

# **Polymer Circuits**

**Name: Chetan Mistry**

**Date: 2001/04/09**

**Student No: 951646530**

**Professor: Khoman Phang**

**Course: ECE1371 – Advanced topics in analog circuits**

## Introduction

The study of organic materials to create field effect transistors has recently emerged and is gaining much interest. Polymer materials are studied extensively in the optical domain as an electro-optic material (for electro-optic modulators) [1], photodetectors, and some light emitting applications [1,2]. It is only in recent years where polymer materials were studied for their charging carrying capability and their application into field effect transistor devices. Obviously all-polymer electronic devices are currently in their infancy, much like semiconductor devices when they first appeared. As a result, the performance of these devices is in no way comparable to current state of the art semiconductor devices.

However, all-polymer devices have a few possible appealing advantages. Firstly, all-polymer devices have the potential to be produced at very low cost because of their ease of manufacturability, and fewer and simpler processing steps compared with semiconductor devices [2,3,]. Secondly, polymer devices offer the ability of material flexibility [3,11,12]. Of course this advantage can only be exploited if the environment demands flexible material. Lastly, polymer devices may prove to be an excellent contender for the interconnection technology between the electronic and optical domains. There already exists a great interest in polymer material for optical devices, so in some instances it may be easier to interconnect two polymer devices rather than a polymer and semiconductor device.

Processing technology and material properties are two of the major issues researchers are still struggling with in order for polymer devices to compete with amorphous silicon devices. Polymer circuits are poised to compete with hydrogenated amorphous silicon devices in the application of switching devices for active matrix liquid crystal displays [4,6,7,9,11,12]. Low cost applications, such as identification tags or barcodes, have also been discussed in the literature [5,8,9,10,12]. In these applications the flexible nature, ease of application onto plastic surfaces, and the disposable nature of polymer circuits make them ideal for it use compared to those of rigid silicon or amorphous silicon devices.

## Polymer Materials

Polymer materials are basically repetitive chains of carbon-based molecules. Considering that these types of materials can be chemically manipulated to create new synthetic materials, there have been many organic compounds that researchers have studied as possible materials for electronic devices. Regioregular polymers are an example of these types of materials, an example of which is shown in figure 1.

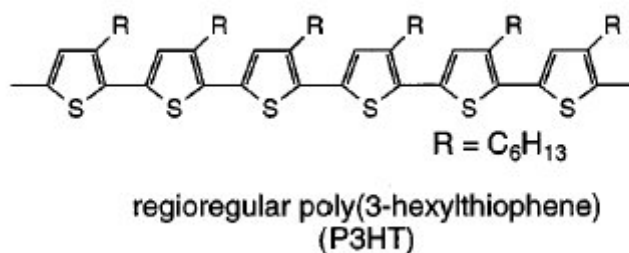


Figure 1: Chemical structure of regioregular poly(3-hexylthiophene) [13].

The polymer shown in figure 1 is regioregular poly(3-hexylthiophene) which was used by Z. Bao and colleges in order to achieve field-effect mobilities between  $0.01$  to  $0.04 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  for p-channel polymer field-effect transistors (FETs)[13]. In their paper they achieved on/off current ratios of up to  $10^3$ . However, these characteristics are still no match to amorphous silicon materials that boasts field-effect mobilities from  $0.05\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  and greater than  $1\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  and on/off current ratios greater than  $10^6$ . Another research group, using the same material, created FETs with mobilities between  $0.05$  and  $0.1\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  with on/off ratios greater than  $10^6$  [2]. H. Sirringhaus, *et. al.* attributed this improved performance to optimized device fabrication, namely improved polymer ordering. Many researchers have found that the structure of the polymer material used in field-effect transistor devices has a direct impact on the mobility of the charge carriers, the more ordered the polymer the higher the mobility [14].

Another type of material that is also studied for thin-film transistor devices are organic-inorganic hybrids such as perovskite,  $(C_6H_5C_2H_4NH_3)_2SnI_4$ . C. R. Kagan and colleges used this material to create a p-channel thin-film transistor with alternating layers of organic-inorganic

material [11]. Figure 2 shows a schematic of the device structure that they used to test this material along with the orientation of the layered active material.

