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Introduction

1.1 Introduction

The development of plastic in the late 1800s revolutionised manufacturing technology and led to what is now commonly known as the Plastics Age [1]. These new materials were flexible, durable and formable in ways that natural materials were not. The first plastic material was developed by Alexander Parkes and was revealed publicly at the 1862 Great Exhibition held at South Kensington in London. Parkesine, as the new material was dubbed, was a cellulose-based material akin to celluloid that could be moulded when heated [2]. In 1899, Arthur Smith patented the use of phenol-formaldehyde resins for use as an ebonite substitute in electrical insulation and this invention led to the development of Bakelite by Leo Baekeland in 1907; probably the best known early plastic [3]. Further developments in the twentieth century led to the invention of Vinyl (polyvinylchloride) by Walter Semon in 1926, Teflon (polytetrafluoroethylene) by Roy Plunkett in 1938 and Nylon by Wallace Carothers in 1939. These materials, and other related plastics, share many similar properties: they are inexpensive, flexible and easy to process. Another property that appeared to be systemic to plastics up until the 1960s was that they were all electrical insulators. Indeed, one of the first domestic applications for Bakelite was as electrical insulation.

However, there are a group of organic, polymeric materials that exhibit electrical conductivity that date back to the pre-historical era. Known as *carbon blacks*, these materials are typically formed from the partial burning of organic substances (such as oils or wood) and have been an important commercial product for centuries, primarily due to their colour (used in pigments and dyes), high electrical conductivity (~50 Ω^{-1} cm^{-1}) and excellent thermal and mechanical properties [4].

Prior to the 1950s, these so-called carbonaceous polymers were thought to consist of three-dimensional cross-linked units with chemical structures that were complex and ill-defined [5]. In order to address these problems, several researchers started to work on developing synthetic routes with the goal of developing controlled conducting polymers, such as polyvinylenes and polyphenylenes [6]. However, the first demonstration of the synthesis of a substantially conductive polymer was achieved in Australia in 1963 by Donald Weiss and co-workers with the thermal polymerisation of tetraiodopyrrole to produce polypyrrole with resistivities of 11–200 Ω cm [7–9].

Conducting polymer research changed significantly in 1977 with the discovery by Alan Heeger, Hideki Shirakawa and the late Alan MacDiarmid that polyacetylene becomes a metallic conductor upon iodine doping, with conductivities as high as 500 S cm^{-1} [10]. This discovery ultimately created an entirely new field of organic electronics and has led to extremely rapid developments in the areas of organic light emitting diodes (OLEDs), organic photovoltaics (OPVs) and organic field effect transistors (OFETs), to name but a few. The rapid development of organic electronics as a research area has paved the way for the rapid development of commercial devices based on this new technology. The first applications have come from the commercialisation of OLED-based display technology, with initially small screens for consumer products ultimately resulting in the development of the OLED-based XEL-1 TV released by Sony in 2008. These new OLED-based displays offer enhanced contrast ratios, wider viewing angles and much thinner formats than comparable LCD or plasma displays (Figure 1.1).

The defining feature of organic electronics is that it allows us to combine the flexibility, formability and economy of plastics with the technological capability of electronics. We are now in the exciting position of being able to envisage a world where consumer electronics devices can be printed at such low cost as to be disposable, where every building has a flexible photovoltaic coating on its roof and where integrated bioelectronic sensors and transistors are routinely available [11].

1.1.1 Origins of Semiconductivity

Inorganic semiconductors, such as silicon, are crystalline solids with an electronic structure that can be described in terms of energy bands, where each energy band is actually an array of allowed energy levels (or states) that can be occupied by an electron (Figure 1.2). Just as audience members have to occupy seats in a theatre, electrons have to occupy states within the energy band. In the idealised case, the electronic structure consists of a higher energy conduction band and a lower energy valence band separated by an energy gap, the size of which depends upon the material. Indeed, one can stretch the theatre analogy a little further to think of the valence and conduction bands as corresponding to the stalls and upper circle seats, respectively. This concept of an energy gap, which is entirely a consequence

Figure 1.1 An OLED electronic display watch (top left), mp3 player (top right) and OLED television (bottom panel)

of quantum mechanics, is crucial to our understanding of conductivity in materials and its subsequent exploitation in a vast range of electronic devices. The high electrical conductivity of metals is a consequence of the fact that the highest occupied band is only half full and, hence, there are many empty states within the band that electrons can move to. In the case of insulators, however, the highest occupied band is full and, thus, for current to flow the electrons have to cross an energy gap of several electron volts, hence their conductivity is very low. Inorganic semiconductors tend to have band gaps typically in the energy range of 0.1–2.2 eV. In the case of silicon, for example, the band gap is 1.12 eV, whereas for gallium arsenide it is 1.4 eV. It is energetically feasible, therefore, that there is sufficient thermal energy at room temperature to excite an electron from the valence band into the conduction band of the material, thus producing two charge carriers: an electron in the conduction band and a so-called hole in the valence band. Although the hole that is produced is simply an empty electronic state, which can be occupied by other electrons in the valence band, it behaves to all intents and purposes as though it is an independent carrier of positive charge. However, to

