

# Optimizing Polymeric Field-Effect Devices

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## Abstract

Field-effect devices were fabricated with poly(3,4-ethylenedioxy-thiophene)/poly(4-styrenesulfonate) (PEDOT/PSS) as the active material. Normally in a conductive “on” state, these transistor-like devices switch to a less conductive “off” state at an applied gate voltage in  $< 1$  second; a switch back to the “on” state requires considerable more time (1 min. – 1 hr.). The physical model for these devices suggests that this recovery time might improve if the channel length is minimized. A channel length  $\approx 5000$  Å was achieved using vertical channel construction, but device performance did not improve. It is therefore proposed that recovery time is mainly governed by ion motion normal to the gate, while ion motion parallel to the gate is ancillary.

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## 1 Introduction

### 1.1 Field-Effect Transistors

At the beginning of the twentieth century, vacuum tubes were used to amplify telephone signals as they travelled across the country. However they were huge, unreliable, and produced too much heat. Shortly after World War II, Bell Laboratories, a branch of American Telephone & Telegraph (AT&T), organized a group of scientists to develop a solid-state device to replace vacuum tubes. John Bardeen, Walter Brattain, and William Shockley developed the technology, and in 1948 Bell Laboratories unveiled the *transistor*, an electronic device used either as an amplifier or an electrical switch. Transistors soon replaced vacuum tubes in everything from phone lines to radios to computers.[1] Since then the computer industry has grown exponentially, and transistors continue to be an important area of research.

Today there are a variety of transistors, but the most common is the field-effect transistor (FET, see Fig. 1). These transistors operate by controlling the current through a semiconductor using an electric field. The current runs from a source electrode through a semiconducting material to a drain electrode. The voltage difference between a third, insulated gate electrode and the source generates an electric field that essentially depletes the semiconducting region of its charge carriers and turns the current off. Therefore, the gate voltage ( $V_g$ ) can control (on/off) the source-drain current ( $I_{sd}$ ).

### 1.2 Conducting Polymers- PEDOT/PSS

Conductivity is the ability of a substance to conduct current and can best be explained using Molecular Orbital Theory (MOT). The electrons of atoms in free space occupy atomic orbitals that have discrete energy levels. However, few atoms are so isolated. The interactions between atoms in solids creates *molecular*

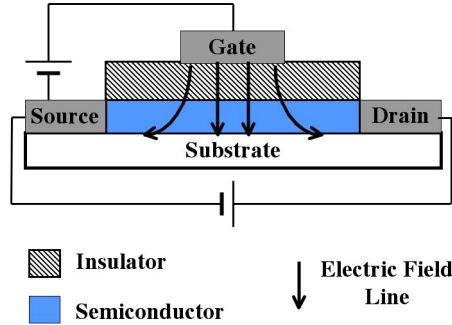


Figure 1: General schematic of a field effect transistor with a conventional planar design. The distance between the source and the drain is the *channel length*.

*orbitals*. These orbitals generate regions of tightly packed energy levels called *bands* because the Pauli Exclusion Principle prevents two electrons in an atom from having the same quantum number. Low energy electrons occupy the *valence* band and are bound to the atom. High energy electrons occupy the *conduction* band and have enough energy to escape the atom and move freely. The differences in energy between orbitals (i.e. 1s orbital and 2s orbital) creates *band gaps* which are forbidden regions where no electron can reside.

A material's physical properties are determined by the size of its band gaps. For insulators, such as glass, the gap is large and very few electrons are able to reach the conduction band. For semiconductors, such as silicon, the gap is relatively small and a few electrons are able to absorb enough energy and jump to the conduction band. As a result, semiconductors can be insulators or conductors depending on the conditions. For conductors, such as silver, there is no gap at all, the two bands overlap and there are always electrons in the conduction band. Fig. 2 compares the bands of these materials.

