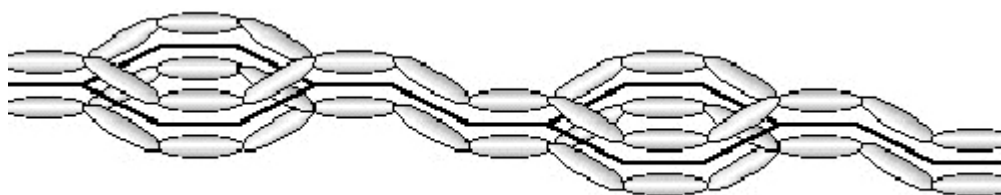


## Introduction to Polymer Light Emitting Diodes (PLEDs)

Plastic materials have long been known to provide useful insulating characteristics in electrical applications. Over the last 30 years there has been increasing interest in exploiting more exciting characteristics of some conjugated polymer materials which emit light when stimulated electrically. These are polymers which possess a delocalised pi-electron system along the polymer backbone. The delocalised pi-electron system confers semi-conducting properties to the polymer and gives it the ability to support positive and negative charge carriers with high mobility along the polymer chain.



*Overlap of  $P_z$  orbitals leads to the formation of a delocalised pi-electron cloud above and below the plane of the sigma bonds, which form the structural framework*

The semiconductor properties of these materials arise from the overlap of  $P_z$  orbitals that originate from the double or triple bonds. If the overlap is over several sites, the formation of well delocalised pi valence and pi\* conduction bands occurs, with an energy gap between them - the recipe for this semi-conductive behaviour. The mechanism for charge transport in these materials is not the same as in more traditional inorganic semiconductors: the amorphous chain morphology results in an inhomogeneous broadening of the energies of the chain segments and leads to hopping type transport. A secondary effect is the distortion of the chain around a charge carrier, with the result that the charged excitations are usually best described as 'polarons' in these materials.

Nevertheless, device engineering of the materials can take advantage of many of the lessons previously learnt for classical semiconductors. Thus device designs and material structures can be translated into the new technology. For example the use of heterostructures, commonplace in III-V technology can also be applied to polymer devices for improved carrier confinement, or for varying offsets with respect to injection electrodes.

Of course there are enormous advantages over the classical semiconductors both in terms of the ease of fabrication (compare spin-coating to epitaxial growth!), as well as the design of new materials with different band gaps and electron affinities. In III-V materials one looks to achieve this by forming different compositions of ternary and even quaternary compounds - however, there are some severe constraints, not least phase diagram access to the required stoichiometry and the need to lattice match to the underlying substrate to prevent debilitating defect density levels. In the polymer case the structure is effectively

amorphous, but the defects tend to have energy states outside the band gap (i.e. they are confining), and since the sigma bonds provide a strong structural framework, there are no dangling bonds (therefore the interfaces are not as sensitive to the environment and UHV processing is not required). The principal disadvantages are lifetime and mobility. Mobility is low due to the largely amorphous nature of conjugated polymer films. Carrier transport across thin films is limited by the mobility values. The hole mobility in PPV is of order  $10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  allowing transport across a  $1000 \text{ \AA}$  layer with typical fields of  $5 \times 10^5 \text{ V/cm}$  in  $0.5 \mu\text{s}$ . (Nevertheless, these switching times are quite adequate for use in many diode devices, such as light emitters, detectors and solar cells.)

In Field Effect Transistor devices, however, channel lengths are substantially larger and the total device size has to be comparatively large (large channel width) to allow reasonable current densities, e.g. for driving LEDs in an active-matrix configuration. Many of the applications of interest are for large area devices where the polymer materials would be an alternative to amorphous silicon. In the latter case typically large devices ( $> 100 \mu\text{m}^2$ ) are used which in combination with a-Si mobility of between  $0.1$  and  $1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  is sufficient to achieve the switching speeds required in active matrix displays. Mobility of this order have been achieved through different techniques primarily by the deposition of ordered (more crystalline) materials and recently also for well-ordered soluble polyalkylthiophenes.

Lifetime is also a big concern when considering commercial applications of the technology. Much work has taken place over the last 50 years to improve the resistance of everyday polymers to photo oxidation principally through the use of additives to prevent discolouration. It should come as no surprise that similar problems exist with conjugated polymers, particularly since in most electronic applications excited  $\pi^*$  states are necessary intermediates - oxidation of these states can lead to degradation of the performance of the materials.

Storage lifetimes of at least five years are typically required by most consumer and business products, and operating lifetimes of  $> 20,000$  hours are relevant for most applications. Conducting polymer materials based on doped polyaniline (a conjugated polymer material that has been known for over 100 years) and polypyrrole are already demonstrating the stability required for commercial applications. In the area of light emitting polymers, significant activity is taking place to improve material lifetimes both through use of materials that are resistant to oxidation and through improved encapsulation.