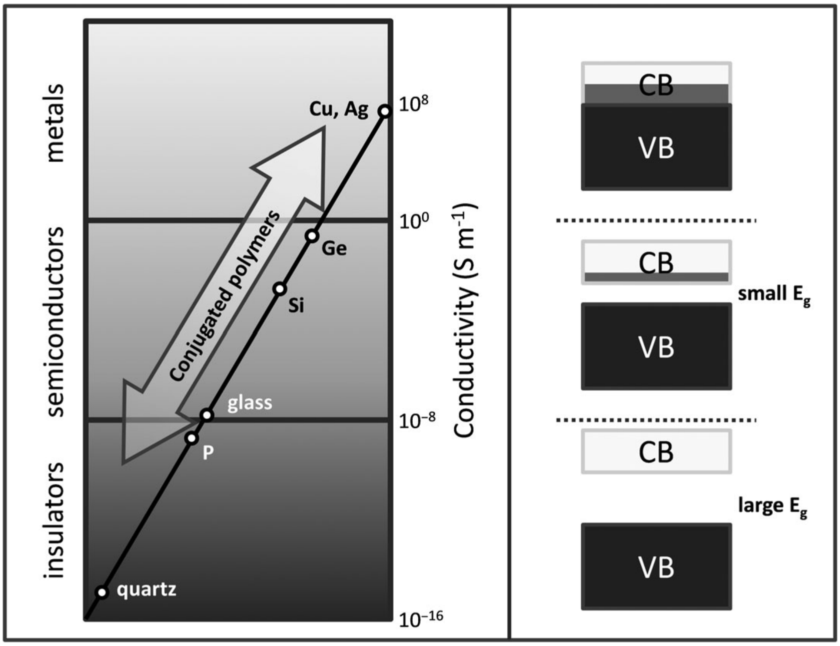

Figure 1.2 Left hand panel: Electrical conductivity of conjugated polymers encompasses the range of conductivities from insulators to semiconductors to metals. Right hand panel: The corresponding band structures for metals, semiconductors and insulators. In an insulator, the valence band (VB) is full and no electrons can cross the band gap (E_g) to occupy the conduction band (CB). For a metal there is no E_g and the CB is partially filled. In a semiconductor, E_g is small enough to permit thermally activated occupancy of CB.

make practical devices, inorganic semiconductors typically need to be doped in order to increase their conductivity by making them rich in either electrons (n-type) or holes (p-type).

Organic semiconducting materials are not limited to polymers but also encompass the small molecule systems, such as the arenes, pthalocyanines and the vast range of organic dye materials. The common feature of all of these organic semiconductors is that they possess chains of alternating single and double carbon bonds, producing what is known as a conjugated π−electron system that is delocalised over the entire molecular system. Effectively, the extra electrons from the double bonds are only loosely held and can move along the polymer chain (intra-chain transport) or between chains (inter-chain transport). More accurately, it is the characteristics of the π-bonds that actually lead to the electronic properties of conjugated polymers. Firstly, the π-bonds are delocalised over the entire molecule and, secondly, the quantum mechanical overlap of p_z orbitals actually produces *two* orbitals, a bonding (π orbital) and an anti-bonding (π^* orbital). The lower-energy π orbital produces the valence band while the higher-energy π* orbital forms the conduction band, with the difference in energy between the two levels producing the band gap that determines the optical properties of the material. Interestingly, most semiconducting polymers appear to have a band gap that lies in the range of 1.5–3 eV, making them ideally suited as optoelectronic devices working in the optical light range.

Rather than the usual electron wave picture that is used to describe conductivity in crystalline inorganic semiconductors, electron transport in the more amorphous conjugated polymers is better described by a hopping transport model. As such, carrier mobilities in conjugated polymers are not as high as those observed in the best crystalline inorganic materials and, thus, it is unlikely that these organic materials will be able to truly compete with inorganic semiconductors in terms of speed or ultimate device miniaturisation. Indeed, the initial mobility values in these organic materials were very low (~10^{-5} cm^2 V^{-1} s^{-1}) in comparison with silicon-based inorganic devices (0.1–1 cm^2 V^{-1} s^{-1}). However, with the development of new organic semiconductors these mobilities have improved, with, for example, OFETs made from pentacene exhibiting mobilities in excess of 1 cm^2 V^{-1} s^{-1}. Indeed, mobilities in excess of 10 cm^2 V^{-1} s^{-1} have been reported for organic molecular crystal materials, with DC mobilities as high as 43 cm^2 V^{-1} s^{-1} measured for rubrene [12].

The vacuum deposition of short chain oligomers on the other hand tends to lead to polycrystalline or single crystalline films. These materials tend to assume π−π stacked structures parallel with the OFET substrate, thus allowing efficient charge transport in the plane of the film. However, defect scattering occurs at the grain boundaries in these materials, thus lowering the mobility of the polycrystalline films with respect to the single crystal materials. The polymers that show the most promise in this area contain thiophene units. Indeed, solution processed films of poly(3-hexylthiophene) (P3HT) have high field effect mobilities of between 10^{-2} and 1 cm^2 V^{-1} s^{-1} and, hence, are well within the range of amorphous silicon-based devices and, as we will discuss in Chapter 8, copolymers of thiophene and other units have been made with reported mobilities between 1 and 20 cm^2 V^{-1} s^{-1}. The mobilities of these more ordered thiophene-based polymers are much higher than those found in amorphous π-conjugated polymers such as polyacetylene and polythiophene and, thus, it appears that the degree of polymer crystallinity plays an important role in device performance.

