Linköping Studies in science and technology
Dissertation No. 1582

Light-Emitting Electrochemical Transistors

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Norrköping 2014

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Linköping Studies in Science and Technology. Dissertation No. 1582

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Printed by LiU-Tryck, Linköping, Sweden, 2014

ISBN: 978-91-7519-382-3

ISSN: 0345-7524

ABSTRACT

Since the discovery of conductive polymers in 1977, the implementation of organic conjugated materials in electronic applications has been of great interest in both industry and academia. The goal of organic electronics is to realize large-area, inexpensive and mechanically-flexible electronic applications.

Organic light emitting diodes (OLEDs), as the first commercial product made from organic conjugated polymers, have successfully demonstrated that organic electronics can make possible a new generation of modern electronics. However, OLEDs are highly sensitive to materials selection and requires a complicated fabrication process. As a result, OLEDs are expensive to fabricate and are not suitable for low-cost printing or roll-to-roll process.

This thesis studies an alternative to OLEDs: light-emitting electrochemical cells (LECs). The active materials in an LEC consist of a conjugated light-emitting polymer (LEP) and an electrolyte. Taking advantage of electrochemical doping of the LEP, an LEC features an in-situ formed emissive organic p-n junction which is easy to fabricate. We aim to control the electrochemical doping profile by employing a "gate" terminal on top of a conventional LEC, forming a light-emitting electrochemical transistor (LECT). We developed three generations of LECTs, in which the position of the light-emitting profile can be modified by the voltage applied at the gate electrode, as well as the geometry of the gate materials. Thus, one can use this structure to achieve a centered light-emitting zone to maximize the power-conversion efficiency. Alternatively, LECTs can be used for information display in a

highly integrated system, as it combines the simultaneous modulation of photons and electrons.

In addition, we use multiple LECs to construct reconfigurable circuits, based on the reversible electrochemical doping. We demonstrate an LEC-array where several different circuits can be created by forming diodes with different polarity at different locations. The thereby formed circuitry can be erased and turned into circuitry with other functionality. For example, the diodes of a digital AND gate can be re-programmed to form an analogue voltage limiter. These reprogrammable circuits are promising for fully-printed and large-area reconfigurable circuits with facile fabrication.

SVENSK SAMMANFATTNING AV AVHANDLINGEN

Allt sedan upptäckten av elektriskt ledande polymerer 1977 har konjugerade organiska material för elektroniska tillämpningar rönt stort intresse både i den industriella och den akademiska världen. Ett viktigt mål med organisk elektronik är att realisera elektronik som kan täcka stora ytor samtidigt som den är mekaniskt flexibel och billig att tillverka.

Organiska lysdioder (OLEDs) är den första kommersiella produkten som bygger på konjugerade polymerer, och har förtjänstfullt visat att organisk elektronik möjliggör en ny generation av modern elektronik. OLEDs är dock känsliga för materialval och kräver en relativt komplicerad tillverkningsprocess. De är därigenom inte lämpliga för rulle-till-rulle-tillverkning med kostnadseffektiva tryckmetoder.

Denna avhandling behandlar ett alternativ till OLEDs: ljusemitterande elektrokemiska celler (LECs). De aktiva materialen i en LEC är en ljusemitterande polymer (LEP) och en elektrolyt. Tillverkningsproceduren är enkel och funktionen bygger på att en ljusemitterande p-n-övergång formas genom elektrokemisk dopning av polymeren. I avhandlingen presenteras en metod att kontrollera dopningsprofilen genom att tillföra en gate-elektrod ovanpå en konventionell LEC och därigenom skapa en ljusemitterande elektrokemisk transistor (LECT). Vi har utvecklat tre generationer av denna LECT, där positionen hos den ljusemitterande zonen kan regleras såväl genom applicerad spänning på gate-elektroden som genom geometrin hos densamma. På så vis kan en centrerad ljusemitterande zon åstadkommas, vilket maximerar energieffektiviteten hos komponenten. LECTs har även potential att

användas i displayer i integrerade system, eftersom de kombinerar funktionaliteten hos en transistor med möjligheten att emittera ljus.

Utöver det ovanstående har multipla LECs använts för att konstruera programmerbara kretsar, baserade på reversibiliteten hos den elektrokemiska dopningen. En LEC-array demonstreras, där flera olika kretsar kan realiseras genom att dioder med olika polaritet skapas elektriskt i olika positioner. När en sådan krets har använts, kan den raderas och därefter omprogrammeras till en ny funktionalitet. Exempelvis kan dioderna i en digital AND-krets programmeras om till att istället forma en analog spänningsbegränsare. Dessa programmerbara kretsar är enkla att tillverka och är därför ett lovande koncept för tryckt elektronik på stora ytor.

ACKNOWLEDGEMENTS

*Above all, I want to thank my co-supervisor **Isak Engquist**, for your guidance, encouragement as well as your trust and patience in me throughout the past years. I would also like to thank you for being an open person to ideas, and for encouraging and helping me to shape my interest and ideas. This dissertation would not have been possible without your help.*

*I would like to thank my main supervisor **Magnus Berggren**, for your inspiring enthusiasm, optimism and invaluable scientific input, specifically, for your bright solution to that obstacle that I had been stuck with for two years in the first LECT project.*

*I also want to thank **Tom Aernouts** in IMEC, who introduced me to the research field of organic electronics, and who helped me in the TEM measurement for the transistor project.*

*I want to thank **every member of Organic Electronics Group and Acreo** for creating such a friendly and cheerful working atmosphere, with special thanks to:*

***Xavier**, for your help in interpreting all the tricky physics, from inspiring talks and the course you gave.*

***Sophie**, for all the kind help in administration work and daily life.*

***Lasse and Bengt**, for all the handicraft work in the lab.*

***Ek**, for your jokes and warm friendship, for the help in work and, more importantly, in daily life.*

Hiam and Olga, for sharing the joy and complaints in the same office. I hope both of you can make it to my dissertation.

