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**BISTABILITY IN DOPED ORGANIC
THIN FILM TRANSISTORS
(PREPRINT)**



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14. ABSTRACT Organic thin film transistors (TFTs) with the conducting polymer poly(3,4-ethylenedioxythiophene):poly(styrene sulfonic acid), PEDOT:PSS, as the active layer and crosslinked, layer-by-layer assembled poly(allylamine hydrochloride)/poly(acrylic acid) (PAH/PAA) multilayers as the gate dielectric layer were investigated. A combination of spectroscopic data and device performance characteristics were used to study the behavior of these TFT devices under a variety of controlled environmental test conditions. It was shown that depletion and recovery of the device can be induced to occur in a means that is consistent with the electrochemical oxidation and reduction of water contained in the film. In addition to acting as a reactant, moisture also acts as a plasticizer to control the movility of other species contained in the film and thereby permits bistable operation of these devices. Raman spectroscopy was used to show that the observed device switching behavior is due to a change in the PEDOT doping level.					
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Introduction

Organic electronic devices such as light emitting diodes,¹ photovoltaics,² and transistors³ have been of particular interest since the discovery that the conductivity of conjugated polymers can be varied over many orders of magnitude through chemical doping.⁴ In particular, poly(3,4-ethylenedioxythiophene) (PEDOT) has been studied for a variety of applications because of its chemical stability, high visible light transmissivity, and relatively high conductivity.⁵ Some examples include antistatic coatings,⁶ electrode materials in capacitors,⁷ buffer layers in light emitting diodes,⁸ electrochromic materials,⁹ and electrochemical microactuators.¹⁰ Although pristine PEDOT is insoluble in common solvents, it can be dispersed in water when polymerized in the presence of polystyrene sulfonate (PSS). The PEDOT:PSS complex that results is readily processable, doped and highly conductive, and is available commercially from a number of sources.

The use of doped conjugated polymers as the active layer in thin film transistors (TFTs) has been investigated by a number of groups. MacDiarmid¹¹ and Epstein^{12,13,14,15} have reported on devices using PEDOT:PSS that exhibit an unexpected field effect upon the application of a positive gate bias. While the operating mechanism of these devices is not completely understood, possibilities include the existence of an ion-leveraged mechanism to disrupt the percolation path,¹³ an electrochemical de-doping effect,¹⁶ or a combination of both.¹⁷ Electrochemical transistors have also been reported by Wrighton^{18,19,20,21,22} and others.^{17,23,24} These are commonly laterally arranged devices with a conjugated polymer whose redox state is modified by a gate bias. These types of transistors generally have slower response times than transistors based on undoped

conjugated polymers (e.g. poly(3-hexylthiophene)) and small molecules (e.g. pentacene). As such, they do not necessarily compete with these more typical organic transistors, but rather have pertinence in areas such as sensors, molecular and flexible electronics, and fundamental materials chemistry.

We have recently demonstrated that layer-by-layer assembly is an effective method of incorporating ultra-thin gate dielectric layers into these types of transistors.²⁵ This method of assembly involves dipping a substrate between two dilute polyelectrolyte solutions of opposite charge to build up a thin film via the electrostatic interactions between the polyelectrolytes. The depletion mechanism for these devices was shown to depend on an electrochemical redox reaction resulting in a de-doping of the active layer through the oxidation of water. Here, the corresponding recovery behavior of doped organic TFTs using crosslinked PAH/PAA bilayers as the gate dielectric layer was investigated. By examining the device performance under different environmental test conditions, a more complete understanding of the device operation and of the role that water plays in the mechanism was achieved. In addition, *in-situ* Raman spectroscopy was used to quantify the influence that these effects have on the intrinsic doping level of the PEDOT:PSS active layer.