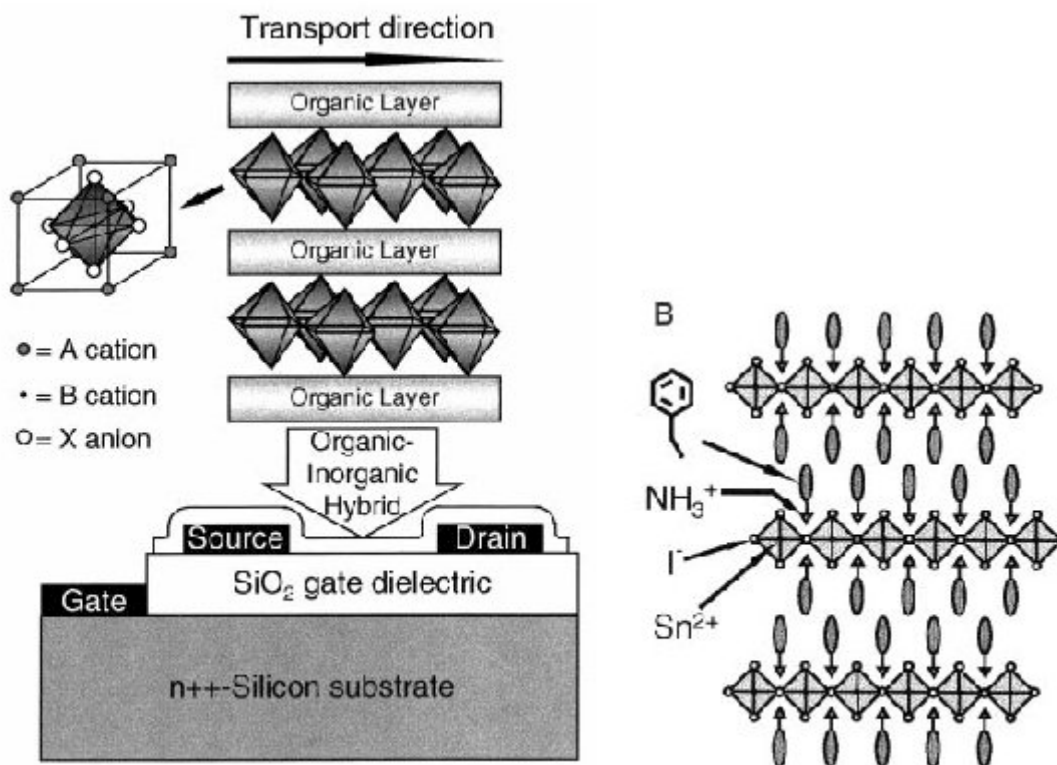


Figure 2: Schematic of a hybrid organic-inorganic based transistor device [11].

The layered channel material was processed only from the perovskite polymer material as described in their paper. They had created several devices with different characteristics including various gate oxide thicknesses, and different metal contacts. The group had found that their devices attained field-effect mobilities from  $0.55 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$  to  $0.62 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , along with on/off current ratios greater than  $10^4$  [11]. This group had also found that the field-effect mobility was a function of the gate voltage, the higher the gate voltage the lower the carrier mobility. This is not a phenomenon held strictly against organic-inorganic materials, it was also found in all organic devices and amorphous silicon devices.

Complementary FETs would be ideal for the applications sought after for polymer circuits in order to reap the benefits of CMOS technology; namely lower power consumption and

faster switching speeds. The majority of polymer materials, that are studied for electronic devices, are limited to p-channel transistors because most polymer materials act as p-type semiconductors. All of the transistors made from polymer materials are enhancement mode devices, meaning they are “normally-on” devices and require a voltage to turn them off. There are polymer materials that act as n-type semiconductors, such as C<sub>60</sub>[5,7] and perlenetetracarboxylic dianhydride (PTCDA)[5], however their performance characteristics are very poor (very low mobilities) or degrade very quickly when exposed to air or moisture.

One proposed solution to creating complementary devices was a hybrid polymer/amorphous silicon complementary structure studied by A. Dodabalapur *et. al.*[7]. In their paper the authors used  $\alpha$ -hexathienylene ( $\alpha$ -6T) as the polymer p-channel material and a well-established amorphous silicon n-channel material to obtain a complementary inverter device. The authors optimized the individual transistors for material properties and device dimensions in order to obtain similar drain currents. Figures 3a and 3b show the device layout and transfer characteristics obtained through experimentation and simulation.

