - V_{TH})^2$$
(1)

Where  $\mu$  was the charge mobility, W and L are the channel width and length respectively,  $C_i$  (30  $\mu$ F/cm<sup>2</sup>) was the IL specific capacitance and V<sub>TH</sub> was the threshold voltage required to deplete the channel. The specific capacitance of the SiO<sub>2</sub> substrate does not affect the measurements as it is a passive component in the device architecture. The inset to Fig. 5 shows the plot of  $\sqrt{I_{DS}}$  vs.  $V_{GS}$  at fixed V<sub>DS</sub>(= -1 V). From the slope (*m*) of the straight line fit to the data as seen in the inset, the mobility can be calculated as follows:

$$\mu = \frac{m^2 2L}{WC_i} \tag{2}$$

The hole mobility in the enhancement mode was calculated to be  $1.8 \times 10^{-4} \, \mathrm{cm}^2/\mathrm{V}$ -s, similar to previous results [30]. The intercept of this line with the voltage axis at zero current was the threshold voltage and was  $+1.8 \, \mathrm{V}$ . The on/off ratio calculated as the ratio of the "on" current to the "off" current measured at  $V_{\rm DS} = -1 \, \mathrm{V}$  was 2, and the sub-threshold swing (SS) was 3.7 V/decade. For reference, in a semiconductor FET, the theoretical SS for electrons at room temperature is 66 mV/decade [31]. These values are tabulated in Table 1 for all the devices studied.

Figs. 6–8 show similar plots as seen in Fig. 5, but for FET's with PEO concentrations of 6 wt%, 22 wt% and 33 wt% in the PANi-CSA/PEO blends respectively. The corresponding device parameters are tabulated in Table 1. For the 6 wt% PEO-FET, the amount of PEO was insufficient to cause major changes in the  $I_{DS}$ - $V_{DS}$  curves compared to 0 wt% PEO-FET. Since the PANi-CSA fraction in the film was above the percolation threshold, the current through the channel was largely unaffected by the PEO chains. The device performance was similar to that of pure PANi-CSA (i.e. 0 wt% PEO) having similar on/off ratio, mobility and SS. From Fig. 1(a) and (b) we see that the thin films for these PEO concentrations are similar in morphology. The higher currents for 6 wt% as seen in Fig. 6 could be due the larger channel width compared to the 0 wt% FET. The channel conductivity values however are similar. The tendency toward current saturation in the 6 wt% PEO-FET was more

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**Fig. 6.** Drain-source current (I<sub>DS</sub>) vs. drain-source voltage (V<sub>DS</sub>) for the 6 wt% PEO device as a function of gate-source voltage (V<sub>GS</sub>). The gate voltage was varied from +2 V to -2 V in steps of 0.2 V. Inset:  $\sqrt{I_{DS}}$  vs.  $V_{GS}$  for V<sub>DS</sub> = -1 V. The slope of the line shown was used to calculate the hole mobility and the threshold voltage (V<sub>TH</sub>).



Fig. 7. Drain-source current  $(I_{DS})$  vs. drain-source voltage  $(V_{DS})$  for the 22 wt% PEO device as a function of gate-source voltage  $(V_{GS})$ . The gate voltage was varied from +2 V to -2 V in steps of 0.2 V. Inset:  $\sqrt{I_{DS}}$  vs.  $V_{GS}$  for  $V_{DS}=-1$  V. The slope of the line shown was used to calculate the hole mobility and the threshold voltage  $(V_{TH})$ .

gradual compared to the 0 wt% PEO-FET. The addition of PEO allowed deeper penetration of the electric field into the film due to increased entanglement with the PANi-CSA chains. A major change was seen in the  $I_{DS}$ - $V_{DS}$  curves for the FET with 22 wt% PEO in Fig. 7. The most significant feature of this Figure was the low off state current for  $V_{GS} = +2$  V while the high throughput "on" state current for  $V_{GS} = -2$  V was similar to other devices. The on/off ratio exceeds 2000 and there was a slight increase in the mobility, decrease in the threshold voltage and SS. All of these changes suggest a superior FET compared to the previous devices. For the 33 wt% PEO-FET there was no discernible field effect as can be seen in Fig. 8, most likely due to severe disorder introduced by the larger fraction of PEO in the blend.