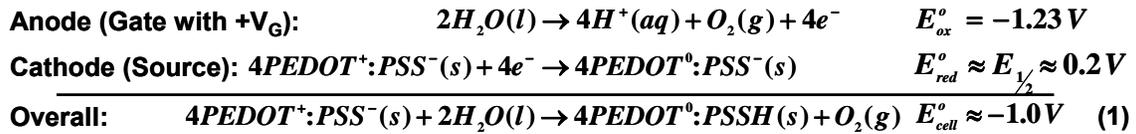
Experimental

Aqueous stock solutions of PEDOT:PSS, under the trade name of Baytron[®] P (H.C. Stark Inc.) with a reported concentration range of 1 – 5%, were filtered prior to use. Spin-coated films of PEDOT:PSS were prepared with solutions comprised of a mixture of the aqueous Baytron P stock solution with ethylene glycol in an 80/20 weight ratio with a small amount (< 1%) of dodecabenzenesulfonic acid. The films were fabricated by spinning at 500 rpm for 10 s and then 3000 rpm for 60 s. Polyelectrolyte solutions (10 mM) were pH adjusted with NaOH and HCl using an Orion model 230A pH meter. Each monolayer deposition cycle (~ 15 min) was followed by multiple rinse steps in deionized H₂O (18 MΩ·cm) in a Carl Zeiss Microm DS-50 automatic slide stainer. Silver and aluminum electrodes were thermally evaporated at a rate of 3 and 4 – 5 Å/s, respectively, in an Explorer 18 Denton Vacuum system (< 10⁻⁷ Torr) using a Telemark model 860 deposition controller. The aluminum gate electrode was deposited to a thickness of 350 – 400 Å. The size of the active channel was approximately 2 mm wide by 3 mm long. Film thicknesses were measured with a Tencor P-10 surface profiler at a stylus force of 0.6 mg. The TFT device performance was characterized with two Keithley 2400 SourceMeters.[®] Gases (air or N₂) were bubbled through deionized water (18 MΩ·cm) to create humidified conditions (relative humidity (RH) ~ 75%), purged through Drierite[®] to create dry conditions, and a mixture of both to create intermediate conditions (RH = 30%) in the test chamber. Raman spectra were obtained with a Renishaw inVia Raman Microscope using a Melles Griot Argon Laser.

Results and Discussion

Thin film transistors using PEDOT:PSS as the active layer and layer-by-layer assembled PAH/PAA films as the gate dielectric were recently shown to operate via an electrochemical de-doping process.²⁵ By way of describing this process, equation (1) is presented to illustrate the means by which depletion occurs in these devices. Upon application of a positive gate bias, the gate electrode serves as the anode at which water is oxidized to produce $O_2(g)$. The source electrode serves as the cathode at which PEDOT becomes reduced back to its neutral state ($E_{1/2} \sim 0.2 \text{ V}$)²⁶ resulting in a decrease in the conductivity of the active layer and device “turn-off.” Sulfonic acid (SO_3H) groups are generated on the PSS due to proton migration from the gate electrode. As a result, the *depletion* behavior was shown to depend critically on the level of water and $O_2(g)$ in the test environment.²⁵

Depletion Mechanism



To gain a better understanding of the overall device operating mechanism, we were also interested in examining the *recovery* behavior. Our findings as a function of test environment serve as the subject of this report, and are presented below. Figure 1 shows the time-dependent performance characteristics of a TFT device using a spin-coated film of PEDOT:PSS (thickness = 500 – 900 Å) as the active layer and a crosslinked, layer-by-layer assembled film of PAH/PAA (thickness = 60 Å) as the gate dielectric. Upon application of a positive gate bias ($V_G = 2.5 \text{ V}$), the source-drain current (I_{DS}) decreases to turn the device to the “off” state. This initial switching of the device was conducted

