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Organic-Based Transistors and Sensors

Aristide Gumyusenge[1], Tianbai Xu[2], Xiaozhi Wang[2], and Jianguo Mei[1,3]

[1] *Purdue University, Department of Chemistry, 560 Oval Drive, West Lafayette, IN 47907, USA*
[2] *Zhejiang University, Department of Information Science and Electronics Engineering, Hangzhou 310027, P. R. China*
[3] *Purdue University, Birck Nanotechnology Center, 1205 W State Street, West Lafayette, IN 47906, USA*

3.1 Introduction

With the emerging popularity of wearable electronics, with the high expectations from robotics engineering, with the desire and need for implantable electronics, and the quest to mimic nature in medicine engineering and artificial intelligence, we are seeking to achieve flexible—bendable and stretchable—electronics. Even though silicon remains the highest performing material in electronics, and is still being studied to be rendered thinner and flexible, silicon-based technology seems to lack the desired easy processability for low-cost manufacturing. The research community is thus dedicating tremendous efforts toward coming up with materials that can potentially complement the traditional inorganic systems used in electronics industry, not to rival silicon technology, but fulfilling the needs mentioned above. Among studied materials are organic semiconductors owing to their tunable optical, electronic, and redox properties, in combination with their ability to be processed at ambient conditions, and their biocompatibility [1–5]. The starting point for achieving large-area processing is making flexible transistors and sensors, and eventually, high-performance large-scale flexible electronics can be achieved [6–9]. Organic semiconductors have already shown promising results for commercial devices, and are being investigated for further uses in flexible circuitry [3, 10]. In this chapter, we give an overview of current approaches on achieving flexible all-organic transistors and transistor-based sensors. In the first section, we will introduce how all-organic devices can be achieved in terms of choosing substrates, electrodes, dielectric layer, and operating channel, as well as the device geometry. The second section will focus on the current state-of-the-art design of transistors; the fundamental working principles that ought to be preserved in flexible hybrids will be introduced. The third section will be dedicated to currently studied fabrication techniques suitable for organic-based transistors. In the last section, applications of flexible transistors will be discussed as we review ongoing efforts in transistor-based sensors design.

Flexible and Stretchable Medical Devices, First Edition. Edited by Kuniharu Takei.

3.2 Materials Consideration for Flexible Organic-Based Transistors

To achieve organic flexible transistors and sensors, we first ought to discuss what makes any material suitable for flexible transistors fabrication and then review how performances can be improved. This section will thus attempt to define flexibility at the level of a transistor, discuss the choice of substrates and electrodes, and introduce the choice of the dielectric layers, as well as the organic functional channel layers. Representative literature will be provided for those readers interested in further learning about current efforts in organic-based flexible electronics.

3.2.1 How Flexibility is Achieved

How we define flexibility becomes an important talking point in organic-based electronics as a first step toward deviating from the traditional robust silicon-based technologies. Some material chemists argue that for a material to be considered flexible, this should be an intrinsic property [11–13], while the counterargument suggests that any material could be rendered flexible if made thin enough [14, 15]. The word "flexible" will be used in this chapter to refer to both bendable and stretchable, and the distinction between these two terms will become crucial as we discuss the applications of organic transistors. Flexibility will here be viewed in terms of the physical strain that a device (material) can sustain when bent and/or stretched. Organic materials oftentimes tend to be associated with flexibility—ergo the common appellation of "plastics"—despite many cases that display high crystallinity and brittleness [16]. The organic systems we consider here are those that are able to provide excellent flexibility at the level of all major components of a transistor—substrate, electrodes, and active layer. We herein review materials under investigation for each component toward achieving large-area organic flexible systems.

3.2.1.1 Flexible Substrates

The approach to thin-out the silicon-based technology, of transferring it onto thinner and bendable substrates to fabricate lighter electronics has recently been a key feature in many tech companies. It could thus be envisioned that the same approach could be used to apply existing technology on flexible substrates; flexible TV displays, for instance, could be fabricated. Among substrate candidates, metals such as steel and aluminum have been investigated to be made thinner, therefore flexible [17]. Thin glass is another candidate mostly for groups interested in applying flexibility to displays (e.g., curved and bendable TVs, wearable displays, etc.) Glass provides excellent optical properties desired for displays (transmittance and birefringence), but it showed great difficulty when trying to achieve desired thinness without damaging the rather fragile and brittle glass sheets [18]. The preferred alternatives have been plastic polymer substrates. Plastic substrates have gained more popularity than the last two counterparts, not only because they tend to tolerate strain better, but also because they display several other properties that metals, for instance,

cannot provide: easy processability, low melting points (whenever desired), biodegradability, not to forget their low-cost. Plastic substrates have then been used in roll-to-roll processing owing to their ability to be printed in long foldable and pliable sheets at low temperatures [19, 20]. Most of the plastic substrates are based on thermoplastics, as well as other high glass-transition points (Tg) polymers. The most widely used polymers include polyethylene terephthalate (PET), polyethylene naphthalate (PEN), polycarbonates (PCs), and polyimides (PIs) [21–23], to name a few. Depending on their crystallinity, these polymers have thus been advanced as candidates to replace glass in fabrication of devices that require excellent optical properties combined with bendability and/or stretchability. Most newly developed fabrication techniques aim to lower the cost and unsustainability associated with the high temperatures required for metal-based substrates.

3.2.1.2 Flexible Electrodes

The use of metal electrodes remains prominent in electronics due to their excellent electronic properties. It is however worth mentioning that the most popular electrode being gold in competition with other precious metals such as platinum and silver, the cost aspect in device fabrication cannot be undermined. Most research groups take advantage of vapor deposition and sputtering to pattern thin layers of the desired metal onto substrates of choice [24–26]. Using special processing methods, transparent and pliable metal electrodes can be achieved [27–29]. Note that most of these generally used methods require high vacuum and/or high temperatures. The meticulous nature of these methods used to achieve flexibility of metal electrodes thus calls for easier and cheaper alternatives to fabricate flexible electrodes.

A special appraisal is presented on the discovery of charge conductivity in conjugated polymers by Heeger and coworkers [30]. Thanks to their work, conducting polymers have shown to be excellent candidates that can replace metal electrodes in device fabrication [31, 32]. Not only have conducting polymers shown great electronic conductivity, but they have also opened doors to easier and low-cost electrode patterning routes as they can be solution-processed at low temperatures. Free-standing flexible polymer electrodes have been achieved and incorporated in several device designs proving their ability to obviate the use of metals [33–36]. In addition to their plastic properties, conductive polymers show great conductivities, excellent charge, and discharge cycles, as well as low band gaps owing to the conjugated π-system along their backbone [36–38]. These metallic properties have also shown to be greatly enhanced in carbon nanotubes owing to their ability to be fabricated in highly oriented nanowires [39, 40]. Carbon nanotubes have thus been used to be incorporated in flexible arrays for sensing applications [41–43]. Free-standing polymer electrodes are thus being investigated as they are more suitable for low-cost fabrication of flexible electronics—they can easily be patterned as thin films.