In the metallic island model used to explain charge transport in doped PANi, the polymer film consists of highly ordered (crystalline) metallic islands surrounded by lowly conducting amorphous regions. Overall charge transport through the film is determined by charge flow



Fig. 8. Drain-source current ( $I_{DS}$ ) vs. drain-source voltage ( $V_{DS}$ ) for the 33 wt% PEO device as a function of gate-source voltage ( $V_{GS}$ ). The gate voltage was varied from +2 V to -2 V in steps of 0.2 V.

in the amorphous regions [32]. The field effect seen in Fig. 5 could be explained as follows: When a voltage was applied to the IL, a closely spaced electric double layer was quickly set up at the metal (gate)/IL and IL/polymer interface. A positive voltage applied to the gate electrode therefore causes a layer of cations (EMI<sup>+</sup>) to appear at the surface of the PANi-CSA film. Some of the cations penetrate the polymer, likely in the amorphous regions and de-dope it (electrochemical) or neutralize CSA<sup>-</sup> counterions (electrostatic) by acting as an electron acceptor. In either case, charge transport in the amorphous regions was reduced thereby lowering the channel current. A finite current however still flows in the channel even when  $V_{GS} = +2$  V. Since the ion penetration was confined to a few nm below the surface, its effect does not penetrate through the bulk of the film. There will be a layer of doped PANi-CSA carrying a current between the S/D electrodes that was unaffected by the gate voltage. This is what we propose occurs in the case of the  $0\,wt\%$  and  $6\,wt\%$  devices where the "off" state currents are fairly high and the device stays "on" at  $V_{GS}$  =  $\,+\,2\,V$  as seen in Figs. 5 and 6. It must be pointed out that the channel conductivity does not change much as  $V_{GS}$  was reduced to  $0\,V$  from  $\,+\,2\,V$  for  $0\,wt\%\mbox{-PEO}$  and  $6\,wt$ %-PEO devices. A gate voltage larger the +2V was avoided in order to stay within the electrochemical window of the IL. Also, the minimal changes in the  $I_{\text{DS}}\text{-}V_{\text{DS}}$  curves for positive gate voltages as seen in Figs. 5–8, did not warrant the use of voltages higher than +2V in all the measurements. Applying a negative gate voltage reverses this effect and now brings anions (TFSA<sup>-</sup>) to the polymer surface. These too diffuse into the polymer, doping it and also contributing additional electronic states in the amorphous regions that raise its conductivity and assist in charge transport between metallic islands. The current through the channel therefore increases with negative gate voltage. The changes in channel current as V<sub>GS</sub> changed from 0 V to -2 V are much larger i.e. the accumulation mode FET operation was greater than the depletion mode. Similar effects were observed in a PEDOT-PSS/PEO nanoribbon FET with IL gating [33]. The on/off ratio was seen be 2 in the 0 wt% and 6 wt% PEO devices.

In the case of the 22 wt% PEO-FET, the on/off ratio increases three orders of magnitude because the off-state current was reduced. Several reasons could account for this change. PEO is a hydrophilic and linear polymer that can easily entangle itself with hydrophilic CSA<sup>-</sup> ions on the PANi-CSA chain. At this concentration, the polymer solution had the right consistency and hydrophilicity to yield good quality spin coated films as seen in Fig. 1(c). PEO is polar, and electrostatic interactions with ions in the IL would be felt along the length of the PEO



**Fig. 9.** Integrated 810 nm polaron band peak area versus PEO wt% bar graph together with the mobility versus PEO wt%. The peak integration interval was 1 nm. Inset: Mobility versus polaron band peak area. Solid lines are guides to the eye.