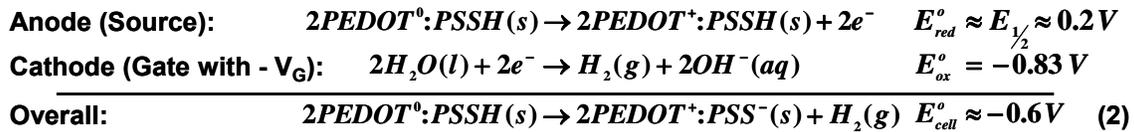
under humidified N₂ conditions. After the gate bias was removed (still under humidified N₂ conditions), the device immediately began to recover as evidenced by an increase in I_{DS}. This recovery is due to trapped O₂(g) remaining in the film, which causes the reverse of reaction (1) to occur and the concomitant increase in the level of doped PEDOT when the gate bias is removed. When water is removed from the test environment by exposing the device to a purge of dry N₂, this recovery behavior becomes almost completely arrested. Although subsequent exposure of the device to dry air results in the resumption of the recovery due to a higher concentration of O₂(g), the magnitude of I_{DS} does not reach its initial value. Only when the device is exposed to a humidified air environment does I_{DS} reach (and even surpass) its initial value. This behavior is consistent with the reversal of the mechanism put forth in equation (1). In order for spontaneous recovery (i.e. re-doping of the active layer) to occur, O₂(g) must be present in the film in a high enough concentration and with sufficient mobility. Correspondingly, moisture contained in the film acts as both the reductant, as well as a plasticizer to increase the mobility within the film.

It is interesting to note that if a *negative* gate bias is applied after the device has been depleted (i.e. turned “off”), it can be induced to quickly recover. In Figure 2, a *positive* gate bias of 3.0 V was used to initially deplete the device under humidified N₂ conditions (75% relative humidity (RH)) to an I_{on/off} ratio ~ 70. If this bias is applied for a relatively short amount of time (~ 5 min), and then removed, the device begins to recover due to trapped O₂(g) remaining in the film, consistent with the discussion above. If, however, this positive gate bias is applied for a longer period of time (~ 27.5 min) and then removed (at time ~ 35 min in the figure), the recovery is completely inhibited because the

O₂(g) has diffused out of the film. The device remains in the “off” state despite the fact that the gate bias has been removed. If a negative gate bias ($V_G = -2.5$ V) is subsequently applied, recovery is induced as seen by an increase in I_{DS} . However, once this gate bias is removed, I_{DS} again begins to decrease. This same negative gate bias was applied three more times, each for approximately two minutes with about nine minutes in between each application. As shown, each time the gate bias was removed, I_{DS} began to decrease, but at a slower rate and to a lesser extent. In fact, if the negative gate bias is applied long enough, I_{DS} does not decrease upon its removal, but remains stable and the device remains in the “on” state. It should be noted that care must be taken to avoid overoxidation of the PEDOT in the active layer upon induced recovery. The overoxidation of PEDOT is commonly suspected as the cause for permanent degradation of the active layer in analogous devices upon prolonged application of a negative gate bias.^{11,27}

This induced recovery behavior is similar in nature but opposite in magnitude to the depletion behavior discussed above and in our previous report.²⁵ The PEDOT:PSS active layer is electrochemically de-doped with a positive gate bias and it is subsequently induced to recover (i.e. re-doped) with a negative gate bias. Equation (2) is thus presented to illustrate the means by which recovery occurs in these devices. Upon

Induced Recovery Mechanism



application of a negative gate bias, the gate electrode serves as the cathode at which water is reduced to generate H₂(g) and OH⁻ ions. The source electrode serves as the

corresponding anode to re-oxidize (i.e. re-dope) neutral PEDOT⁰ that was generated during depletion. The OH⁻ ions can subsequently migrate from the cathode to the anode to de-protonate the SO₃H groups of PSS. The overall net effect of a negative gate bias is to induce the recovery of the de-doped active layer through an electrochemical reduction of water to generate H₂(g). Maintaining the negative gate bias for a long enough period of time will enable H₂(g) to diffuse out of the device, thereby shifting the state of reaction equilibrium to favor the “on” state. It should be noted that the gate current observed during the switching of similar doped organic TFTs (Figure 2) has previously been attributed to an ionic current.²⁸ For the devices shown here, the I_G observed with an applied gate bias is attributed to a combination of both faradaic (redox) and non-faradaic (ionic) processes associated with the electrochemical reactions put forth in equations (1) and (2). In addition, when the gate bias is removed, the magnitude of I_G reverses direction and decays exponentially, which is attributed to the ions drifting back to their original state of equilibrium as the reverse of reactions (1) and (2) proceed. It can be seen that the longer the negative gate bias is applied, the resulting gate current decreases due to the device being switched back to a stable “on” state. This type of behavior involving the oxidation and reduction of water to control the doping level of organic materials systems has previously been demonstrated²⁹ and is similar to what is observed here.

