Addressability and GHz Operation in Flexible Electronics

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The first principle is that you must not fool yourself and you are the easiest person to fool.

- Richard Feynman
Abstract

The discovery of conductive polymers in 1977 opened up a whole new path for flexible electronics. Conducting polymers and organic semiconductors are carbon rich compounds that are able to conduct charges while flexed and are compatible with low-cost and large-scale processes including printing and coating techniques. The conducting polymer has aided the rapidly expanding field of flexible electronics, leading to many new applications such as electronic skin, RFID tags, smart labels, flexible displays, implantable medical devices, and flexible sensors.

However, there are several remaining challenges in the production and implementation of flexible electronic materials and devices. The conductivity of organic conductors and semiconductors is still orders of magnitude lower compared to their inorganic counterparts. In addition, non-flexible inorganic semiconductors still remain the materials of choice for high frequency applications; since the charge carrier mobility and thus operational speed of the organic materials are limited. Therefore, there remains a high demand to combine the high frequency operation of inorganic semiconductors with the flexible fabrication methods of organic systems for future electronics.

In addition to the challenges in the choice of materials in flexible electronics, the upscaling of the flexible devices and implementing them in circuits can also be complicated. Lack of non-linearity is an issue that arises when flexible devices with linear behavior need to be incorporated in an array or matrix form. Non-linearity is important for applications such as displays and memory arrays, where the devices are arranged as matrix cells addressed by their row and column number. If the behavior of cells in the matrix is linear, addressing each cell affects the adjacent cells. Therefore, inducing non-linearity and, consequently, addressability in such linear devices is the first step before scaling up into matrix schemes.

In this work, non-linear organic/inorganic hybrid devices are produced to overcome the limitations mentioned above and leverage the advantages of both organic and inorganic materials. Two novel methods are developed to incorporate non-flexible inorganic semiconductors into ultra-high frequency (UHF) flexible devices. In the first method, Si is ground into a powder with micrometer-sized particles and printed through standard screen printing. For the first time, all-printed flexible diodes operating in the GHz range are produced. The energy harvesting application of the printed diodes is demonstrated in a flexible circuit coupling an antenna and the display to the diode.
A second and simpler room-temperature method based on lamination was later developed, which further improves device performance and operational frequency. Here, a flexible semiconducting composite film consisting of Si micro-particles, glycerol, and nano-fibrillated cellulose is produced and used as the semiconducting layer of the UHF diode.

The diodes fabricated through both mentioned processes are demonstrated in energy harvesting applications in the GHz range; however, they can also serve as rectifiers or non-linear elements in any other flexible and/or UHF circuit.

Furthermore, a new approach is developed to induce non-linearity and hence addressability in linear devices in order to make their implementation in flexible matrix form feasible. This is accomplished by depositing a ferroelectric layer on a device electrode and thus controlling charge transfer through the electrode. The electrode current becomes limited to the charge displacement current established in the ferroelectric layer during polarization. Thus, the current does not follow the voltage linearly and non-linearity is induced in the device. The polarization voltage is dictated by the thickness of the ferroelectric layer. Therefore, the switching voltage of the device can be tuned by adjusting the ferroelectric layer thickness. In this work, the organic ferroelectric poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) is used due to its distinctive properties such as stability, high polarizability and simple processability. The polarization of P(VDF-TrFE) through an electrolyte and an electrophoretic liquid is investigated. In addition, a simple model is presented in order to understand the field and potential distribution, and the ferroelectric polarization, in the P(VDF-TrFE)-electrolyte contact. The induction of non-linearity through P(VDF-TrFE) is successfully demonstrated in novel addressable and bistable devices and memory elements such as non-linear electrophoretic display cells, organic ferroelectrochromic displays (FeOEDCs), and ferroelectrochemical organic transistors (FeOECTs).
Populärvetenskaplig sammanfattning

Flexibel (i betydelsen böjarbart) elektronik är viktig inom många olika tillämpningsområden, såsom elektronisk hud, trådlösa smarta etiketter, böjarbara displayer, elektroniska implantat, flexibla sensorer, etc. Detta fält har expanderat kraftigt under senare år och vissa produkter, såsom trådlösa etiketter och flexibla sensorer, finns redan på marknaden. Forskningen inriktas på att komma förbi nuvarande tekniska begränsningar och finna nya produktionsmetoder för flexibla elektroniska kretsar.


Givet de för- och nackdelar som finns med både organiska och inorganiska elektroniska material, blir det viktigt att välja rätt material för en viss tillämpning. Flexibel elektronik kräver ofta att organiska och inorganiska material kombineras.

I denna avhandling designas och studeras icke-linjära organiska/inorganiska hybridkomponenter för två olika tillämpningar: i) användning vid ultrahögfrekvenser (UHF) och ii) adresserbarhet i kretsar ämnade för böjarbart elektronik.