In case of special properties that tend to be solely characteristic for metals—magnetism for instance—metal-polymer hybrids have been studied. These hybrids are usually achieved by immersing metal nanoparticles in a polymer medium; this combination affords the desired properties of the

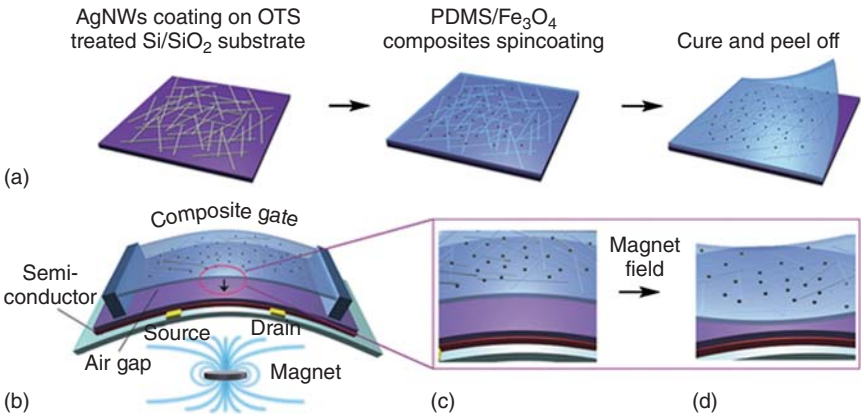


Figure 3.1 Gate electrode engineering achieving highly flexible magnetic sensors using the gate suspension technique. Silver nanoparticles are immersed in a solution of PMDS yielding a magnetically active composite. (Adapted from Ref. [47].)

metal with the flexibility of the polymer. Several composite systems have been explored and polymers such as polyamides, polyacrylamide, and other hydrogels have been used to achieve highly flexible conductive arrays [33, 44–46]. For instance, Zang *et al*. demonstrated a flexible magnetic sensor achieved by taking advantage of gate-electrode engineering. The group incorporated magnetically active nanoparticles (silver nanowires and iron oxide nanoparticles) into poly-dimethylsiloxane (PDMS), a flexible medium, and flexible composites could be fabricated. Using a gate suspension technique (as depicted in Figure 3.1) a flexible magnetic sensor was achieved [47]. Such sensors would find great applications in soft robotics.

3.2.2 Organic Dielectric Layer

Another crucial component in transistor fabrication is the layering of a dielectric layer on the top of the patterned electrodes. This step remains relevant for charge injection in organic systems [48, 49]. Given how thin the dielectric layer is made, it does not play a crucial role in limiting device flexibility. It has however been shown that by using polymer gate dielectrics in place of the inorganic dielectrics, the overall performance can be significantly improved in thin-film transistors (TFTs) [50]. An effective dielectric layer requires to be a very thin and pinholes-free film of an insulator that can allow electric field injection at low voltages. This task, however, becomes challenging as most polymer insulators tend to yield thicker films (100 nm) and require high voltages [51]. In order to circumvent this leakage issue while retaining thinness, polymers such as poly-4-vinyl-phenol (PVP) [50, 52–55], poly(methyl methacrylate) (PMMA) [51], polystyrene (PS) [56], and polyvinyl alcohol (PVA) [57] have been used. These polymers have showed the ability to be cross-linked achieving desired thinness, uniformity, and of excellent charge injection. Note that instead of relying on traditionally used methods such as vapor deposition, sputtering, and thermal growing as it is the case for inorganic dielectrics—usually silicon

(or aluminum) oxides and nitrides [48]—the polymers listed above could be deposited by solution processing. Using all-organic dielectric materials thus becomes more suitable for the fabrication of flexible devices; no harsh conditions are required and desired results can be achieved.

3.2.3 Organic Functional Layer

The use of organic materials in transistor fabrication emerged in the late 1980s with the discovery of (semi)conducting polymers [30, 58, 59]. Ever since, organic semiconductor-based transistor fabrication has seen tremendous attention to the point of achieving performances approaching that of polycrystalline silicon [5, 60]. Polymer backbone engineering, as well as side chain engineering are two crucial tools to improve charge carrier mobility in semiconductor polymer systems. With the manipulation of conjugated backbones, as well as functionality tuning of side chains, charge carrier transport in polymer systems has thus seen tremendous improvements in the past two decades. Mobilities exceeding 40 $cm^2 V^{-1} s^{-1}$ have been achieved [61].

One of the specialties for which organic semiconductors are popular is their ability to be processed as thin films at ambient temperatures. This low temperature processing has made organic thin-film transistors (OTFTs) potential candidates for devices processed on flexible polymeric substrates such as smart paper, radio frequency tags, smart cards, flexible displays, and sensors as will be discussed later in this chapter [62, 63]. In addition, this ease of achieving OTFTs provides an appealing alternative to industry as a way to obviate the meticulous and harsh protocol required for achieving thin layers of silicon [64, 65]. Organic semiconductors from small molecules, to oligomers, and conjugated polymers have shown the ability to be processed into thin films, and several device designs have been studied [2, 4–6]. We will not discuss the material design and engineering for organic semiconductors in detail. We will however revisit what has been accomplished in terms of improving charge carrier transport when we get to transistor designs; materials design and device performance tend to be inseparable in this field.

3.3 State-of-the-Art Designs and Fabrication of Organic-Based Transistors

OTFTs for different applications adopt various designs namely organic field-effect transistors (OFETs) [3, 6, 8], electrolyte-gated organic field-effect transistors (EGOFETs) [66–68], organic electrochemical transistors (OECTs) [66–72], and the list goes on. These designs aim to substitute inorganic materials with organic alternatives as the active layers in transistor fabrication. Using organic materials has promised to decrease, if not completely eliminate, the cost of high temperature ramping that is usually required for inorganic systems. Thin-film processing has also opened doors to several fabrication techniques including screen printing, inkjet printing, and different photolithographic techniques—we will revisit fabrication techniques in later sections. For all the

designs discussed further, we will need to keep in mind that charge transport in the channel layer tends to be associated to the first few layers of molecules. This concentration of charge in the bottom layers becomes crucial when choosing the optimal film thickness, as well as strategic electrodes placement for particular transistor designs [62, 64, 65]. In this section, we introduce representative transistor designs, explain their working mechanisms, and discuss their potential applications in organic electronics.

3.3.1 Organic Field-Effect Transistors

3.3.1.1 Structure

OFETs are by far the most widely studied transistor configuration in organic transistors. This design provides amplifying and/or switching of electronic signals, while maintaining a rather simple layout. The first demonstration of a solid-state OFET was reported by Tsumura *et al.* [73], which was around the same time when Kodak research laboratory had just demonstrated an organic light-emitting diode [58, 59]. Since then, the field of OFETs has been widely studied to the extent of improving the primitive charge carrier mobilities from 10^{-5} to higher than tens of $cm^2\,V^{-1}\,s^{-1}$ [4, 6, 61]. An OFET consists of an organic semiconducting layer deposited between two ohmic contacts (source and drain), separated by a thin dielectric layer from a third contact (gate). The gate can be positioned either on the top (top gate) or at the bottom (bottom gate). In some cases, the gate can also serve as the substrate, otherwise, the assembly can be patterned on a substrate (traditionally glass or heavily doped silicon).

Choosing the right device geometry is another crucial step to achieving high performance of a transistor. One of the main challenges in OFET fabrication is to ensure that neither the functional layer nor the electrodes are damaged in the process. Generally, in order to minimize atmospheric and/or harsh environment exposure, electrodes are deposited on a substrate, followed by the channel layer, and then the assembly is protected with a dielectric layer (plus the gate contact). The geometry varies depending on the intended functions of the OFET and the materials of choice. For instance, n-type materials, that is, electron-transporting semiconductors tend to be associated with low air stability. It is thus common to adopt device geometries that encapsulate the semiconductor materials between the more stable layers—insulating layer and/or passivation layer—achieving bottom-contact or top-contact geometries as shown in Figure 3.2.

It is also to be noted that many researchers are investigating the use of the vertical geometries as opposed to lateral planar geometries to increase OFETs performance and device stability [74–78]. In the vertical geometry, the semiconductor layer is sandwiched between the source and drain pads, thus reducing the channel length to the film thickness of the deposited functional layer. This geometry still faces challenges mainly due to the difficulty of charge injection through the source contact, which, in this configuration, becomes significantly close to the gate electrode yielding a capacitive unit. One of the proposed ways around this issue is the use of perforated source contacts. The electric field accumulated at the dielectric–source interface can be allowed to tunnel through the

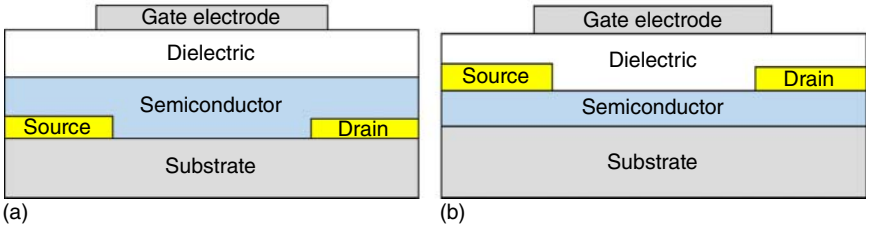


Figure 3.2 Transistor structures preferred for sensitive materials (a) bottom-contact top gate, (b) top-contact top gate. Contact is in reference to the position of source and drain with the semiconductor.

intentionally placed holes within the source electrode. High OFET performances have been achieved and reported affording potential applications for these structures in achieving flexible arrays [79, 80].