As a result of being able to systematically control the doping state of the film by the application of either a positive or negative gate bias, bistable device operation can be achieved as shown in Figure 3. Although bistable operation of PEDOT/PSS electrochemical transistors has previously been demonstrated using lateral architectures of non-closed circuits,²³ the bistability observed herein is obtained with controlled

environmental conditions. In this case, the device was tested under a lower relative humidity (RH ~ 30%) than that described above for Figure 2 (RH ~ 75%). The device was alternately switched between stable “off” and “on” states with a positive ($V_G = 4$ to 6 V) and negative ($V_G = -4$ to -5 V) gate bias, respectively. The magnitude of I_{DS} changed from approximately 0.5 μA in the “off” state to approximately 10.5 μA in the “on” state. Due to the fact that this device was tested at a lower RH than those discussed above, a higher V_G was required to induce a change in I_{DS} , the magnitude of I_G (for any given V_G) was lower, and the tendency to overoxidize PEDOT (as indicated by a rapid, irreversible drop in I_{DS} ¹¹) appeared to decrease.

Under these test conditions, each time the gate bias was removed (either positive or negative), the magnitude of I_{DS} remained constant at the current value, and did not tend towards what it was previously, as was shown in Figures 1 and 2. In those cases, the magnitude of I_{DS} became stable only when the gate bias was applied for a long enough time to allow all of the $\text{O}_2(g)$ or $\text{H}_2(g)$ generated (see equations 1 and 2) to diffuse out of the film, thereby prohibiting the back reaction. In this case, the gate bias was applied for a sufficiently short amount of time to suppress diffusion of $\text{O}_2(g)$ or $\text{H}_2(g)$ out of the film. Instead, the lower level of humidity that is used in the test environment is unable to “plasticize” the matrix enough to allow for significant diffusion of these species. Apparently, enough moisture is present to act as the reactant for both oxidation and reduction of PEDOT:PSS in equations (1) and (2), but not enough to permit whole-scale diffusion of the reaction products. Consequently, while water acts as both the reactant and plasticizer in these devices, a lower RH provides a means to enable bistable device operation by reducing the mobility of other species in the film.

Figure 4 offers additional support of this effect whereby a device was first equilibrated in a humidified N₂ environment before operation. Immediately before applying a positive gate bias, the test environment was switched to dry N₂. The device becomes depleted in approximately 5.5 minutes with an I_{on/off} ratio ~ 300 due to the presence of moisture still contained in the film. Upon removal of the gate bias, I_{DS} did not begin to recover as before, but rather the device remained in the “off” state because of the low mobility of the reactant products generated during depletion. Once moisture was re-introduced into the film by exposing it to a humidified N₂ environment, the device began to recover because of the increased mobility of the O₂(g) trapped in the film and the ability to re-oxidize the neutral PEDOT⁰ generated during depletion. It should be noted that when the device was operated in a dry environment, an unexpected increase in I_G was sometimes observed. This effect could be eliminated by re-equilibrating with moisture. While not completely understood, this behavior is believed to be due to defects introduced into the polyelectrolyte multilayer gate dielectric resulting in an increase in the leakage current.