A semiconducting substance can be made more conductive via doping. Doping is the process by which a substance is injected with dopants. A dopant is a substance that changes the number of electrons in the conduction or valence bands and affects the semiconductor's conductivity. For example, pure silicon is a poor conductor because the valence band is completely filled. However, if it is treated with a Group V element such as phosphorus, then it becomes conductive. The phosphorus atom has five electrons compared to silicon's four, and the extra electron has no place to go but into the conduction band. The electron is a *negative* charge so this is known as n-type doping. Another method of doping is when a semiconductor is doped with a Group III element such as indium. The indium atom has three electrons compared to silicon's

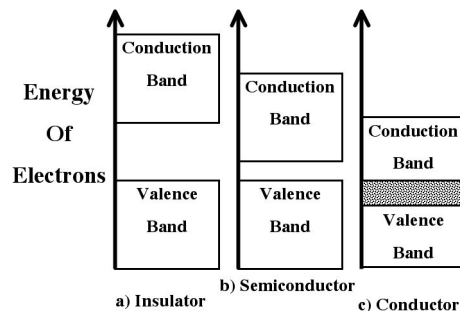


Figure 2: The valence and conduction bands of various solids. Electrons cannot occupy the forbidden region between the bands.

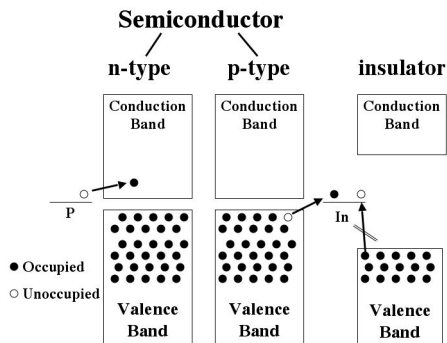


Figure 3: N-type semiconductors are doped with a Group V element and the conduction band is partially filled. P-type semiconductors are doped with Group III element and the valence band is partially empty. Insulators cannot be easily doped.

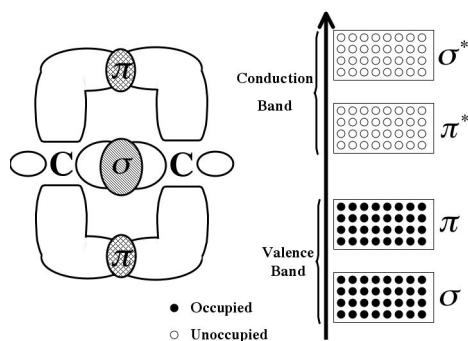


Figure 4: (Left) The  $\sigma$  and  $\pi$  bonds that form between two  $sp_2$  hybridized carbon atoms. (Right) The conduction and valence bands created by these bonds; the  $\pi$  and  $\sigma$  bonds are lower energy *bonding* orbitals and the  $\pi^*$  and  $\sigma^*$  are higher energy *anti-bonding* orbitals.

four, and this creates a *hole* in the valence band. This hole is essentially a net *positive* charge that can be conducted through the material. This is known as p-type doping. Fig. 3 illustrates the various methods of doping.

Organic polymers also have valence and conducting bands. A common polymer bond is the alternating single-double-single carbon chain. These carbon atoms are  $sp_2$  hybridized, and these orbitals form strong  $\sigma$  bonds. The remaining  $p_z$  orbitals form weaker  $\pi$  bonds. This  $\pi$ -conjugated polymer backbone is not naturally conductive because the valence band is completely full. However, like silicon it can be doped to become a p-type conductor. Fig. 4 shows how two carbon atoms bond and the energy bands that these bonds create.

The first intrinsic electrically conducting polymer, doped polyacetylene, was reported in 1977.[2] Organic polymer blends have since been developed and reported to have conductivity comparable to good metals.[3, 4] For a conductivity comparison see Table 1.

The co-polymer poly(3,4-ethylenedioxy-thiophene) (PEDOT) doped with poly(4-styrenesulfonate) (PSS) has recently generated interest for its potential application.[5] PEDOT is not intrinsically conductive; the  $\pi$ -conjugated carbon chain does not conduct. However, when doped with PSS it becomes a p-type conductor (See Fig. 5).

