

# Effects of humidity on unencapsulated poly(thiophene) thin-film transistors

Michael L. Chabiny<sup>a)</sup> and Fred Endicott  
PARC, 3333 Coyote Hill Road, Palo Alto, California 94304

Bryan D. Vogt, Dean M. DeLongchamp, and Eric K. Lin  
Polymers Division, National Institute of Standards and Technology, 100 Bureau Drive, Mail Stop 8541,  
Building 224, Room A325 Gaithersburg, Maryland 20899-8541

Yiliang Wu, Ping Liu, and Beng S. Ong  
Xerox Research Centre of Canada, 2660 Speakman Drive, Mississauga, Ontario, Canada L5K 2L1

(Received 9 December 2005; accepted 23 January 2006; published online 17 March 2006)

The effects of humidity on unencapsulated polymeric thin-film transistors (TFTs) of poly[5,5'-bis(3-dodecyl-2-thienyl)-2,2'-bithiophene] (PQT-12) were investigated. The field effect mobility of PQT-12 TFTs decreases and the rate of trapping of charge carriers increases under increasing humidity. The amount of water absorbed by the PQT-12 films was measured using a quartz crystal microbalance. Thin films of PQT-12 absorb comparable amounts of water to the carrier concentration in TFTs under routine operating conditions (humidity of 30% relative humidity and gate voltage of  $-30$  V); the changes in electrical characteristics under humid atmospheres are attributed to the interaction of absorbed water with the carriers in the film. © 2006 American Institute of Physics. [DOI: 10.1063/1.2181206]

Exposure of unencapsulated thin-film transistors (TFTs) made with semiconducting polymers to the ambient environment is known to degrade their electrical performance.<sup>1-4</sup> The degradation has typically been attributed to the presence of oxygen<sup>1,4</sup> and water.<sup>3</sup> Although in finished electronic devices polymeric TFTs will be encapsulated, it is important to understand the intrinsic effects of absorbed impurities. We present here a study of the impact of water absorption on the electrical performance of TFTs made with poly[5,5'-bis(3-dodecyl-2-thienyl)-2,2'-bithiophene] (PQT-12).<sup>5</sup>

Most organic polymers adsorb small molecules from the ambient vapor phase, e.g., water or volatile organics, in relatively large quantities ( $10^{20}$  to  $10^{21}$  molecules/cm<sup>3</sup>) (Ref. 6), when compared to the density of states in electronic devices ( $10^{22}$  cm<sup>-3</sup>). Impurities that are well-below readily detectable concentrations can potentially have a large impact on device performance. Most data on the diffusion of environmental species, such as water, in polymer films are for films with thicknesses in excess of  $1\text{ }\mu\text{m}$ , a relatively large value compared to the thickness of the semiconducting layer in a TFT ( $<50$  nm). Recent studies have shown that interfacial effects can play a strong role in the absorption of water in thin polymer films suggesting that measurements should be made on surfaces that most closely resemble the configuration in actual devices.<sup>7</sup>

Due to its large dipole moment and electrochemical reactivity water is expected to affect charge transport in organic TFTs.<sup>2</sup> Indeed, gate bias stress in polythiophene vinylene-based TFTs has been shown to increase during operation under humid environments.<sup>3</sup> The field-effect mobility of several molecular organic semiconductors has been shown to decrease with increasing humidity.<sup>8</sup> Hoshino and co-workers<sup>9</sup> attempted to separate the effects of oxygen and water on the performance of poly(3-hexylthiophene) P3HT-based TFTs. They observed that water increased the off-state conduction and caused a lack of saturation in the output characteristics of TFTs with an initial mobility of

$1 \times 10^{-4}$  cm<sup>2</sup>/V s formed on bare SiO<sub>2</sub> dielectrics. The effects of humidity on organic TFTs with polymeric gate dielectrics have also been studied; but in these cases, it is difficult to disaggregate the contribution of water in the semiconducting layer and in the dielectric.<sup>10,11</sup>