Raman scattering was used to elucidate the role that these effects have on the doping level of the PEDOT:PSS active layer during device operation under the environmental conditions described above. The Raman spectra shown in Figure 5 were obtained using an excitation wavelength ($\lambda_{exc} = 514$ nm) that exhibits a resonance with the $\pi \rightarrow \pi^*$ transition of PEDOT.³⁰ Spectra A, B, and C were obtained *in-situ* during device operation at the times and under the conditions shown in Figure 4. Before depletion, the spectrum appeared almost completely featureless (A), but after applying a gate bias ($V_G = 2.5$ V), peaks appeared at 989, 1365, 1428, and 1506 cm⁻¹ (B). These peaks have

previously been assigned to the ring deformation, $C_{\beta} - C_{\beta}$ stretch, $C_{\alpha} - C_{\beta}$ symmetrical stretch, and the $C_{\alpha} - C_{\beta}$ asymmetrical stretch of PEDOT, respectively.³¹ An increase in the intensity of these peaks has been shown to correlate with a reduction in the doping level of PEDOT.³⁰ These trends agree with the decrease in I_{DS} after the gate bias was applied. As the device begins to recover upon exposure to a humidified N_2 environment, the peak intensities again decrease (C), consistent with an increase in both the PEDOT doping level and I_{DS} .

The remaining spectra shown in Figure 5 were obtained by continued testing of this device under a humidified N_2 environment. The device performance characteristics associated with these spectra are shown in Figure 6. The data for points D through H show that as the gate bias is increased from 0.0 to 2.0 V, the device becomes depleted (I_{DS} decreases) due to an increase in the level of de-doping of the PEDOT (i.e. increasing peak intensities in the Raman spectra). In addition, by comparing spectra B (dry N_2) and H (humidified N_2), the effects of humidity on the PEDOT doping level can be seen. In particular, the level of de-doping that occurred under a dry N_2 environment (B) was significantly lower than that under humidified N_2 (H), despite the fact that a higher gate bias was applied for B. The lower moisture content in the film at B limits the level of de-doping that can occur, however, more subtle effects present themselves when comparing results obtained under these different conditions. It can be seen from the Raman spectra that at point B, the PEDOT has a higher level of doping (smaller peak intensities) than at point F. However, I_{DS} (and hence the conductivity) is larger for point F (see Figures 4 and 6). This effect is not completely understood but is possibly the result of a

morphology-dependent change in conductivity upon exposure to moisture that is analogous to the known, secondary doping effect of PEDOT:PSS.^{32,33,34}

The effects of induced recovery observed upon application of a negative gate bias are shown for points I through K. As expected, a negative gate bias induces the recovery of the device by re-doping the PEDOT active layer as seen by a decrease in the Raman peak intensities. The data for points L through P reiterate the ability to achieve bistable device operation by switching the device between “on” and “off” states and associating these changes to a change in the PEDOT doping level, as seen in the Raman spectra. All of these effects are consistent with the electrochemical device operation put forth in equations (1) and (2).

Conclusions

A bistable, doped organic TFT has been demonstrated under a controlled N₂ environment. Under humidified conditions, the depletion and recovery of the active layer can be induced with a positive and negative gate bias, respectively. This behavior was explained through electrochemical reactions involving the oxidation and reduction of water. Upon removal of V_G, both I_{DS} and I_G slowly return to their original value due to the reversal of the electrochemical depletion and recovery reactions put forth. Longer applications of the gate bias were required to stabilize the state of the device by allowing the reaction products to diffuse out of the film. Moisture contained in the film was shown to act as the reactant for both oxidation and reduction in addition to acting as a plasticizer to control the mobility and diffusion of other species (O₂(g) and H₂(g)) in the

film. Raman spectroscopy was utilized to show that the observed switching behavior in these devices is due to a change in the PEDOT doping level.