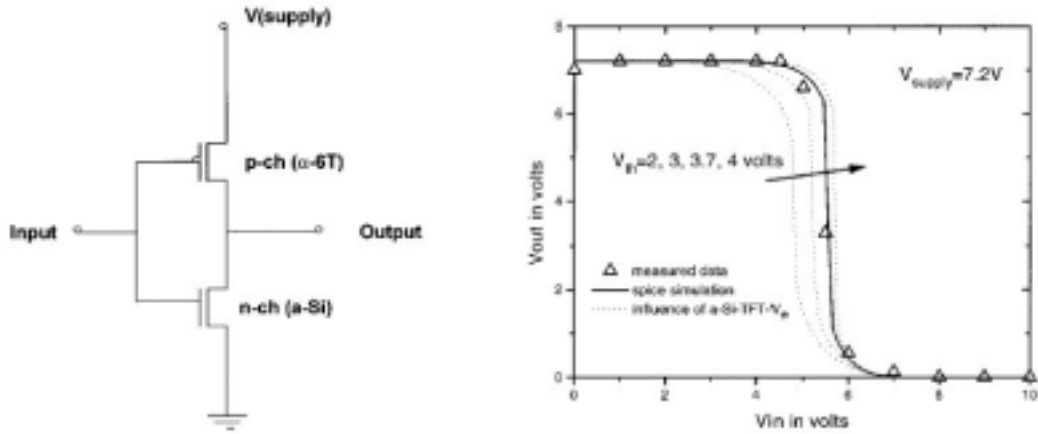


Figure 3: (a) Schematic of a complementary inverter using a polymer and amorphous silicon device. (b) Results of inverter experiments and simulations [7].

The authors achieved field-effect mobilities of 0.1 to 1 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for the amorphous silicon devices and mobilities of 0.01 to 0.03 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> for the  $\alpha$ -6T polymer devices; which are typical values for these materials. However good the performance of such a hybrid

complementary device is, the trade-off lies in the fact that now a crystalline material is used instead of an all-polymer approach. Meaning that low cost, ease of processing, and flexible devices is given way to functionality. I do not believe the authors investigated the switching speeds of this complementary arrangement, which would have been good to see the results of.

Eventually, stable n-channel materials were found and integrated into complementary transistor devices. A. Dodabalapur and his colleges did some of the earliest work on all-polymer complementary transistor devices. In a 1996 paper the group used an n-channel material of naphthalene tetracarboxylic dianhydride (NTCDA), which was shown to provide the highest mobilities for n-channel devices at that time [5]. Along with several p-channel active materials such as copper phthalocyanine,  $\alpha$ -sexithiophene, and pentacene the group created and tested several complementary FET inverter devices. Using sub optimal material processing they obtain transfer characteristics as shown in figure 4. The reason for the poor transfer functions obtained by their devices were attributed to leakage current due to the fact that the polymer channel layers was not patterned between the source and drain contacts (the polymer covered the entire region of the device).

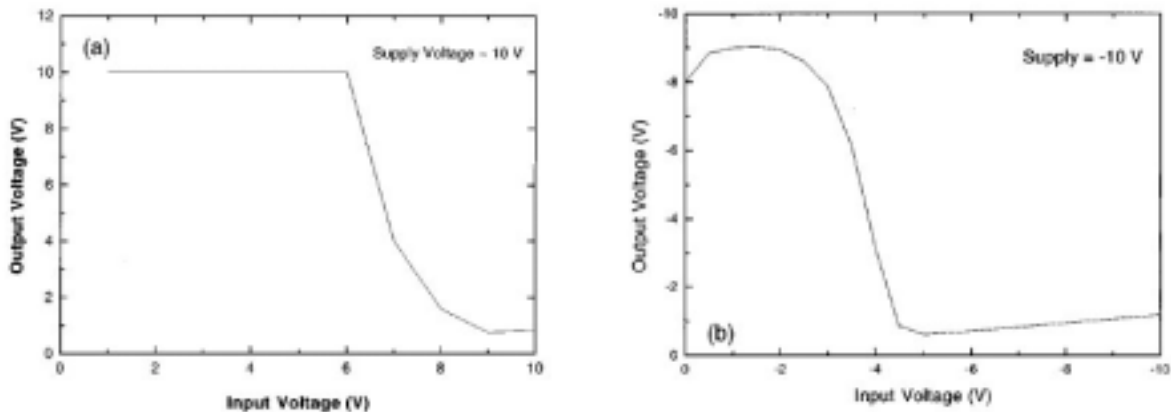


Figure 4: (a) Transfer characteristics of a polymer based inverter with the p-channel device as the load. (b) Transfer characteristics of an inverter with the n-channel device as the load [5].