We have studied the effects of humidity on the operation of PQT-12 TFTs with an inorganic gate dielectric.<sup>12</sup> All of the TFTs studied here were fabricated in the coplanar geometry on glass substrates using photolithography. The dielectric layer was a plasma-enhanced chemical vapor deposited SiO<sub>2</sub>/Si<sub>3</sub>N<sub>4</sub> dielectric stack ( $C=28$  nF/cm<sup>2</sup>). The source and drain contacts were made of gold ( $2000\text{ }\text{\AA}$ ) with a chromium adhesion layer ( $30\text{ }\text{\AA}$ ) and were patterned using wet etching. A self-assembled monolayer formed from octyltrichlorosilane (OTS) was applied to all dielectrics using previously reported procedures.<sup>13</sup> PQT-12, ( $\approx 30$  to  $50$  nm thick) was deposited by spin coating and was thermally annealed at  $120\text{ }^\circ\text{C}$ . Current-voltage characteristics of the PQT-12-based TFTs were measured using both continuous and pulsed gate bias measurements in the dark. All of the devices tested were exposed to different ambient environments at room temperature in a home-built flow chamber. Nitrogen gas was humidified by bubbling through a water bath and could be controlled within  $\pm 5\%$ . Current-voltage measurements were acquired for three to four TFTs on the same substrate; the mobility varies  $\pm 5\%$  device-to-device and  $\pm 20\%$  substrate-to-substrate.

Measurements of the transfer characteristics of PQT-12 TFTs exposed to different relative humidity (RH) environments for 30 to 60 min showed that the extracted mobility is influenced by the timescale of gate bias. The extracted parameters of TFTs measured under dry nitrogen were nearly identical when measured using a pulsed gate (width  $\approx 100$  ms) and with continuous application of the gate voltage ( $\mu_{\text{linear}}=0.03$  cm<sup>2</sup>/V s and  $V_T=-5$  V) [Fig. 1(a)]. Upon exposing the TFT to a RH of  $\approx 45\%$  for 30 min, a noticeable difference was observed between the continuous and pulsed gate measurements. Pulsed-gate measurements yielded the same threshold voltage as measured under dry conditions,

<sup>a)</sup>Electronic mail: mchabiny@parc.com

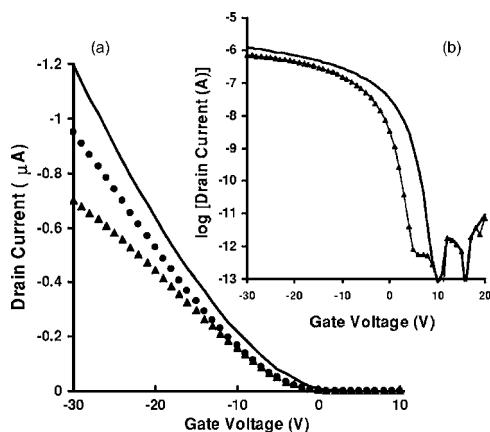


FIG. 1. (a) Linear regime transfer characteristics of a PQT-12 TFT under dry nitrogen (solid line) using continuous gate measurements, 45% RH in nitrogen (dots) using pulsed gate voltages, and using continuous application of the gate voltage (triangles). The source-drain voltage was  $-5\text{ V}$ . (b) Log-scale plot of transfer characteristic in (a) under dry nitrogen (line) and under 45% RH (triangles).

$V_T = -5\text{ V}$ , but a different mobility  $\mu_{\text{linear}} = 0.024\text{ cm}^2/\text{V s}$ . Continuous gate measurements showed a reduced apparent mobility ( $\mu_{\text{linear}} = 0.016\text{ cm}^2/\text{V s}$  and  $V_T = -3\text{ V}$ ), and a curvature in the characteristic at high gate voltage, a sign of gate bias stress. The off-current was relatively unaffected by humidity, but signs of a shift in the onset voltage were observed [Fig. 1(b)]. Figure 2 shows the mobility extracted in the linear regime using measurements of the current  $\approx 20\text{ ms}$  after application of the gate voltage. The decrease in mobility was nearly linear from 0 to 70% RH and the absolute decrease was  $\approx 60\%$  at high RH. The change in mobility was reversible upon removal of the humidified atmosphere and purging under dry nitrogen for 4 h or longer at room temperature.

