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4.2 Organic Polymer Field Effect Transistors

Jerzy Kanicki and Sandrine Martin

4.2.1 Introduction

Conjugated organic polymers are a novel class of semiconductors that combine the optical and electronic properties of semiconductors with the advantages of low-cost processing, large-area scalability, compatibility with flexible substrates, and mechanical properties of polymers. Important examples of polymers within this class include poly(p-phenylene vinylene), poly(p-phenylene), polythiophenes, polyfluorene derivatives, and others. In general, the conducting polymers contain extended π -conjugated systems composed of single and double bonds alternating along the polymer chain (for an explanation of π -conjugation, see Chapter 2). The strong relation between electronic structure and backbone conformations is a fundamental feature of π -conjugated polymers. The extent of the π -conjugation is the essential structure parameter that controls the physical properties of conducting polymers. Within conducting polymers, carriers can be created by adding impurities. These impurities act as electron donors or acceptors, where the *carrier concentration* depends on the doping level (*i.e.*, amount of impurities present). For example, the introduction of acceptors into a polymer creates holes (positive charge carriers), resulting in structural defects in the alternation of the double and single bonds. These defects can travel along the polymer chain without changing its shape and represent localized solitary waves; they are responsible for localization of the electron states along the polymer chain. The defects can also be called *polarons* if single-charged and *bipolarons* if double-charged. A polaron is a *quasiparticle* that repulses adjacent electrons while attracting the nuclei of neighboring atoms. This results in the polarization of the lattice in its closest vicinity. This accompanying cloud of polarization causes an increased effective mass of the particle, decreasing the mobility of those quasiparticles. Those quasiparticles can be identified by additional energy levels, which appear within the semiconductor bandgap. Polarons in conjugated systems affect not merely the polarization in their vicinity but they can also change the nature of bonds from σ to π and vice versa via excitation and while traveling. The strong electron-lattice coupling is responsible for the existence of polarons in conjugated systems.¹

In general, the conductivity in polymers is one-dimensional on the molecular scale. Therefore, the polymers can be represented as a one-dimensional disordered system, in which electron states are localized due to defects along the chain. The physical reason for localization is interference of forward- and backward-scattered electron wave functions, forming

standing waves. The situation changes if electrons can be transferred between the chains. If the electrons can move off the chain before they scatter backwards, they become effectively delocalized. Let the inter-chain exchange rate be I_{RE} and the mean free time of an electron moving along chain τ . Then the condition of delocalization is expressed by

$$I_{RE} > \frac{1}{2} \tau \quad (4.2.1)$$

There exists a threshold value of I_{RE}

$$I_{RE}^C \approx \frac{1}{\tau} \quad (4.2.2)$$

above which electron states become three-dimensional, and below which they are localized on a single chain. Therefore, three-dimensional conductivity will occur when the interchain transfer rate is high enough.² However, even if the conductivity in polymers is one-dimensional on the molecular scale, the bulk samples (and device structures) have a three-dimensional conductivity because macromolecules are assembled into three-dimensional structures, and their conductivity will be highly dependent on the thin film morphology. In conducting polymers, one can distinguish *intra-chain* and *inter-chain* transport mechanisms. Intra-chain transport depends on intrinsic properties of macromolecules and the doping level. Inter-chain transport is a function of the polymer morphology and the packing density.

Bulk electronic conduction that is observed in device structures described in this chapter is a result of these processes. If the polymer chain packing is not perfect, inter-chain disorder will reduce the inter-chain transfer rate, and hence decrease the conductivity. It can be argued that polymer chains are packed into a bundle and are well ordered within the bundle, and that the electronic behavior of particular films is controlled by the dimensions and ordering of the bundles. The conductivity in randomly oriented polymers used in OFETs depends on the pathways that are available for carriers to organize a macroscopic electronic current between two contacts. It is expected that the structural order (that can be influenced by solvent polarity, solid content in the solution, thermal treatment and film deposition method) in an intrinsically conducting polymer will have a pronounced influence on its charge transport and device electrical characteristics. For instance, it is expected that the inter-chain transport will

be favorable for high-density crystalline packing of macromolecules because of the relatively small value of the energetic barriers. Therefore, film conductivity will increase with the thermal annealing of samples, leading to an increase in the degree of crystallinity.

In summary, order is one of the key properties of conducting polymers that can have a major effect on electrical performance of devices such as field-effect transistors. The organic materials used in device structures described in this chapter are as-deposited disordered organic polymers.

4.2.2 Device Structures

Since in most of the published papers, the electrical properties of organic thin-film transistors (OFETs) are analyzed using models and carrier transport equations developed for inorganic thin-film transistors (TFTs),^{3,4} it is important first to summarize the physics of the TFTs before describing the electrical properties of OFETs. Inorganic TFT operation is based on the crystalline silicon (c-Si) metal-oxide-semiconductor field-effect transistor.

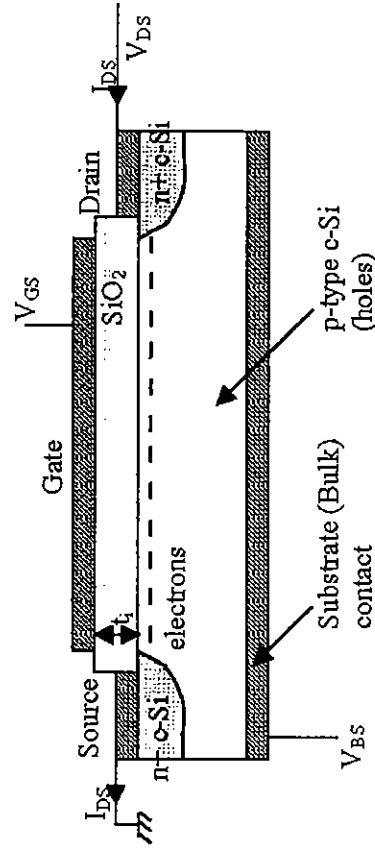


Figure 4.2.1. Typical MOSFET device structure.

The structure of a typical metal-oxide-semiconductor field-effect transistor (MOSFET) is shown in Figure 4.2.1. This cross-section shows an *n*-channel enhancement mode inorganic device built on a *p*-type single crystal silicon (c-Si) substrate, designated as *B* (bulk). The source and drain electrodes are heavily doped *n*-type (*n*⁺) c-Si regions covered with metal. (An *n*-type material contains impurities, such as phosphorous, which create a