Another important question is whether the performance of a given organic transistor material is dominated by extrinsic factors, such as oxidation, the presence of moisture or chemical impurities, or whether the intrinsic structural and energetic disorder of the organic semiconductor and/or specific structural defects are responsible for the measured device properties, particularly with regard to their stability [13]. For example, large hysteresis effects and threshold voltage shifts are often observed for polar un-cross-linked polymer dielectrics such as polyvinylphenol (PVP) [14], which are then markedly reduced in poly(4-vinylpyridine) (PVPy)-based organic thin film transistors [15].

Overall, therefore, even considering their lower transport properties, solution processed polymers still offer the greatest potential for the production of low-cost so-called soft electronics, since they can be easily processed as liquid, unlike the organic crystals and short chain oligomers, which are typically vapour deposited.

1.2 Developing Flexible Displays: Organic Light-Emitting Diodes

The initial application focus for organic electronic device development was in the area of organic light-emitting diodes (OLEDs) [16]. The small area of these devices, coupled with the high value of consumer products such as cameras, mobile phones and televisions, meant that research into electroluminescent displays (ELDs) based on OLEDs rapidly gained traction in the early 1990s.

Although ELDs based on an organic molecule (anthracene) were first demonstrated in the early 1960s [17], it wasn’t until the late 1980s that Tang demonstrated the first real OLED based on 8-hydroxyquinoline aluminium (Alq) [18]. The first ELD based on solution deposited polymers was reported by the Cambridge group in 1990 using a polyphenylenevinylene derivative [19]. These two seminal papers provided the foundation for the modern development of the field of OLED research, both for systems based on small organic molecules (deposited primarily via vapour-phase deposition) and semiconducting polymers (fabricated from solution-based processing such as spin-coating and printing).

1.2.1 Basic Operation

In an OLED device, an applied voltage results in charge injection at the electrodes, with electrons injected at the low work function cathode and holes injected at the high work function anode (Figure 1.3). Charge transport occurs via a hopping mechanism and in an OLED device culminates in the recombination of differing charges to form a neutral exciton. As will be discussed in more detail in Section 1.3, the exciton is a bound electron-hole pair that can diffuse a short distance through the polymer system, primarily via a Förster resonant energy transfer (FRET) mechanism [20]. The recombination of the exciton results in light emission and thus the OLED design has to be tailored to ensure efficient charge injection, charge transport, exciton formation and subsequent light emission.

The mobility of electrons in organic materials is typically much lower than holes (especially in semiconducting polymers), primarily due to the presence of trapping sites (such as oxygen-containing functional groups or other electronegative

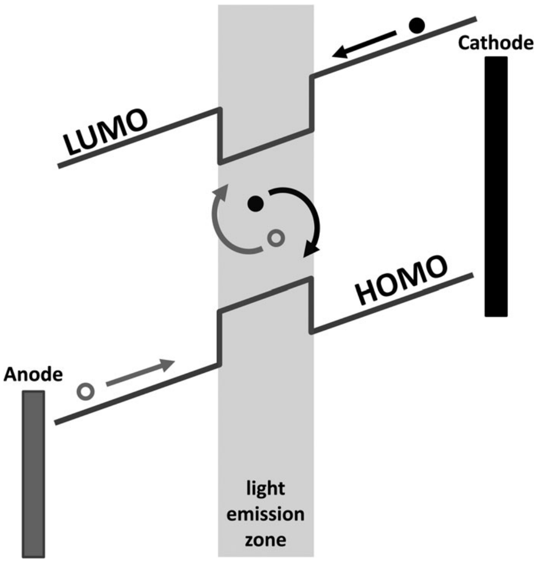

Figure 1.3 Basic operation of an OLED. Holes are injected from the high work function anode while electrons are injected from the low work function cathode. They combine to form an exciton in the light emission region, which subsequently recombines, resulting in light emission

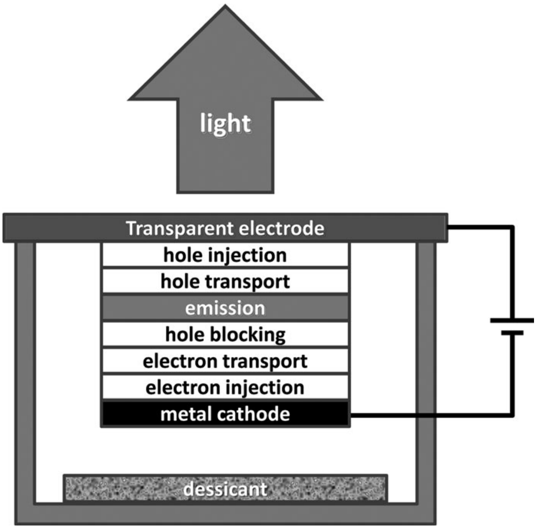

Figure 1.4 Multi-layered OLED structure with layers tailored for carrier injection, transport and blocking characteristics

impurity materials). Consequently, OLED devices have a multi-layered structure (Figure 1.4) incorporating layers that are tailored for electron and hole transport as well as hole-blocking layers to ensure equal electron and hole densities in the light emission layer.