Amanda, Björn, Elina, Henrik, Loïg, Negar, Skomantas, Simone and Zia, for the joyful moments we shared outside work, for the songs we sang from Lucia tåg, for the sweat dripped in the football field and ice ring, for the nature we explored in the kayaks, and for the laughers in all the parties.

Dan, Jun and Hui, for being my Asian companion and sharing my nostalgia in the same(or similar) language.

Finally, I would like to thank my dear love, Linjing Fu, who has provided me with care, passion and support, and who has shared with me all the joy and frustration during the last few years. Furthermore, I would also like to thank my parents for their endless love.

A handwritten signature in black ink, consisting of stylized, overlapping loops and lines, likely representing the name Jiang Liu.

February 16, 2014 in Norrköping

Jiang Liu

LIST OF INCLUDED PAPERS

Paper I

Vertical Polyelectrolyte-Gated Organic Field-Effect Transistors

Jiang Liu; Lars Herlogsson; Anurak Sawatdee; Paula Favia; M Sandberg; Xavier Crispin; Isak Engquist; Magnus Berggren.

Applied Physics Letters **97**, 103303 (2010).

Contributions: All experimental work except TEM characterization. Wrote the first draft and contributed to the final editing of the manuscript.

Paper II

Organic Reprogrammable Circuits Based on Electrochemically-Formed Diodes

Jiang Liu; Isak Engquist; Magnus Berggren.

Manuscript in preparation.

Contributions: All experimental work. Wrote the first draft and contributed to the final editing of the manuscript.

Paper III

Spatial Control of p–n Junction in an Organic Light-Emitting Electrochemical Transistor.

Jiang Liu; Isak Engquist; Xavier Crispin; Magnus Berggren.

Journal of the American Chemical Society **134**, 901 (2011).

Contributions: All experimental work. Wrote the first draft and contributed to the final editing of the manuscript.

Paper IV

Double-Gate Light-Emitting Electrochemical Transistor: Confining the Organic p–n Junction

Jiang Liu; Isak Engquist; Magnus Berggren.

Journal of the American Chemical Society **135**, 12224 (2013).

Contributions: All experimental work. Wrote the first draft and contributed to the final editing of the manuscript.

Paper V

Half-Gate Light-Emitting Electrochemical Transistor to Achieve Centered Emissive Organic p-n Junction

Jiang Liu; Isak Engquist; Magnus Berggren.

Manuscript in preparation.

Contributions: All experimental work. Wrote the first draft and contributed to the final editing of the manuscript.

RELATIVE WORK NOT INCLUDED IN THE THESIS

Integration of Two Classes of Organic Electronic Devices into One System.

J. Liu; I. Engquist; M. Berggren; P. Norberg; M. Lögdlund; S. Nordlinder; A. Sawatdee; D. Nilsson; H. Gold; B. Stadlober; A. Haase; E. Kaker; M. König; G. Klink; K. Bock; T. Blaudeck; U. Geyer; R. Baumann.

Proceedings of LOPE-C, article number P 3.8 (2009).

Simplified Large-Area Manufacturing of Organic Electrochemical Transistors Combining Printing and a Self-Aligning Laser Ablation Step.

Thomas Blaudeck; Peter Andersson Ersman; Mats Sandberg; Sebastian Heinz; Ari Laiho; **Jiang Liu**; Isak Engquist; Magnus Berggren; Reinhard R. Baumann.

Advanced Functional Materials **22**, 2939 (2012).

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Chapter 1. Introduction

1.1 ORGANIC ELECTRONICS

Since the invention of transistors in 1947, integrated circuits based on silicon transistors have monumentally impacted our society. As Moore's law says, the number of transistors on integrated circuits doubles every 18 months(7). Nowadays in a personal computer the transistor count has exceeded 5 billion. With the silicon technology continuing to revolutionize our world, other materials science has been developed to introduce new functional electronics that silicon chips cannot offer.

Organic electronics uses organic conjugated materials as the core materials in electronic devices and systems. The unique properties that organic materials possess open new routes for electronic applications.

First of all, most organic materials can be dissolved into solution. This makes it possible to use conventional "printing" techniques to fabricate

organic devices, which leads to large-area, inexpensive processing methods.

Secondly, polymers can be deposited onto flexible substrates such as paper or plastic, and flexible organic solar cells as well as stretchable light-emitting components have already been demonstrated.

Moreover, organic materials are mainly composed of carbon and hydrogen atoms with addition of other elements such as nitrogen, oxygen, phosphorus etc., which is essentially the same as many biological molecules. Thus, organic electronics can be made to be highly biocompatible when integrating into biological systems.

Last but not least, organic molecules can be synthesized with unlimited variations. A single molecule can be made to function as a resistor, an insulator or even a rectifier. Building more complex electronic systems from multiple organic molecules is still a great challenge but it provides a potential approach to extend beyond the physical limitations of silicon technologies.

The organic light-emitting diode (OLED) was the first commercial electronic component made from organic materials. Products incorporating OLEDs range from mobile phones' displays to TV panels, which are already existing in the market. As an alternative product to OLED, the light-emitting electrochemical cell (LEC) shows similar electroluminescent behavior with a simpler structure; LECs are also more

versatile due to their reversible electrochemical system. In this thesis the main focus is on LECs, and the aim is to exploit new functionalities of these components.

1.2 OUTLINE OF THE THESIS

The thesis is structured as follows: Chapter 2 introduces organic semiconductors and electrolytes which are essential in the materials system; in chapter 3 a variety of organic devices such as transistors and LECs are discussed, together with related circuit constructions; chapter 4 introduces the fabrication and characterization methods to realize those devices. Following that, chapter 5 summarizes the manuscripts and chapter 6 provides an outlook towards future perspectives.

Chapter 2. Materials

2.1 CONJUGATED POLYMERS

Polymers are widely used in modern society, from industry packaging to construction materials, from automobile parts to doll parts, from electronic components to clothing. The wide range of usage is attributed to the versatility of polymers: they are physically flexible, lightweight, durable, reusable, and most of the polymers are good electrical insulators.