The difference in results between continuous and pulsed measurements is easily reconciled because they suggest that carriers are being trapped on a timescale that is somewhere between the duration of the gate bias both measurements (total time of applied bias is  $\approx 30\text{ s}$  for continuous measurements and  $\approx 1\text{ s}$  for pulsed measurements). Figure 3(a) shows the channel current at fixed gate voltage over time at different humidities; these data demonstrate that the rate of decay in current at a fixed gate voltage increases with increasing humidity. This decay in current is attributable to

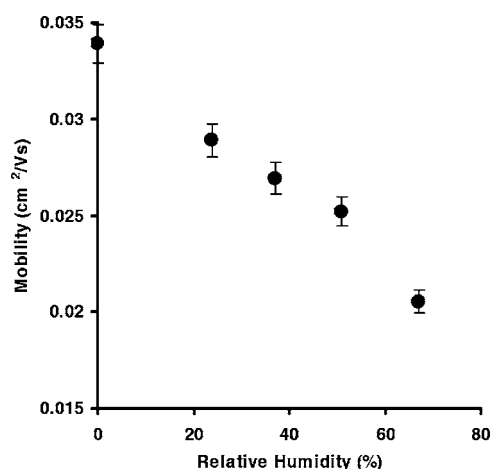


FIG. 2. Linear regime field-effect mobility as a function of RH in nitrogen measured using pulsed gate voltages with the current measured  $\approx 20\text{ ms}$  after the beginning of the gate pulse.

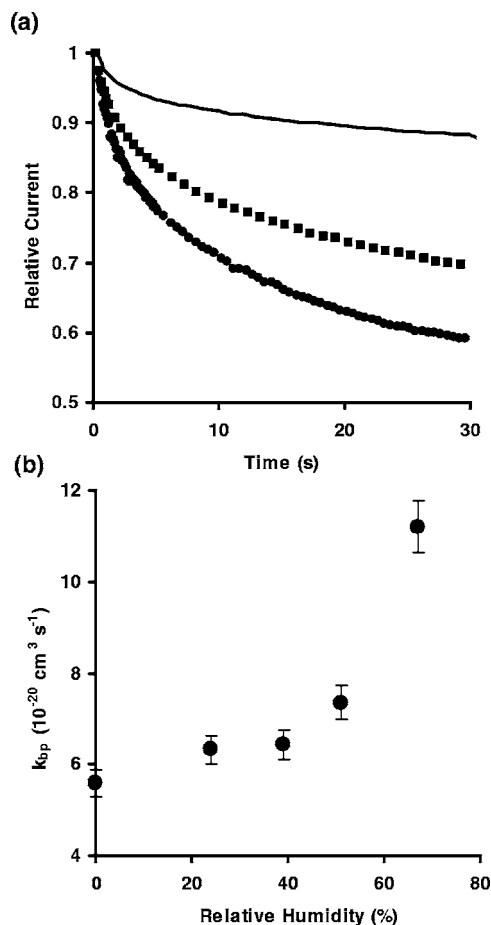


FIG. 3. (a) Current measurement at a fixed gate voltage ( $-30\text{ V}$ ) with respect to time at  $V_{SD} = -2\text{ V}$ . Solid—dry nitrogen; squares: 25% RH in nitrogen; dots: 65% RH in nitrogen. (b) Rate constant for bipolaron formation as a function of relative humidity in nitrogen.

trapping of carriers into immobile electronic states. This hypothesis is supported by the measured shift in the threshold voltage after biasing at a fixed gate voltage and a constant mobility. The carriers are reversibly trapped at short times; for a constant shift in threshold voltage,  $\Delta V_T \approx -4\text{ V}$  (times of 1 to 30 s depending on the ambient), the trapped carriers released in  $\approx 100\text{ s}$  at all humidities that were studied.

Similar to a previous analysis of charge trapping in PQT-12, current transients were measured at a several gate voltages and humidities to characterize the dependence of the decay in current on charge carrier concentration.<sup>14,15</sup> The rate of change of the carrier concentration ( $dN/dt$ ) was measured at short time ( $< 40\text{ ms}$ ) by extracting the change in threshold voltage from the measured current and calculating the aerial density of the trapped charge using the gate capacitance. For devices measured under a vacuum, it was found that the trapping kinetics are approximately second order with respect to hole concentration suggesting the presence of bipolaron traps in these materials.<sup>14</sup> The trapping kinetics remain second-order under humidified atmospheres and the rate constant for formation of the bipolaron increases nonlinearly with increasing ambient humidity [Fig. 3(b)].

