Patterning Acene-Inspired p-type Semiconductors for Organic Field Effect Transistors

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Field effect transistors (FETs) are of immense importance to modern society. The most ubiquitous transistor device is the metal-oxide semiconductor FET (MOSFET) found in microprocessors, solid-state memories, and many other electronic devices. Second to the MOSFET is the hydrogenated amorphous silicon transistor (a-Si:H), which is widely used in active-matrix-liquid-crystal displays (AMLCD).[1] Combined, the two types of transistors amounted to a market value of approximately 280 billion dollars in 2009.

Although there are several designs for FETs, they all operate on the same basic principles (Figure 1A). A gate, an insulator, a semiconductor, and contacts (named source and drain), are mounted on a substrate. A voltage is applied to the source and drain (V_{DS}) and current flows between the two contacts through the semiconductor. A voltage is also applied to the gate (V_{GS}). The amount of current that flows through the semiconductor depends on V_{GS}. A sufficiently large V_{GS} can completely stop current between the source and drain contacts, effectively turning off the device.[2,3]

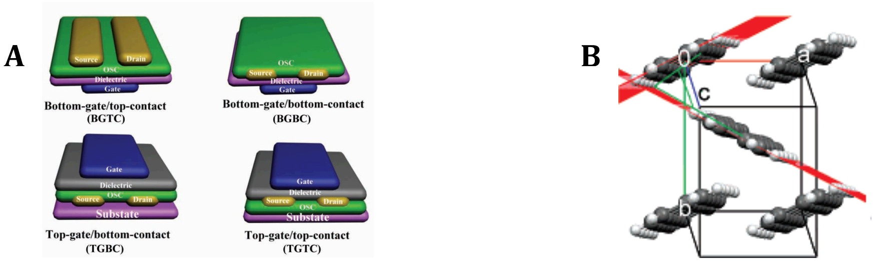

Figure 1. A) Schematic of four common designs for OFETs.[3] B) Crystal structure of pentacene viewed down c-axis. Herringbone angle is the intersection of the red planes.[7]

Over the past 20 years, there has been increasing interest in developing organic semiconductors (OSCs) organic field effect transistors (OFETs) to compete with the a-Si:H transistors.[1] OFETs can generally be processed at low temperatures and could be cheaper to produce than their a-Si:H competitors. Low process temperatures and low cost can lead to OFETs being used in devices such as flexible displays, smart cards, and radio frequency tags.[2]

In the mid 1990's, pentacene emerged as an OSC of interest for p-type OFETs. Gundlach *et al*. made thin films of pentacene and found that the mobility (μ) was comparable to amorphous silicon FETs (~1 cm^2/Vs). They proposed that the observed high mobility was related to a well-ordered crystalline thin-film of pentacene.[4]

This sparked research into correlating high hole mobility in pentacene with crystal structure and orbital overlap. In 2003, Mattheus *et al*. showed that there existed four polymorphs of pentacene that all packed in a triclinic, herringbone structure (Figure 1B).

They are, however, distinguishable by differences in the (001) d-spacing.[5] Two years later, calculations to determine the HOMO-HOMO overlap in the pentacene polymorphs were completed. The authors found that, for all polymorphs, hole mobility along the c-axis was extremely low and that mobility in the a-b plane was significantly higher. Of the four, calculations suggested that the d(001) = 15.4 Å polymorph is the best for thin-film applications.[6] To better understand the 15.4 Å polymorph, Schiefer *et al.* used grazing incidence crystal truncation rod method to observe that growing pentacene thin-films on different substrates slightly altered the herringbone angle.[7] This series of work concluded that a high degree of crystallinity led to good orbital overlap in the a-b plane, which accounted for the high mobility observed in pentacene.

Consequently, work to improve mobility in pentacene films was conducted by coating the dielectric surface onto which pentacene was deposited with a polymer. Kim *et al.* compared SiO_2 dielectric surfaces coated with polystyrene (PS) and poly(4-vinylpyridine) (PVPyr). They found that under all conditions, pentacene layers grown on PS surfaces showed higher hole mobility than the PVPyr counterparts. The lower hole mobility on PVPyr was attributed to the electron-donating nature of the pyridine group as well as more surface defects, both of which lead to more hole traps. The authors went on to show that the grain size of pentacene films (and therefore hole mobility) also depended on the temperature of the dielectric (T_s) during deposition as well as deposition rate (κ).[8]

Problems the with solubility and air stability of pentacene, however, have led researchers to investigate new systems.[1] To deal with solubility issues, pentacene was modified to a Diels-Alder adduct to make it more soluble. Following spin-coating from chloroform onto a substrate and thermal decomposition of the adduct at 200 °C, pentacene OFETs were made showing mobility as high as 0.89 $cm^2\ V^{-1}\ s^{-1}$.[9] To address air stability, Youn *et al.* investigated a family of dithiophenes. The dithiophenes showed improved air stability due to having a larger band gap than pentacene.[10]

The authors also performed studies on the thin film structure and showed that the dithiophenes crystallized very similarly to pentacene; thus structure and orbital overlap arguments could be extended to cover this family of compounds. In a study similar to Kim *et al.*, the authors modified the SiO_2 dielectric surface with hexamethyldisilazne (HMDS) and octadecyltrichlorosilane (OTS) to show that hole mobility in dithiophenes depends on surface treatment. In agreement with hydrophobicity arguments, OTS-treated surfaces showed the best hole mobility in thiophenes. The authors also experimented with a two-stage deposition method that involved first a slow deposition of the dithiophene followed by rapid deposition of the dithiophene. This created large grains during the slow deposition and then connected the large grains during the fast deposition leading to improved mobility in almost all cases.[10]

Finally, Gundlach *et al.* showed that surface treating the contacts in an OFET can also lead to higher hole mobility in dithiophenes. The source and drain contacts were coated with pentafluorobenzene thiol (PFBT) and using 5,11-bis(triethylsilylethynyl) anthradithiophene (diF-TESADT) as the OSC, the authors obtained mobility exceeding 1 $cm^2\ V^{-1}\ s^{-1}$. The authors went on to build a flexible seven-stage ring oscillator on a polyimide substrate that had mobilities between 0.1-0.2 $cm^2\ V^{-1}\ s^{-1}$.[11]

OFETs are approaching a stage in development where they will be commercially viable. Processing techniques, air stability, and transistor size still require significant improvements, however. These issues need to be addressed quickly as the rapid rise of flexible inorganic electronics[12] could soon compete in the market with OFETs.

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