

MSE 542 – Final Term Paper

Title: Organic Semiconductor for Flexible Electronics

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### **Introduction:**

An organic semiconductor is an organic compound that possesses similar properties to inorganic semiconductors with hole and electron conduction layer and a band gap.<sup>4</sup> Organic semiconductors differ from other organic material in that the molecules that they are made of have  $\pi$  conjugate bonds which allow electrons to move via  $\pi$ -electron cloud overlaps. Conduction mechanisms for organic semiconductor are mainly through tunneling, hopping between localized states, mobility gaps, and phonon-assisted hopping.<sup>5</sup> Like inorganic semiconductors, organic semiconductors can be doped in order to change its conductivity. Although inorganic semiconductors such as silicon, germanium and gallium arsenide have been the backbone of semiconductor industry, for the past decade, demands for pervasive computing have led to a dramatic improvement in the performance of organic semiconductor. Recently, organic semiconductors have been used as active elements in optoelectronic devices such as organic light emitting diodes (OLED), organic solar cells, and organic field effect transistors (OFET). There are many advantages of using organic semiconductors, such as easy fabrication, mechanical flexibility, and low cost. Organic semiconductors offer the ability to fabricate electronic device at lower temperature and over large areas on various flexible substrate such as plastic and paper. They can be processed using existing techniques used in semiconducting industry as well as in printing industries such as roll-to-roll

manufacturing.<sup>3</sup> These manufacturing advantages can create low-cost, pervasive electronic applications such as flexible displays and RFID tags. However, the mobility of organic semiconductor cannot match the performance of field-effect transistors based on single-crystalline inorganic semiconductor such as silicon or germanium. These inorganic semiconductors have charge carrier mobilities nearly three order of magnitude higher than typical organic semiconductor.<sup>3</sup> As a result of this limitation, organic semiconductors are not suitable for use in electronic applications that require very high switching speeds. However, the performance of some organic semiconductors, coupled with their ease of processing makes it competitive in electronic applications that do not require high switching speed such as amorphous silicon used for TFT-LCD.

### **Main Body:**

Organics semiconductors are possible because carbon atoms can form  $sp_2$ -hybridisations where the  $sp_2$ -orbitals form within a plane and the  $p_z$  orbitals are in the plane perpendicular to it.<sup>4</sup> For organic molecules, a  $\sigma$ -bond between two carbons are formed by creating an orbital overlap of two  $sp_2$ -orbitals (Figure 1). This creates a large energy difference between the occupied binding orbitals and the unoccupied anti-binding orbitals. This large energy difference leads to insulating properties, and thus longer chains of carbon atoms would have a larger gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). However, in  $sp_2$ -hybridisation, the  $p_z$  orbitals form additional  $\pi$ -bonds. These bonds have much smaller energetic difference between the HOMO and LUMO, leading to semiconducting properties.

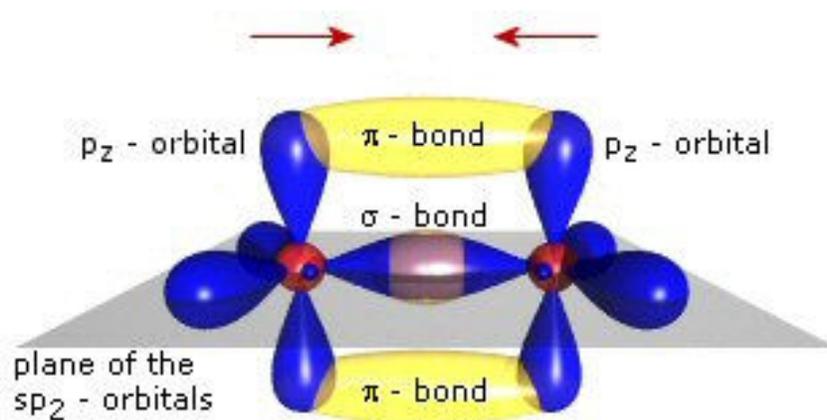


Figure 1

Organic semiconductors can be divided into two types, short chain (oligomers) and long chain (polymers).<sup>5</sup> Typical examples for semiconducting oligomers are pentacene, anthracene and rubrene. Some semiconducting polymers are Poly(3-hexylthiophene) and poly(p-phenylene vinylene).