3.3.1.2 Performance and Characterization

As previously stated, an OFET is a three-terminal device that operates by switching and/or amplifying a current passing through an organic semiconducting layer deposited between two ohmic contacts (source and drain). This current flow is usually a response to a certain voltage (V_G) applied on a third plate (gate) lying underneath or on the top of the semiconductor layer. The amount of current that is able to flow between the source and drain—through the active layer—subsequently marks the device's performance in terms of its ability to transport charge carriers. The question of whether organic materials could perform to the same level as the inorganic counterparts has been the driving force to finding organic materials with high conductivities, as well as facile processability. With such materials in hand, flexible all-organic transistors can be achieved to fabricate large-area devices for daily uses. OFETs have shown promising results and we hope to be able to say the same for flexible hybrids by the end of this chapter.

Ordinarily, transistor performance is tested by analyzing the channel layer's transductance (or capacitance) as a response to an applied V_G. By applying another voltage (V_{DS}) between source and drain contacts, the performance of the channel layer can be monitored from the decrease in voltage as the current travels through the organic material. Extrapolating transfer and output curves, a few key parameters are usually reported to characterize OFET performance. First, charge carrier mobility (μ), ON/OFF ratio, as well as the threshold voltage (V_{TH}) are to be evaluated. Charge carrier mobility tells how fast the charge carriers can move from one contact to the other, while the ON/OFF ratio shows the difference between currents before the device could be turned on and when the device is switched on. The threshold voltage is an indication of the minimum voltage V_{DS} that has to be applied before the device can be "tuned on". V_{TH} is oftentimes reported with its subthreshold slope (SS) which is the voltage difference required to increase the current between source and drain by a factor of ten. This slope is usually an indication of how fast the device can switch from the OFF state to the ON state. Notice the dependence of the threshold voltage on

any fabrication defects, since any holes or leakages—contact resistance—would have to be filled before the device can turn on. Also note that the organic-based systems borrow these parameters from the inorganic systems that are used by physicists to derive the parameters [81]. The extraction of these parameters is normally done in either the linear regime or the saturation regime of the I/V transfer curves, from which the following equations are derived [4]:

$$I_{ds} = \mu \frac{W}{L} Ci(V_g - V_t)V_{ds}, V_g - V_t \gg V_{ds} \text{ (linear regime)} \tag{3.1}$$

$$I_{ds}(\text{sat.}) = \mu \frac{W}{L}(V_g - V_t)^2,\ V_g - V_t < V_{ds} \text{ (saturation regime)} \tag{3.2}$$

Equation (3.1) and (3.2) are compiled for OFET performance characterization. I_{DS} is the current between the source and drain electrodes, μ the charge carrier mobility, mostly referred to as mobility, W and L are the width and the length of the operating channel, respectively, and V_G and V_{TH} are the applied gate voltage and the threshold voltage, respectively.

Note the occasional overestimation of charge carrier mobility from the nonlinear slopes of the transfer curve, as shown in Figure 3.3, which tends to be characteristic for many semiconducting polymers including cyclopentadithiophene-benzothiadiazole copolymer (CDT-BTZ) (Figure 3.3a), diketopyrrolopyrrolethieno[3,2-*b*]thiophene copolymer (DPP-T-TT) (Figure 3.3b), and indacenodithiophene-co-benzothiadiazole (IDTBT) (Figure 3.3c) [82]. The presence of kinks within the transfer curve can lead to inaccurate performance results. The research community in this field is thus debating the linearity of transfer curves is required for accurate charge mobility reporting [83]. Nonetheless, OFETs have shown excellent performances and have shown potential to be applied to large-area processing. The ongoing quest for improving their functionalities has thus enriched the library of (semi)conducting oligo/polymers, and remarkably high charge carrier mobilities have been achieved [61]. For the readers interested in further learning about the evolution of OFETs material engineering, representative examples of highly functionalized materials were reviewed and respective mobility milestones were presented [5].

3.3.2 Modifications of OFETs for Sensing Applications

Several OFETs modifications have been designed in accordance with the desired applications especially in sensing as shown in Figure 3.4. In the next section, we show a few of the proposed designs, explain their working mechanisms, while providing their potential applications in organic electronics. The operating mechanism of OECT will be used to discuss the device performance; the other configurations tend to operate in a similar manner and will not be discussed in detail. Readers may consider the work of Piet Bergveld for more insights on ion-sensitive field-effect transitors [85].

3.3.2.1 Electrolyte-Gated and Ion-Sensitive Organic Field-Effect Transistors

An EGOFET is a proposed device design that slightly differs from an OFET mainly for biological interfacing purposes. In addition to the major components of an OFET, EGOFETs are topped with an electrolyte layer that is

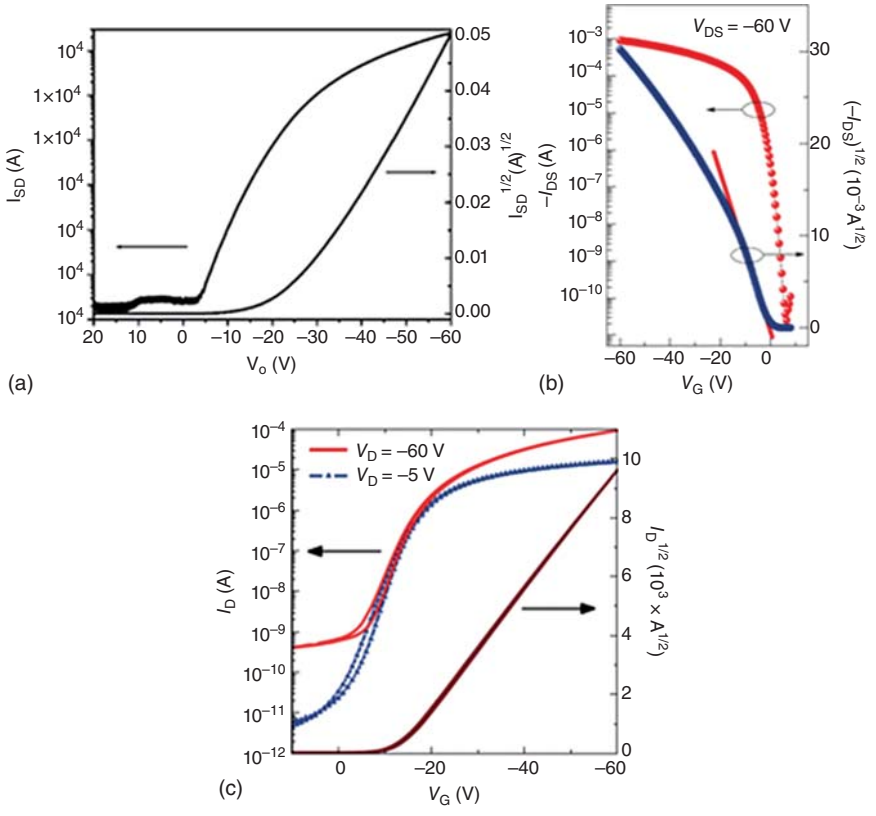


Figure 3.3 Transfer characteristics curves for mobility extraction from high-performance conjugated polymer OFETs showing occasional non-ideal transfer characteristics: (a) CDT-BTZ bottom-gate, top-contact FET. (b) DPP-T-TT bottom-gate, top-contact FET. (c) IDTBT top-gate, bottom-contact FET. (Adapted from Ref. [4].)

meant to interface with charged analytes [84]. This design has mainly been used in designing biosensors as the latter require a soft and benign interface between the device and the physiological environment. This interfacing ability has allowed for the coating of traditional metal electrodes in order to access and monitor neurons activity [86], intra- and extracellular stimulation [68], physiological pH sensing [67], as well as bio-transduction sensing [66, 87]. The working principal of electrolyte-gated transistors relies on the ability of their electrolyte/semiconductor interface to selectively detect any potentiostatic change due to ionic injection in the electrolyte layer. The amplified capacitance of the transistor is usually explained by the formation of a double Helmholtz layer between the electrode/electrolyte interface, and then the electrolyte/semiconductor interface. This double layer formation was extensively studied by Salleo research group at Stanford University [88]. With the combination of the flexibility that was discussed for OFETs—which still applies here—and the "softness" offered by electrolyte coating, EGOFETs have thus been potential candidates for interfacing with physiological tissues.