In an OLED, the light emission region (or recombination zone) is typically designed to be in the middle of the emissive layer, thus requiring that equal fluxes of electrons and holes arrive in the centre of the OLED device. Consequently, balanced and efficient charge carrier injection and mobility need to be achieved since any unbalance results in a shifting in the position of the recombination zone. Unfortunately, neither balanced charge carrier injection nor mobility is usually obtained in single-layer OLEDs, due to non-radiative recombination of charges at the electrodes (dark current) or recombination of excitons in the near-electrode region, resulting in decreased quantum efficiencies [21]. In particular, the mobility of electrons in organic materials is typically much lower than holes (especially in semiconducting polymers), primarily due to the presence of trapping sites (such as oxygen-containing functional groups or other electronegative impurity materials). In order to address these issues, OLED devices have a multi-layered structure (Figure 1.4) incorporating layers that are tailored for electron and hole transport as well as hole-blocking layers to ensure equal electron and hole densities in the light emission layer. In a typical multi-layered OLED structure, the emitting layer is sandwiched between the hole and electron transport layers (Figure 1.4), which facilitate enhanced recombination of electrons and holes in the emissive layer, hence ensuring that light emission is maximised in the centre of the device.

As can be seen in Figure 1.3, the colour of the emitted light (wavelength) depends on the energy difference between the LUMO and HOMO levels (taking into account the exciton binding energy) and, thus, is controlled by the electronic structure of the polymer or molecule. At both electrodes a low barrier to charge injection is required. For the anode, indium tin oxide (ITO) is commonly used since its high work function (typically 4.8–5.0 eV) is well matched to the typical HOMO levels (5–6 eV) of most organic electronic materials and can be further enhanced by oxygen plasma treatment [22]. On the cathode side, a low barrier relative to the LUMO level of the organic material (typically 2–3 eV) is required for electron injection. OLED researchers pioneered the use of low work function metals such as calcium and magnesium as electron injection layers, but the low stability of these materials meant that they were superseded by more stable cathodes, such as magnesium/silver alloys [23], thin (~1–5 nm) lithium fluoride layers capped with aluminium [24], caesium fluoride [25] and magnesium oxide layers [26].

Another key criterion for OLED devices is a high solid state photoluminescent (PL) quantum yield. Quantum mechanically, an exciton is the bound state of an electron and a hole, forming a quasiparticle with zero net charge. Both electron and hole are particles with spin ½ and thus can be combined either symmetrically to form a triplet state (total spin quantum number, $S = 1$) or anti-symmetrically to form a singlet state ($S = 0$). Whereas the transition from the singlet state to the ground state (S = 0) occurs rapidly in nanoseconds leading to light emission, decay from the triplet state to the ground state is quantum-mechanically forbidden (since ΔS must be zero). The probability that a triplet or singlet state will form depends on the number of possible spin orbital configurations that are possible in each state, which for singlets is one and for triplets is threefold. Consequently, given the random nature of spin production in electroluminescent devices simple statistics predicts that only 25% of the injected charges should result in light emission from singlet states, whereas 75% of excitations will involve triplet states and thus, in principle, the internal quantum efficiency should be limited to 25%. However, the formation cross-section of singlet excitons can be much higher than triplet excitons in π-conjugated polymers [27] and it has been shown recently that singlets generated from triplet–triplet annihilation can reach 40% of all excitons generated by charge recombination [28]. Moreover, incorporating heavy atoms (such as platinum and iridium) into the emitter structure can allow triplet to singlet intersystem crossing (ISC), which can lead to highly efficient devices with potentially up to 100% of the excitons emitting light and very high PL quantum yields [29]. More recently, donor–acceptor complexes have been used to demonstrate highly efficient ISC without the use of heavy atoms [30].

Another important factor that governs the luminescence of OLEDs is the surface out-coupling efficiency, ξ, which relates the external electroluminescent (EL) efficiency, η_{EL}^{ext}, with the internal electroluminescent (EL) efficiency, η_{EL}^{int}, such that:

$$\eta_{EL}^{ext} = \xi \eta_{EL}^{int}. \tag{1.1}$$

Given that only the external EL efficiency can be measured, understanding the origin of ξ is therefore crucial to provide an estimate of the internal quantum efficiency and hence an insight into the device physics of OLEDs [31].

For isotropic emission, where there are no optical interference effects with the reflector, the external and internal EL efficiencies are simply related by the refractive index of the emitter layer, n, with $\xi \sim {}^{1}\!/_{2n^2}$ for large n. In the case of in-plane dipoles (and no optical interference) the relationship is modified slightly so that $\xi \sim {}^{3}\!/_{4n^2}$ [32]. However, for OLEDs, which consist of a thin organic light emitting layer sandwiched between a metal cathode and a transparent anode, the situation is far more complicated. Multiple optical reflections at the metal anode combined with complex refraction at the various multiple interfaces in the device result in optical interference effects that can significantly influence the value of ξ. For OLED devices where the emission location is optimal, optical modelling shows that $\xi \sim {}^{3}\!/_{4n^2}$ and $\xi \sim {}^{6}\!/_{5n^2}$ for isotropic and in-plane dipoles, respectively. More importantly, this analysis also revealed that the probability of forming an emissive singlet exciton from electrical injection was substantially larger than the value of 0.25 predicted from quantum mechanical spin statistics [33].

Table 1.1 *Summary of performance characteristics of various lighting technologies*

Light Source	Efficiency ($\mathrm{lm\ W^{-1}}$)	CRI	Lifetime (hours)
Incandescent lamp	10 – 15	>90	1,000
Fluorescent tube	40 – 80	70	10,000
High-pressure sodium lamp	140	<10	10,000
Light-emitting diode (LED)	>80	80	>10,000
Organic light-emitting device (OLED)	>110[1]	>90	10,000

Table adapted from So et al. [37].