The discovery of conductive polymers in the late 70s has changed one's perception of what a polymer can be used for. In 1977, Alan J. Heeger, Hideki Shirakawa and Alan MacDiarmid reported iodine-doped polyacetylene with high conductivity(2). The researchers were later rewarded the Nobel Prize of Chemistry in 2000.

2.1.1 MOLECULAR STRUCTURE

To understand the origin of conductivity in polymers, one must look at the molecular structure. As the most common materials in conventional plastic bags(3), polyethylene has a repeating unit of $-(CH_2)_n-$, as depicted in figure 2.1b. Each carbon atom in polyethylene has four sp^3 molecular orbitals and bonds to the adjacent four atoms by strong σ **bonds**. In those orbitals, the valance electrons are highly localized; thus no free charge carrier is present, which is reflected by the fact that the energy difference between the valance band and the conduction band is as large as 8 eV(4). This large band gap is the reason why polyethylene is transparent and nonconductive.

Figure 2.1 (a) plastic bags made from polyethylene; (b) the chemical structure of polyethylene.

As the first organic material known to be conductive, polyacetylene (the chemical structure shown in figure 2.2a possesses carbon atoms which have three sp^2 molecular orbitals and one p_z orbital. The three electrons in sp^2 molecular orbitals form three σ bonds which connects two

neighboring carbon atoms and one hydrogen atom. The remaining electron travels in the p_z orbital, which overlaps with the p_z orbital of a neighboring carbon atom. The overlaps of the p_z orbits form so-called **π bond** (see 2.2b), in which the electrons are delocalized between the two carbon atoms. This delocalization along the polymer backbone results in the electrical conductivity of polyacetylene. The band gap of polyacetylene is 1.5 eV (4).

Figure 2.2 (a) the chemical structure and (b) the π bonds of polyacetylene.

As can also be seen from the structure of polyacetylene in figure 2.2a, it possesses a structure of alternating single and double bonds. Any polymer having these alternations is considered being a **conjugated polymer**. A few examples of conjugated polymers/molecules are given in figure 2.3.

Figure 2.3 Examples of conjugated materials.

2.1.2 OPTICAL PROPERTIES

The repeat unit of a conjugated polymer interacts with its neighboring units, creating the electronic bands(5). The highest occupied levels of the electronic bands construct the valence band, and the lowest unoccupied levels constitute the conduction band. The edge of the valence band and the edge of the conduction band are termed **HOMO** (highest occupied molecular orbital) and **LUMO** (lowest unoccupied molecular orbital), respectively; see figure 2.4. The energy difference between LUMO and HOMO defines the bandgap (E_g) of the polymer.

Figure 2.4 schematic of energy bands.

When a photon with energy larger than E_g is incident onto a light-emitting polymer (LEP), an electron in the valance band of the LEP absorbs the photon and thus is promoted to the excited state, forming a hole in the valance band. The electron-hole pair is called an **exciton**. Following the absorption process, the electron relaxes to the ground state. The energy released from this decay is emitted either radiatively as a photon or non-radiatively to heat.

This photon emission phenomenon induced by photon absorption is called **photoluminescence** (PL). Alternatively, a photon can be generated from the passage of an electric current; this process is called **electroluminescence** (EL)(6). In EL, electrons and holes are injected into the LEP and recombine to form excitons, which then produce photons through decay.

2.1.3 ELECTRONIC PROPERTIES

Although free charge carriers are present in pristine conjugated polymers, their conductivity is usually low. Typical values of conductivity in pristine conjugated polymers are in the range of 10^{-10} to 10^{-5} S/m.

Doping is commonly used to boost the conductivity by a few orders of magnitude, and is usually achieved by introducing impurities into the intrinsic polymer.

Doping can be seen as removal of electrons from the polymer chain (p-doping or oxidation) or addition of electrons onto the polymer (n-doping or reduction). Assume that an electron is removed from a conjugated polymer chain. A positive mobile charge is in this case created, which induces distortion of the local lattice. This free charge together with local distortion is called a **polaron**, which carries a spin of $\frac{1}{2}$. The energy level of the polaron is situated in the bandgap of the polymer, as shown in figure 2.5b. One polaron can be delocalized over a few repeat units of a polymer chain.

Removing a second electron would create another polaron. When two polarons are close enough the distortion is shared, creating a **bipolaron**. A bipolaron is thermodynamically more stable than two single polarons and it has zero spin. The band structure of the bipolaron is depicted in figure 2.5c.

High oxidation level creates more bipolarons and the overlap of bipolaron states leads to the formation of a **bipolaron band**; see figure 2.5d. A widened bandgap also results because the electrons that form the bipolaron bands are taken from the edge of valance band.

Figure 2.5 Illustration of the band structure of a polymer as the doping level increases.

Doping can be performed by various methods. The first example of a conductive polymer was made by exposing polyacetylene to oxidizing or reducing agents. Such a redox process is characterized as **chemical doping**.

Conjugated polymers can also be doped electrochemically. In **electrochemical doping**, an electric current is driven through the polymer, and the surrounding ions migrate into the soft and porous polymer chain to compensate the injected charge. As a result, the

polymer can be n-doped or p-doped depending on the polarity of the ions:

where p^0 , p^- and p^+ represents neutral, n-doped and p-doping polymer respectively, C^+ and A^- indicates cation and anion.

2.2 ELECTROLYTE

An electrolyte is a substance that consists of ionizable compounds when dissolved in a solvent. A classic example is NaCl dissolved in water solution. Electrolyte is a vital component inside the human body, as it conducts various minerals (ions) and regulates biological functions, such as muscle contraction and neuron activities. In industry, electrolytes are widely used in energy storage applications, such as lithium batteries and fuel cells. In this section we discuss electrolytes in the form of ionically conductive polymers.