In more recent work, Y. Lin, *et. al.* used  $\alpha$ -6T for the active p-channel material and hexadecafluorophthalocyanine ( $F_{16}CuPc$ ) for the active n-channel material to create complementary FET inverters, which were ultimately used in a ring oscillator structure, which

will be discussed in a later section [10]. Figure 5 shows a schematic of the transistor structures that they utilized.

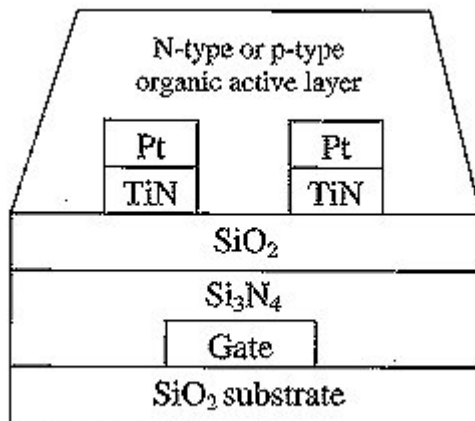


Figure 5: Schematic of a polymer transistor device, which can be used as both a p-channel, and an n-channel device depending on the polymer used [10].

This “upside-down” geometry was used so as to limit the amount of processing for the polymer materials thereby optimizing the device performance, which was also found by G.H. Gelinck, *et. al.* [15]. Ultimately, the authors used a different p-channel active material,  $\alpha$ ,  $\omega$ -dihexyl quinquethiophene (DH $\alpha$ 5T), to obtain better performance from their ring oscillator.

## Pentacene

One the most promising materials for the use in polymer integrated circuits is pentacene. Figure 6 shows the molecular structure of this polymer, a fused-ring aromatic hydrocarbon.

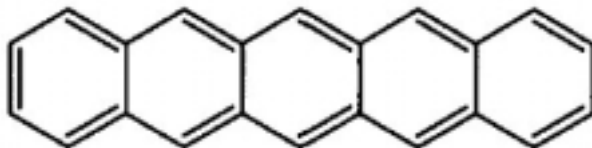


Figure 6: Chemical structure of a pentacene molecule [9].

Several research groups have, and still are, working on various aspects of this material for transistor devices. In 1996 C.D. Dimitrakopoulos and his group used pentacene in a metal-insulator-semiconductor field-effect transistor (MISFET) device, the schematic of which is shown in figure 7 [9]. The group obtained field-effect mobilities from 0.02 to 0.038  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  and rather poor current-voltage characteristics, nothing comparable to amorphous silicon devices. However, they did mention several possibilities of improving device performance [9].

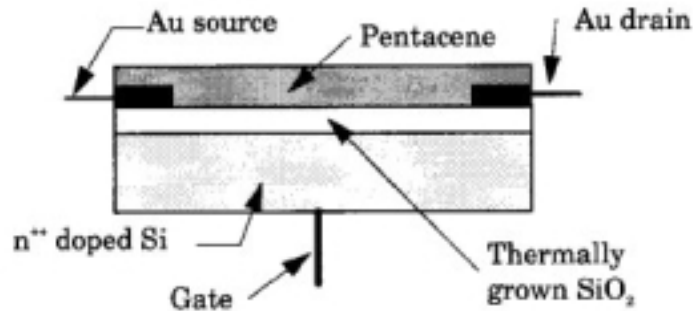


Figure 7: Schematic of a MISFET with pentacene as the active semiconducting material [9].

In a series of papers from a group led by Y.Y. Lin, they managed to obtain mobilities greater than 0.60  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ . In their first paper in 1996 the group used pentacene in a thin-film transistor structure as shown in figure 8a [6]. From this device they obtained a field-effect mobility of about 0.62  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$  and an on/off current ratio greater than  $10^8$ . This group, for the first time, created a polymer device with characteristics that are comparable to hydrogenated amorphous silicon devices, however they also found that the threshold voltage and subthreshold slope were too large for the device to be of any use. In the following year the group overcame the problem of threshold voltage and subthreshold slope by optimizing the order of the polymer material using a thin octadecyltrichlorosilane (OTS) layer, and using a prepatterned polymer layer [16]. Figure 8b shows the device structure that the group used. They found mobilities between 1.3 and 1.5  $\text{cm}^2\text{V}^{-1}\text{s}^{-1}$ , with on/off ratios greater than  $10^8$ , and low threshold voltages and subthreshold slope.