[1] Panasonic announced the world's highest efficiency white OLED for lighting on 24 May 2013.

1.2.2 White OLEDs and Application to Solid State Lighting

The development of the first white organic OLED was reported by Kido and co-workers in 1994 [34, 35]. The luminous efficacy of a source is a measure of the efficiency with which the source provides visible light and is the ratio of luminous flux to input power and is measured in lumens per watt ($\mathrm{lm\ W^{-1}}$). Since this first report, the field developed rapidly with the white light efficacy improving from initial values of less than 1 $\mathrm{lm\ W^{-1}}$, to figures of ~100 $\mathrm{lm\ W^{-1}}$; comparable to that of a fluorescent tube [36]. White OLEDs offer a number of attractive features as a white light source. They are a lightweight, flexible and mercury-free illumination light source and already meet the requirements of the EU directives on Waste Electrical and Electronic Equipment (WEEE) and Restriction of Hazardous Substances (RoHS). As such, these devices are expected to usher a revolution in lighting design, including such developments as transparent lighting panels and luminescent wallpapers [37].

The requirements for general illumination lighting are: (a) sufficient luminous flux (where a typical office lighting fixture emits ~ 5000 lm), (b) a colour rendering index (CRI) greater than 80 (where the CRI measures the ability of a light source to render all of the colours that it illuminates) and (c) a lifetime of greater than 10,000 hours at high brightness. The comparative performance characteristics of various lighting technologies are listed in Table 1.1.

1.2.3 Conjugated Polymers for Lasing Applications

One of the holy grails of organic optoelectronics has been the development of the semiconducting polymer laser. The first report of the use of a conjugated polymer as the gain medium in a lasing system was in 1992, when MEH-PPV was used in solution as the dye in an optically pumped dye laser system using a Q-switched Nd:YAG laser [38]. Apart from their excellent material processing properties, conjugated polymers also have high photoluminescence yields, even in the solid state, which means that they have been identified as potentially attractive candidates for solid state lasing for a number of years [39]. Optically pumped lasing has been reported for a wide range of conjugated polymers, including in the polyphenylenevinylenes (PPVs) [40–42] and polyfluorenes [43, 44]. In addition, the lasing of host–guest systems composed of MEH-PPV (see Chapter 3) doped into F8BT (see Chapter 6) have been described [45].

The challenge faced in developing an electrically pumped organic solid state laser is, however, more significant [46]. In particular, the issues around overcoming the inherent losses, which lead to extremely high lasing thresholds, need to be overcome. These losses arise from optical leakage at the metal electrodes [47], polaron–exciton quenching in the active layer [48] and absorption by triplet excitons [49]. Thus, although the electrically pumped organic laser has yet to be achieved, despite more than 15 years of development since the first optically pumped organic laser, the underlying issues are now understood and are being quantitatively determined.

1.3 Developing Solar Paint: Organic Photovoltaics

The development of novel photovoltaic (PV) devices based on conducting polymers is one of the most rapidly developing areas in the field of organic electronics. The increasing demand for energy coupled with the rising world population provides a significant driver for the expansion of global energy resources. Moreover, the constraints of climate change and sustainability mean that meeting this so-called Terawatt Challenge will only be possible using non-CO_2 emitting energy generating technology. Indeed, ever since their first discovery, conducting polymers have been used to form the active elements of PV devices. The motivation is clear: of all the non-traditional renewable energy resources currently available, arguably only solar power has the potential to provide the world with the increased electrical generating capacity that it requires in a sustainable manner. Moreover, within the more specific area of solar photovoltaic devices, solar cells made from polymers can be printed at high speeds across large areas using roll-to-roll processing techniques, thus creating the tantalising vision of coating every roof and other suitable building surface with photovoltaic materials at extremely low cost.

1.3.1 Basic Operation

The photocurrent generation mechanism for inorganic semiconductors, such as silicon, is well established. In a conventional inorganic photovoltaic device, the photocurrent is generated across junctions between n-type and p-type semiconductors with the photoexcited electron and hole being separated by the strong internal electric fields that exist at the junction and thus becoming free to migrate to the opposite electrode, whereupon they can do useful work. In the case of semiconducting polymers, however, the photocurrent generation mechanism is more complex than for inorganic semiconductors. Although the action of an incident photon upon a conducting polymer excites an electron from the valence band into the conduction band, the low relative dielectric constant of organic materials (typically 2–4) means that the electron and hole that are produced are bound and their motion through the material is coupled. These coupled moieties are known as *excitons* and are responsible for many of the electronic properties found in the most common and efficient polymer-based electronic devices.

How then, can we obtain any useful work from a conducting polymer if the electron and hole are not separated? It turns out that the bound exciton can be split at interfaces with the simplest interface being created at the junction between the electrode and the conducting polymer. Under open circuit conditions, holes are collected at the high work function electrode (which is typically made of indium tin oxide (ITO), a transparent conductor) while electrons are collected at the low work function electrode (which is typically a metal electrode such as aluminium). Indeed, the open circuit voltage generated by these devices depends upon the work function difference between the two electrodes. Unfortunately, the exciton splitting process that occurs at a conducting polymer/electrode interface is not very efficient and was one of the causes of the low quality of early polymer photovoltaics. Another cause of the very low efficiencies of early devices was the effect of impurities, such as oxygen, which acted as traps for the migrating charge carriers.

