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Threshold voltage control in organic thin film transistors with dielectric layer modified by a genetically engineered polypeptide

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Precise control over the threshold voltage of pentacene-based organic thin film transistors was achieved by inserting a genetically engineered quartz-binding polypeptide at the semiconductor-dielectric interface. A 30 V range was accessed with the same peptide by adjusting the pH of the solution for peptide assembly while leaving other device properties unaffected. Mobility of $0.1\text{--}0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and on/off current ratio of $>10^6$ could be achieved for all devices regardless of the presence of the neutral peptide or the peptide assembled in acidic or basic conditions. This shift in threshold voltages is explained by the generation of charged species and dipoles due to variation in assembling conditions. Controlling device characteristics such as threshold voltage is essential for integration of transistors into electronic circuits. © 2010 American Institute of Physics. [doi:[10.1063/1.3459978](https://doi.org/10.1063/1.3459978)]

Significant research has been carried out in organic thin film transistors (OTFTs) due to their potential applications in low-cost, large-area electronic circuits, sensors, and displays.¹ Controlling device performance is essential for the integration of OTFTs into electronics. Typical methods of improving device performance include developing high-performance organic semiconductors, dielectrics, and electrodes, utilizing various device architectures, and tuning device properties via interface engineering.^{1,2} Important device parameters for OTFTs include driving voltage, stability, on/off current ratio, charge carrier mobility, and threshold voltage (V_T). Controlling V_T can yield higher circuit performance and lower power consumption in electronics.^{3,4} It can be shifted by modifying the dielectric with self assembled monolayers (SAMs) to shift V_T by tens of volts.^{5,6}

A less studied route in the pursuit of improved device performance involves integrating functional biological materials into OTFTs.⁷ Singh *et al.* demonstrated using deoxyribo-nucleic acid as a gate dielectric to produce memory effect.⁸ Malliaras *et al.* utilized a lipid bilayer in an organic electrochemical transistor for ion sensing.⁹ Bao *et al.* fabricated a transistor using biomaterials as part of the substrate and active layers.¹⁰ One set of biomaterials that have not been explored in OTFTs are genetically engineered peptides for inorganics (GEPIs).^{11,12} GEPIs have been studied for applications in interface engineering ranging from bionanotechnology¹³ to bionanomedicine.¹⁴

The conformation and structure of GEPIs are dependent on their composition and environment. By tuning the pH of its solution, the secondary structure of the peptide can be changed as a result of variation in hydrogen bonding and interaction between residues. Additionally, at pHs near the pK_{a} s of the C-terminus (1.8–2.5 depending on the residue),¹⁵ N-terminus (8.7–10.7),¹⁵ or side chain groups (the phenol side chain on tyrosine has a pK_{a} of ~10.5, for example) (Ref. 15) of the peptide, these groups can be protonated or

deprotonated, depending on the direction of pH adjustment.

Since GEPIs are composed of amino acids linked by peptide bonds, their structures can produce dipoles as a result of their amide bonds and side chains, and adjusting the pH to change peptide conformation or structure can affect the produced dipoles. Control over these conformational and structural properties combined with the surface binding abilities of GEPIs suggest that GEPIs can be explored for OTFT applications. One well studied GEPI, quartz binding polypeptide (QBP, PPPWLPYMPWWS, Fig. 1), strongly binds to silicon dioxide (SiO_2) surfaces.^{16,17} Here we demonstrate the use of QBP to modify the organic semiconductor/ SiO_2 interface in an OTFT and tune the threshold voltage through the control of the peptide assembling conditions.