Även om en stor del av forskningen inom flexibel elektronik har fokuserat på organiska material, är det nödvändigt att använda inorganiska material i vissa tillämpningar, t.ex. i kretsar som ska användas vid frekvenser i GHz-området. Bland tillämpningarna märks kommunikation och energiskördning för mobila enheter. I avhandlingen presenteras två nya metoder att åstadkomma flexibla dioder baserade på mikrometerstora kiselpartiklar. Kisel, som används på grund av sin höga mobilitet, mals i den första metoden till mikropartiklar för att bli tryckbart och därigenom användbart i flexibla kretsar. Partiklarna trycks ovanpå ett lager av en isolerande polymer, och pressas därefter in i detta lager för att åstadkomma det aktiva materialet i kretsen. Den andra metoden bygger på
laminering och ger både en förenklad produktion och förbättrad prestanda. Här blandas samma typ av kiselpartiklar med nanofibercellulosa och glycerol och formar därmed en självbärande film. Båda typerna av diod har demonstrerats fungera som likriktare vid energiskördning men kan också användas i andra tillämpningar i flexibla kretsar och vid frekvenser upp till GHz-området.

Publications

Included Papers

I. Negar Sani, Mats Robertsson, Philip Cooper, Xin Wang, Magnus Svensson, Peter Andersson Ersman, Petronella Norberg, Marie Nilsson, David Nilsson, Xianjie Liu, Hjalmar Hesselbom, Laurent Akesso, Mats Fahlman, Xavier Crispin, Isak Engquist, Magnus Berggren, & Göran Gustafsson.

All-printed diode operating at 1.6 GHz. PNAS 111, 11943 (2014)

Contribution: Designed and performed experiments analyzed data and modelled the device.

II. Negar Sani, Xin Wang, Hjalmar Granberg, Peter Andersson Ersman, Xavier Crispin, Peter Dyreklev, Isak Engquist, Göran Gustafsson and Magnus Berggren

Semiconducting Composite Film of Silicon Micro-Particles and Nano-Fibrillated Cellulose. (Submitted)

Contribution: Designed and performed the experiments and the data analysis and contributed to the idea.

III. Henrik Toss, Negar Sani, Simone Fabiano, Daniel T Simon, Robert Forchheimer, Magnus Berggren

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Contribution: Contributed to the idea and experiments and editing of the final manuscript.

IV. Simone Fabiano, Negar Sani, Jun Kawahara, Isak Engquist, Xavier Crispin and Magnus Berggren

Ferroelectric polarization induces nonlinearity in the ionic compensation of highly doped conducting polymers. (Manuscript)

Contribution: Contributed to the design of the device and the experiments, and writing of the manuscript and performed experiments.
V. Negar Sani, Deborah Mirbel, Simone Fabiano, Daniel Simon, Isak Engquist, Georges Hadzioannou, Magnus Berggren

**Introducing Non-Linearity and Threshold to Electrophoretic Display Cell.** (Manuscript)

Contribution: Contributed to the idea, designed the device and the experiments, performed the experiments and wrote the manuscript.

**Patents**

I. **Diode and Method for Producing the Same.** Appl. No. 1650220-5 (2016) (Related to paper II)

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1 Introduction

The role of electronics in different aspects of human life, such as communication, medicine and healthcare, transportation, etc. is indispensable and prominent. A rapid expansion of the research, development and commercialization of modern electronics occurred after the Nobel prize winning invention of the first transistor by John Bardeen and Walter Brattain at AT&T’s Bell Labs in United States in 1947 [1]. This was followed by tremendous development in science and technology based on electronics [2].

The idea of producing electronics on flexible substrates has been circling for several decades and it has recently gained new momentum following the development of new materials and processing techniques accompanied by the increasing market demand for flexible electronics [3]. Among the new materials that are compatible with flexible electronics, organic materials have received increasing attention [4-6]. Several printing and coating techniques for large area and low cost production of organic materials have been successfully developed [5, 6]. However, the science and technology behind organic materials is not as established as for inorganics. Both organic and inorganic materials are utilized in flexible electronics. It is common practice to incorporate a hybrid of organic and inorganic materials to meet the requirements of specific applications [7-9].
1.1 Organic Electronics versus Conventional Electronics

Polymers were considered electrically insulating for a long time and traditionally, were used only as insulators in electronic devices and circuits. In 1977, Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa reported the possibility of inducing considerable electrical conductivity in the polymer polyacetylene [10]. This experiment, which is considered the birth of conductive polymers, has been recognized with the Nobel Prize in Chemistry in 2000. The substantial interest in organic materials is due to their exclusive advantages such as easy processing, low cost manufacturing and possibility to tailor their physical properties such as light absorbance, luminescence, and electrical conductivity [11, 12]. The most mature organic electronic devices are arguably organic light emitting diodes (OLEDs), thin film transistors (TFTs), solar cells, and memory devices [11-15]. Some of these technologies, like OLEDs for instance, have been implemented in electronic products currently available on the market [11, 16]. Despite all the advantages organic materials offer, certain limitations persist. For example, the fact that n-type organic semiconductors have seldom been reported is problematic as semiconductor devices often require both p-type and n-type materials [17-19]. In addition, the conductivity and the charge carrier mobility levels of the organic materials are still orders of magnitude lower compared to their inorganic counterparts [7]. For instance, the conductivity and charge carrier mobility of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), used as both conductor and semiconductor in organic electronics, are on the order of $10^3$ S cm$^{-1}$ and 10 cm$^2$ V$^{-1}$ s$^{-1}$ respectively [20-23]. In comparison, the conductivity of metals, used as conductors in conventional electronics, is typically between $10^4$ and $10^6$ S cm$^{-1}$ and the mobility of silicon, one of the most commonly used inorganic semiconductors, is on the order of $10^3$ cm$^2$ V$^{-1}$ s$^{-1}$ [2, 23, 24]. The charge carrier mobility of the semiconductor is a key factor in the speed and operation frequency of semiconductor devices. Therefore, for ultra-high frequency (UHF) applications, especially in the Ghz range, organic materials are not suitable due to their poor mobility, which makes the use of inorganic materials inevitable. Thus, the design of flexible electronic devices and components requires dedicated attention in the selection of the materials depending on the targeted application. An optimum design is a trade-off between the simple processing and flexibility of the organics and the favorable electronic properties of inorganics and the mature technology and research behind them. The flexible electronic devices are hence usually a hybrid of organic and inorganic materials.
1.2 Printed Electronics