Attempts to improve the efficiency of the exciton splitting process led to the development of new conducting polymer species that contained electron-donating and electron-accepting species. By creating interfaces between conducting polymer molecules of differing electron affinities it is possible to enhance the probability of electron transfer between molecules. This process (photoexcited charge transfer) causes the bound charges to separate and the junction formed at the donor–acceptor interface is analogous to a semiconductor heterojunction. These heterojunctions work very well at separating excitons that arrive at the junction. Unfortunately, the lifetime of excitons is short such that only excitons that are formed within about 10 nm of the junction will ever reach it. This short exciton range clearly limits the efficiency of these photovoltaic devices. In an attempt to develop a more efficient photovoltaic structure, interpenetrating networks of electron-accepting and electron-donating polymers were produced by blending electron-donating and electron-accepting materials together. With these materials, the number of heterojunctions within the polymer blend is greatly increased, thus so is the probability that an exciton will encounter a junction and be separated.

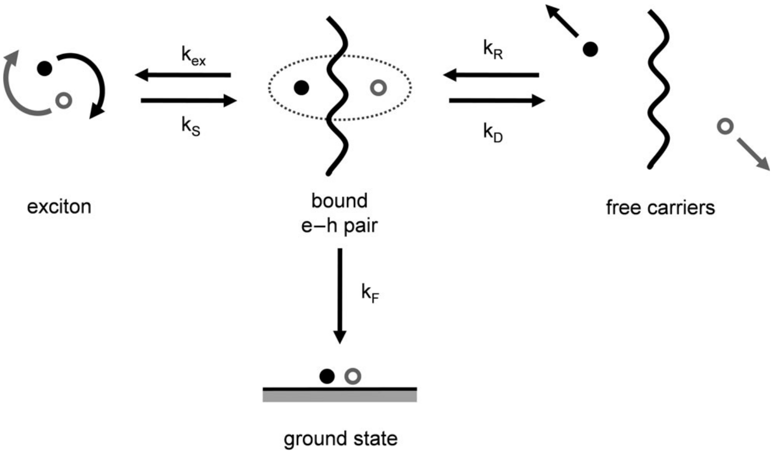

Figure 1.5 Schematic of free carrier generation in organic photovoltaic cells. The wavy line denotes an interface and the dotted ellipse denotes a Coulombic binding between an interface separated electron–hole pair

The model for exciton dissociation and recombination at these heterojunction interfaces is now well-established and is summarised in Figure 1.5. Dissociation of photogenerated excitons at donor–acceptor interfaces (with rate constant k_S) does not initially result in the production of free charges, but rather a bound electron-hole pair [50] (also known as a charge transfer state [51], bound radical pair (BRP) state [50] or bound polaron pair [52]) due to the Coulomb attraction across the interface between the charge carriers. Thus, a further dissociation step (with rate constant k_D) needs to occur, whereby the bound electron-hole pair separates into free charge carriers via a process that is dependent upon the temperature and electric field across the interface, before it decays to the ground state (with rate constant k_F). This bound pair is metastable and can also be regenerated via recombination (whether geminate or bimolecular) of free charge carriers (with rate constant k_R) [51]. Finally, it is thought that excitons can be regenerated at donor–acceptor interfaces (with rate constant k_{ex}) and can be transferred back into the bulk [52, 53].

The ratio of the dissociation, k_D, and recombination, k_R, rate constants can be expressed in terms of the charge separation, a, the temperature, T, and the binding energy, E_B, such that [51]:

$$\frac{k_D}{k_R} = \frac{3}{4\pi a^3} e^{-E_B/kT} \left[1 + b + \frac{b^2}{3} + \frac{b^3}{18} + \frac{b^4}{180} + \ldots, \right], \tag{1.2}$$

where, for a given electric field, E, relative permittivity, ε, and temperature, T, b is a constant defined by:

$$b = \frac{e^3 E}{8\pi\langle\varepsilon\rangle\varepsilon_0 k^2 T^2}, \tag{1.3}$$

where e is the electronic charge, k is, the Boltzmann constant and ε_0 is the permittivity of free space, and:

$$E_B = \frac{e^2}{4\pi\langle\varepsilon\rangle\varepsilon_0 a}. \tag{1.4}$$

Substituting Equation (1.3) into Equation (1.1) and rearranging:

$$\frac{k_D}{k_R} = A\left(\frac{1}{a^3}\right) exp\left\{-\left(\frac{B}{a}\right)\left(\frac{1}{kT}\right),\right\}, \tag{1.5}$$

where

$$A = \frac{3}{4\pi}\left[1 + b + \frac{b^2}{3} + \frac{b^3}{18} + \frac{b^4}{180} + \ldots\right] \tag{1.6}$$

and

$$B = \frac{e^2}{4\pi\langle\varepsilon\rangle\varepsilon_0}. \tag{1.7}$$

Thus, from Equation (1.4) we see that the ratio of the dissociation and recombination rates is a function of both the separation of the bound electron–hole pair (a) and the effective thermal energy of the bound state (kT) [54]. The overall probability that a bound electron–hole pair dissociates into free charge carriers is also a function of k_F [51], which is likely to have a similar dependence upon charge separation and effective thermal energy since a strong coupling between the bound electron and hole is also expected to increase k_F [52]. Therefore, the overall dissociation probability is a function of both initial charge separation (a) and effective thermal energy of the bound state (kT).