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Figures

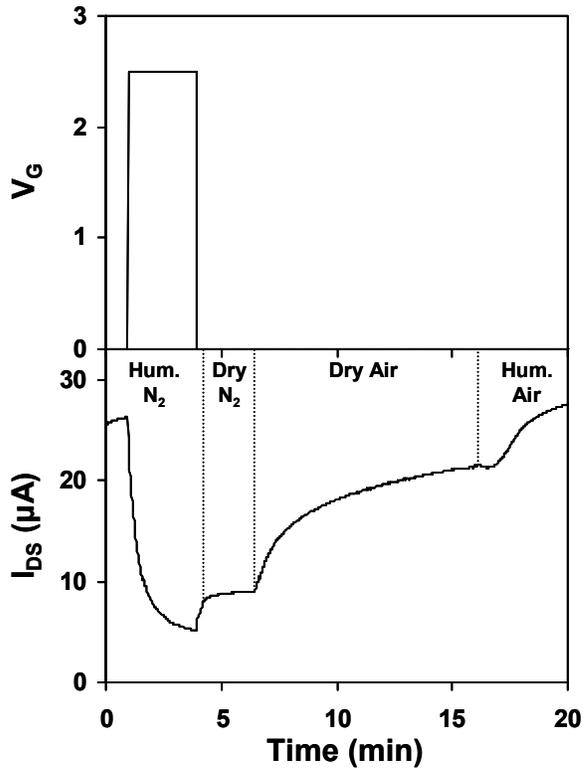


Figure 1. Time-dependent performance characteristics (at $V_{DS} = 0.1$ V) under different test conditions of a TFT device with PEDOT:PSS as the active layer and 20 PAH/PAA bilayers as the gate dielectric (deposited at a pH of 6 – 6.5 with a total thickness ~ 60 Å).

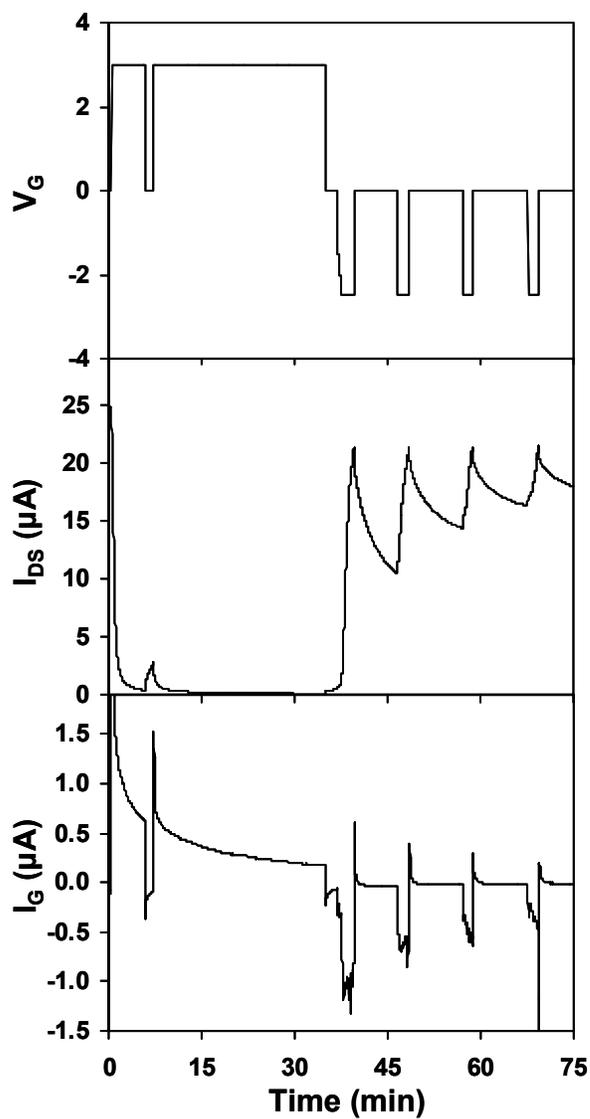


Figure 2. Time-dependent performance characteristics (at $V_{DS} = 0.2$ V) of a TFT device with PEDOT:PSS as the active layer and 40 PAH/PAA bilayers as the gate dielectric layer (deposited at a pH of 6 – 6.5 with a total thickness ~ 130 Å). The device was tested under humidified N_2 conditions (RH $\sim 75\%$).