chain, also affecting the PANi-CSA chains. The tight wrapping of PEO around the PANi-CSA chains imply stronger interaction and therefore allow the field effect to be felt deep into the amorphous regions and through the bulk of the polymer film. Applying a positive gate voltage therefore results in (EMI<sup>+</sup>) ions affecting the entire film reducing the channel current via de-doping and neutralization of CSA<sup>-</sup> counter ions to a much lower value. Thus, the off currents in this device are several orders of magnitude lower compared to those in the previous devices. Applying a negative gate voltage would reverse this effect and increase the channel current through the amorphous regions via a combination of hopping and tunneling processes through energetic barriers. The relatively constant specific capacitance at low frequency for negative voltage in a similar MIS device (as seen in Fig. 3(b)) is another sign of electrostatic doping via hole injection into the channel for negative gate voltage [26]. A slight increase in the mobility could be due to the better quality of the film as seen in Fig. 1(c) that has fewer grain boundaries which imply fewer charge traps and scattering. The better-quality film also results in high "on" state current, smaller values of the threshold voltage and of the sub-threshold swing as seen in Table 1. For the device with 33 wt% PEO, the PANi concentration was still above the percolation threshold. This is why the currents remain high as seen in Fig. 8. The channel conductivity was slightly smaller mostly due to larger inter-chain separation caused by the higher PEO concentration. As seen in Fig. 1(d) for this PEO concentration, the film was not uniform. At such high concentrations it was possible that excess PEO would remain undissolved or a fraction of the doped PANi-CSA could precipitate out. These undissolved particles then would lead to the spin coated films being non-uniform and grainy in appearance. The rough surface morphology and phase separation in the film would lead to a large number of scattering centers and charge traps that suppress the depletion and accumulation mode operation of the device. Thus, the field effect was minimal for this device as seen in Fig. 8. Fig. 9 shows the polaron band (810 nm) integrated peak area versus PEO wt% together with  $\mu$  versus PEO wt% (right axis). A smaller peak area for the 22 wt% PEO film is seen to indicate that the film has semiconducting properties (i.e. higher on/off ratio). This, we suggest, is due to a more compact film that results from efficient PEO binding with the PANi-CSA polymer chains that permits deeper penetration of the electric field into the film. The inset to Fig. 9 shows that the mobility decreases with increasing peak area. A higher polaron band peak area for the 33 wt% PEO-FET is consistent with a low expected mobility and subsequent suppression of the field effect. Our results therefore point to an optimum PEO concentration in the PANi-CSA/PEO blend that would lead to enhanced FET parameters due to better film quality and internal charge dynamics.

#### 4. Conclusions

PANi-CSA blended with PEO at concentrations of 0, 6, 22 and 33 wt % were used to fabricate thin film field effect transistors that were gated via an IL. The film having 22 wt% PEO was much more uniform compared to the films spun from other concentrations. Upon contact with the IL, the film (channel) conductivity increased regardless of the PEO content in the blend. This was attributed to an increase in the polymer work function combined with IL induced doping. Applying a positive gate voltage reduced the channel current while a negative voltage increased it. The observed field effects occurred due to electrochemical and electrostatic doping caused by the ions in the IL. PANi-CSA with 0 wt% and 6 wt% PEO were difficult to turn off due to the highly conducting nature of polyaniline. However a 22 wt% PEO-FET showed the highest on/off ratio exceeding 2000 and improved mobility. This was primarily due efficient PEO entanglement with the PANi chains, better film quality and lower off state current. Excessive PEO (33 wt%) leads to severe damping of the field effect due to the poor film quality and associated disorder. Analyzing the mobility dependence on the 810 nm polaron band peak area points to an optimum PEO wt% in the blend that would enhance device performance. A detailed study using additional PEO in the range 10%-25% is planned in the future to find the optimum concentration that yields the highest on/off ratio. The high "on" state throughput currents together with low operating voltages via IL gating make PANi-CSA/PEO blends attractive materials for use in low power consumption electronics.

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