Compensation Doping in Conjugated Polymers: Engineering Dopable Heterojunctions for Modulating Conductivity in the Solid State

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Limitations related to material properties and the fabrication process used for the creation of complementary metal oxide−semiconductor (CMOS)-based electronics have resulted in a drive to develop new materials and novel mechanisms to advance microelectronics.[1] For example, systems that provide a means for modulating resistance are being pursued for memory applications.[2] Recent reports have demonstrated that field-induced changes in carrier concentrations in amorphous semiconductors such as TiO_2 provide a useful mechanism for memory applications.[3,4]

Our groups recently demonstrated a memory design based on field-induced ion drift[5] resulting in spatial variation in doping and conductivity changes in conjugated polymer-based junctions. Through the use of this mechanism, it should be possible to increase the magnitude and tune the time scale of conductivity changes by combining semiconductors capable of electrochemical doping through the field-induced movement of ions. While the electrochemical modulation of conductivity and doping level in conjugated polymers in contact with an electrolyte is well-known,[6] achieving similar behavior in a solid-state junction in the absence of electrolyte requires a new approach. For example, a mechanism by which a single ionic species can cross an interface between two semiconductors, resulting in both becoming doped, would provide a means for modulating conductivity of the entire system in the solid state.

In this work, we used compensation doping[7] to create an intrinsic form of a conjugated polymer that contains a sufficient level of ions to support the doped form of the polymer upon removal of the compensating ion. Interfacing this form of conjugated polymer with another semiconductor capable of becoming doped upon uptake of the compensating ion allows a field-driven change in conductivity to be achieved.[8] As a result, this system is capable of rectification and storage of charge. The system is tunable through control of the energy difference between the undoped and doped states as well as the barriers to ion drift in both the bulk semiconductors and their interfaces.

To demonstrate this approach, we combined polypyrrole (PPy) containing immobilized dodecylbenzenesulfonate (DBS⁻) compensated by Li⁺ [PPy(Li⁺DBS⁻)][5,9] with tungsten oxide (WO_3)[10] in a state (i.e., −0.5 V vs Ag/AgCl) where both are undoped with low conductivities (see Scheme 1). Upon application of a positive voltage to the polymer relative to WO_3, the field drives mobile Li⁺ from the polymer into the WO_3, forming p-type polymer and n-type WO_3. Unlike a typical p/n junction between lightly doped (ppt to ppb) inorganic semiconductors with immobile dopants, these materials become heavily doped (∼30%) with mobile dopants, resulting the formation of polaron states in the band gaps[11] and no significant barriers at the interfaces (i.e., an ohmic contact).

Scheme 1. Band Structure Diagrams for a PPy(Li⁺DBS⁻)|WO₃ Heterojunction in the Undoped and Field-Induced Doped States
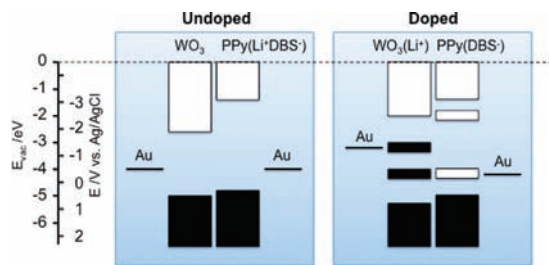
By creation of a heterojunction of conducting polymer and metal oxide on transparent indium tin oxide (ITO) contacts, which can also be separated into two components, it is possible to differentiate the faradaic current associated with doping of the two materials (and the movement of Li⁺ between them) from the total current passing through the junction when in contact as a function of applied field. When the two halves of the junction are biased in a two-electrode configuration separated by electrolyte, a bidirectional current is observed for the net redox process (Figure 1). Spectroelectrochemical measurements [Figure S2 in the Supporting Information (SI)] confirm the conversion of both materials to their doped state. Upon contact, the sum of the faradaic current and the ohmic current is observed (Figure 1), with the same net spectral changes (Figure S4 in the SI).

Higher conductivity occurs only when the compensating ions are driven in one direction. Hence, the junctions are rectifying. The threshold voltage of the junction is determined by the voltage difference required to drive the Fermi levels of the contacting electrodes to potentials where electrons are both injected and removed from the polaron states formed as a result of the movement
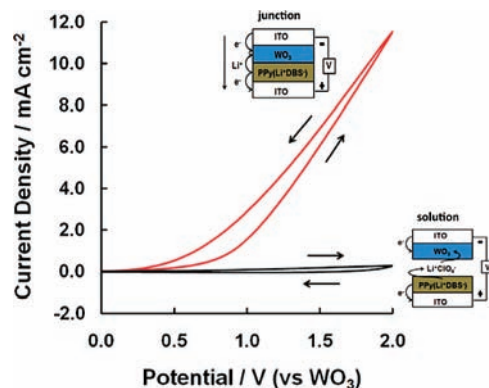

Figure 1. Current−voltage curves for PPy(Li⁺DBS⁻) vs WO₃ on ITO at a scan rate of 10 mV/s. Black trace: electrodes separated in 0.1 M propylene carbonate LiClO₄ solution. Red trace: sandwiched electrodes.