Heavily doped p-type silicon substrates with a 300 nm SiO_2 dielectric (Montco Semiconductors) were cleaned by ultrasonication in acetone and isopropyl alcohol, followed by drying with nitrogen gas and UV-ozone cleaning. Substrates were further rinsed with acetone, isopropyl alcohol, ethanol, then dried with nitrogen gas. Aqueous QBP solutions (80 μM) were prepared at pHs of 1.3, 3.3, 3.8, 4.1, 4.4, 7.0, 9.5, 9.9, 10.2, and 10.5 by varying the concentration of acid (HCl) or base (KOH) in solution. The pHs of these solutions were selected based on peptide concentration and estimated pK_{a} values of the QBP termini as discussed previously.¹⁵ QBP solutions were drop-cast onto cleaned SiO_2/Si substrates and left to sit for 3 h. After peptide assembly the substrate was rinsed thoroughly with the similar concentration of acid or base it was assembled in, then dried with nitrogen gas. Surface characterization of QBP on SiO_2/Si was performed at ambient conditions via atomic force microscopy (Digital Instruments) and contact angle measurements (AST Products.) A separate experiment was performed where quantum dot-linked QBP was assembled on SiO_2/Si substrates in order to take fluorescence measurements (Nikon).

Top-contact pentacene based OTFTs were fabricated on top of QBP-modified substrates [Fig. 1(a)]. 50 nm pentacene

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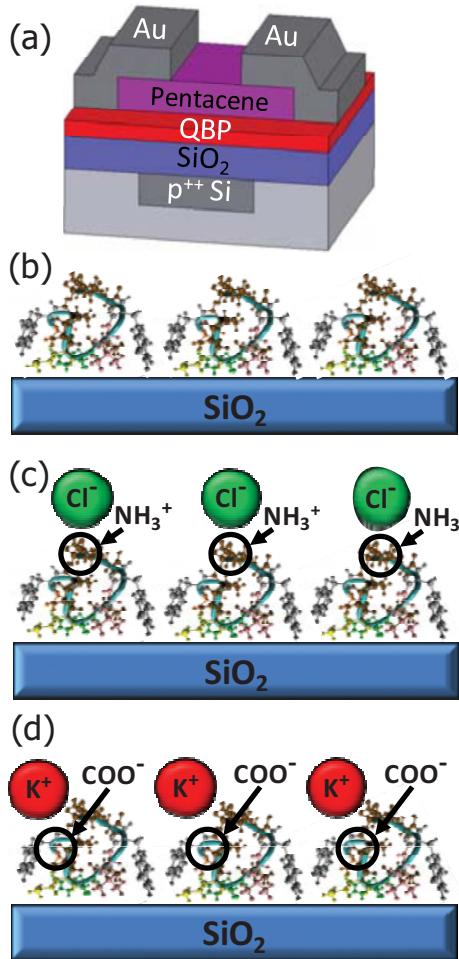


FIG. 1. (Color online) (a) Device schematic for peptide-modified thin film transistor. (b) When assembled in water, no ions are present to pair with peptide termini. (c) When assembled in HCl solution, the N-termini pair with chloride ions to produce a dipole pointing away from the substrate surface. (d) When assembled in KOH solution, the C-termini pair with potassium ions to produce a dipole pointing toward the substrate surface. Solvated model of QBP (PPPWLPYMPWPS) predicted using HYPERCHEM 7.5.

(99.995%, Aldrich) was deposited at $0.2\text{--}0.3 \text{ \AA s}^{-1}$ at 2×10^{-6} torr from a resistively heated quartz crucible onto the substrates maintained at room temperature. Interdigitated source and drain electrodes ($W=9000 \mu\text{m}$, $L=90 \mu\text{m}$, and $W/L=100$) were defined on top of the pentacene by evaporating a 50-nm-thick gold film at 1.0 \AA s^{-1} through a shadow mask from a resistively heated W boat at 2×10^{-6} Torr. All OTFT characterization was performed under ambient conditions using an Agilent 4155B semiconductor parameter analyzer. The saturation field-effect mobility was calculated in the saturation regime from the linear fit of $(-I_{ds})^{1/2}$ versus V_g using the saturation current equation: $I_{ds} = (W/2L)C_1(V_{gs} - V_T)^2$. V_T was estimated as the x-intercept of the linear section of the plot of $(-I_{ds})^{1/2}$ versus V_g . Reported electrical characteristics are an average of five devices from two different batches.