Type	Material	Purity	Conductivity ( $S \cdot cm^{-1}$ )
Inorganic	Ag	pure	$10^5$
	Si	pure	$4.3 \times 10^{-6}$
	Si	doped	1-2
Organic	polyphenylenevinylene	doped	$10^4$
	polypyrrole	doped	500-7500
	PEDOT	doped	$2 \times 10^{-2}$

Table 1: Comparison of conductivity for organic and inorganic, doped and undoped materials.

### 1.3 Polymeric FET's

The versatility and low cost fabrication of organic electrical devices has generated much interest in recent years. A crucial step in creating organic electrical devices is the development of organic FETs. Several FETs, based on small organic molecules such as pentacene, have been developed using relatively expensive fabrication techniques.[6] However, such techniques defeat the purpose of organic devices. Recently several field-effect devices, based on large organic molecules such as polymers, have been developed using inexpensive construction processes.

One such polymeric device utilizes the highly conductive PEDOT/PSS polymer mixture as the semi-conducting material. Devices with planar designs similar to Fig. 1 and a channel length of  $40 \mu m$  (width of a razor blade) have been reported to have a current ratio ( $I_{on}/I_{off}$ ) exceeding  $10^4$  at room temperature for high gate voltages.[7] These devices have a relatively fast switching-off time of  $< 1$  second but a relatively slow switching-on time (1 min. - 1 hr., See Fig. 6).

Ion motion is the suspected cause of this slow recovery. When an electric field penetrates PEDOT/PSS, the positively charged  $H^+$  ions are forced to the polymer's extremes. This essentially depletes the polymer of its dopant. Without the  $H^+$  dopant, PEDOT is not conductive and therefore  $I_{sd}$  turns off. Ion motion is relatively fast in an electric field so  $I_{sd}$  switches off relatively quickly. When the electric field is then turned off, the  $H^+$  ions *slowly* diffuse back into the polymer and therefore  $I_{sd}$  switches back on slowly.

It is possible to optimize the recovery time by changing the geometry of the device. If ions diffusing parallel to the gate had a shorter distance to travel (i.e. shorter channel length), then the polymer would be re-doped more quickly (See Fig. 7). One method of decreasing channel length is utilizing a vertical design as opposed to the conventional planar design; instead of building the source and drain next to each other, they are built on top of each other. In this vertical design the two electrodes are separated by a thin insulating layer, and the channel length is defined as the thickness of the insulating layer. This is known as vertical channel (VC) construction. VC field-effect devices have been fabricated using PEDOT/PSS as the active material, however their time dynamic was not reported.[8]

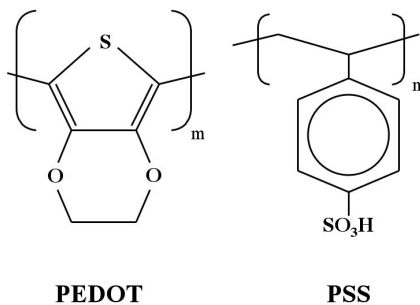


Figure 5: The chemical structure of PEDOT and PSS. An  $H^+$  disassociates from the PSS and dopes the PEDOT polymer backbone.

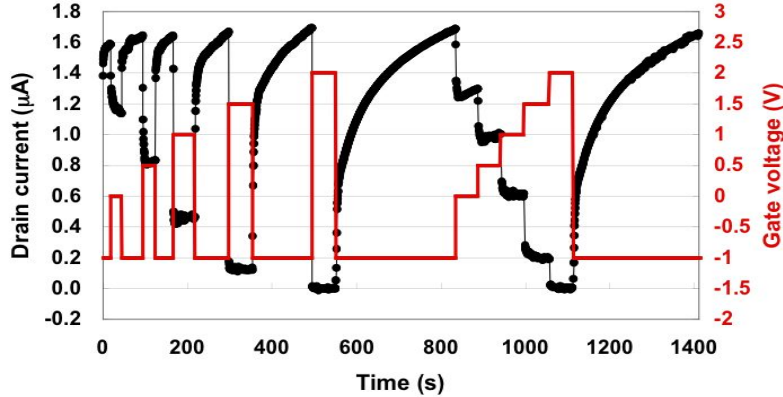


Figure 6: Variation of  $I_{sd}$  with  $V_g$  modulation as a function of time.