Short chain organic semiconductors are usually formed by a series of benzene rings in which the  $\pi$ -bonds become delocalized to form a  $\pi$ -system. The gap between occupied and empty states in these  $\pi$  systems becomes smaller with increasing delocalization, leading to smaller bandgap (Figure 2).

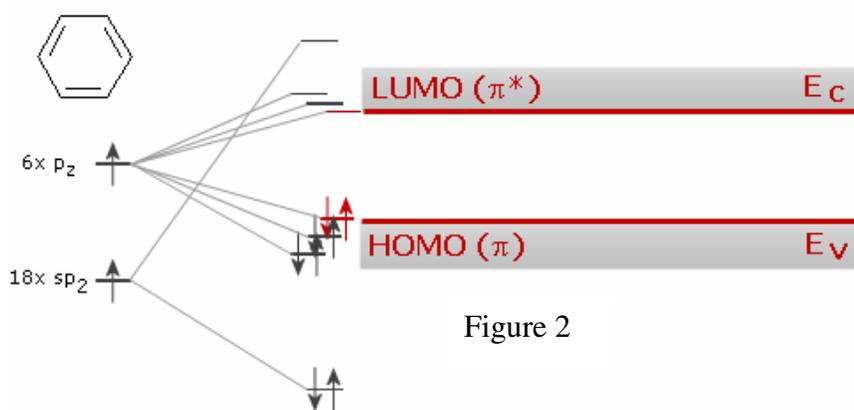


Figure 2

Organic semiconductors can be prepared as molecular single crystals by vacuum evaporation. This brings closer the coupling of the  $\pi$  systems and increases the band transport mobility.

Long chain organic semiconductors are usually polymers that have  $\pi$  bonds that are delocalized along the chain to form a one-dimensional system resulting in a 1D-band structure that has considerable band width. The transport properties of such polymers are usually determined by defects in the 1D-chains or by hopping from chain to chain.

Polymer organic semiconductors are usually deposited in wet processes, like spin coating or doctor blading.

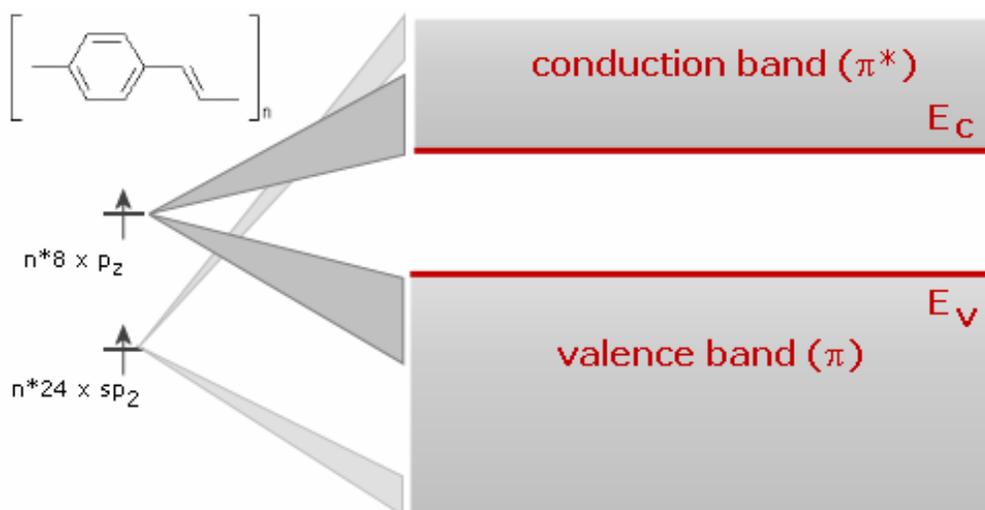


Figure 3

Delocalization in polymer semiconductor is accomplished by forming a conjugated backbone of continuous overlapping orbitals. This includes alternating single and double carbon-carbon bonds, which leaves a continuous path of overlapping p orbitals (figure 4).