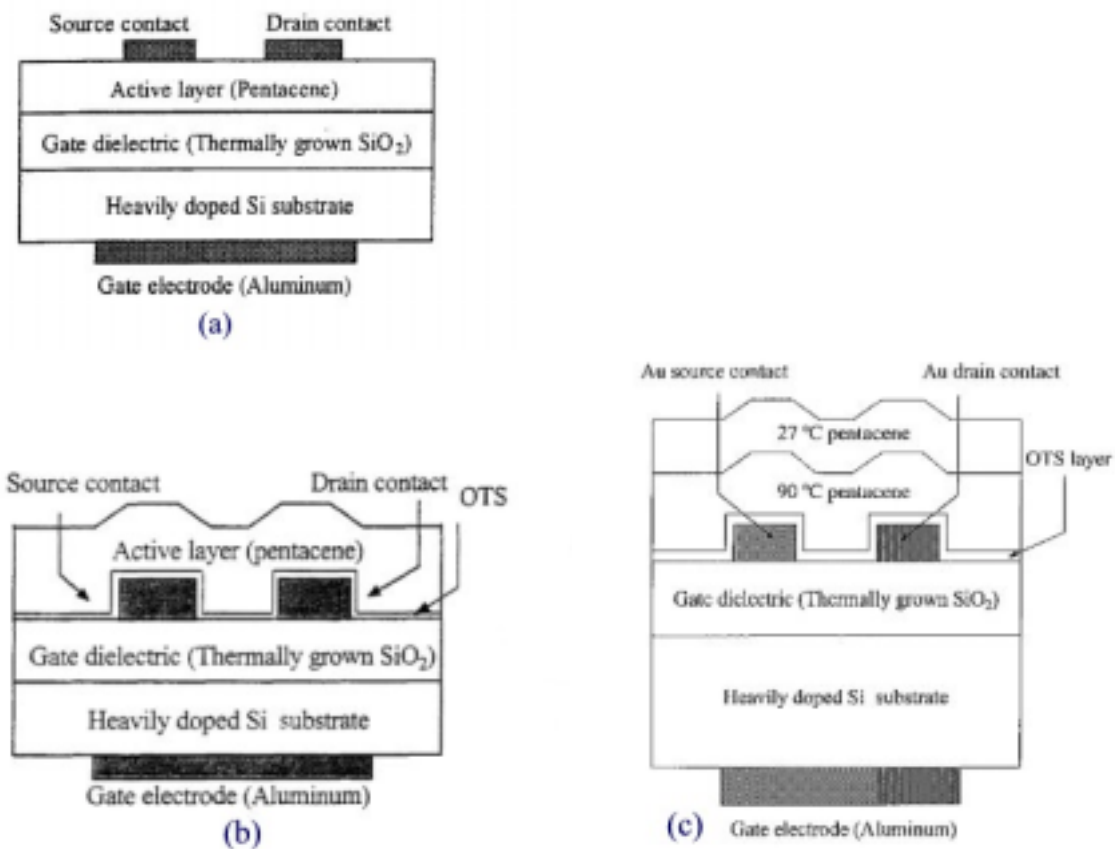


Figure 8: Schematics of (a) a top contact pentacene polymer transistor, (b) a bottom contact pentacene transistor, and (c) a stacked pentacene transistor [6,16,17].

Again, in the same year, the group added a second pentacene layer as shown in figure 8c and obtained similar results as before [17]. This was done to confirm ideas related to interface issues between the dielectric and polymer. The devices created by Lin *et. al.* were grown on silicon wafers for simplicity, however for practical implementation thermally grown silicon dioxide will not be possible on a polymer substrate. A related group led by H. Klauk created pentacene thin-film transistors on a glass substrate using a different processing techniques, a cross section is shown in figure 9. The group achieved a field-effect mobility of  $0.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ , an on/off ratio of about  $10^8$ , and a subthreshold slope of  $0.7\text{V/dec}$  [12].