2.2.1 POLYMER ELECTROLYTE

A polymer electrolyte consists of a salt that is dissolved in a polymer host. It was first discovered by Fenton in 1973, who observed that polyethylene oxide(PEO) can be used to dissolve and conduct alkali salt(7).

Ion conductivity in polymer electrolytes is governed by the fact that ions move between many co-ordinate sites induced by the local movement of the chain segments of the polymer host(8). It is generally believed that in such systems, it is more energetically favorable that the cations form co-ordinate bonds to the polymer backbone, while the anions diffuse freely(9). Therefore, it is desirable for the polymer host to possess a strong electron donor group so that it forms a strong coordination bond to the cations. PEO with a repeating oxygen group, which is a strong electron donor, is the most commonly used polymer in polymer electrolytes. It has a chemical structure of $-(\text{CH}_2\text{CH}_2\text{O})_n-$, as shown in figure 2.6a. It also has a distance between neighboring oxygen groups that is ideal for ion transportation, evidenced by the fact that both $-(\text{CH}_2\text{O})_n-$ and $-(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_n-$ show lower ion conductivity(10).

Figure 2.6b shows a schematic of ion transportation in PEO-based electrolytes. As the cation moves from one co-ordinate site to another, its movement is assisted by the segmental motion in the PEO chain (11, 12). It is believed that the ionic transport is closely correlated to the flexibility of the polymer host backbone, therefore the ion conductivity is highly dependent on temperature. Indeed, below the glass transition temperature (T_g), PEO is crystalline and the ion conductivity is negligible. In contrast, above T_g PEO is amorphous and flexible, displaying a relatively high ion conduction capability. The conductivity-temperature

relation follows the Vogel-Tamman-Fulcher behavior and is formulated as below:

$$\sigma(T) = \sigma_0 e^{-\frac{E_A}{R(T-T_0)}}$$

Where σ_0 is the conductivity at temperature T_0 , and E_A the activation energy.

Figure 2.6 (a) chemical structure of PEO. (b) Illustration of ion transportation in PEO-ion complex.

2.2.2 POLYELECTROLYTE

Polyelectrolytes are polymers bearing ionic groups. This ionic group would dissociate while dissolving in a solvent, leading to a charged polymer backbone and mobile ions with opposite charges. A polyelectrolyte possessing anionic groups is termed polycation because the polymer backbone is positively charged, while the one carrying cationic groups is called polyanion. Examples of polyelectrolytes are shown in figure 2.7.

In the solid state, the polymer backbone is considered immobile due to its large size, while the counter ions are relatively freer to move. Because polyelectrolytes are mostly hygroscopic, the solid state electrolytes usually contain a certain amount of water in ambient atmosphere. Upon the dissociation of counter ions from the polymer backbones, solvent molecules form a shell surrounding each counter ion and move together with them. Therefore, the ion conductivity in a polyelectrolyte depends on the viscosity of the solvent, the size of the counter ions and the amount of solvent in the materials system, with the latter parameter being heavily influenced by the humidity level(13).

Figure 2.7 examples of polyelectrolytes.

Chapter 3. Devices and Circuits

In this chapter we review various devices and circuits that are mentioned in paper I-V.

3.1 POLYMER LIGHT-EMITTING ELECTROCHEMICAL CELLS

A light-emitting electrochemical cell (LEC) is a two terminal electrochemical device that generates light through electroluminescence. The first LEC was invented by Pei et al. in 1995(14), and LECs have attracted great research attention ever since(15-48). The conventional LEC consists merely of a layer of active materials sandwiched by two charge-injection electrodes. The active material is an intermixture of an LEP and an electrolyte.

As displayed in figure 3.1, an LEC can be structured according to different geometries. The most conventional LEC is constructed in a vertical manner, where the cathode/active material/anode are

vertically stacked (figure 3.1a). This structure is optimal for practical application as the light emissive area per device is large. LECs can also be made in a planar way as shown in figure 3.1b. In this structure, the active material is not covered by the electrodes, which is suitable for studying the dynamic working mechanism at run-time by the means of scanning probe(19, 23, 49-52) and imaging techniques(53-58). In a planar LEC, the LEP and electrolyte can also be separated, as shown in figure 3.1c. In this so-called “bi-layer” LEC, the ionic and electronic transports are separated, and thus a better stability of the device is achieved(48).

Figure 3.1 Geometries of LECs. (a) A vertically structured LEC; a planar LEC with electrolyte and LEP (b) intermixed and (c) separated.

Although the geometry of LECs varies, the working principle is basically the same; see figure 3.2. Once an electric potential larger than E_g/e is applied to the electrodes, holes start to inject from the anode and electrons from the cathode; see figure 3.2b. The LEP near the anodic interface is then oxidized (p-doped), and the polymer near the cathode is reduced (n-doped). The counter ions in the electrolyte dissociate and migrate towards the electrodes to compensate the injected charges, so

the redox composites of LEP/hole/anion (or LEP/electron/cation) are neutralized and stabilized. Since the doped LEP is a good electric conductor, it serves as an extension of the charge-injection electrodes. As the n- and p-doped polymer regions expand towards the center, the intrinsic LEP region shrinks in size. Intrinsic LEP is reduced to a point where the electrons and holes injected from the doped polymer are close enough to recombine, leading to the formation of excitons; see figure 3.2c. The as-formed excitons will decay to generate light radiatively or heat non-radiatively.

Figure 3.2 working mechanism of an LEC. (a) an intrinsic device; (b) initial electrochemical doping starts from the region close to electrodes; (c) both doped parts extend towards the center where electroluminescence occurs.

LECs are promising candidates for next-generation solid-state lighting applications as they possess several unique properties. First of all, the efficient charge injection at the electrodes is attributed to the existence of ions at this interface, and is insensitive to the work-function of the electrodes. Thus, any conductive materials can be used as electrodes, varying from the organic materials PEDOT:PSS and graphene to inorganic gold and ITO(59-62). Secondly, the electrochemical process in an LEC is largely independent of film thickness and roughness, which makes it suitable for large-area roll-to-roll process(78). The robust feature of the LEC also makes it possible to use for stretchable lighting applications(21, 63).