1.3.2 Progress towards Organic Solar Coatings

Photovoltaic devices made from organic semiconductors have come a long way since the first devices, using organic crystals such as anthracene and perylene, were reported in 1959 [55]. These early organic electronic devices were typically sandwich-type structures, with films or single crystals of thickness between 1 and 100 μm arranged between two conducting electrodes. Unfortunately, these molecular semiconductor-based devices tended to show low photo-voltages (typically less than 500 mV) and poor energy conversion efficiencies. These poor efficiencies were attributed to difficulties in achieving efficient ionisation of the photo-generated excitons together with inherently poor electron or hole mobility in these materials. However, different device architectures were devised to circumvent some of these limitations. In 1986, Tang demonstrated that exciton dissociation could be made more efficient in molecular photovoltaic devices by creating a heterojunction of two organic layers with different electronegativities (namely CuPc (copper phthalocyanine) and PV, a perylene tetracarboxylic derivative) [56]. This was the first heterojunction structure and showed that efficiencies could be improved by bringing the electron donor (D) closer to the electron acceptor (A) material. In 1992, Sariciftci et al. showed that, by combining a semiconducting polymer (D) with C_{60} (A), ultrafast D–A electron transfer occurs and they demonstrated for the first time the potential for fullerenes (and their derivatives) to act as highly efficient electron acceptors in these devices [57, 58]. In 1995, Yu et al. showed how the bulk heterojunction (BHJ) concept could be used to massively increase the number of excitons that reach an interface by intimately blending the donor and acceptor components [59]. Moreover, the soluble fullerene derivative phenyl-C_{61}-butyric acid methyl ester (PCBM) material that was developed as part of this work has gone on to become the mainstay electron acceptor material in OPV devices for more than a decade. In 2001, Shaheen et al. showed how surface morphology was a critical determinant for device performance and that the choice of solvent system could have a profound effect upon OPV efficiency [60]. Since then, OPV devices based on polythiophene derivatives have gone on to achieve routine efficiencies of around 4%. Further efforts to improve device efficiency have focussed upon the development of tandem cells; combining two or more OPV cells with complimentary absorption characteristics in series [61]. This architecture increases the open circuit voltage of the overall device and enables broadband absorption over the solar spectrum. The importance of controlling the light distribution in these devices has been recognised. Combining this architecture with the use of a TiO_2 spacer layer which can enhance device performance by ~50% through maximisation of the light field within the very thin active layer, has led to the most efficient OPV devices so far, with efficiencies as high as 6.5% reported in 2007 by Heeger's group for the first tandem cells involving two polythiophene derivatives combined with PCBM [62], which was increased in 2013 to over 10% for devices using alternating donor–acceptor copolymers [63, 64].

More recently, as will be expanded upon in Chapters 7 and 8, many more high-performance polymers have been developed [65]. The majority of these improvements have been based on extending the spectral response of the materials to longer wavelengths to produce so-called low band-gap materials. Materials such as poly [2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']dithiophene)-alt-4,7-(2,1, 3-benzothiadiazole)] (PCPDTBT) have extended the wavelength response of these materials up to 900 nm, and have produced device efficiencies of up to 5.5% with appropriate alkanethiol additives [66]. Further synthetic developments led to the introduction of donor–acceptor (D–A) systems such as the thieno[3,4-b]-thiophene (TT) and benzodithiophene (BDT) D–A systems [67–69], capable of delivering power conversion efficiencies approaching 20%, as will be discussed in Chapter 8.

1.4 Developing Disposable Integrated Circuits: Organic Transistors

The first solid state organic field effect transistor (OFET) was demonstrated by Tsumura and co-workers in 1986 using polythiophene as the semi-conducting layer [70], with a similar device being reported by Burroughes et al. in 1988 [71]. In an OFET (Figure 1.6) the current between the source and drain electrodes (I_{SD}) is controlled by a voltage (V_G) applied to a third electrode known as the gate. The gate electrode is separated from the source–drain region by a thin insulating dielectric region and thus is capacitively coupled to the semiconductor. By altering the bias voltage applied to the gate region, the source–drain region can be altered from conducting to insulating and, hence, the device can be turned on or off. Importantly, the presence of a relatively small number of charges on the gate electrode (I_G) alters the flow of a great many charges (I_{SD}) controlled by the

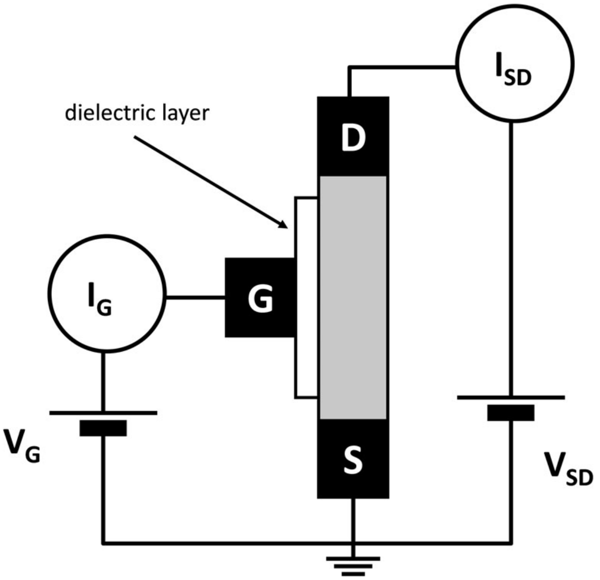

Figure 1.6 Schematic of free carrier generation in organic field–effect transistor. The letters **D**, **G** and **S** denote the drain, gate and source electrodes, respectively

voltage (V_{SD}) between the source and drain electrodes and, thus, as well as acting as a *switch*, the FET acts as an *amplifier*.