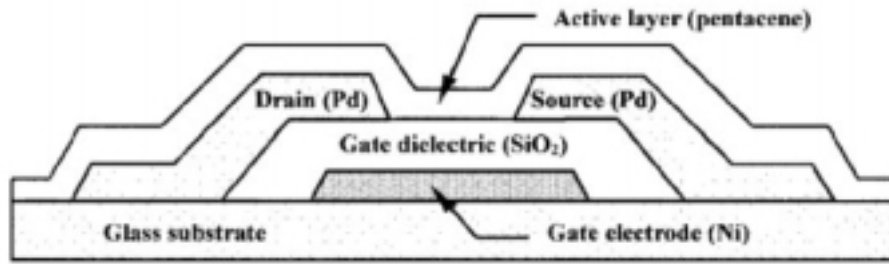


Figure 9: Schematic of a pentacene based polymer transistor [12].

## Polymer Processing

The processing of polymer material is a major issue when considering device implementation. In order to achieve the low-cost electronics envisioned for polymer circuits simple processing steps must be used to create these circuits, such as spin coating, dip coating, and print screening. Also, processing environments play a role in this respect; using high or low temperature ranges, inert gas, vacuum, or pressure environments just adds to the cost of processing. Hence room temperature processing in air is the ideal candidate to provide for low cost production.

Material organization is also an important issue facing polymer circuit design. If multiple polymer materials are used in a circuit careful attention must be made in order to ensure that subsequent processing steps do not interfere with the material already deposited. This in effect limits the choice of materials that can be used.

Many researchers have studied polymer circuits that have been grown on silicon wafers for simplicity. For example, Lin et. al. have done most of their pentacene polymer work on highly doped silicon substrates, making silicon dioxide (gate oxide) fairly simple to make [6,16,17]. This resulted in very good device characteristics. However, this would not be suitable for low cost, flexible applications. A related group then used a similar device with more appropriate processing steps and found that, while certain device characteristics were improved others were not (for example the carrier field-mobility had dropped from  $1.5$  to  $0.6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ ) [12].

Another processing issue to keep in mind for commercial circuit applications is material stability and lifetime. Many early polymer materials were very unstable when exposed to air or moisture, meaning the material's performance would simply degrade (sometimes in a matter of minutes) when released from their sealed environments. Early experiments with pentacene had this problem. And of course, many polymer materials have very short shelf lives making commercial applications a waste of time.

## Polymer Circuits

There have been a few endeavors into fully functioning polymer circuits with some interesting results. The majority of these applications fall into the digital realm. Y. Lin, *et. al.* had used a complementary polymer transistor structure using both  $\alpha$ -6T and F<sub>16</sub>CuPc to create a five-stage all-organic ring oscillator [10]. In the end they replaced the  $\alpha$ -6T with DH $\alpha$ 5T to improve the circuit's performance and obtained an oscillation frequency of about 2.63 kHz with possible optimizations leading to frequencies above 50kHz. The circuit schematic and sample result are shown in figures 10a and 10b.

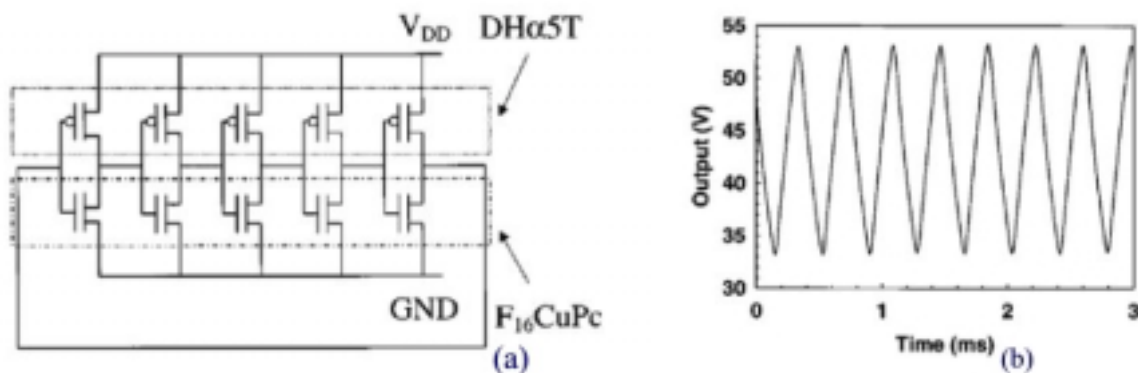


Figure 10: (a) Schematic of an all-polymer based ring oscillator and (b) and result from experimentation [10].