Despite the many attractive merits of LECs, one of the critical drawbacks has been the limited operational lifetime, mainly due to the undesired side reaction between the ion conductor and injected charge(64, 65). However, by using more stable ion conductors, a lifetime of 27,000 hours has been recorded, which is close to OLEDs for commercial applications(20). Another disadvantage of LECs is the slow turn-on time, which can be circumvented by fixing the junction and will be discussed in section 3.1.2.

3.1.2 LECs WITH FIXED JUNCTIONS

The ions in LECs must migrate to their desired positions during the electrochemical reaction, in order to form the emissive p-n junction. This process can take from one second up to a few minutes, depending on

the physical dimensions and ionic conductivity of the particular LEC. Moreover, the electrochemical reactions are reversible, meaning that once the external potential is removed, the p-n junction will gradually relax⁽³⁴⁾ due to the internal “built-in” potential⁽⁴⁹⁾, and the same amount of time will be needed later to turn on the LEC again. To achieve instantaneous response in an LEC, the junctions can be stabilized after turn-on, by the means of physical or chemical methods.

The physical method is usually termed “frozen junction”, which takes advantage of temperature-dependent ion conductivity. After the desired ion distribution is obtained in the LECs, the temperature is decreased to a point where the ions are relatively immobile⁽⁶⁶⁻⁷⁴⁾. In a frozen junction, the turn-on time has shown to be significantly improved; it shows rectification behavior which means it only emits light at the positive cycle.

Alternatively, various chemical approaches have been used to stabilize the junction. It has been demonstrated that after the initial electrochemical charging, the ions can be polymerized at the desired position within the LEC, thus preventing the reversibility of the device^(22, 75, 76). Similarly, the ion conductor can be cured after the p-n junction is initially formed, eliminating the ion conductance in the LEC⁽²⁶⁾. The devices prepared by chemically-fixed junction also display fast response and unipolar light emission.

3.2 ORGANIC FIELD-EFFECT TRANSISTOR

An organic field-effect transistor (OFET) is a three terminal device that is used to control electric signals through manipulation of an internal electric field. As in the schematic of an OFET shown in figure 3.3, a typical OFET consists of three electrodes (drain, source and gate), An organic semiconductor and a dielectric layer. The “channel” is a conductive part of the semiconductor layer that accounts for charge transport. A current (I_{DS}) flows from the source to the drain through the channel. The gate voltage (V_G) controls the electric field that acts to induce charge carriers into the channel, and hence regulates the conductivity of the channel.

Figure 3.3 The schematic of an OFET.

The gate/dielectric/semiconductor stack functions as a capacitor, with the capacitance per area C_i given by

$$C_i = \frac{\epsilon_0 k}{d} \quad (3.1)$$

where ϵ_0 is the vacuum permittivity, k is relative permittivity and d is the thickness of the dielectric layer.

When there is no voltage applied between gate and source electrodes, the transistor is "off" as the intrinsic organic semiconductor usually has a high electrical resistance. When a voltage is applied at the gate electrode, the charge carriers accumulate at the interface between the dielectric and semiconductor layer. The accumulated charge is proportional to V_G and C_i . However, some of the charges are trapped and do not contribute to the conduction of the channel. Thus the effective accumulated charge density Q is given by

$$Q = C_i(V_G - V_T) \quad (3.2)$$

where V_T is threshold voltage, above which the traps are filled.

When a V_G greater than V_T is applied, a uniform distribution of charge carriers is induced, and the transistor is turned on. Under this condition, the relation between drain-source voltage (V_{DS}) and I_{DS} is detailed as follows (figure 3.4):

- When V_{DS} is small, the channel conductance is almost unaffected by V_{DS} , resulting in a linear increase of I_{DS} in response to the increase of V_{DS} ; see figure 3.4a. Therefore this region is called the linear region and we obtain the current in this regime:

$$I_{DS, Lin} = \frac{W}{L} \mu_{lin} C_i (V_G - V_T) V_{DS} \quad (3.2)$$

Where μ_{lin} is the field-effect mobility in the linear region and W , L are the width and length of the transistor channel, respectively.

- As V_{DS} is further increased, the accumulated charge carriers adjacent to the drain electrode start to decrease, leading to a gradual increase of the channel resistance. This is reflected as a decrease of the slope in the curve of figure 3.4b. When V_{DS} reaches a point equal to the effective gate voltage ($V_{DS}=V_G-V_T$), a charge depleted region is created. This phenomenon is called pinch-off.
- A further increase of V_{DS} causes the pinch-off region to grow towards the source electrode, and a space-charge limited current flows in this region. Since the potential at the pinch-off point is equal to V_G-V_T , the potential drop between the pinch-off point and source electrode remains constant, resulting in a constant drain-source current; see figure 3.4c. Thus the transistor saturates. The saturation current is given by:

$$I_{DS,sat} = \frac{W}{2L} \mu_{sat} C_i (V_G - V_T)^2 \quad (3.3)$$

where μ_{sat} is the field-effect mobility in the saturation regime.

Figure 3.4 The charge distribution during the channel formation and V-I characteristics of OFET in three regimes: (a) linear regime; (b) start of pinch-off; (c) saturation regime.

Depending on which type of charge carrier the transistor conducts, there are three types of transistors: p-type transistor in which holes are the mobile charge carriers, n-type transistor in which electrons are the mobile charge carriers, and ambipolar transistor which conducts both holes and electrons.

3.2.1 SCALING OF TRANSISTORS

Down-scaling of transistors has been a continuous trend since their invention, as transistors with smaller feature size enable higher packing density. Moreover, a smaller channel length leads to higher channel current, as shown in equations (3.2) and (3.3). As the channel shrinks, the time for a charge carrier to travel between drain and source reduces, and therefore a transistor switches faster with a shorter L .