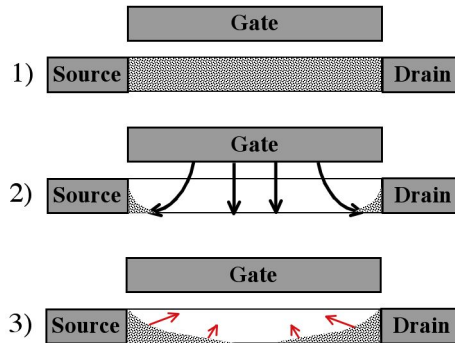


Figure 7: (1) The  $H^+$  ions permeate the entire active material when  $V_g$  is off. (2) When an electric field is applied, the ions are forced to the polymer's extreme. (3) When the electric field is turned off, the ions slowly diffuse back into the polymer. A smaller channel length could potentially optimize the recovery time.

## 2 Experiment

### 2.1 Materials & Fabrication

Devices were constructed on glass substrates pre-coated with indium tin oxide (ITO). Polymer layers were fabricated using a Headway Research Inc., Photo-Resist spin coater. In this process a substrate is mounted on the spin coater and a polymer solution is spun off, leaving a polymer film. The spin rate, duration of the spin, and the concentration of the solution all affect the thickness of the film. The active polymer solution used to construct the devices was a mixture of PEDOT/PSS (80% by wt., Aldrich, Baytron P) and ethylene glycol (20% by wt.). Ethyleneglycol linearizes the polymer chains and increases conductivity to as much as  $20 S \cdot cm^{-1}$ . A drop of dodecylbenzene sulfonic acid (Acros Organics) was added for adhesive purposes. This mixture is very stable to 200 °C annealing. The polymeric insulating layer was fabricated using a mixture of polyvinylphenol (PVP) (Aldrich, mol. wt. = 2000) dissolved in isopropanol. PVP layers were strengthened by annealing above 150 °C. Materials were massed with a Mettler H54AR balance. Metal layers were fabricated using thermal evaporation. In this process a vacuum is pulled inside a bell jar to  $8 \times 10^{-6}$  torr using at first a mechanical pump and then a diffusion pump. A heated boat is then placed at the bottom of the bell jar and used to evaporate metal onto an inverted substrate mounted at the top of the

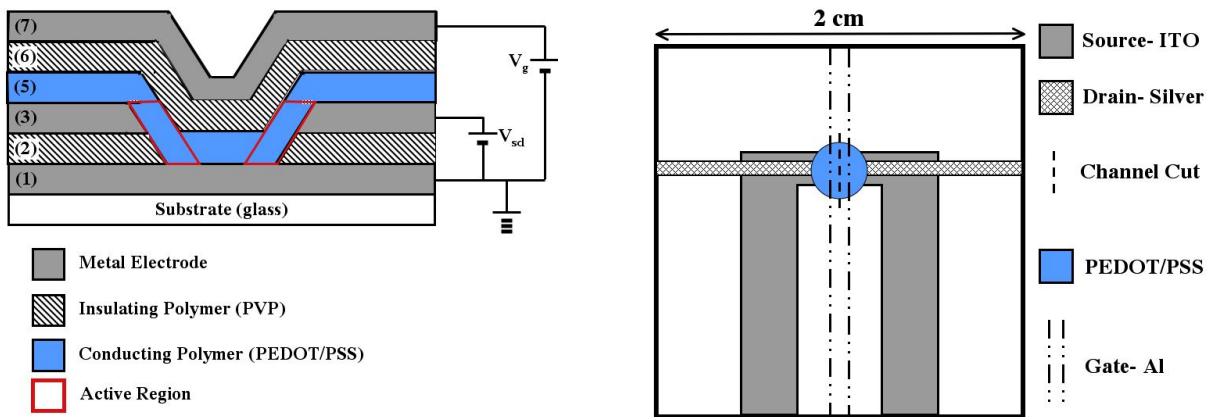


Figure 8: (Left) Cross section of a vertical channel field-effect device. The channel length is defined as the thickness of the insulating layer (2) between the source and drain electrodes (1,3). There are two transistors for each substrate: one on each side of the channel. Note that this diagram is ideal. (Right) Topview of a vertical channel field-effect device on a square glass substrate. PVP layers cover the entire substrate.

bell jar. All layer thicknesses were directly measured using a Tencor Alpha-Step 500 surface profiler.