C.J. Dury, *et. al.* had created several test circuits using a polyimide foil substrate, doped polyaniline (with some processing) for the contacts, and polythiénylenevinylene (PTV) as the semiconducting polymer. This is a true all-polymer circuit, the details of which can be found in reference 8. This group also created a seven-stage ring oscillator, which operated at voltages as

low as 3V and achieved oscillation frequencies between 40 and 200 Hz. They had also created a 15-bit mechanically programmable code generator, which contained an onboard clock generator, a 5-bit counter, and decoder logic [8]. They managed a bit rate of 30 bits/s. Then, recently, G.H. Gelinck, *et. al.* (a related group) used the same circuit but with a new transistor layout and increased the bit rate to 100 bits/s [15].

H. Sirringhaus, *et. al.* used regiorregular poly(hexythiophene) to create a transistor driven polymer light emitting diode, which could rival currently used amorphous silicon drivers [2].

Figure 11 shows the full device structure and the implemented structure.

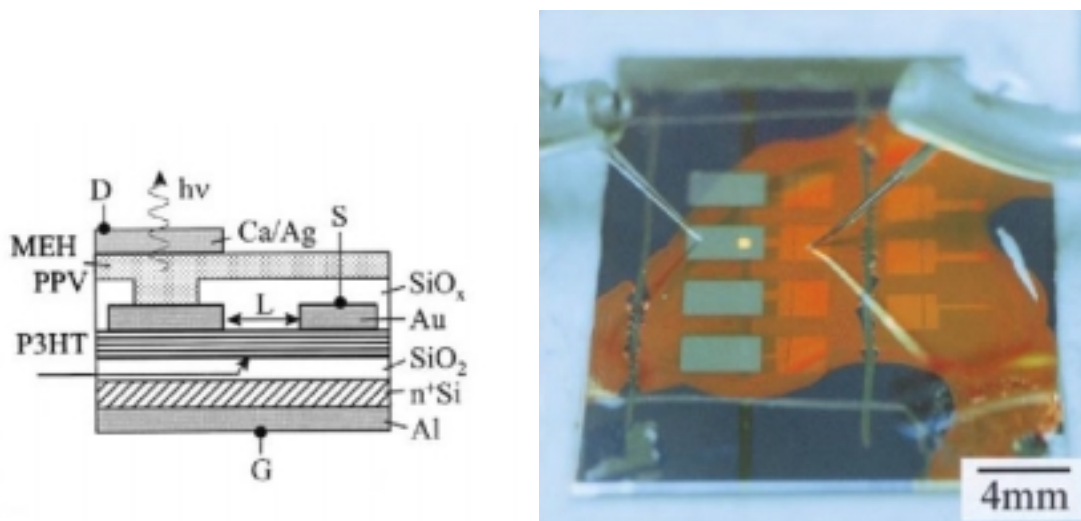


Figure 11: Schematic and pictorial version of an all-polymer based LED and driver transistor [2].

On a more analog side of things, J.H. Bechtel, *et. al.* discuss polymer circuit possibilities for high speed analog-to-digital converters using multiple Mach-Zehnder modulators [1]. The authors also mention applications into radio frequency manipulation, and high data rate modulators, however this uses the electro-optic properties of polymers. Finally, one group had mentioned an unpublished paper citing the creation of an all-polymer integrated circuit of an audio amplifier with a 5 kHz bandwidth [10].

## Conclusions

Polymer based devices and circuits have, in the past decade, exploded onto the research community. Material characteristics and device performance have gone through several optimizations such that polymer devices are now comparable, in performance, with hydrogenated amorphous silicon devices. Their application into low-cost, large area processing is inevitable.

Many issues, however, need to be resolved in order for this to happen. Room temperature and ambient air processing techniques must be studied further in order to produce low-cost devices. Material stability and lifetime must be improved to make devices commercially viable. A good understanding of carrier mobility and charge flow in polymer materials is still lacking. A better understanding may lead to better device characteristics.

In any event, many successful attempts have been made to create all-polymer devices and circuits, from simple ring oscillators to complex code generators and even some analog circuits. Considering the wide interest in polymer circuits from consumer to aerospace applications, polymer materials are close to becoming a commercially viable technology.