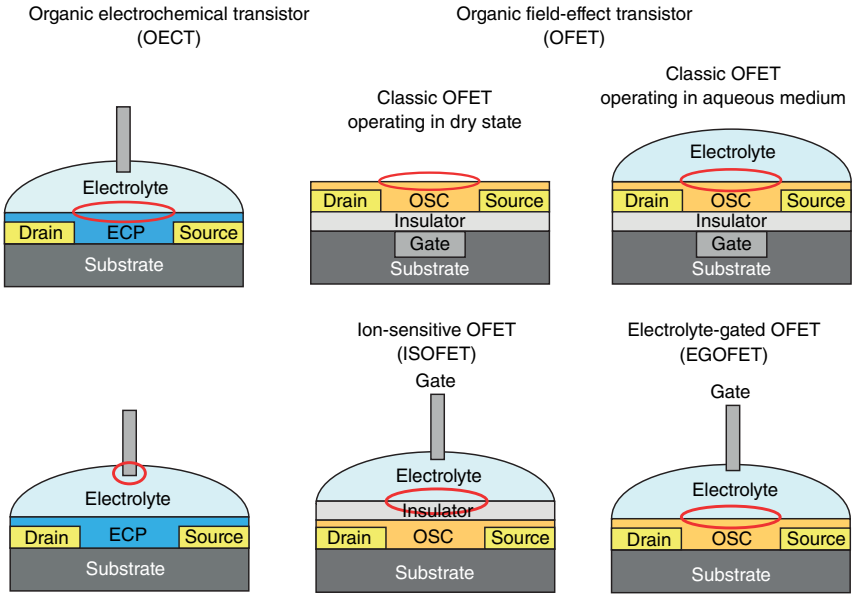


Figure 3.4 Representative modifications of OFET design for sensing applications. The red circle indicates the interface of the functional layer (OSC: organic semiconductor, ECP: electrically conductive polymer) and the electrolyte-sample solution. (Adapted from Ref. [84].)

Ion-sensitive electrolytes have been employed to achieve ion-sensitive organic field-effect transistors (ISOFETs). This OFET modification has been proposed and used for pH sensors [89, 90], various water-soluble metabolites sensing [91, 92], as well as anionic and cationic sensing [93, 94]. The injection of ions at the electrolyte interface can be translated into an electrical signal and the device's response can be monitored. Note that most of the studied electrolytes are in their aqueous phases as depicted in Figure 3.4, and oftentimes need to be contained in a well of inert polymers such as PDMS. Ideally, a solid state electrolyte or a hydrogel would be more applicable for easy manipulation of the device and for flexible arrays. To further improve the device design and sensitivity, a structure that exploits similar working mechanism as an ISOFET (as well as EGOFET) but on a wider spectrum of analytes has been studied, namely OECT.

3.3.2.2 Organic Electrochemical Transistors

This rather newly developed organic transistor design gained its popularity in the past two decades due to its promising ability to interface with the biological systems. OECTs were a timely development after the argument that the field of biomedicine has not fully benefited from the currently available technologies—compared to other fields such as entertainment and telecommunication. The validity of this argument is simply rooted in the fact that the currently available technologies are rather rigid and cannot be in direct contact with the soft and fragile bio-physiological tissues. In efforts to establish the missing link between the soft biological tissues and the robust silicon-based technologies, OECTs have shown promising performances to be suitable candidates [35, 70,

95, 96]. Owing to their ability to translate change in ionic concentration—one of the most common mechanism in signal recognition in physiology—OECTs have been identified as device designs that can render the possible fabrication of implantable technologies. Long-term implantation of high-tech devices would be a crucial addition to fields of bio-medicine and drug delivery.

The ion-detecting ability of OECTs has thus been widely explored to design biomedical devices from glucose sensors to brain activity monitors [35, 96]. Being a newly studied design, OECTs have seen tremendous advancement as researchers started to design ionic-conducting materials that could be matched with the physiological functions. When poly(3,4-ethylenedioxythiophene)-polystyrene sulfonate (PEDOT-PSS) was first synthesized, its unprecedented performance in electro-ionic conductivity allowed the fabrication of improved devices significantly exceeding what had been reported by Wrighton's research in the 1980s [96, 97]. PEDOT-PSS remains the most widely studied electro-ionic conducting polymer for OECTs mostly due to its commercial availability, and also its excellent electrochemical performance [71, 95, 96, 98]. One of the remaining challenges for OECT design, however, is a full understanding of the device's working mechanism. The device's physics becomes complicated due to the combined electronic and ionic conductivity.

3.3.2.3 Operating Mechanisms

All three modifications of OFETs rely on one major working principal: when the electrolyte comes in contact with a charged analyte (or when a voltage is applied), the change in chemical potential within the electrolyte is detected by the underlying (semi)conducting layer. This principal becomes more complicated for an OECT since the later requires a combination of electric conductivity and ionic conductivity of the organic layer (shown as ECP in Figure 3.4 above). The current consensus of an OECT operating mechanism is that upon injection of ions in the electrolyte layer, the latter becomes doped. With the presence of negatively charged sites in the subsequent conducting layer, the anions migrate to de-dope the now positively charged electrolyte layer, leaving behind an electron-conducting layer. This doping and de-doping cycle results in the movement of holes (positive charge carries) correlating to a generated current and detectable potential change. This injection of holes at the source electrode is oftentimes studied in the depletion mode of the device [95]. OECT performance is then evaluated as the ability of the active material to detect change in electrochemical potential at the electrolyte interface, and its ability to translate it into a current flow.

3.4 Fabrication Techniques for Organic-Based Transistors and Sensors

The fabrication technology for flexible organic-based transistors and sensors has been greatly dictated by the materials of choice and the desired structures of the devices. Generally, the gate, source, drain electrodes, and inorganic dielectric

layer can be patterned using traditional methods, for example, photolithography or shadow mask [24, 25]. The organic layer, however, requires less harsh fabrication methods employing newly developed "softer" technologies such as transfer printing, inkjet printing, or even direct writing. In addition, many organic materials are incompatible with most solvents used in traditional microfabrication processes, which means appropriate methods have to be predetermined depending on the sensitivity of the material in use. The ultimate goal of being to able to achieve low-cost printing of circuits, techniques such as spin coating, drop casting, inkjet printing, screen printing, gravure printing, to name a few, have been studied [52, 99]. Not only are these methods low-cost, they are also more compatible with achieving flexible, pliable, and even stretchable devices as most of them can be conducted at room temperature. Low temperature processing provides low-cost fabrication and also obviates thermal expansion of flexible substrates; this thermal expansion is oftentimes linked to the misalignment of the different device layers and can affect patterning resolution. These methods have been used to achieve long pliable sheets of integrated circuits [19, 20, 100].