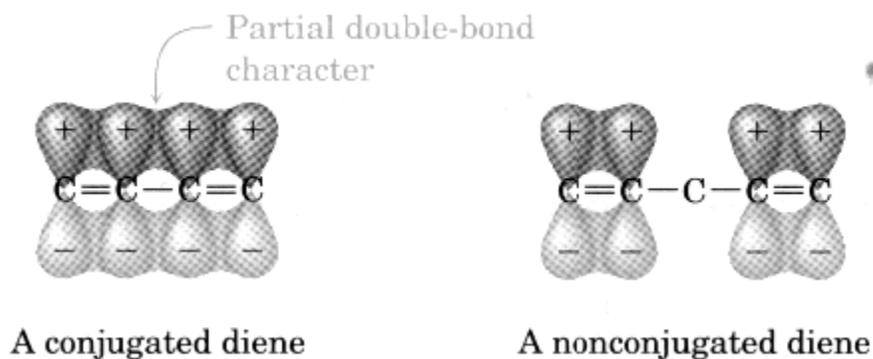


Figure 4

In organic semiconducting polymer, this continuous string of orbitals creates degeneracy in the highest occupied and unoccupied orbitals and leads to the filled and unfilled bands that define a semiconductor. However, conductive polymers generally exhibit very low conductivities. This is because conduction in such relatively disordered materials are due to mobility gaps with phonon-assisted hopping, tunneling between localized states but not band gaps as in crystalline semiconductors.<sup>8</sup>

As mentioned before, organic semiconductor can be doped either by removing an electron from valence band or adding an electron to the conduction band to increase its conductivity. Doping organic semiconductor creates more charge carriers which move in an electric field. This movement of charge is responsible for electrical conductivity in organic semiconductor. Doping a polymer is different from that of inorganic semiconductor in which elements with excess and shortage of electrons are introduced. In polymer, both doping process involves an oxidation and reduction process. The first method involves exposing a polymer to an oxidant such as iodine or bromine or a reductant such as alkali metals.<sup>2</sup> The second is electrochemical doping in which a polymer-coated electrode is suspended in an electrolyte solution. The polymer is

insoluble in the solution that contains separate counter and reference electrodes. By applying an electric potential difference between the electrodes, counter ion from the electrolyte diffuses into the polymer in the form of electron addition (n doping) or removal (p doping).<sup>2</sup> One of the problem with organic semiconductor is that p-type material is much more prevalent than n-type because electron rich n-type is unstable in the presence of oxygen. Organic semiconductor can only be useful for devices if both p-type and n-type are both incorporated. The most widely used organic semiconductors are pentacene, thiophene oligomers, and regioregular polythiophene.<sup>3</sup>

In organic semiconductors, the macroscopic properties of the material can be attributed to both the properties of the individual molecules and the structural order of the molecules in the film. These properties can be controlled by either synthesizing molecules with optimal characteristics or by controlling the fabrication conditions. For example, carrier mobility in rod-like molecules can increase if the organic material has long  $\pi$  conjugation length along the long axis and close molecular packing of the molecules.<sup>3</sup>

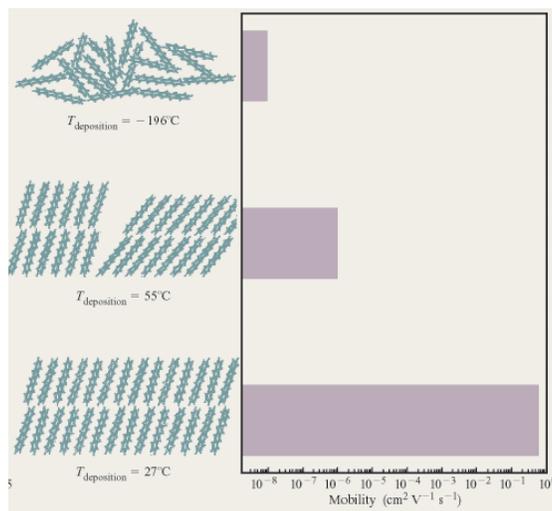


Figure 5

Another example of fabrication affecting carrier mobility is growing amorphous films of pentacene which is achieved by keeping the substrate temperature low during deposition. This makes an insulating film. However, when the substrate temperature is kept at room temperature during deposition, a very well-ordered film is deposited with a high mobility.<sup>3</sup> Figure 5 demonstrates that ordered organic material has higher charge transport mobility.