To best interpret these experiments, it is important to know the concentration of water in the carrier accumulation layer of the device. We have measured the mass uptake of water into these films using a quartz crystal microbalance method.<sup>7,16</sup> PQT-12 films were spincoated on quartz crystals with an OTS-coated layer of  $\text{SiO}_2$  and the absorption of wa-

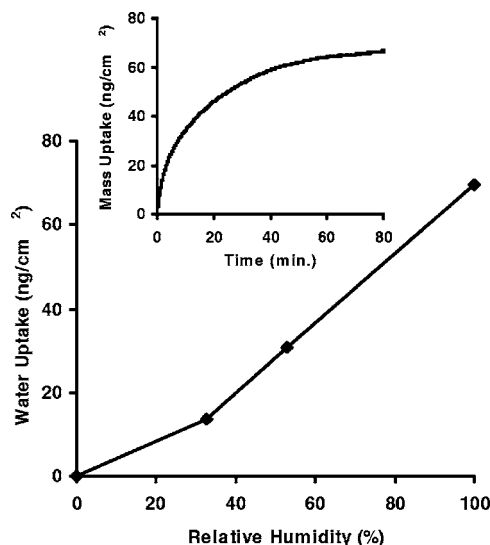


FIG. 4. (a) Mass uptake of water into a PQT-12 film on OTS-coated  $\text{SiO}_2$  at varying humidity in nitrogen measured using a quartz crystal microbalance (the line is provided as a guide for the eyes and does not represent a fit to the data). (b) Mass uptake of water as a function of time at 30% RH in nitrogen for a film of PQT-12 on bare silicon dioxide.

ter was measured under flowing humidified nitrogen (see Fig. 4). The mass uptake is nearly linear with increasing humidity and is  $\approx 2\%$  by weight at the highest humidity tested (100% RH). The timescale for saturation of the film at a given ambient is shown in the inset and is  $\approx 60$  min, which correlates well with the observation that devices immediately measured in ambient after thermal annealing under dry nitrogen show little bias stress. From these data, we can estimate the number of water molecules relative to the number of carriers in the accumulation layer. This analysis is inherently qualitative because we must assume that the water is uniformly distributed in the film, both through the thickness of the film and in both laterally through crystalline and disordered regions. If we consider the case of relatively high carrier concentrations, at  $V_G = -30$  V with a gate capacitance of  $30 \text{ nF/cm}^2$ , the induced carrier concentration is  $\approx 5.6 \times 10^{12} \text{ carriers/cm}^2$ . These carriers are confined with  $\approx 1$  nm of the surface of the gate dielectric. At  $\approx 100\%$  RH the film contains  $\approx 70 \text{ ng/cm}^2$  of water in a film that is  $\approx 30$  nm in thickness; assuming that the water is uniformly distributed in the film, the concentration of water in the accumulation layer is  $\approx 8 \times 10^{13} \text{ molecules/cm}^2$ , or  $\approx 10$  water molecules/carrier. Even at lower relative humidity, e.g., 30%, the accumulation layer contains nearly equal numbers of water molecules and carriers.

The number of water molecules absorbed in PQT-12 films under humidified atmospheres is large relative to the number of charge carriers under operation, thus they are likely to interact strongly with the charged polymer molecules in the film. The presence of water both decreases the field-effect mobility and increases the rate constant of carrier trapping. While the water molecules can affect the molecular packing in the films, even without such an effect they can stabilize the holes in the material and reduce their ability to hop from chain to chain, thus reducing their mobility. It has been suggested that dipolar disorder in polymeric dielectrics can reduce mobility of carriers and it is possible that ran-

domly distributed water molecules in the semiconducting layer could exert a similar effect.<sup>17</sup> The observed increase in rate constant for the formation of bipolarons is consistent with the speculation that the water molecules stabilize the charged species in PQT-12; the presence of water should reduce the barrier to the formation of bipolaron traps by reducing the Coulomb barrier caused by the approach of two positively charged species. While we cannot rule out structural changes in the PQT-12 films by absorption of moisture, it is likely that electrostatic interactions with the carriers are a substantial contributor to the change in electrical characteristics.