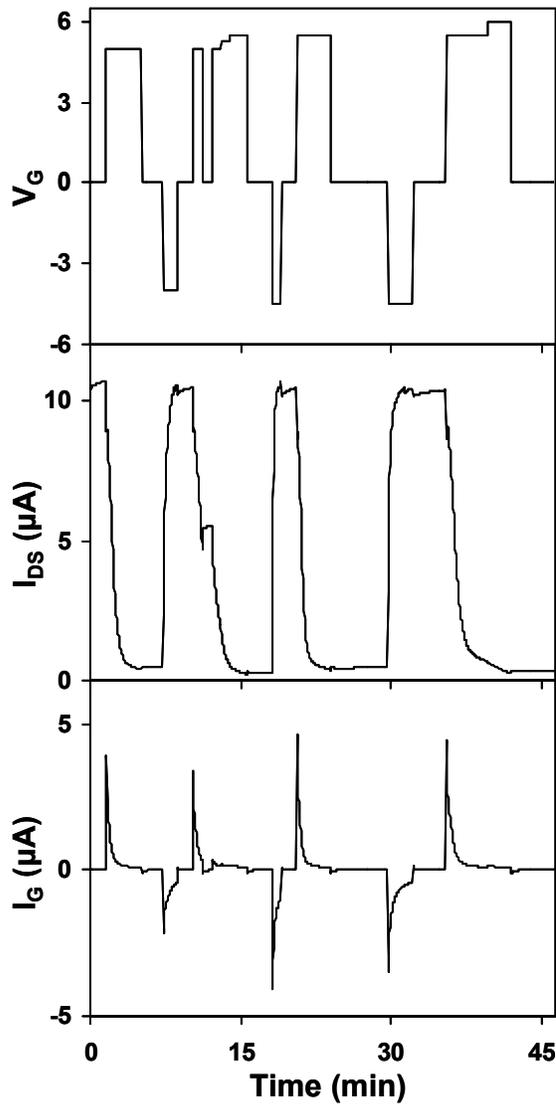


Figure 3. Time-dependent performance characteristics (at $V_{DS} = 0.2$ V) of the same device described in Figure 2, but tested under humidified N_2 at 30% RH.

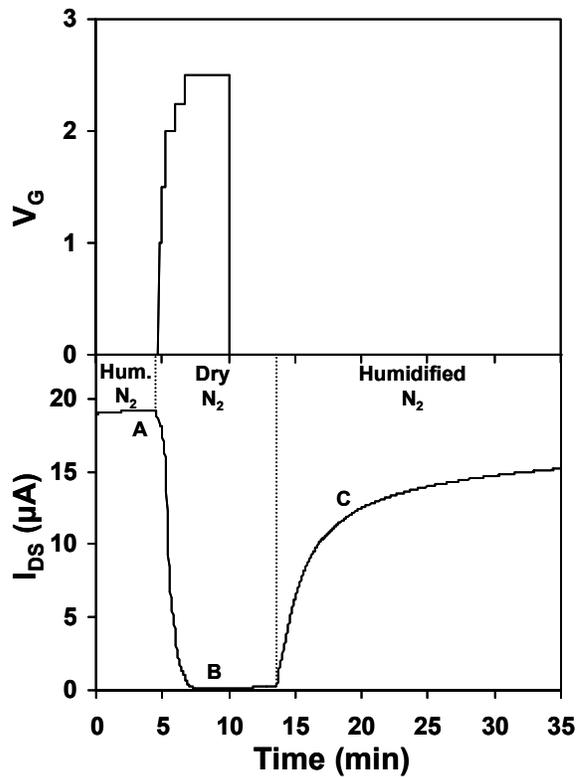


Figure 4. Time-dependent performance characteristics (at $V_{DS} = 0.2$ V) of a TFT device with PEDOT:PSS as the active layer and 40 PAH/PAA bilayers as the gate dielectric layer (deposited at a pH of 6 – 6.5 with a total thickness ~ 130 Å). The device was initially exposed to humidified N₂ (RH $\sim 75\%$) and then purged with dry N₂ immediately before the gate bias was ramped up to 2.5 V. The labels A through C indicate the time at which the Raman spectra shown in Figure 5 were obtained.