Organic semiconductors have found applications in solar cells because it has the potential for low cost manufacturing. Solar cell incorporating organic semiconductor can be made by depositing patterned electrode and semiconductors on plastic substrate using roll-to-roll coating machines. This would produce cheaper solar cells, but also allow solar cells to be easily installed on roof, clothes, and electronic devices. However, the efficiency of organic solar cell is still very low compare to solar cells made using traditional silicon technology. Another application of organic semiconductor is in organic thin film transistor (OTFT). Organic transistors (Figure 6) are transistors that use organic molecules rather than silicon for their active material. This active material can be composed of a wide variety of molecules. The advantage of organic transistor is that they are compatibility with plastic substrates, have lower manufacturing temperature, lower fabrication cost (spin-coating, printing, evaporation), and no need to worry about dangling bonds.<sup>6</sup>

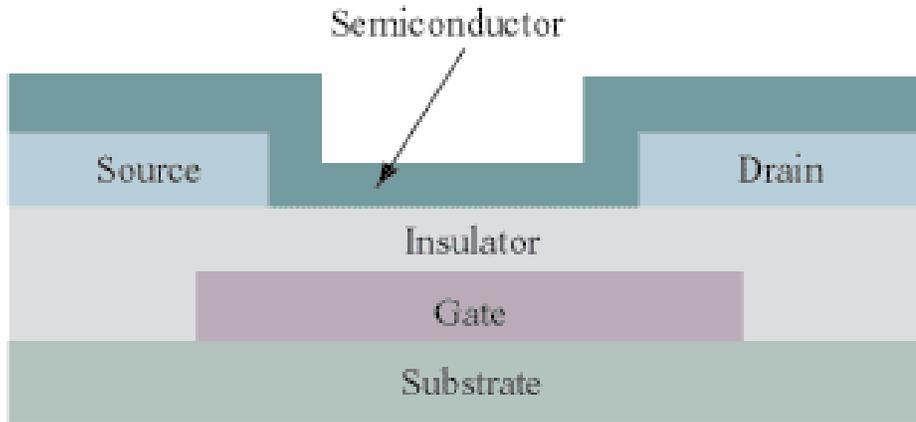


Figure 6

Organic TFT differ from silicon TFT in that it only operates in accumulation mode. This makes complementary logic more difficult to implement, although there are several solutions to this problem. One technique to overcome this shortfall involves using layers in organic semiconductors to make heterostructures which allow p and n channels.<sup>7</sup> The disadvantage of OTFT so far is their lower mobility and switching speeds compared to silicon and that they usually do not operate under inversion mode.<sup>7</sup> For organics to compete with amorphous silicon, their mobility should be greater than  $0.1 \text{ cm}^2/\text{V S}$ .

### **Conclusion:**

Organic semiconductors are relatively new class of materials that offer the ability to create devices using plastic substrate. Organic semiconductors work because of  $\pi$  conjugated bond within its molecules. Without conjugation, electrons are shared very closely between molecules creating a large band gap compared to molecules with conjugation, thus making it an insulator. The conducting mechanism of organic semiconductor is charge hopping which allows electron to jump from one molecule to another. Phonons assists charge hopping, therefore increasing temperature also increases

the mobility of the material. In addition, highly order structures and arrangements may facilitate the intermolecular hopping process, by bringing closer the coupling of  $\pi$  bonding system and increase carrier mobility. The upper limits of carrier mobility in organic semiconductor fall between  $1\text{-}10\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ .<sup>1</sup> This is because intermolecular interaction in organic semiconductor is via van der Waal force which is quite weak. Van der Waal interaction account for bonding energy smaller than  $10\text{ kcal mol}^{-1}$  and sets the upper limit for mobility because the vibrational energy of the molecules reaches a magnitude close to that of the intermolecular bond energies at or above room temperature.<sup>3</sup> One of the most exciting things about organic semiconductors is that their electric performance has increased dramatically in the past decade and that makes them competitive in electronic devices that do not need high speed switching. Although their mobility is still three order of magnitude smaller compare to inorganic semiconductor, they have the ability to enable applications that are not achievable using current silicon technology by taking advantage of their unique processing characteristics. Some of the characteristics include low temperature deposition on large substrate area, low cost manufacturing using printing and spin-coating. Organic semiconductors enable displays to be fabricated on a plastic substrate which currently is not possible because of the high processing temperature of amorphous silicon. Organic semiconductors will allow devices such as OTFTs to be processed at room temperature, thus making it compatible with flexible electronics.

## **References:**

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