Printed electronics is the utilization of printing techniques to fabricate electronic devices on different substrates [25]. Printed electronics and flexible electronics overlap in a wide range of aspects and objectives and they have been developed in a close interconnection. However, the idea of fabricating flexible electronics was put forth before research on “printed” electronic devices started jointly with the development of organic conductors and semiconductors [3, 10]. Simple, low cost and large area manufacturing of electronic devices are among the primary goals of both flexible and printed electronics [4, 26]. Organic materials developed for organic electronics can be processed from solution and this makes them good candidates for printed electronics. Therefore, most of the research on printed electronics has been devoted to the implementation of soluble organic materials [6, 12, 27]. However, several reports have been published also on printed devices based on inorganic materials. Inkjet printing is among the common techniques used for deposition of both organic and inorganic materials [28-30]. In case of inorganic components and circuits, transfer printing (a.k.a. lift-off) is one of the frequently used methods [31]. Screen-printing is also widely used in printed electronics both for organic and inorganic materials [28, 29, 32, 33].

1.3 Motivation and Goal

Electronic devices can be divided into two groups based on the current-voltage relation: namely, linear and non-linear devices. Linear devices, as the name suggests, are devices with a linear current-voltage relation that follows the superposition principle:

\[ C \times I(V_1 + V_2) = C \times I(V_1) + C \times I(V_2) \]

where \( I \) is the device current, \( V_1 \) and \( V_2 \) are the voltage amplitudes applied to the device, and \( C \) is a constant. Resistors, inductors and capacitors are examples of linear devices. Note that the phase shift between the current and voltage in capacitors and inductors is not considered as non-linearity.

Diodes and transistors are examples of non-linear devices in which the current and voltage do not have a linear relationship. One of the most important aspects in which a non-linear device is required is switching, i.e. enabling or disabling an element, circuit or part of a circuit.
The goal of this thesis is to develop non-linear devices that are compatible with printed and/or flexible electronics. This includes designing new structures for the devices, characterization and modeling of the devices, and coupling them with other devices or circuits. Here we are processing two non-linear devices for different applications in flexible electronics: diodes and ferroelectric capacitors.

Diodes are the fundamental non-linear semiconductor devices and are broadly used in electrical circuits such as AC/DC converters, signal transmitters and receivers, voltage regulators, etc.

For high speed and high frequency applications such as telecommunication, semiconductor devices with GHz operation range are necessary. Organic semiconductors cannot be used for GHz range applications due to their limited charge carrier mobility, hence inorganic materials like silicon should be implemented [7]. Several flexible diode and transistor structures with GHz operation range have been demonstrated based on silicon. The suggested fabrication processes for these devices include modifying silicon wafers into ribbons or thinning them until they are flexible, using peel-and-stick, lift-off or transfer printing techniques, depositing silicon nanomembranes, or solution processing of silanes followed by annealing [8, 9, 23, 34-40]. Besides silicon, other materials such as ZnO, Ge and indium–gallium–zinc–oxide have also been used for high frequency (HF) or UHF devices [41-43]. Nevertheless, all the above works report production steps including high temperature, vacuum or other processes that are not feasible for industrial, mass-production procedures.

In the present work, we have suggested two novel methods to produce flexible silicon diodes with GHz operational range (papers I and II). The first proposed method is based on different printing techniques and Si wafers are grinded in a powder with micrometer-sized particles to become printable. All the device layers are printed and no high temperature or vacuum steps are included in the process. The energy harvesting application of the diode is demonstrated using a circuit comprising a flexible antenna connected to the input and a printed electrochromic display coupled to the output of the diode. The transmitted signal from an ordinary mobile phone working in the GSM (Global System for Mobile Communications) band can be transferred to the diode via the antenna. The diode rectifies this signal producing a DC voltage to turn on the display (paper I).

A simpler method for producing flexible silicon diodes is also developed, where the speed of the device is further improved (paper II). In this method, which is based on lamination, a flexible semiconducting composite film consisting of silicon micro-particles, glycerol and nano-fibrillated cellulose is produced and used as the
semiconducting layer of the diode. The devices fabricated through both mentioned processes are demonstrated in energy harvesting applications; however, their use as rectifiers or non-linear elements in any other flexible and especially UHF circuit can be envisioned.