For flexible devices, spin coating and drop casting remain the two most widely used methods in transistor fabrication. The two methods allow for achieving very thin films of the semiconductor layer, especially spin coating, and have shown great results in large-area flexible arrays. However, these methods still rely heavily on the use of organic solvents and remain less appealing to industrial-scale manufacturing. Industrial production prefers a more robust and fast fabrication route: roll-to-roll printing. For roll-to-roll manufacturing, preferred alternatives would be inkjet printing, screen printing, as well as other routes that allow for a continuous process. The organic semiconductor materials can be prepared as inks with proper viscosity and the channel layers can be readily printed. In this case, the channel length and the amount of material needed in transistor fabrication can be determined by the printer's resolution. Much efforts are currently being put into achieving high resolutions as the roll-to-roll printing route promises low-cost manufacturing of desired circuits [19, 53]. Figure 3.5 summarizes the current

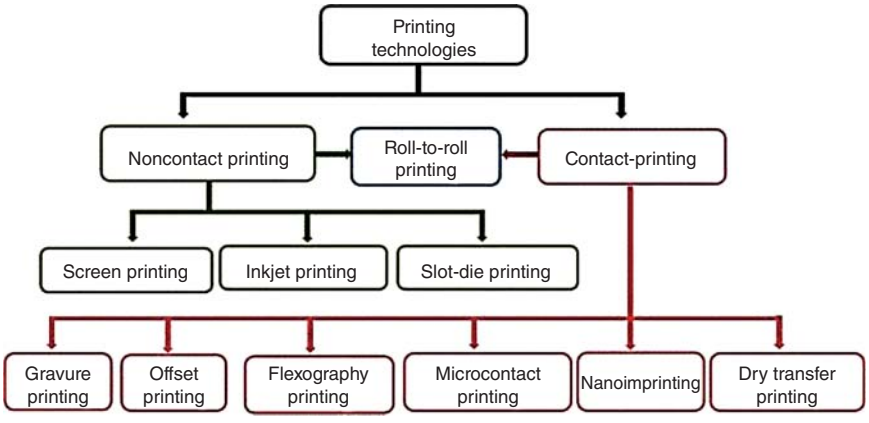


Figure 3.5 Printing technologies for roll-to-roll printing of flexible electronics under investigation. (Khan *et al*. 2015 [101]. With permission from IEEE.)

approaches toward achieving easy and reliable roll-to-roll printing; for the readers interested in further details, a review by Khan *et al*. [101] is recommended.

3.5 Flexible Organic Transistor-Based Sensors

Compared with inorganic systems, organic materials present many advantages in sensing owing to their mechanical properties, electrical properties and their biocompatibility. Throughout the previous sections, we showed different designs of organic-based transistors and we repeatedly hinted on their applications. In this section, we focus on organic-based transistors that have been studied to design sensors. We thus present a few examples of sensors namely for strain, temperature, pressure, as well as bio-analytes using organic materials as active layers. Note that for most sensors under investigation, the use of metal electrodes and/or glass substrates still remains popular, therefore many figures shown in this section are only partially organic.

3.5.1 Flexible Organic Strain Sensors

Flexible strain sensors, different from the traditional strain sensors, put forward a higher demand on material design as well as device geometry. Intrinsically stretchable materials would be ideal choices for strain sensing, but many material candidates lack the ability to combine stretchability with other desired properties—electrical and stability. For organic-based designs, this stretchability remains an issue as most of OTFT-based systems manifest low moduli [16, 102]. If the strain applied on the devices exceeds the crack-on-set strain of the material, cracks will form within the film, and the device will lose its function. Flexible organic-based strain sensors are thus oftentimes fabricated on thin and unstretchable plastic substrates to acquire the required bendability. Generally, strain-sensitive materials, piezoelectric, for example, are used to be incorporated in a device in order to detect applied strain. For instance, Hsu *et al*. designed a flexible strain sensor using an OFET structure patterned on polyvinylidene fluoride (PVDF) [103]. To fabricate the OFET devices on PVDF, a layer of parylene-C was used as the dielectric layer, and an aluminum layer at the bottom acted as a reference electrode. When strain was applied on the device, the PVDF layer could generate an accumulation of charge because of its piezoelectricity. The accumulated charge then acted as the gate voltage and turned-on the channel layer. Different strain conditions induced different drain currents (Figure 3.6b). Using an array of devices, the strain applied on a large area could be detected.

Besides piezoelectric devices, other device structures and different fabrication processes have been introduced for strain sensing. For instance, Nam *et al*. demonstrated a kind of strain sensor based on heptazole TFTs [104] as shown in Figure 3.7. An inverter-type TFT circuit was introduced to measure the large elastic strain (up to ca. 2.5%), owing to excellent mechanical properties of heptazole. Despite the anisotropic electrical properties of heptazole under strain—which caused little current variation under horizontal strain—the

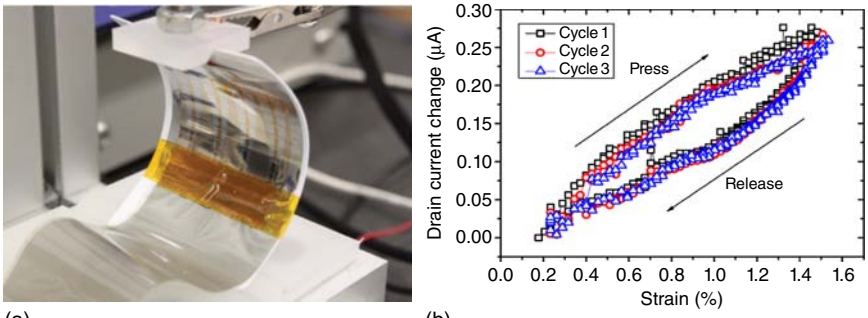


Figure 3.6 Illustration of a piezoelectric-based strain sensor (a) strain is applied from both ends of the sensor, and (b) is the performance of the devices under different strain. (Hsu *et al*. 2011 [103]. With permission from IEEE.)

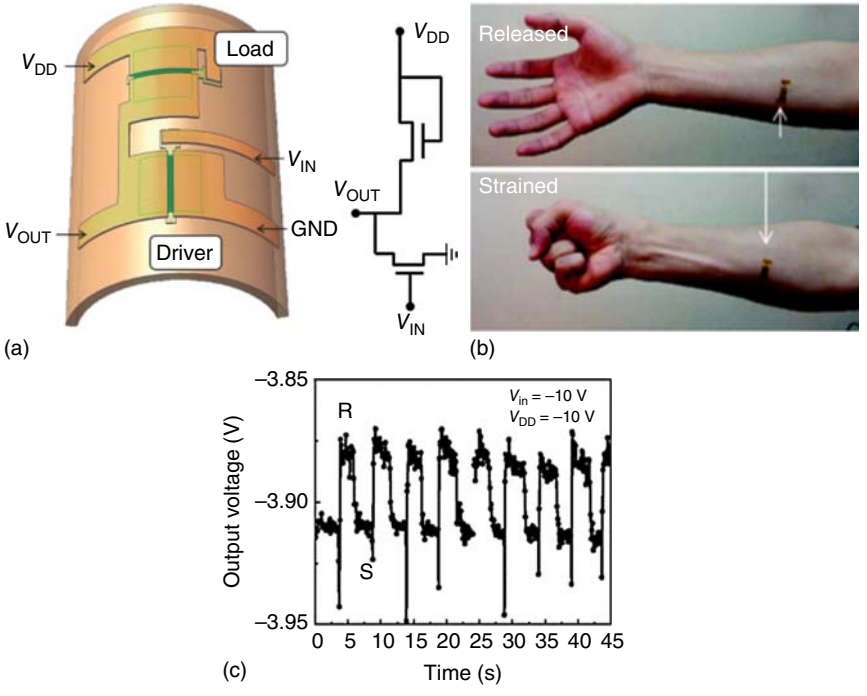


Figure 3.7 Demonstration of an elastic strain sensor based on heptazole: (a) device structure and junctions layout, (b) strain gauge mounted on a fore arm, (c) muscle movement detected by the sensor. (Adapted from Ref. [104].)

current could change dramatically under vertical strain. The performance of the device could be tuned by controlling the orientation of the heptazole. The strain gauge was used to detect the movement of a muscle, as shown in Figure 3.7b.