As the channel length of transistor is reduced, the lateral electric field originating from drain and source becomes more significant and starts to influence the transverse electric field induced by the gate electrode. As a result, the short-channel transistor characteristics deviate from those of a long-channel transistor(77-87). This phenomenon is called "short-channel effect".

Short channel effects include insufficient saturation(77), threshold voltage reduction and an increase of drain-source leakage current(88). The short channel effect can be suppressed by proportional increase of the transverse electric field induced by the gate electrode(79).

3.2.2 ELECTROLYTE GATED FIELD-EFFECT TRANSISTOR

As equations (3.2) and (3.3) suggest, in order to achieve low-voltage operation of an OFET, a large C_i is highly desired. Two common approaches to increase this parameter are utilization of a high-k dielectric and use of an ultrathin dielectric(89). Alternatively, the

electrolyte gated organic field-effect transistor (EGOFET) employs a solid electrolyte as gate insulator(90-96), because of the large capacitance of this material.

The working principle of EGOFETs is analogous to a conventional transistor, except for the polarization mechanism of the solid electrolyte. As depicted in figure 3.5, when a gate voltage is applied, electric double layers (EDLs) are formed at the gate/electrolyte and electrolyte/semiconductor interface. The EDLs can be considered as capacitors with nanometer thickness. The typical capacitance per area of an EGOFET is on the order of 1-10 $\mu\text{F}/\text{cm}^2$, which is a few orders of magnitude larger than those prepared by high-k or ultrathin dielectric(97).

Figure 3.5 The schematic of an EGOFET, also showing the ionic polarization.

3.2.3 LIGHT-EMITTING TRANSISTOR

The geometry of a light-emitting transistor (LET) is analogous to that of a conventional FET, as shown in figure 3.6. LETs usually possess a light-emissive semiconductor layer that is ambipolar, i.e. it conducts both electrons and holes.

Figure 3.6 The schematic of an ambipolar LET.

Depending on the biasing conditions, there are three working regimes for an LET: (i) unipolar electron transport when $V_G > V_{th,e}$ (the threshold voltage for electron transport) and $V_G - V_D > V_{th,h}$ (the threshold voltage for hole transport); (ii) unipolar hole transport when $V_G < V_{th,e}$ and $V_G - V_D < V_{th,h}$; (iii) ambipolar transport when $V_G > V_{th,e}$ and $V_G - V_D < V_{th,h}$. For light emitting behavior, the ambipolar regime is the most interesting, as both electrons and holes are flowing through the channel and have a possibility to recombine and emit light.

Several groups have employed the electrolyte components in LETs to investigate the charge transport and electroluminescence under the influence of ions(98-105), which will be discussed in detail in paper III-V.

3.3 P-N JUNCTION DIODES AND CIRCUITS

3.3.1 P-N JUNCTION

A p-n junction is formed when a p-type semiconductor having positive charge carriers (holes) is brought into contact with an n-type semiconductor possessing negative charge carriers (electrons); see figure 3.7. After contact, the great concentration gradient of charge carriers at the interface causes diffusion of holes and electrons. Holes in the p-type semiconductor diffuse into the n-type material, leaving negatively charged ions N^- . Electrons in the n-type material diffuse to the p-type material, leaving positively charged ions N^+ . The region where the mobile charge carriers are depleted is called the depletion region. In this region, the ions with uncompensated charge create an electric field that is directed from the n region towards the p region, as indicated in figure 3.7b. This electric potential across the depletion region is called "built-in" potential V_{bi} and causes the electrons and holes to drift in the opposite direction of the diffusion force. Once the drift current is equal to the diffusion current, i.e., $J_n(\text{drift}) + J_n(\text{diffusion}) = 0$ and $J_p(\text{drift}) + J_p(\text{diffusion}) = 0$, the p-n junction has reached its equilibrium and there is zero net current flowing through the junction.

Figure 3.7 (a) p- and n-type semiconductor before they are joined. (b) The formation and band structure of the p-n junction.

The potential barrier across the junction is the obstacle for charge carriers to diffuse freely. It is possible to vary the potential barrier by applying an external voltage. A forward bias V , which is a positive potential applied on the p-side relative to the n-side, reduces the depletion region and potential barrier to $V - V_{bi}$, leading to a high diffusion current of both electrons and holes flowing through the junction; see figure 3.8a. Once a hole (electron) from the p(n)-side crosses the depletion region, it recombines with an electron (hole) at the n (p)-side. If the external potential is reversed, as depicted in figure 3.8b, the depletion region expands and the barrier height is increased, resulting in a negligible diffusion current.

Figure 3.8 Depletion region and band structure for p-n junction under (a) forward bias and (b) reverse bias.

The current-voltage behavior of a p-n junction is given by:

$$I = I_0 \left(e^{qV/KT} - 1 \right) \quad (3.4)$$

where I_0 is the reversed saturation current, V is the voltage across the junction, K is the Boltzmann constant and T is the temperature. A typical current-voltage plot is shown in figure 3.9.

Figure 3.9 Ideal current-voltage plot for a p-n junction.

3.3.2 CIRCUITS BASED ON P-N DIODES

A p-n diode is a two-terminal electric component based upon the p-n junction. The p side is termed anode and the n side is the cathode, corresponding to the circuit diagram symbol displayed in figure 3.10. The diode conducts when the anode is positively biased with respect to the cathode, and becomes an isolator when the bias is reversed. This so-called “rectification” property makes diodes useful in circuit construction.

Figure 3.10 The symbol of a p-n diode.

Using diodes, it is possible to construct diode-resistor logics, which is Boolean logic gates composed of a diode and resistor network. Although these logic gates can be made with high simplicity, only non-inverted Boolean logic (AND gate and OR gate) can be constructed. To achieve inverted logic (NOT, NAND, NOR etc.), a diode-transistor network must be used.