The second non-linear device typology explored in this work for flexible electronic applications is ferroelectric capacitor (papers III, IV and V). Ferroelectrics are materials containing permanent electrical dipoles that can be reoriented under sufficient electric field and maintain their orientation even when the field is removed. Here the organic ferroelectric poly(vinylidene fluoride-co-trifluoroethylene) (P(VDF-TrFE)) is used due to its distinctive properties such as stability, high polarizability, low leakage and high resistance [44, 45]. Another important advantage of this material is that it can be processed from solution via simple and low temperature methods that are compatible with printed and flexible electronics [46]. P(VDF-TrFE) has been implemented in different devices such as transistors, capacitors and diodes intended for memory and energy storage applications or for inducing bistability in organic field effect transistors (OFETs) and light emitting diodes (OLEDs) [15, 47]. Here we are investigating the possibility of introducing non-linearity and bistability to electrochemical transistors and electrochromic and electrophoretic displays. We have developed a model to understand the polarization of P(VDF-TrFE) through electrolytes in ferroelectric capacitor structures (paper III) [48]. These capacitors are further implemented in the structure of electrochemical transistors and electrophoretic and electrochromic displays (papers IV and V).

Transistors are basic building blocks of flexible electronics and flexible displays are one of the biggest and most explored flexible electronics applications [49]. In this work we show that a P(VDF-TrFE) film can be employed in the gate of a PEDOT:PSS-based electrochemical transistor to induce bistable on-off states to produce a memory element.

Electrochromic and electrophoretic display technologies are among the promising candidates for the production of flexible displays [50-53]. All common display types consist of addressable pixels. Active matrix addressing is a method commonly used in the display technology to selectively switch the pixels on and off according to the image. However, since low cost and simple manufacturing processes are crucial parameters in flexible electronics, passive matrix addressing, which is simpler and more cost effective than active matrix addressing, is preferable in flexible display technology. In this work we are using a P(VDF-TrFE)
ferroelectric layer to induce non-linearity and consequently passive addressability to the display cells.
2 Materials

From an electronics point of view, materials can be divided to three main categories according to their electrical conductivity: insulators, metals and semiconductors. Insulators are a class of materials with very low electrical conductivity ($10^{-18}$-$10^{-8}$ S/cm); metals, on the other hand possess very high electrical conductivities ($10^4$-$10^6$ S/cm) [54]. The conductivity of the semiconductor materials lies in between the insulators and metals. One important characteristic of semiconductors is that their conductivity depends on several factors such as impurities, temperature, electric and magnetic field, illumination, etc., and hence, can be tuned. This property of semiconductors is widely used in electronic devices and it contributes enormously to the many technological advances in today’s life. In this chapter, properties of different classes of materials and the physical phenomena they are correlated with, are discussed.

2.1 Atomic and Molecular Orbitals

In classical physics, there is a clear difference between particles and waves. Electromagnetic waves, such as light, are interpreted as oscillations of electric and magnetic fields spread in space, and their properties like speed, wavelength, frequency etc. depend on the properties of the source and the media they
propagate in. Particles, on the other hand are defined as fragments of matter with a certain speed and position in space that can be precisely identified.

In the beginning of 20th century scientists started reporting wave like behavior of particles and particle like behavior of waves and the concept of wave-particle duality was introduced. The American scientists Clinton Davisson and Lester Germer conducted an experiment showing an electron, which is considered as a particle in classical physics, can be diffracted like a wave by a crystal. In quantum physics, particles such as electrons are described by a wavefunction (usually noted by Greek letter \( \psi \)). Wavefunction of a particle or a system, that can be calculated by solving the famous Schrödinger equation, explains different properties of the particle such as probability of finding it at a specific position in space [55].

In 1900, the German physicist Max Planck introduced the concept of energy quantization for the first time [55]. Energy quantization indicates that the energy levels are only composed of integer multiplications of a basic unit and as such, the available energy states are limited to defined discrete levels, and cannot take any arbitrary value. This concept is hardly noticeable in larger-scale macroscopic material systems that are well explained using classic physics. However, it becomes significantly important in case of small particles (with small mass) such as atoms and subatomic particles confined to a small region of space. Electrons in an atom for example can only have certain energy levels.

An atom consists of neutrons and protons in its core and electrons in orbitals around the core. Each atomic orbital, which is defined by the quantum numbers \( n \), \( l \), and \( m_l \), can accommodate two electrons with opposite spins. The shells in an atom are identified by the principal quantum number \( n \), each shell has \( n \) subshells defined by the quantum number \( l \) (\( l = 0, 1, ..., n-1 \)) and each subshell has \( 2l+1 \) orbitals identified by the quantum number \( m_l \). The orbitals having the same principal quantum number (\( n \)) have identical energy levels. As the principal quantum number of the orbital increases (the outer shells of the atom), the interaction between the electrons occupying the orbital and the core becomes weaker. Therefore, the electrons of the outer most shell, also referred to as valence electrons, are more likely to move to or form bonds with other atoms. The subshells are generally referred to by a letter instead of their subshell number. The subshells with \( l = 0, 1, \) and 2 are called “s”, “p”, and “d” respectively. The first shell in an atom has only one “s” subshell with atomic numbers \( n=1 \), \( l=0 \) and \( m_l=0 \). Having only one orbital, the “s” subshell can accommodate two electrons. The second shell has one “s” and one “p” subshell, the “p” subshell in turn has three orbitals. One simple and commonly used way to visualize the orbitals is to plot
their boundary surface that identifies the volume where there is a high probability (typically 90%) of finding the electrons occupying an orbital. The boundary surface of the “s” and “p” orbitals are shown in Figure 2-1. The three “p” orbitals are called “pₓ”, “pᵧ”, and “pₓ” since they are symmetric around x-, y-, and z-axes respectively.