This study suggests that a range of measurement times is required to interpret the effects of environmental impurities on polymer TFTs. Exclusion of water from TFTs will be required in applications, such as displays, to prevent an increased rate of bias stress that will degrade the performance of the backplane. These studies have only examined the effects of moisture on short-term operation; long-term studies are required to determine the absolute stability of these semiconducting polymers to chemical damage under operation.

The authors gratefully acknowledge A. Salleo, and R. A. Street for useful discussions, and the process line at PARC for fabrication of the transistor substrates. One of the authors (D.M.D.) acknowledges support from the NIST-NRC post-doctoral program. This work was partially supported by the Advanced Technology Program of the National Institute of Standards and Technology (Contract No. 70NANB0H3033).

- <sup>1</sup>D. M. Taylor, H. L. Gomes, A. E. Underhill, S. Edge, and P. I. Clemenson, *J. Phys. D* **24**, 2032 (1991).
- <sup>2</sup>D. M. de Leeuw, M. M. J. Simenon, A. R. Brown, and R. E. F. Einerhand, *Synth. Met.* **87**, 53 (1997).
- <sup>3</sup>M. Matters, D. M. De Leeuw, P. T. Herwig, and A. R. Brown, *Synth. Met.* **102**, 998 (1999).
- <sup>4</sup>H. Sirringhaus, N. Tessler, and R. H. Friend, *Synth. Met.* **102**, 857 (1999).
- <sup>5</sup>B. S. Ong, Y. Wu, P. Liu, and S. Gardner, *J. Am. Chem. Soc.* **126**, 3378 (2004).
- <sup>6</sup>G. K. v. d. Wel and O. C. G. Adan, *Prog. Org. Coat.* **37**, 1 (1999).
- <sup>7</sup>B. D. Vogt, C. L. Soles, H.-J. Lee, E. K. Lin, and W.-L. Wu, *Polymer* **46**, 1635 (2005).
- <sup>8</sup>D. Li, E.-J. Borkent, R. Nortrup, H. Moon, H. Katz, and Z. Bao, *Appl. Phys. Lett.* **86**, 042105 (2005).
- <sup>9</sup>S. Hoshino, M. Yoshida, S. Uemura, T. Kodzasa, N. Takada, T. Kamata, and K. Yase, *J. Appl. Phys.* **95**, 5088 (2004).
- <sup>10</sup>T. Jung, A. Dodabalapur, R. Wenz, and S. Mohapatra, *Appl. Phys. Lett.* **87**, 182109 (2005).
- <sup>11</sup>H. G. O. Sandberg, T. G. Backlund, R. Osterbacka, and H. Stubbs, *Adv. Mater. (Weinheim, Ger.)* **16**, 1112 (2004).
- <sup>12</sup>Certain equipment, instruments or materials are identified in this paper in order to adequately specify the experimental details. Such identification does not imply recommendation by the National Institute of Standards and Technology nor does it imply the materials are necessarily the best available for the purpose.
- <sup>13</sup>A. Salleo, M. L. Chabinyk, M. S. Yang, and R. A. Street, *Appl. Phys. Lett.* **81**, 4383 (2002).
- <sup>14</sup>R. A. Street, A. Salleo, and M. L. Chabinyk, *Phys. Rev. B* **68**, 085316 (2003).
- <sup>15</sup>R. A. Street, J. E. Northrup, and A. Salleo, *Phys. Rev. B* **71**, 165202 (2005).
- <sup>16</sup>C. L. Soles, R. L. Jones, J. L. Lenhart, V. M. Prabhu, W.-L. Wu, E. K. Lin, D. L. Goldfarb, and M. Angelopoulos, *Proc. SPIE* **5039**, 366 (2003).
- <sup>17</sup>J. Veres, S. D. Ogier, S. W. Leeming, D. C. Cupertino, and S. M. Khaffaf, *Adv. Funct. Mater.* **13**, 199 (2003).