Of the ten batches of VC field-effect devices made over a seven week time period, only the last exhibited transistor-like behavior; the first six batches refined fabrication techniques via trial and error. Each layer is fabricated individually, resulting in a seven step process that took approximately three days. The planar patterning of the layers minimized the probability of shorts and optimized contact location. Fig. 8 is the VC device design.

Step-1 The U-shaped source was etched in the ITO. The substrates were cleaned with methanol, masked with scotch tape, and soaked in a 1.0 molar HCl bath for one hour. The acid etched away the unmasked ITO. The substrates were then removed from the bath, cleaned with distilled water, unmasked, and air dried with pressurized nitrogen gas.

Step-2 The first PVP insulating layer was spin coated over the entire substrate at 1500 RPM for 30 seconds using a 10% solution by weight. This layer was then annealed for 3 hours at 160 °C at room pressure resulting in layer  $\approx 5000 \text{ \AA}$  thick.

Step-3 The silver drain was evaporated at a rate of  $< 2.0 \text{ \AA/s}$  to a thickness of  $\approx 400 \text{ \AA}$ . A teflon mask patterned the silver as a thin strip overlapping the ITO source.

Step-4 The channel was cut with a clean razor blade. The razor cut through the silver drain and PVP insulating layer but not through the ITO source.

Step-5 The active material, PEDOT/PSS, was spin coated over the channel cut at a rate of 3000 RPM for 60 seconds and allowed to dry at room conditions, yielding a layer  $\approx 1.1 \mu\text{m}$  thick.

Step-6 The second PVP insulating layer was spin coated over the entire substrate at 3000 RPM for 60 seconds using a 5% solution by weight. This layer was not annealed but allowed to dry at room conditions resulting in a layer  $\approx 1000 \text{ \AA}$  thick.

Step-7 The aluminum gate was evaporated at a rate of  $< 2.0 \text{ \AA/s}$  to a thickness of  $\approx 400 \text{ \AA}$ . A teflon mask patterned the aluminum as a thin strip overlapping the channel.

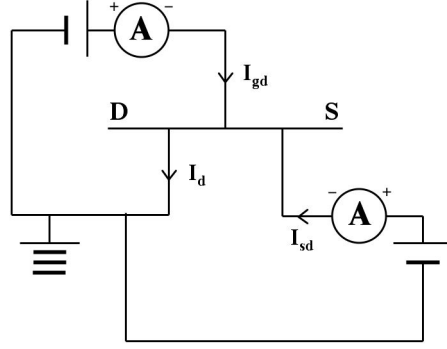


Figure 9: Schematic of the circuit used to test the field-effect devices.

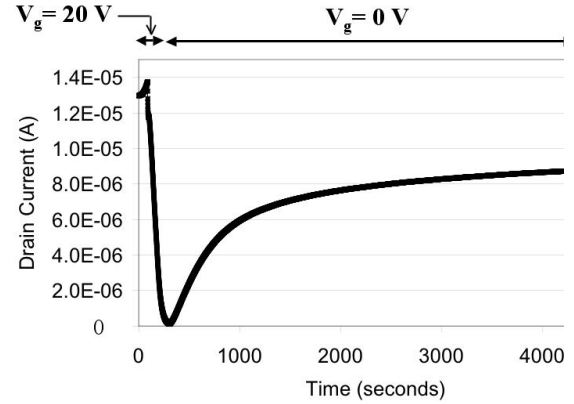
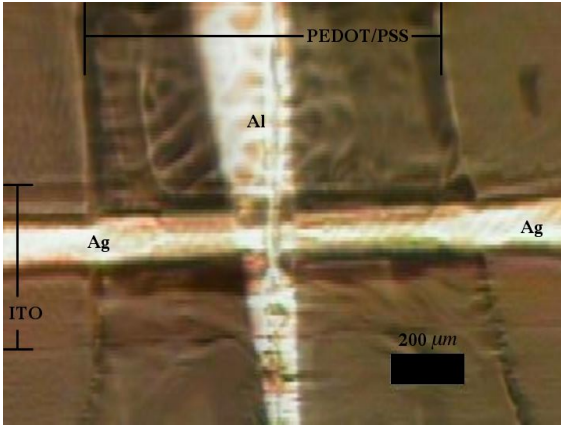