Figure 2-1 (a) An “s” orbital. (b) “pₓ” orbital. (c) “pᵧ” orbital. (d) “pₓ” orbital.

When the atoms approach each other and bond, their orbitals combine and form molecular orbitals, which are the superposition of the atomic wavefunctions. If the combining orbitals are aligned along the line connecting two atoms, they can form sigma bonds (σ-bonds). A σ-bond formed from a combination of the s-orbitals of two hydrogen atoms along the z-axis is shown in Figure 2-2(a). Bonding orbitals that are not aligned, like in case of two pᵧ-orbitals combining along z-axis, form pi-bonds (π-bonds) as shown in Figure 2-2(b). If two atoms share an electron pair via combination of two orbitals, the bond is called a single bond. If two or three electron pairs are shared between two atoms, the bonds are called double and triple bond respectively.

The interaction between atoms to form molecules can lead to a combination of different types of orbitals to form new hybrid orbitals. Figure 2-2(c) shows an
example of hybridization of one s-orbital and three p-orbitals forming four identical “sp$^3$” hybrid orbitals in a methane molecule that is composed of one carbon atom bonding four hydrogen atoms. Note that the hybrid sp$^3$ orbital, shown in the inset of Figure 2-2(c), has a shape, which is neither the shape of an s-orbital nor of a p-orbital, but a combination of both. An example of sp$^2$ hybridization in ethylene (C$_2$H$_4$) molecule is shown in Figure 2-2(d). In this molecule, the s-orbital and two p-orbitals of each carbon atom combine and form three sp$^2$ hybrid orbitals. Each carbon atom shares two of its valence electrons with hydrogen atoms through σ-bonds. The other two electron pairs are shared between the two carbon atoms via a double bond: one σ-bond along the y-axis and one π-bond in y-z plane. The electrons in the σ-bonds in this molecule are strongly bound to the atom cores, while the π-bond electrons have a weaker interaction with the cores and are therefore less restricted.

Figure 2-2 (a) The wavefunction of a σ-bond. (b) The wavefunction of a π-band. (c) A methane (CH$_4$) molecule where the s and three p orbitals are combined to form four sp$^3$ hybrid orbitals. The inset shows one of the sp$^3$ orbitals. (d) Hybridization of one s-orbital and two p-orbitals to form three sp$^2$ orbitals in ethylene (C$_2$H$_4$) molecule.
2.2 Energy Levels

If two identical atoms are brought close to each other, their energy levels with the same principal quantum number split into two levels, as a result of the interaction between the atoms. In a system with many atoms, the split energy levels become so dense that they start forming energy bands instead of energy levels. Figure 2-3(a) shows the energy diagram of the outer shell of silicon consisting of one “s” orbital (3s: n=3, l=0, m_l=0) that can accommodate 2 electrons and three “p” orbitals (3p: n=1, l=1, m_l=0, ±1) that can accommodate 6 electrons. Notice that in the case of a single Si atom the s and p orbitals of the same shell have identical energies since they have the same principal quantum number, however within a system of many atoms they are split into two different energy levels. As the distance between the atoms decreases, they start to interact stronger and the 3s and 3p energy levels overlap and form an energy band. At the interatomic distance of 2.35 Å, which is the equilibrium distance in a Si crystal with diamond structure, the bands split to an energy band with higher energy (conduction band) and another one with a lower energy (valence band). The lowest energy of the conduction band is called E_C and the highest energy of the valence band is called E_V. There is an energy band gap between the conduction and valence bands, which is called the forbidden energy gap; E_g, meaning that no electron in the system can be found with an energy within this band. Note that E_g is the difference between E_V and E_C. The conduction and the valence bands can each accommodate 4N electrons with N being the total number of atoms in the system, since each Si atom has four electrons in its outer shell.

Although the energy band diagram shown in Figure 2-3(a) belongs to a system of Si atoms, it can be generalized for other materials as well. The conductivity of different materials can be explained via their outer shell energy band diagram since the electrons in the outer shell of the atoms contribute to the conductivity. In a semiconductor at the temperature of absolute zero, all the electrons in the outer shell occupy the valence band, and thus the valence band is filled. As a result, there are no empty energy levels for the electrons to move to and contribute to the conduction. The only way for the electrons to contribute to the electrical current is to reach the levels in the conduction band by gaining some thermal energy. Therefore, as the temperature increases from 0 K, some of the electrons start to appear in the conduction band and the conductivity of the material increases [56].
Insulators have a similar band structure as the semiconductors, but with a much wider band gap. Therefore, the electrons in the valence band need to gain much more energy before they can contribute to electrical conduction. There is no sharp line to distinguish semiconductors and insulators, but in general the materials that are classified as semiconductors have a bandgap below 3 eV\(^\text{[57]}\).