3.5.2 Flexible Organic Pressure Sensors

As mentioned above, organic materials tend to be delicate and sensitive to harsh conditions. This delicate nature thus makes many organic materials unsuitable for direct use in pressure sensing. In order to achieve organic-based pressure sensors without direct use of the organic functional layer, two methods are generally used. One method is to branch a pressure-sensitive resistor in series with an organic-based amplifier (OFET for instance) [105, 106]. A few thin-film organic pressure sensors have then been demonstrated using the field-effect transistor configuration [107, 108]. In these sensors, the output current will change due to the change in the resistance under applied pressure. These devices tend to be very thin, which allows them to withstand bending. For example, Kaltenbrunner *et al*. presented an ultralightweight pressure sensor that could be bent even to radii as low as 5 μm [23]. In this work, the device was fabricated on a 1 μm-thick plastic foil making it lighter than a similar size feather (as shown in Figure 3.8a). The transistor was patterned in series with a tactile sensor through a "via hole," and all the fabrication processes were compatible with CMOS (complementary metal oxide semiconductor) technology, which showed the potential for large-scale fabrication. The source and drain current could be tuned by the pressure applied on the tactile sensor, and the mapping of the pressure was achieved by scanning the current changes of the array. A second method to achieve a pressure sensor is to incorporate a pressure-sensitive unit as one of the TFT components. For instance, a pressure-sensitive dielectric layer, which can also tune the output current under different pressures (Figure 3.9a) [109, 112].

Most of the flexible organic pressure sensors mentioned above still face a few challenges as the response times are usually poor and the sensitivities tend to be low. In addition, detection methods also remain a challenge as it becomes difficult to directly and accurately monitor the pressure changes within the

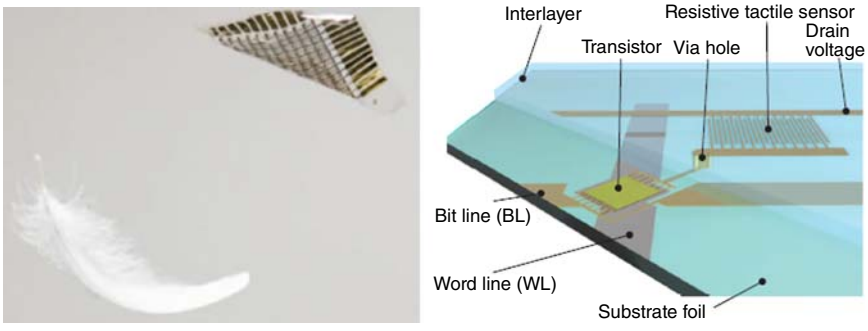


Figure 3.8 An ultralightweight device for pressure sensing (a) device weight compared to a feather in air, (b) structure of a single pressure sensor in the array on a flexible foil. (Adapted from Ref. [23].)

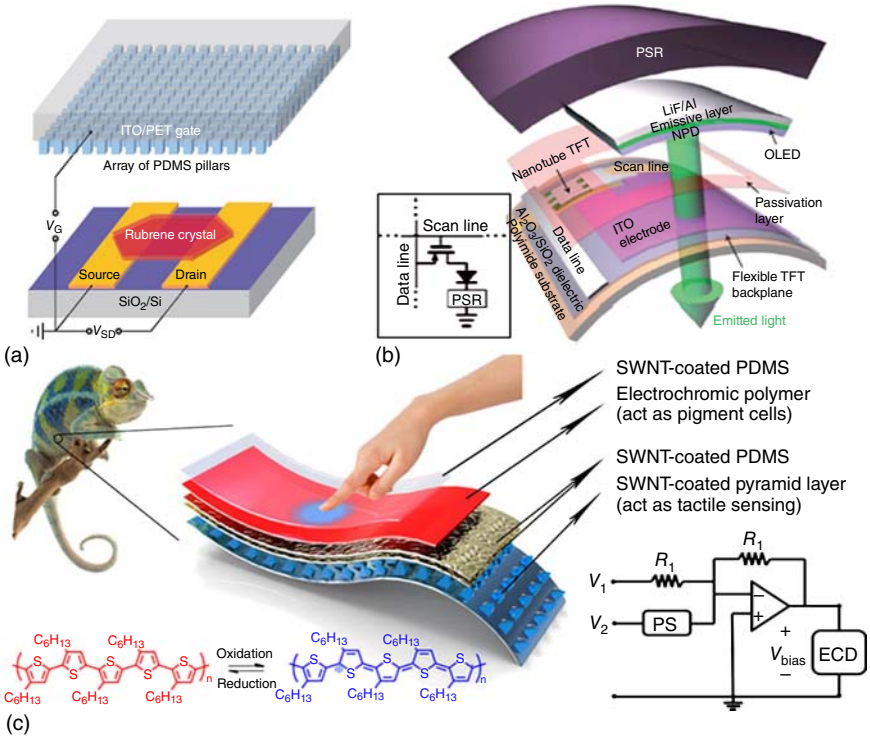


Figure 3.9 (a) A pressure sensor equipped with a flexible and microstructured dielectric layer. (b) Structure of an OLED-based pressure sensor. (c) A kind of pressure sensor mimicking the chameleon's skin. The organic layer is oxidized upon applied pressure resulting into a color change. (Adapted from Refs [109–111].)

device. In their efforts to directly visualize the device's response, Wang *et al*. demonstrated a new kind of flexible pressure sensor [110] by integrating an organic light-emitting diode (OLED) in the sensor. The pressure distribution could directly be displayed according to the pixels (Figure 3.9b). In the area of applied pressure, the OLEDs would turn on and the device's response was evaluated from the intensity of the emitted light.

However, this incorporation of OLEDs within the sensors has its shortcomings as it leads to complex device structures, as well as the robust nature of the device. To address the device complexity issue, a rather simpler concept was introduced by Chou *et al*. as shown in Figure 3.9c. The group proposed an idea of e-skin mimicking chameleon's skin, where an applied pressure would stimulate a color change in the channel layer due to the redox reaction induced within the polymer system [111]. The device's response could then be easily monitored via a color change. Note that the original material, P3HT, showed low stability and this appealing concept is yet to be commercialized. We can however project that this concept could be put to use by addressing device stability using more stable p-type materials, or making use of device passivation.

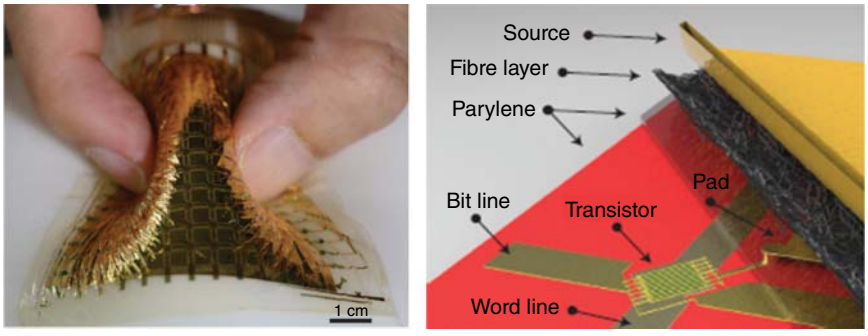


Figure 3.10 Bending insensitive pressure sensor. (a) Array of nanofibers insensitive to bending strain. (b) Structure of the sensor showing different layers encapsulating a transistor. The fiber layer underlies the source electrode making the device insensitive to bending strain. (Adapted from Ref. [113].)

Another puzzling issue for flexible pressure sensors is that it is oftentimes difficult to distinguish pressure from other mechanical deformations, for instance, bending of the device. Most flexible pressure/strain sensors will respond to both kinds of deformations, in other words the pressure change during the strain test will interfere with the anticipated result and vice versa. In their efforts to obviate the signal interference and stable performance, Lee *et al*. presented a new kind of pressure sensor [113], which is insensitive to bending—the device only responds to normal pressure. The pressure sensor is composed of bending-insensitive nanofibers and TFT arrays as shown in Figure 3.10. The insensitivity of the sensor to strain was mainly attributed to the nanofibrous structures, that is, the alignment of the fibers would change during the bending to help release the strain in each fiber. The device as a whole thus showed insignificant sensitivity to strain while applied pressure could be detected.