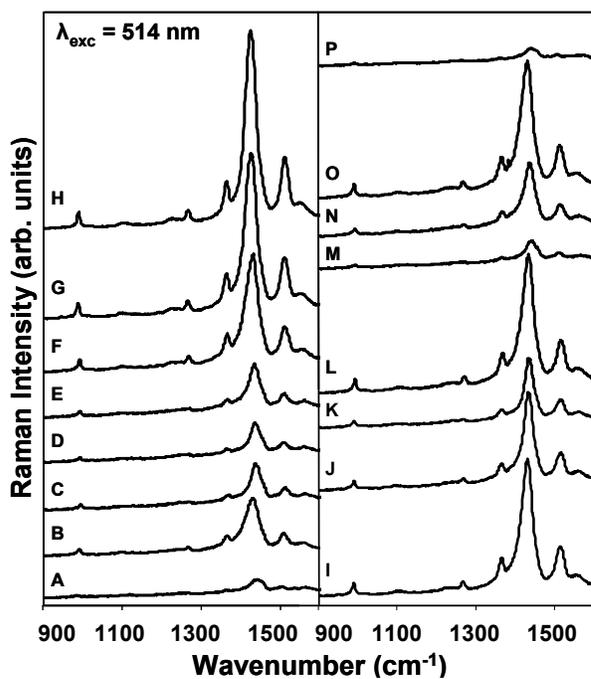


Figure 5. Raman spectra obtained *in-situ* during operation of the device described in Figures 4 and 6. Labels A through P correspond to the times indicated in Figures 4 and 6.

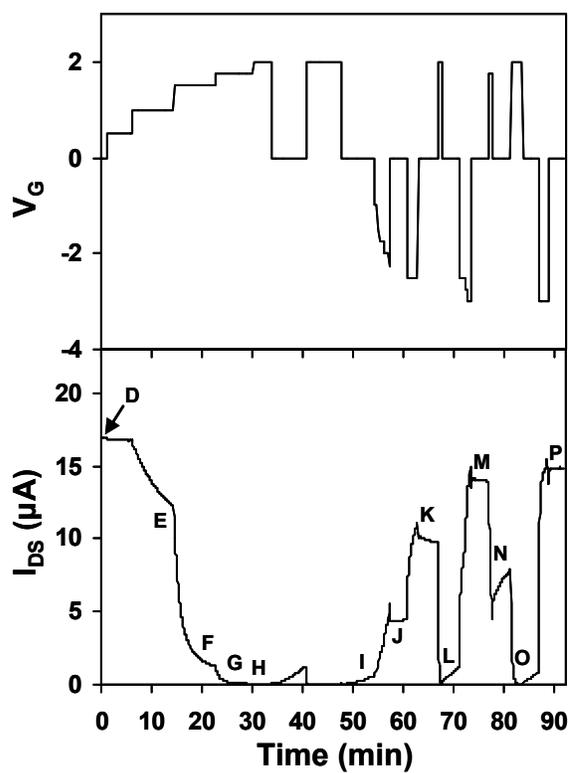


Figure 6. Time-dependent performance characteristics of the same device discussed in Figure 4, but tested under humidified N_2 conditions. Labels D through P correspond to the time at which the Raman spectra shown in Figure 5 were obtained.

Table of Contents Synopsis

Bistability of a thin film transistor with an ultra-thin layer-by-layer assembled gate dielectric and poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) as the active layer is demonstrated through control of environmental conditions. Device operation is shown to require water as a redox reactant, which induces a corresponding change in the active layer doping level.