- [1] J.H. Bechtel, C.B. Morrison, & Y. Shi, "Polymer Optoelectronics and Semiconductor Grafting for Aerospace Applications", 1999 IEEE Aerospace Conference Proceedings, vol. 3, pp.317-27, 1999.
- [2] H. Sirringhaus, N. Tessler, & R.H. Friend, "Integrated Optoelectronic Devices Based on Conjugated Polymers", Science, vol. 280, pp.1741-44, June 1998.
- [3] C. Marshall, "Welcome to Plastic Valley", Business 2.0, January 2001, <http://www.business2.com/content/magazine/breakthrough/2001/01/29/25559?page=1>
- [4] M. Matters, D.M. de Leeuw, M.J.C.M. Vissenberg, C.M. Hart, P.T. Herwig, T. Geuns, C.M.J. Mutsaers, & C.J. Drury, "Organic field-effect transistors and all-polymer integrated circuits", Optical Materials, vol. 12, no. 2-3, pp.189-97, June 1999.
- [5] A. Dodabalapur, J. Laquindanum, H.E. Katz, & Z. Bao, "Complementary circuits with organic transistors", Appl. Phys. Lett., vol. 69, pp.4227-29, December 1996.
- [6] Y.Y. Lin, D.J. Gundlach, & T.N. Jackson, "High-Mobility Pentacene Organic Thin Film Transistors", 54<sup>th</sup> IEEE Device Research Conference Digest, pp.80-81, 1996.
- [7] A. Dodabalapur, J. Baumbach, K. Baldwin, & H.E. Katz, "Hybrid organic/inorganic complementary circuits", Appl. Phys. Lett., vol. 68, pp.246-48, 1996.
- [8] C.J. Drury, C.M.J. Mutsaers, C.M. Hart, M. Matters, & D.M. de Leeuw, "Low-cost all-polymer integrated circuits", Appl. Phys. Lett., vol. 73, pp.108-110, 1998.
- [9] C.D. Dimitrakopoulos, A.R. Brown, & A. Pomp, "Molecular beam deposited thin films of pentacene for organic field effect transistor applications", J. Appl. Phys., vol. 80, pp.2501-08, 1996.
- [10] Y.Y. Lin, A. Dodabalapur, R. Sarpeshkar, Z. Bao, W. Li, K. Baldwin, V.R. Raju, & H.E. Katz, "Organic complementary ring oscillators", Appl. Phys. Lett., vol. 74, pp.2714-16, May 1999.
- [11] C.R. Kagan, D.B. Mitzi, & C.D. Dimitrakopoulos, "Organic-Inorganic Hybrid Materials as Semiconducting Channels in Thin-Film Field-Effect Transistors", Science, vol. 286, pp.945-47, October 1999.
- [12] H. Klauk, D.J. Gundlach, J.A. Nichols, & T.N. Jackson, "Pentacene Organic Thin-Film Transistors for Circuit and Display Applications", IEEE Trans. Electron Dev., vol. 46, no. 6, pp.1258-63, June 1999.
- [13] Z. Bao, A. Dodabalapur, & A.J. Lovinger, "Soluble and processable regioregular poly(3-hexylthiophene) for thin film field-effect transistor applications with high mobility", Appl. Phys. Lett., vol. 69, pp.4108-10, December 1996.

- [14] P.T. Herwig, & K. Mullen, "A Soluble Pentacene Precursor: Synthesis, Solid-State conversion into Pentacene and Application in a Field-Effect Transistor", Advanced Materials, vol. 11, no. 6, pp.480-83, 1999.
- [15] G.H. Gelinck, T.C.T. Geuns, & D.M. de Leeuw, "High-performance all-polymer integrated circuits", Appl. Phys. Lett., vol. 77, no. 10, pp.1487-89, September 2000.
- [16] Y.Y. Lin, D.J. Gundlach, S.F. Nelson, & T.N. Jackson, "High-mobility Pentacene-Based Organic Thin Film Transistors", 55<sup>th</sup> IEEE Device Research Conference Digest, pp.60-61, 1997.
- [17] Y.Y. Lin, D.J. Gundlach, S.F. Nelson, & T.N. Jackson, "Stacked Pentacene Layer Organic Thin-Film Transistors with Improved Characteristics", IEEE Electron Device Lett., vol. 18, no. 12, pp.606-8, December 1997.