3.5.3 Flexible Organic Temperature Sensors

The availability of traditional thermometers might overshadow the need for temperature sensors until one starts considering the need for flexible thermometers—temperature sensors. Ideally, a surgeon should not need an assistant to hold a thermometer during the procedure if a flexible temperature sensor can be directly inserted. Another futuristic example would be having a patch-like sensor that can monitor the thermal activity of, for instance, babies and patients in critical condition. If connected to a monitor system, patients and/or doctors can respond according to continuous monitoring. Here, we turn our focus onto ongoing investigation on designing temperature sensors based on organic materials. Most currently studied flexible organic temperature sensors take advantage of the OTFT structure and the temperature-sensitive resistance [114–116]. Several similarities between these designs and the TFT-based pressure sensors discussed earlier may become easily noticeable to many readers.

Recently, Yokota *et al*. have demonstrated one kind of OTFT-based ultrathin flexible temperature sensor [116]. The sensor shows high sensitivity above 20 mK and a high-speed response time of less than 100 ms, in combination with a working range that can be tuned from 20 to 50 °C. The device design was laid out so that each pixel of the active-matrix-based temperature sensor consisted of an OTFT and a block of acrylate copolymer with graphite particles fillers. The thermal sensitivity of the mixture could be tuned by changing the ratio of the fillers. In principle, any change in temperature within the device leads to a volume change of the copolymer owing to changes in the distances between carbon fillers. This variation in volume can thus be detected as the source-drain current varies and could be monitored as the device's response to temperature change. Since all the materials used in the devices are biocompatible, this sensor design finds potential applications for *in vivo* monitoring.

Highly flexible and stretchable temperature sensors can also be achieved by altering the device structure or by enhancing the elasticity of the thin-film material. For instance, Hong *et al*. presented a stretchable temperature sensor that could work well under 30% biaxial applied strain, showing potential application of the temperature sensor in stretchable electronics [114]. The device design combines carbonanotubes-based active matrices (AM) [110] with a temperature-sensitive resistor to achieve direct temperature monitoring. In order to achieve high flexibility, the interconnecting material for the devices was chosen to be liquid metal—which has been used for stretchable electronic devices. The channel layer consisted of SWCNTs (single wall carbon nanotubes) which are also suitable for stretchable devices (Figure 3.11a). All the devices were first fabricated on PET substrates and then encapsulated by silicon rubber (Ecoflex 00-30) film. The use of such stretchable substrates (devices on high modulus materials, then embedded in low modulus materials) [117] have shown to dramatically release the strain on the devices. Finite element modeling (FEM) analysis was further used to show strain distribution across the devices during the stretch process, thus indicating the effectiveness of the array layout (as depicted in Figure 3.11b).

3.5.4 Flexible Organic Biosensors

As previously mentioned, organic materials have shown abilities to function inside physiological tissues and have so far demonstrated great sensitivities toward various metabolites. OECTs, as well as other modified designs of OFETs, have been used to detect different metabolites including glucose, urea, and ionic concentration, as well as in brain activity [31, 92, 118–124]. With the need for more advanced medical procedures, organic-based sensors provide a rich platform for sensing several metabolites, thus opening doors to newly desired techniques in biomedicine. Organic-based biosensors also offer the ability to be linked with enzymatic activity thus offering most of the required qualities of a sensor—selectivity, sensitivity, viability, quick response time, as well as reproducibility. These properties have thus been exploited in organic-based sensors producing promising results [125, 126]. For instance, Malliaras' group has pioneered the design of OECT-based bio-sensors, and has demonstrated

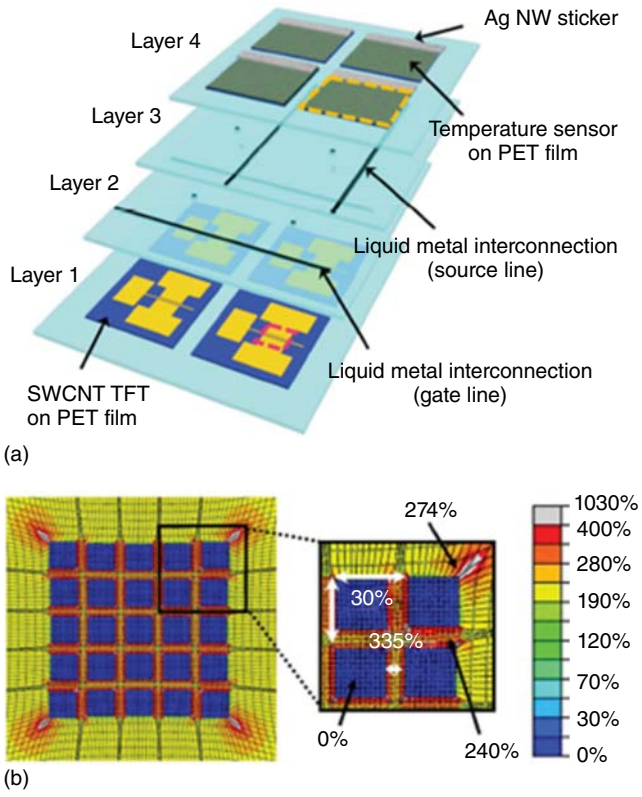


Figure 3.11 (a) Strucrture of a stretchable temperature sensor. (b) Strain distribution of the sensor during the stretching process. (Adapted from Ref. [114].)

applications for soft tissue interfacing. Figure 3.12a shows the layout of an OECT-based glucose sensor utilizing enzymatic sensitivity and selectivity on glucose [96]. The device detects the protons injected in the electrolyte layer as a product of the enzymatic glucose degradation. The device design was later coupled with fluorescent chromophores for direct optical monitoring of glucose levels (as shown in Figure 3.12b) [127]. Furthermore, the group later demonstrated the use of soft organic semiconductors, namely PEDOT:PSS, and achieved flexible and implantable electrodes for electroencephalography (Figure 3.12c) [33, 35]. These flexible arrays showed excellent stability at the brain–tissue interface, in combination with improved neurosignals compared to their inorganic counterparts. These organic-based systems are thus promising in terms of flexible implantable medical device design.

The combination of the properties discussed above allows for organic-based devices to answer questions that could not be answered before particularly in biomedicine. For instance, long-term implantation of the inorganic sensors has been limited by the performance degradation of the sensors due to their rejection by the immune system [35]. Another critical parameter for implantation of the device being their flexibility; rigid devices have the risk of damaging the targeted

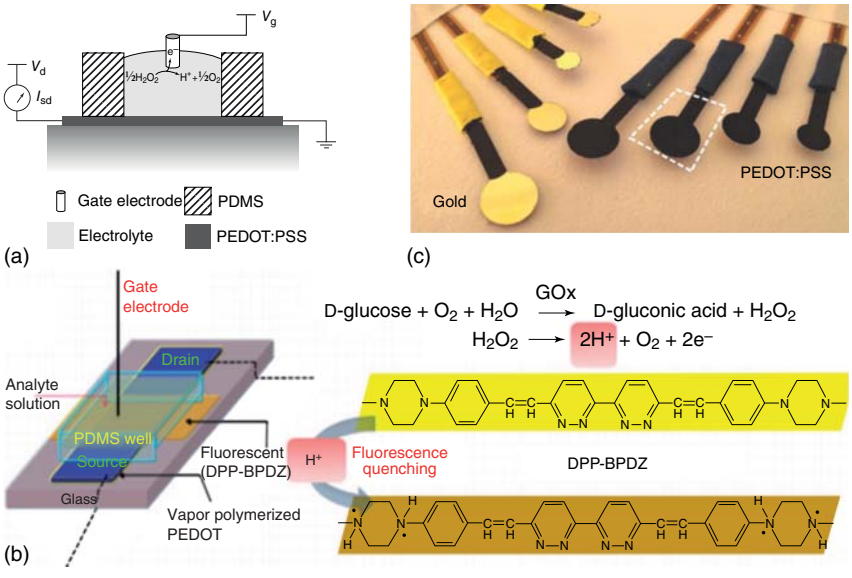


Figure 3.12 (a) Device layout of an organic electrochemical transistor-based biosensor for enzymatic sensing. The presence of analytes can be detected from the change in H^+ at the gate–electrolyte interface. The doping and dedoping of the ionic transporting channel layer is used to detect enzymatic-specific analyte. (b) Glucose monitoring using the detection of proton via fluorescence quenching. (c) Fabricated biocompatible electrodes for brain activity detection. PEDOT:PSS is used to coat the contacts for ionic detection and soft interfacing. (Adapted from Refs [35, 96, 127].)