In the case of metals, either the valence band and the conduction band overlap or the conduction band is partially filled. In both situations, there are empty energy states available for the electrons to move to and contribute to the electric current. As a result, metals have very high electrical conductivities even at very low temperatures.

The order in which the electrons occupy the energy levels can be explained via the Femi-Dirac distribution function \(f(E)\). At the temperature of 0 K, \(f(E)\) is 1 for the energy levels below \(E_v\), implying all these energy levels are occupied and is 0 for the energy levels above \(E_c\), implying all these energy levels are empty (see Figure 2-3(b)). Exactly at the middle of the bandgap the value of \(f(E)\) is \(\frac{1}{2}\). This energy level is called the Fermi level and is the energy level in the material where the probability of an allowed state being occupied is \(\frac{1}{2}\). As the temperature increases, the edges of the Fermi-Dirac function become smoother. This is due to some electrons in the valence band gaining enough thermal energy to move to the conduction band, leaving empty energy states behind. Therefore, the probability of some of the energy levels being occupied in the valence band is below one and the probability of some energy levels being occupied in the conduction band is above zero \(\text{[2, 54, 56]}\).
The difference between the Fermi level and the vacuum level (energy of a single electron in vacuum) is called work function ($e\varphi$) and the difference between the bottom of the conduction band $E_C$ and the vacuum level is called electron affinity ($e\chi$). Electron affinity and work function are determining parameters in the charge transfer and conduction in a material or a junction of two different materials.

2.3 Doping

In a perfectly pure semiconductor crystal with no impurity atoms, the Fermi level lies in the middle of the bandgap. However, sometimes impurities are added to the semiconductor crystal in order to tune different properties of the material such as conductivity. This process is called doping of the semiconductor. Doping usually alters the symmetry of the Fermi-Dirac function so that the Fermi level is no longer positioned in the middle of the bandgap. Doping can be divided into two types, p-type and n-type. Donors or n-type dopants have electrons in their outer shell that are weakly bound to the core, and therefore can improve the conductivity. Donors cause the Fermi level to move up in the energy axis towards the conduction band. The majority charge carriers in n-type semiconductors are electrons. Acceptors or p-type dopants improve the conductivity by providing unoccupied energy states (holes) in the valence band and cause the Fermi level to move towards the valence band [2, 54]. The majority charge carriers in p-type semiconductors are holes.

2.4 Metal-Semiconductor Junction

When an electric field ($E$) is applied to a semiconductor, the charge carriers i.e. electrons in the conduction band and holes (empty states) in the valence band, experience a force proportional to the product of their charge and the applied field. The charges start moving towards the side with lower energy (more stable) as a result of the force. The current generated from transferring the charge carriers by applying electric field is called drift current. When two different materials are in contact with each other, the charge transfer under the applied field becomes more complicated. In the junction between two materials, the energy band diagram is altered. The charge carriers on one side of the junction might not be at the same energy levels as the empty energy states on the other side. Therefore, the charge
carriers have to pass an energy barrier to reach to the empty energy states on the other side.

Metal-semiconductor junctions are used repeatedly in electrical circuits to transfer signals, apply voltage, or for current rectification [2, 54, 56]. There are two types of metal-semiconductor junctions, Schottky and ohmic. An ohmic contact is formed when the charge carriers and the energy states in both sides of the junction are at the same or similar energy levels. As a result, the charge carriers can pass through the junction by applying an electric field and do not need to overcome any energy barriers. A Schottky contact is formed when there is an energy mismatch between the energy states of the materials in contact so that the majority charge carriers in the semiconductor encounter a high energy barrier blocking them from passing the junction.

Figure 2-4(a) shows the energy levels of an n-type semiconductor and a metal with a work function ($\phi_m$) larger than that of the semiconductor ($\phi_s$). This is the case where a Schottky contact can be formed [58]. As the metal and semiconductor are connected (Figure 2-4(b)), some of the electrons in the semiconductor conduction band settle down in lower empty energy states on the metal surface leaving a depleted region with uncompensated positive donors at the surface of the semiconductor. This uneven spatial distribution of charges, results in a potential difference in the junction that is called the built-in potential ($V_{bi}$). In the equilibrium situation when no voltage is applied to the junction, the fermi levels of the semiconductor and the metal are aligned and the built-in potential is equal to the difference between the fermi levels before the junction is formed. The electrons with higher energy levels in the semiconductor settle down in lower empty energy levels in the metal and a depletion region is formed on the semiconductor surface. $V_{bi}$ is the energy barrier the electrons in the semiconductor must surmount in order to move to the metal. By applying a positive voltage to the metal the energy barrier is reduced. Consequently, electrons in conduction band of the semiconductor are able to overcome the energy barrier and move to lower energy states of the metal and generate the forward bias current (Figure 2-4(c)). As more electrons move into the depletion region the width of the region decreases. In a reverse bias situation shown in Figure 2-4(d), a positive voltage is applied to the semiconductor side, which pulls the electrons out of the junction region and increases the width of the depletion region. The barrier height for the electrons to move from the semiconductor to the metal is increased. However, the barrier height for the electrons to move from the metal to the semiconductor is still the same as the zero bias and the forward bias case (Figure 2-4(b) and(c)). In this
situation, the electrons in the high energy states of the metal which have enough thermal energy to pass the energy barrier, move to the semiconductor due to the applied voltage and generate the reverse current ($I_r$). Since the number of the electrons with enough thermal energy in the metal side is not high, the reverse current is usually orders of magnitude smaller than the forward bias. In addition, since the energy barrier for these electrons is voltage independent, in an ideal Schottky contact $I_r$ is also voltage independent.