Figure 10: (Left) Picture of a VC field-effect device. (Right) The  $I_{sd}$  of the device as a function of time.

## 2.2 Measurement

$I_{sd}$  was measured as a function of time while  $V_g$  was varied. Fig. 9 is the standard FET circuit schematic that was used to test the devices. The currents were measured and the voltages were supplied using two Keithley 487 picoammeter/voltage sources.

## 3 Results

Through collaborative efforts a working batch of VC field-effect devices were realized and analyzed (See Fig. 10). A small channel length was successfully obtained:  $\approx 5000 \text{ \AA}$ , 80 times closer than previous devices. Devices exhibited current on/off ratios approaching  $10^4$  at room temperature. Switch off speed was  $< 1$  second but recovery rate was on the order of minutes.

## 4 Discussion

This result calls for scrutiny of the physical model for PEDOT/PSS based field-effect devices. The recovery time of these devices depends on the the diffusion of  $H^+$  ions. It was hypothesized that the recovery

rate would improve if the ions diffusing parallel to the gate had a shorter distance to travel. However, this was not observed. A possible explanation is that the theoretical devices are too ideal and actual devices are much more irregular. Nonetheless, even if the functioning devices were not ideal, some change in recovery time should be observed. Therefore, I propose that the recovery rate is mainly governed by ion diffusion in the direction normal to the gate; a change in the channel length would have a minimal effect on the recovery time.

## 5 Future Research

The potential of inexpensive organic electronic devices has spawned interest in many low cost fabrication techniques. Electrostatic self assembly (ESA) is a process by which polymer layers are built by dipping a substrate alternately between aqueous cationic and anionic solutions. These highly ordered, microscopic bi-layers ( $\approx 40 \text{ \AA}$ ) allow control of macroscopic device characteristics. Ink-jet printing is being investigated as a method of creating polymer layers. I took the liberty of designing a completely polymer field-effect device using either ESA or ink-jet printing.

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## References

- [1] [www.pbs.org/transistor/](http://www.pbs.org/transistor/)
- [2] C.K. Chiang, C.R. Fincher, Jr., Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis, S.C. Gau, and A.G. MacDiarmid, *Phys. Rev. Lett.* **39** (1977) 1098.
- [3] R.S. Kohlman, J. Joo, and A.J. Epstein, in: *Physical Properties of Polymers Handbook*, edited by J.E. Mark, (AIP Press, 1996), Chapter 34 453.
- [4] R.S. Kohlman and A.J. Epstein, in: *Handbook of Conducting Polymers*, edited by T.A. Skotheim, R.L. Elsebaumer, and J.R. Reynolds (Marcel Dekker, Inc., New York 1998) 85.
- [5] L. B. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, and J. R. Reynolds, *Adv. Mater.* **12**, 481 (2000).
- [6] A. R. Brown, A. Pomp, D. M. de Leeuw, D. B. M. Klaassen, E.E. Havinga, P. Herwig, and K. Müllen, *Applied Physics* **79**, 2136 (1999).
- [7] A. J. Epstein, Fang-Chi Hsu, Nan-Rong Chiou, Vladimir N. Prigodin, *Current Applied Physics* **2** (2003) 339-343.
- [8] R. Parashkov, E. Becker, S. Hartmann, G. Gineva, D. Schneider, H. Krautwald, T. Dobbertin, D. Metzendorf, F. Brunetti, C. Schildknecht, A. Kammoun, M. Brandes, T. Riedl, H. Johannes and W. Kowalsky, *Applied Physics* **82**, 4579 (2003).