A common feature of these early organic thin film transistors (OTFTs) was the use of silicon as the substrate material. These hybrid devices were not truly all-polymer electronic devices and thus did not offer all of the advantages offered by organic materials such as flexibility. However, patterning, conducting and insulating regions on silicon is a well-established technology and thus the fabrication of these devices was relatively easy to implement. Subsequently, the first all-polymer FET was reported by Garnier et al. in 1994 and was fabricated by a printing technique [72].

As discussed previously in this chapter, the mobility of the charge carriers is a key parameter in determining the performance of conjugated polymers in organic electronic devices and this criterion is particularly relevant in the case of organic transistors. As such, a great deal of OFET research has focussed upon developing and optimising the charge carrier mobilities of existing and new organic materials. Traditionally, hole carriers (p-type materials) dominated the organic electronic landscape but advances in material design and synthesis have led to an increasing number of n-type molecules where electrons are the dominant charge carrier. A variety of semiconducting organic materials are now commonly available, ranging from small molecule systems based around the acenes to conjugated polymer systems (such as the polythiophenes) to larger macrocycles, with further intense effort aimed at improving morphology, processing and reliability of the materials through modification of side chain functionality, etc.

A much-discussed topic in the OFET field has been whether high polymer crystallinity is an essential determinant of high-mobility devices. Previous advances in polymer mobility appeared to be predicated on the development of highly crystalline polymers and this polymer engineering approach had resulted in OFET mobilities in excess of 1 $cm^2 V^{-1} s^{-1}$ for solution-processed polymer semiconductors [73]. Recently, however, as will be discussed in Chapter 8, mobilities an order of magnitude higher have been reported, despite the fact that these new polymers are actually less ordered [74]. Interestingly, it appears that, although these high-mobility materials are not highly crystalline, they do gain longer-range structural order by having a more rigid polymer backbone [75]. This increased long-range order compensates for the lack of crystallinity by providing high-mobility pathways (which extend for up to 1 μm), which allow the charge carriers to more effectively bypass disordered regions in the material [76]. Excitingly, these discoveries may point towards the development of solution-processible polymers with mobilities as high as their small crystal counterparts [77].

One of the most active areas of current OFET research is focussed on the application of these organic electronic devices as sensors and detectors. Research into OFET-based sensors encompasses a number of areas, including large area detectors, transducers and biosensors. In the case of large area detectors such as pressure sensors, the OFETs are typically used to form active-matrix structures or other electronic circuits for reading data out from each sensing unit. As such, the OFET structures are simply used as electronic switches and are actually designed to be insensitive to their environment. Indeed, research at the University of Tokyo has shown how robots of the future could be endowed with the sense of touch using sensors based on organic electronics. Takeo Someya's group has built high-mobility organic transistors, with pentacene as the channel layer, that were fabricated into a flexible sheet made of carbon and rubber [78, 79]. Upon flexing, the electrical resistance of the carbon–rubber sheet is changed locally and this change in resistance operates on the nearest OFET. Using this so-called e-skin (Figure 1.4), the robot's control system could be made to 'feel', with a sensitivity of about 10 g cm^{-2} that is independent of the OFET array. The initial 16 × 16 sensor devices built by the University of Tokyo team were limited by the response time of the pressure-sensitive rubber (~500 ms) but for larger arrays the overall frequency response is currently limited by the response time of the OFET devices (~30 ms).

OFET devices are also attractive as candidates for sensors in the own right. In particular, the fact that OFETs are fabricated from a material system that can be made liquid soluble and is carbon-based means that they are much more compatible with other organic systems, such as biomolecules, than transistors built from conventional inorganic materials. Research at the University of Newcastle is focussed upon developing new biosensors based on integrating biomolecules (such as enzymes) directly into the OFET structure to create highly specific and highly sensitive detectors that can be printed at low-cost using conventional inkjet printing technology. The ultimate vision for this work, which is at an advanced stage, is the development of a sensor that responds to the much lower salivary glucose levels instead of the usual blood glucose levels [15, 80–83]. Such a development would open the door for a non-invasive glucose meter for diabetes sufferers that would only require a very small amount of saliva to determine glucose level as opposed to current devices that require the patient to provide blood samples via needle stick.

1.4.1 The Organic Electronic Age

Although the fabrication of devices and machines based on organic electronics is still in its infancy, this exciting new field is developing rapidly and this development is accelerating. It is widely anticipated that electronic devices based on organic materials will gradually replace those based on conventional inorganic semiconductors and metals, driven primarily by the material properties of plastics, which allow for the production of arrays of devices on flexible substrates using extremely low-cost printing and coating techniques. Indeed, rapid advances are already being made, with organic electronic materials offering enormous potential across many technologies, ranging from new sources of low-cost renewable energy to arrays of biosensors for medical applications. Optical pumping of organic lasers has also been demonstrated but electrically pumped organic lasers remain out of reach at present. These materials also open up the prospect for new technologies that are not accessible by current materials by providing the interface between biological systems and electronic systems. It is possible to envisage bionic devices based on organic electronics that could be readily interfaced with biological systems and potentially directly linked to a patient's muscles and nerves. Perhaps we will see, in our own lifetime, a world where organic electronics provides both the photovoltaic coating on our roof and the glucose sensor that we printed at home on our inkjet printer.