Figure 2-4  (a) The energy levels of an n-type semiconductor and a metal with a work function larger than the semiconductor (the black circles represent electrons and white ones represent holes). (b) A Schottky junction in zero bias. (c) A Schottky junction in forward bias. (d) A Schottky junction in reverse bias. (Redrawn from ref. [58])

A Schottky junction can be formed between a p-type semiconductor and a metal in a very similar manner, in case the work function of the metal ($\phi_m$) is
smaller than the semiconductor work function ($\phi_s$). The only difference is that the charge carriers are holes instead of electrons.

In a metal and p-type semiconductor junction with $\phi_m > \phi_s$ or in a metal and n-type semiconductor junction with $\phi_m < \phi_s$ the energy levels of the charge carriers on both sides of the junction are similar. Therefore, the charges can move by applying the voltage in both directions. This type of contact is called an ohmic contact.

2.4.1 Tunneling

In classical physics if an object hits a barrier, it stops or bounces back and the probability of the object appearing on the other side of the barrier is zero, unless it has enough energy to surmount the barrier. In quantum mechanics however, if a particle hits an energy barrier, the wavefunction of the particle can still have a finite amplitude in the other side of the barrier even if its energy is lower than the barrier height. This means there is a probability that the particle can pass the barrier. This phenomenon is called tunneling [2, 55].

![Tunneling phenomenon. (Redrawn from ref. [2])](-tunneling.png)

When an electron approaches an energy barrier, part of the wavefunction is reflected back but part of it can be extended to the other side of the barrier (see Figure 2-5). The possibility of the wavefunction having a finite amplitude in the other side of the barrier is identified by the transmission coefficient, which depends on the energy of the particle, the width (d), and the height (q$V_0$) of the barrier.
2.4.2 Charge Transfer Mechanisms

There are different mechanisms for the charges to pass an energy barrier. Three different cases of charge transfer between an n-type semiconductor and a metal are schematically shown in Figure 2-6 [2, 59]. The first case is the thermionic-emission mechanism, which dominates in low-doped semiconductors (Figure 2-6(a)). In this mechanism the electrons with high enough thermal energy can surmount the energy barrier. In the second mechanism that is more dominant in moderately doped semiconductors, the electrons are thermally excited to higher energy levels where the width of the barrier is narrower and they can tunnel through it (Figure 2-6(b)). This mechanism is a combination of thermionic emission and tunneling. In case of highly doped semiconductors (Figure 2-6(c)), the width of the barrier is narrow enough for the electrons to tunnel through without any thermal excitation.

The current is usually a combination of different charge transfer mechanisms. The contribution of each mechanism to the total current can change based on different factors such as temperature, voltage, etc., aside from the properties of the materials and the junction [2].

![Figure 2-6](image)

Figure 2-6 The charge transfer mechanism in three different cases, (a) thermionic emission, (b) combination of tunneling and thermionic emission and (c) tunneling. (Redrawn from Ref. [59]).

2.5 Organic Semiconductors

Polymers are chemicals composed of long chains of repeat units called monomers. Traditionally polymers were assumed electrical insulators. In 1977, however, the pioneers of today’s organic electronics, Alan J. Heeger, Alan G. MacDiarmid, and Hideki Shirakawa reported the possibility of inducing considerable electrical conductivity in the polymer polyacetylene [10].
As the atoms join to form a polymer, the energy levels of the atoms start to overlap and split to conduction and valence bands separated by a bandgap ($E_g$), similar to the case of inorganic materials. The terms HOMO (highest unoccupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) are often used instead of valence and conduction band respectively, in the organic electronic community. Electrical conduction in a material is due to the charges that are loosely bound to the core of the atom and therefore can freely move when an electrical field is applied. Unlike metals and inorganic semiconductors, the electrons in a polymer are quite localized around an atom or within a bond. However, in some polymers the electrons in $\pi$-bonds that have a weak interaction with the atom cores can become delocalized to an extent. The alternation of single and double bonds along the carbon chain promotes this kind of electron delocalization and enhances the electrical conductivity. This kind of alternating single and double bonds is called conjugated structure and the polymers with such a structure are called conjugated polymers. The chemical structure of the simplest conjugated polymer, polyacetylene, is shown in Figure 2-7. The electron pairs in the C-C and C-H $\sigma$-bonds are localized and do not contribute to the electrical conduction. The electron pairs in the alternating C-C $\pi$-bonds, however, are free to move in an electron cloud perpendicular to the plane of C-C $\sigma$-bonds. These electrons are delocalized along the chain and can contribute to the electrical conduction.