Minor changes in surface topography and roughness were observed by AFM before and after QBP assembled on SiO_2 . Fluorescence measurements indicated the presence of quantum dot linked QBP on the SiO_2/Si surface while unmodified SiO_2/Si did not fluoresce. A change in water contact angle was also found before and after surface modification (bare SiO_2/Si : $24.4^\circ \pm 2.0^\circ$; SiO_2/Si with

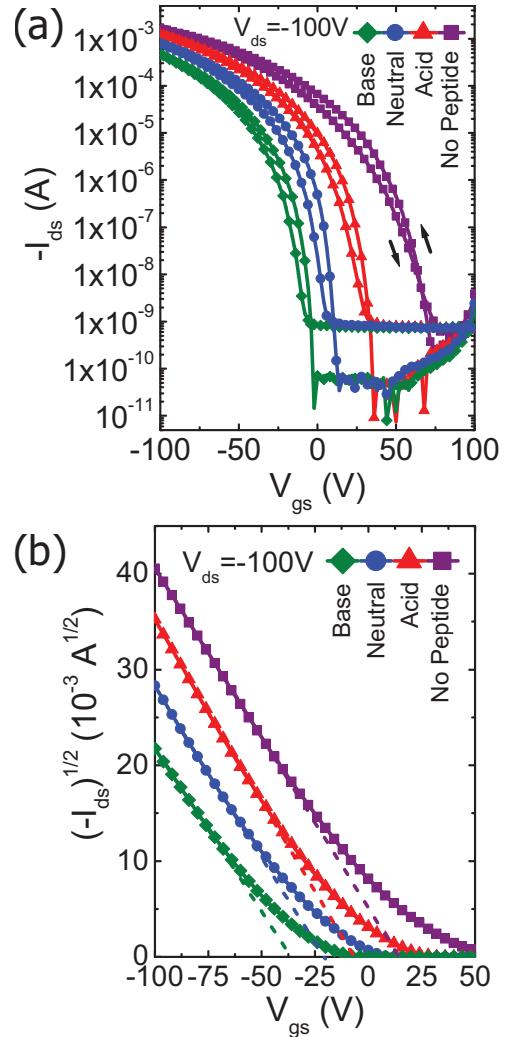


FIG. 2. (Color online) Representative (a) transfer curve characteristics ($-I_{ds}$ vs V_{gs}) and (b) $(-I_{ds})^{1/2}$ vs V_{gs} for pentacene OTFTs modified with QBP assembled on SiO_2 under basic (green diamonds), neutral (blue circles), and acidic (red triangles) conditions, and with no peptide (purple squares) provided for comparison. Acid and base concentrations are $2x$ that of peptide concentration for acid and base curves.

QBP: $50.8^\circ \pm 1.0^\circ$). This shows that QBP readily binds to the SiO_2/Si surface.

The transfer characteristics for top-contact pentacene based OTFTs fabricated on top of QBP-modified SiO_2/Si are shown in Fig. 2. A shift in V_T of about -30 V compared to unmodified SiO_2 was observed upon assembly of the peptide at neutral condition. From this point, a positive shift in V_T was observed when QBP was assembled in varying concentrations of HCl, and a negative shift in V_T was observed when QBP was assembled in varying concentrations of KOH (Figs. 2 and 3). Substrates prepared in acidic or basic assembling conditions without the presence of QBP showed similar V_T with respect to bare SiO_2 . A field-effect mobility of $0.1\text{--}0.2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and on/off current ratio of $>10^6$ could be achieved for all devices regardless of the presence of neutral QBP or the QBP assembled in acidic or basic conditions.

The initial shift in threshold voltage upon the introduction of QBP to the semiconductor-dielectric interface can be explained by the conformation with which QBP binds to the surface. The orientation of QBP on SiO_2 is such that the dipole within the QBP itself points toward the SiO_2 surface, a result of the orientation of the amide bonds and side chains