The diode-resistor circuits for OR and AND gates are shown in figure 3.11. To understand how these circuits work, we assume that a diode is a resistor with zero resistance when forward biased, and infinite resistance when reverse biased. In an OR gate, if any of the voltage inputs is high

(H), the diode connected to this input is forward biased, thus has zero resistance. In this case, the output can be considered to be shorted to that input, therefore $V_{in}=V_{out} =H$. If both inputs are low (L), both diodes are reverse biased and have infinite resistance. In this case, V_{out} is shorted to the ground terminal, and thus $V_{out}=\text{ground}=L$. In an AND gate, if any of the inputs is L, the diode connected to this input is forward biased, so V_{out} is shorted to this input, and thus $V_{in}=V_{out}=L$. If both inputs are H, both diodes are reverse biased and thus have infinite resistance. Then V_{out} is shorted to the high (5 V) input, so $V_{out}=H$.

Figure 3.11 The circuits and truth tables for logic OR and AND gates constructed from diode resistor networks.

However, in reality diodes do not possess a zero resistance when forward biased – a voltage drop across the diode (0.7 V for silicon) is always present. This voltage drop (also called turn-on voltage or threshold

voltage, denoted V_T) leads to a voltage loss for each stage of diode logic. Take the OR gate for example, when the two inputs are H (5 V) and L (0 V), the resulting output would be H (4.3 V), instead of H (5 V) in an ideal case. The voltage loss is more significant when cascading several diode logic gates. As a result, diode logic is only used in single stage logic applications due to the lack of voltage amplification at each stage.

Diodes are also widely used in analog circuits such as voltage limiters and rectifiers. As shown in figure 3.12a, a voltage limiter employs two identical diodes connected in parallel and with opposite polarities. Once an input voltage exceeds the V_T of the diode, the output voltage will be V_T , thus realizing the “limiter” functionality.

Figure 3.12 The circuits for (a) a voltage limiter and (b) a bridge rectifier.

The schematic in figure 3.12b shows how a bridge rectifier is constructed using four identical diodes. It is usually used to convert an AC signal to a DC signal. The rectification mechanism is explained in figure 3.13. When

the input is a positive voltage, diodes D_2 and D_3 are forward biased and function as resistors with 0.7 V voltage drop; diodes D_1 and D_4 are reverse biased and thus function as resistors with infinite resistance that are ineffective in the circuit. In this case, as the effective circuit in figure 3.13a shows, the output voltage equals the voltage drop over R , which is the input voltage subtracted by the voltage drop on D_2 and D_3 . Therefore we obtain $V_{out}=V_{in}-2V_T$ when $V_{in}>0$. Similarly, when a negative voltage is applied, the effective circuit is shown in 3.13b and the output voltage is given by: $V_{out}=-V_{in}-2V_T$ when $V_{in}<0$. In summary, we obtain $V_{out}=|V_{in}|-2V_T$ for input voltages of either polarity.

Figure 3.13 effective circuit for a diode bridge when the input voltage is (a) positive and (b) negative.

Chapter 4. Fabrication and Characterization

Manufacturing methods commonly used for organic electronics were utilized for the devices in this thesis. In this chapter, an overview of these methods is given, together with a short description of the electrical characterization methods employed.

4.1 DEVICE FABRICATION

The fabrication was performed in a cleanroom (class 1 000-10 000). All the manufacturing processes were carried out in ambient atmosphere if not mentioned otherwise. All the devices/circuits were constructed on silicon wafers with a thermally grown oxide (1 μm thick).

4.1.1 DEPOSITION AND PATTERNING OF METAL ELECTRODES

To fabricate electrodes with spacing higher than 400 μm , thermal evaporation in vacuum through a shadow-mask was performed. The plastic shadow mask was made in a plotter machine (Graphtec FC

2200-90Ex). This technique is very powerful for user-customization since the turnaround time is only about one day.

To manufacture electrodes with spacing smaller than 400 μm , photolithography is performed in the following steps (figure 4.1): (a) After a global layer of metal is evaporated onto the substrate, a layer of positive photoresist is deposited and cured; (b) UV exposure is performed through a photo mask; (c) the exposed photoresist is dissolved in a developer, while the unexposed photoresist remains intact in the developer and serves as the protection layer in the following etching process; (d) finally the etching agent dissolves the uncovered metal, leaving the remainder of metal in the desired pattern. Photolithography offers high precision in materials patterning; however, in project planning one needs to take into account that the turnaround time for ordering a photolithographic mask from an external party usually varies from one week to one month.

Figure 4.1 photolithography process: (a) photoresist deposition; (b) exposure; (c) development; (d) etching.

4.1.2 ORGANIC MATERIALS DEPOSITION

Solution processability is important for organic electronics. The solution containing the organic materials can be deposited by various techniques. After the solvent is removed from the system (usually by

heating), the organic materials become solidified. The most common techniques used in this thesis are spin-coating and drop-casting.

In the spin-coating process, the substrate is covered by the solution and is rotated to spread the materials by centrifugal force. As the solvent evaporates during and after the spinning, a homogeneous film results. The thickness of the film is determined by the spinning speed, spinning duration and solution properties (e.g., surface wettability, materials concentration and evaporation rate of the solvent).

Drop-casting is widely used in the work covered in this thesis, due to its simplicity and versatility. A drop of solution containing the active compound was placed onto the substrate and subsequently dried. Drop-casting can be applied to any substrate and is not restricted to surface roughness and wetting compatibility. The resulting film is usually thicker and less uniform than one prepared by spin-coating.

4.2 CHARACTERIZATION

All the characterization in this thesis except the EGOFET measurement was carried out under vacuum in a cryogenic station; see figure 4.2a. As the sketch displayed in figure 4.2b shows, the cryogenic station is equipped with a sample platen with heating/cooling function, four probe manipulators, and an optical window through which images can be recorded using a camera and a microscope. The external UV source

is used to excite the polymer sample in order to induce photoluminescence.