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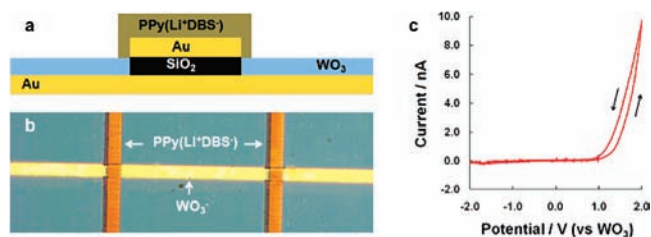‡ Department of Electrical and Computer Engineering.

Figure 2. (a) Schematic diagram of a PPy(Li$^+$DBS$^-$)|WO$_3$ heterojunction on a Au crossbar electrode. (b) Image of a pair of PPy(Li$^+$DBS$^-$)|WO$_3$ heterojunctions on crossbar. The vertical brown bar contains PPy$^+$(Li$^+$DBS$^-$), and the horizontal yellow bar contains WO$_3$. (c) Current−voltage curves for PPy(Li$^+$DBS$^-$) with respect to WO$_3$ on a Au crossbar at a scan rate of 10 mV/s.

of the compensating ions. Junctions of this type are therefore dependent on the thermodynamics of doping of the two materials involved and can be tuned by changing the semiconductors involved (Figure S7 in the SI). Tuning can also be achieved by setting the Fermi levels of the two materials in the presence of electrolyte prior to biasing in the solid state. For example, if the electrochemical potential of both materials in Figure 1 is shifted 0.5 V more negative (upward in Scheme 1), a larger applied voltage (on the polymer side) is required to reach its conducting state. This shifts the threshold voltage in the positive direction (Figure S7 in the SI), changing the threshold voltage.

Under these conditions, the movement of ions is expected to be reversible, and the time scale should depend on the mobility of the compensating ion and any barriers to motion at the interface. For example, residual electrolyte in the sandwich structure speeds up the process by removing limitations on ions moving only through physical contacts associated with surface roughness and the associated void spaces. Regardless, in the dry state, the system exhibits the expected field dependence of the ion drift (Figure S9 in the SI).

The operating principles and fabrication of these junctions have desirable scaling properties, and the junctions can be created on existing crossbar structures. Electrodeposition allows precise control over the deposition without the need for complicated and costly sputtering systems. Therefore, this approach removes junction fabrication from the fab line, avoiding issues related to introducing new procedures into strictly controlled CMOS fab environments. The approach also eliminates the need for evaporation and lithographic processing of contacting electrodes atop the active polymer, which often result in defects and shorts in ultrathin organic films.

To demonstrate the versatility of this approach, junctions were replicated on a prefabricated 10 × 10 crossbar array with a 600 nm SiO$_2$ spacer layer (Figure S10a,c in the SI). A 120 nm WO$_3$ layer was deposited on the bottom electrodes, and the polymer was deposited with a bipotentiostat at +0.65 V versus Ag/AgCl on the top electrodes while the bottom WO$_3$ electrodes were biased at −0.5 V (i.e., in their n-type conducting state). In this way, a WO$_3$ electrode depolarized the adjacent polymer electrode once a contact was made, stopping deposition of the polymer. The process was followed by monitoring current as a function of time; it transitions from a lower faradaic current during polymer deposition to a larger short-circuit current (Figure S10b in the SI). The resulting array of

junctions is illustrated schematically in Figure 2. The final step involved biasing the two electrodes to the same electrochemical potential where both materials are undoped (i.e., −0.5 V vs Ag/AgCl). Individual junctions were addressed by biasing a selected row/column combination. The current voltage curve of a single junction is shown in Figure 2c.

The results herein represent a proof of principle of a new approach for designing dopable semiconductor heterojunctions whose conductivities can be modulated by field-induced ion drift. In addition to the versatility and tunability of this design, the simplicity and reproducibility of fabrication make it ideal for integration with existing electronic platforms.

Supporting Information Available: Details on the deposition, electrochemistry, and spectroelectrochemistry of both the conducting polymer and tungsten oxide and on the temporal behavior of junctions. This material is available free of charge via the Internet at http://pubs.acs.org.

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