organs in our bodies. Oftentimes, for brain–machine interface (BMI) applications, traditional devices made by silicon or metal needles arrays have shown to be unsuitable as the devices have to penetrate inside the brain tissue to acquire accurate and updated signals. With this lack of soft interfacing between the physiological world and currently available silicon-based technologies, flexible organic devices find potential applications in biomedicine and long-term implantation. In their efforts to circumvent these challenges for inorganic systems, Rogers' group recently demonstrated a series of work aimed at wireless optogenetics [128, 129]. These systems mainly include flexible needles, μ-ILEDs, microchannel for *in vivo* pharmacology, and wireless control module as shown in Figure 3.13. Notice that these systems are partially organic. The devices could be implanted either in the brain or in the spinal cord of rats and could be controlled by wireless signals from the outside. In principal, the medicine is primarily stored in the reservoirs and will flow through u-fluidic channels to the brain or spinal tissues. At the same time, the u-ILEDs at the tip of the needle will emit light to activate the ion channels of the cell for the injection of the medicine. The joule heaters will be wirelessly activated and will lead to the expansion of the reservoirs until the rupture of a Cu-membranes.

Despite the efforts of the Rogers group, a fully implantable long-term, flexible device is yet to be approved. Plenty of attention still needs to be paid to details

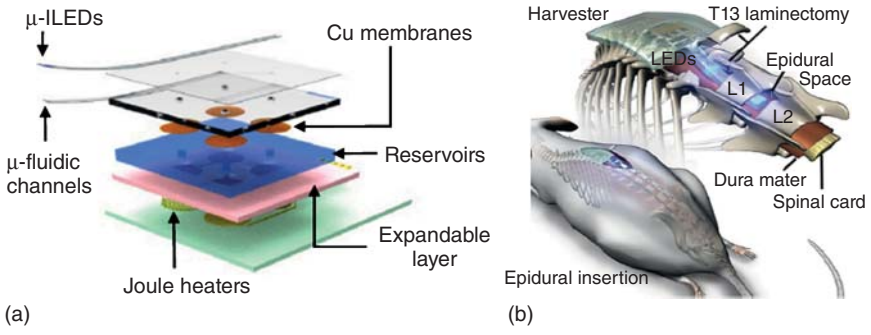


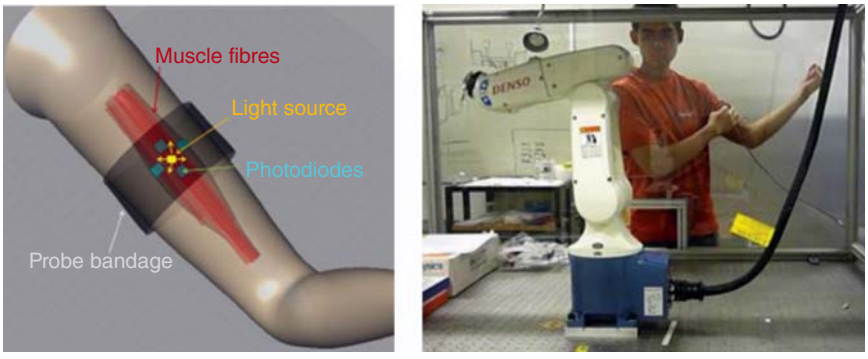
Figure 3.13 (a) Device layer of an μ-ILEDs-based wireless optogenetics system. The joules heaters are separated from medicine reservoirs by an expandable layer. The reservoirs and the encapsulating Cu-membrane can be wirelessly triggered to rupture by the heating and expansion of the expandable membranes. (b) Demonstration of the implatation of the optogenetic device in the spinal cord of a mouse. (Adapted from Ref. [129].)

such as the power source for such a device (implantable batteries [130]), the device's life, and transiency [128, 131, 132], as well as device conformity with physiological tissues; organic-based devices can potentially fulfill these requirements.

3.5.5 Flexible Organic Optical Sensors

There are several ways to design organic-based flexible optical sensors. Depending on the components of the desired devices, organic-based optical sensors can be divided into two main groups: OLED-based devices and devices based on organic wave guide. OLEDs-based sensors are by far the most widely studied structure in optically active electronics while wave-guide-based sensors tend to be coupled to pressure sensors [133]. OLEDs have offered various advantages owing to their rather simple geometry and ease with which they can be achieved on flexible substrates. Flexible displays have been under investigation, and one could safely argue that they might be the next novelistic marketable e-products. All organic-based light-emitting diodes have shown promising results in terms of achieving flexibility, finding applications in e-paper, bendable TVs, wearables, and low-cost monitors [134, 135].

In addition, OLEDs have been studied in combination with organic photodetectors (PDs). This combination of two designs expands the application of these optical sensors to fields requiring continuous monitoring such as healthcare. For instance Bansal *et al*. have demonstrated a wearable optical sensor to medical uses [136]. This sensor could be used in measuring signals from intact muscles to control the movement of active prosthetic devices and tissue oxygenation. In Figure 3.14, the device was fixed in a probe bandage around the upper limb. The wavelength and the location of the PD were carefully chosen to optimize the device performance. With the movement of the muscle, the scattering of the photons was observed to change, which could subsequently be detected by the PDs. In this way, the devices could be used to control a robotic arm.



(a) (b)

Figure 3.14 Demonstration of an optical sensor based on OLED coupled with a PD; (a) the bandage consists of one light source and four photodiodes to detect the movement of muscle fibres. (b) A robotic arm mimicking the arm movement of a volunteer. (Adapted from Ref. [136].)

3.6 Summary and Outlook

In this chapter, we present an overview of the recent advances in organic-based flexible electronic devices, including transistors and sensors. We have shown that organic transistors are excellent candidates for achieving easily patterned circuits for low-cost flexible electronics. We have also shown that by changing the structure and/or materials used, transistors can be designed for specific sensing platforms such as chemical sensors and biosensors. Different kinds of organic flexible sensors, including pressure, thermal, and optical sensors were demonstrated, and most of the sensors mentioned earlier have shown great potential for healthcare and wearable applications. Unlike inorganic materials, organic materials were demonstrated to be suitable for fabrication techniques including inkjet printing and screen printing to achieve roll-to-roll printing. Some organic materials are even compatible with the standard CMOS process, which shows their potential for large-scale and low-cost fabrication. Another important advantage of the organic-based flexible devices is their biocompatibility; how this feature has attracted special research interest for achieving "soft" devices, especially for implantable devices has been discussed as well.

Up to this point, we have described what has been accomplished in order to achieve flexibility and what materials have been studied for organic-based systems. We have even showed the applicability of some of the ubiquitous assays. We have yet to answer the question of what is next for organic-based devices. And the answer will ultimately be rooted in the fact that many researchers in this field would agree that achieving flexible electronics would revolutionize technology to the same level as silicon has. Not only have organic materials showed the ability to perform to the level of silicon, but also have presented properties that the future of technology is demanding. Performance milestones have already been achieved in flexible organic-based devices meeting the requirement for daily-use devices manufacturing. The research community in

this field still ought to focus on the material design, as the intrinsic flexibility of organic materials seems to be taken for granted. Accessing intrinsically flexible (bendable and stretchable) organic semiconductors, organic dielectrics, as well as all transistor components would allow easy fabrication of highly flexible circuitries. A little more attention also ought to be paid to the device engineering in order to overcome resilient challenges such as devices' air stability and device mechanical durability, but nonetheless these platforms are ready to be turned into marketable products. Achieving easy roll-to-roll processing would extremely impact the fields of healthcare, energy, environmental sustainability, and robotics, to name a few. We hope to have guided the readers through current efforts toward achieving all-organic-based transistors and organic transistor-based sensors. We envision the great impact that these devices can potentially have as this seems to be an opportune time to question whether silicon-based technology has reached its apogee.

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