All the electrical measurements were performed by means of a Keithley 4200 Semiconductor Parameter Analyzer. The Keithley 4200 possesses multiple measurement units, each of which can source a current (or voltage) and measure the voltage (or current) at the same time.

Figure 4.2 (a) Photograph and (b) sketch of the cryogenic station.

Chapter 5. Summary of the Manuscripts

In summary, this thesis focuses on organic devices containing ion-conducting elements such as LEC and EGOFET, as well as the merger of these two — light-emitting electrochemical transistor (LECT) — the scientific results of which have produced five manuscripts in these subjects; see figure 5.1.

Figure 5.1 Topics and organization of the manuscripts.

In paper I, we develop an EGOFET having a vertical drain-source structure with a short channel. The fabrication merely requires a low-resolution and mask-free photolithography process. We have demonstrated short-channel transistors with 2.2 and 0.7 μm channel length, which are operational below 1 V and show clear saturation. Vertical EGOFET is promising for large-area, low-voltage circuits with simple fabrication steps.

In paper II, we take advantage of the reversible electrochemical doping of LECs, to develop printable and reconfigurable logic circuits. We constructed an LEC array where several p-n diodes can be simultaneously formed with desired polarity at different locations, thus enabling the creation of various circuits based on this diode-network. Any circuit made can be erased by heating, and turned into another circuit with different functionality by electrically forming diodes in other patterns. For example, the diodes of an AND gate can be reprogrammed to form an OR gate.

In paper III, a device that combines a transistor and an LEC is developed: LECT. We employ an ion-conductive gate made from PEDOT:PSS onto a conventional bilayer LEC, and use it to modify the doping level of the electrochemical p- and n-doping. Through proper control from the gate, we can turn on the LECT already at a voltage below 4 V, and move the emission zone back and forth within a 500 μm channel. This device also

displays a clear transistor behavior: it has an on/off ratio about 50, a gate threshold voltage of -2.3 V and a transconductance value of about 2 μS .

In paper IV, we aim to improve the control of the LECT presented in paper III. To do so, we utilize two gate terminals on the LEC, with one controlling the p-doping and another the n-doping. The location of the light emission zone can be precisely defined, as it aligns with the area that is not covered by any gate. We demonstrate double-gate LECTs with two different gate patterns, showing a homogeneously centered emission zone as well as a zigzag one. We also propose an electrical model to explain the gate-doping process. The double-gate LECT is designed to combat the off-centered emission zone in LEC, which is detrimental in device efficiency.

In paper V, we demonstrate a simplified version of the double-gate LECT from paper IV, by omitting the gate terminal that is responsible for p-doping. Having only one gate terminal covering the n-doping region, this device also displays a centered emissive p-n junction, in a similar manner as the double-gate LECT, because the p-doping is by nature more active than n-doping. Moreover, we prove that this half-gate LECT outperforms the corresponding LEC in efficiency, due to a more centered emission zone. We also calculate the doping level of the semiconductor material in the LECT, and conclude that it reaches a level that is comparable to a conventional LEC.

Chapter 6. Future Outlook

This thesis presents several organic devices with novel functionalities, and there are interesting opportunities for further improvement, some of which will be described here.

The major achievement of this thesis is the development of the LECT, as seen in paper III, IV and V. For the proof of concept, we have chosen to focus on the basic functionality of the LECT with different geometries. One of the ultimate goals for LECT development is to construct a smart pixel in which several LEPs are patterned so that different colors can be selected to emit light by using the gate control; see figure 6.1. Thus, a large-area LECT matrix could be made for information display with no additional control components. To achieve this, process optimization and further understanding of the working mechanism is required.

Figure 6.1 A smart pixel that can be made from LECT.

First of all, control of the emissive zone should be more reproducible and predictable, which necessitates a more homogeneous polymer film. We have used coarse drop-casting to deposit electrolyte layers with high roughness. In a refined device, this can be replaced by other thin-film coating methods such as inkjet printing or slot-die coating, to achieve higher uniformity of the polymer film.

Secondly, the lifetime of the device needs to be greatly increased. The short lifetime is attributed to the presence of water and oxygen, which deteriorates the LEP during n-doping, and the side reaction between the ion-conducting polymer (such as PEO) and the exciton. The ultimate solution for the lifetime issue requires advancement of the materials science: to design an LEP that is inert to oxygen or water upon both p- and n-doping, and a polymer electrolyte with a broad stability window to eliminate the side reaction.

Last but not least, better understanding of the working mechanism is necessary. In paper III we propose an electrical model corresponding to device resistance of the LECT, which varies with time as the doping

progresses. However, the resistance through the device is not homogenous. A resistance mapping with high resolution is strongly desired to study the doping level progression for both p- and n-doping, as well as the doping level to resistance relation. This measurement can be done, for example, by four-probe resistance measurement with a moving stage or a probe array.

As for reconfigurable circuits based on LEC mentioned in paper II, we have demonstrated several simple digital and analog circuits made from the LEC array, and it opens a route to facilitate more complex systems based on the same concept. To realize a system bearing more functionality, one needs to integrate other electronic components that can be made from the same materials. The LEC is made by intermixing or stacking an LEP and an electrolyte. With these two core materials, many other electronic components can be made. An undoped LEP is a resistor; an electrolyte can be made into a capacitor; the LEC is a resistor with tunable resistance, depending on the doping level; an LEC can be turned into a transistor with addition of a gate terminal; LECs also show photovoltaic behavior when charged and frozen. All these multiple functionalities can be achieved by simple fabrication. Together with the circuit design that was demonstrated in paper II, a system with easy integration and fabrication should be achievable. Furthermore, the reconfigurable circuits require a low temperature to immobilize the ions due to the low glass transition temperature ($-67\text{ }^{\circ}\text{C}$) of PEO. Utilizing an

ion conductor with a high glass transition temperature would allow for the formation of the frozen junction at room temperature (RT) (68, 74). If such a material system is adopted, the reconfigurable circuit will be able to function at RT.

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