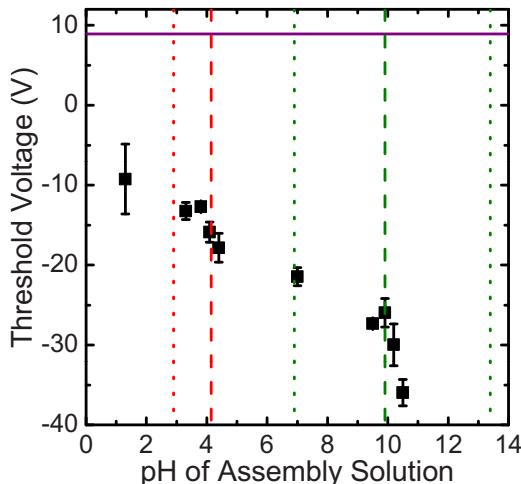


FIG. 3. (Color online) Threshold voltage vs assembling pH for QBP-modified thin film transistors. The horizontal line represents the mean threshold voltage for a nonpeptide modified transistor. The vertical lines represent critical pHs in acidic and basic conditions, respectively. Dashed lines represent equivalence points for the titration of peptide with acid ($\text{pH}=4.2$) or base ($\text{pH}=9.9$). Dotted lines represent the pK_a s of the C-terminus ($\text{pK}_a=2.9$), N-terminus ($\text{pK}_a=6.9$), and phenol side chain on tyrosine ($\text{pK}_a=13.4$).

within the peptide [Fig. 1(b)]. This generates positive dipoles at the semiconductor-dielectric interface that suppress hole accumulation, resulting in a negative gate voltage shift with respect to the bare SiO_2 . Shifts in V_T similar to the shift caused by QBP under neutral assembling conditions have also been reported by using SAMs.^{4,5} However, the ability to vary assembling conditions of the peptide offers an efficient method for controlling V_T .

Addition of acid to the assembling conditions of the peptide causes positive shifts in V_T of 5–15 V with respect to the initial V_T shift resulting from QBP binding to the SiO_2 surface under neutral assembling conditions. The magnitude of the shift became larger as the acidity of the QBP solution was increased. Addition of base yielded negative shifts in V_T of 5–15 V, larger with increasing basicity, with respect to the initial shift. These shifts can be explained by the presence of ion pairs on the QBP layer such as NH_3^+Cl^- or COO^-K^+ dependent on the acidic or basic assembling conditions. Based on the calculations using PROPKA server,¹⁸ the isoelectric point (pI) of QBP is 6.0, and the pK_a s of the C-terminus (Ser-12), N-terminus (Pro-1), and side chain group (the phenol side chain on tyrosine (Tyr-7) are 2.9, 6.9, and 13.4, respectively. When the peptide is assembled in acid (HCl), chloride ions (Cl^-) are present in solution. These Cl^- ions pair with the N-termini (NH_3^+) of the individual peptide units, which are positively charged in acidic solution. Cl^- is electronegative and a dipole is generated pointing away from the SiO_2 surface [Fig. 1(c)]. Analogously, when the peptide is assembled in base (KOH), potassium ions (K^+) are present in solution. These K^+ ions pair with the C-terminus (COO^-) of the peptide, which is negatively charged in basic solution. K^+ is electropositive and a dipole pointing toward the SiO_2 surface is generated [Fig. 1(d)]. These dipoles, generated at the semiconductor-dielectric interface shift V_T positively or negatively based on their direction. The dipoles generated by NH_3^+Cl^- ion pair shift V_T positively while those generated by COO^-K^+ ion pair shift V_T negatively. The ions do not appear to bind to the SiO_2 surface when no peptide is present

as there is no change in device performance if the bare SiO_2/Si substrate is soaked in HCl or KOH solution prior to pentacene and gold evaporation. It is important to note that there is only a small hysteresis seen in the electrical characteristics of QBP modified OTFTs which is independent of acidic or basic assembling conditions and comparable to that for bare SiO_2 [Fig. 2(a)]. This indicates that the presence of QBP as a charged species on the SiO_2 surface only acts to modulate the V_T via dipolar interactions while not acting as a charge-storing species.

In conclusion, we have demonstrated that GEPIs can form a modifying layer at the semiconductor-dielectric interface of OTFTs and adjust the threshold voltages of the devices. V_T can be further adjusted either positively or negatively by assembling QBP in acidic or basic conditions, and the degree of this change is tuned by adjusting the concentration of acid or base. Precise tuning of V_T is desirable for better integration of OTFT devices into electronic circuits. This approach of using a genetically engineered biomolecule as an agent for OTFT modification leads to precise control of device properties and shows the potential of GEPIs as a diverse tool for applications in electronics and surface chemistry.

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