![Figure 2-7 Chemical structure of the conjugated polymer polyacetylene.](image.png)

As the polymer chains grow in length, the $\pi$-bond electrons get more delocalized resulting in the bandgap of the material to decrease and the conductivity to increase. One can thus conclude that increasing the chain length in a conjugated polymer can reduce the bandgap to zero and a conductivity close to metals can be achieved. In reality however, this does not happen since the electrons in the polymer chain cannot be delocalized further than a certain length (conjugation length) and therefore the bandgap of the polymers never reaches zero [60]. Nonetheless, the bandgap of the polymers can be tuned by means of charge injection, photoexcitation, or by doping [61]. Polymers, like inorganic
semiconductors can be p-doped or n-doped by introducing dopants to the material. Within the scientific literature, mostly p-type organic semiconductors have been investigated. One of the most commonly used organic semiconductors is poly(3,4-ethylenedioxythiophene) (PEDOT) which is frequently doped by polystyrene sulfonate (PSS). Introduction of the PSS dopant induces positive charges along PEDOT chain resulting in an improvement in conductivity [62]. The chemical structure of PEDOT and PSS are shown in Figure 2-8. The highly electronegative sulfonate groups within PSS can compensate for the positive charges in the PEDOT chains, and ease the ionization of PEDOT and consequently increase the conductivity.

Figure 2-8 Chemical structure of (a) the conjugated polymer PEDOT and (b) the dopant PSS.

The conductivity of PEDOT:PSS, which is a commercially available conductive polymer blend in aqueous media, can be tuned via electrochemical doping by injecting or withdrawing charges to and from the polymer. The charge neutrality in the material is maintained by injecting or withdrawing counterions from a source of ions i.e. an electrolyte. Electrochemical doping is achieved by applying a potential over a PEDOT:PSS/electrolyte interface. The charges and ions are injected or withdrawn from the PEDOT:PSS blend causing it to go through the following reaction:

\[
\text{PEDOT}^+\text{PSS}^- + \text{M}^+ + \text{e}^- \rightleftharpoons \text{PEDOT}^0 + \text{M}^+:\text{PSS}^-
\]

where \(\text{M}^+\) represents the positive ions in the electrolyte. When a positive voltage is applied to the polymer, the reaction balance moves towards the left side where the electrons are withdrawn from the blend and PEDOT is oxidized. In oxidized state, there are more positive charges along the PEDOT chains and therefore the conductivity increases. When a negative voltage is applied to the polymer, the electrons injected into the material reduce the PEDOT\(^+\) to PEDOT\(^0\) and the
conductivity decreases. In both cases, the ions move in and out of the material to compensate for the injected charges and provide electron neutrality. The conductivity of PEDOT:PSS blend can vary several orders of magnitude by electrochemical doping \[63\]. The variation of the conductivity is due to the changes in the bandgap of the polymer which also causes the absorption and therefore the color of the material to vary. Thin films of PEDOT:PSS are transparent in the oxidized (conductive) state, while in the reduced (low conductivity) state they have a dark blue color. This property of PEDOT:PSS is called electrochromism and is used in electrochromic displays \[64-66\].

2.6 Dielectrics and Ferroelectrics

Dielectrics are a class of insulators that can be polarized by applying electric field. The polarization in most of the dielectrics has a linear relation with the electric field and tends to disappear as soon as the electric field is removed. In some dielectrics with crystalline structure the dipoles that are polarized in an electric field, can stabilize in the crystal and thus maintain their polarization even after the electric field is removed. These materials are classified as ferroelectrics \[67\].

A ferroelectric material contains electrical dipoles with random orientation. By applying a sufficient electric field to a ferroelectric film, ferroelectric domains are nucleated \[68, 69\]. These domains grow and merge by increasing the electric field allowing a small charge displacement current to pass through the film. If the applied field is removed while the domains are forming, the polarization is not stable and vanishes soon after. However, if the field is high enough all the domains merge, the whole film is polarized, and the polarization is stable. The field needed to induce a stable polarization in the ferroelectric is called coercive field (E_c). The polarization can be switched to the opposite direction by applying the coercive field with an opposite polarity.

Organic ferroelectrics have gained a lot of attention due to their advantages over inorganic ferroelectrics, such as flexibility and ease of processing. Work on organic ferroelectrics and their applications started in 1980s \[70, 71\]. Among the ferroelectric polymers poly(vinylidene fluoride) (PVDF) and its copolymers with trifluoroethylene (TrFE) have been the center of interest for many research studies \[45\]. This is due to the particular properties of P(VDF-TrFE) including simple, low temperature and from solution processing and stability \[44, 45\].
The chemical structure of P(VDF-TrFE) is shown in Figure 2-9. The dipole moment in the polymer stems from the highly electronegative fluorine atoms in the VDF molecule. When an electric field is applied, the dipoles twist along the polymer chain to align with the field. The additional PTrFE part improves the ferroelectricity by aligning the dipole moments in the chain; otherwise extra steps are needed to make the polymer ferroelectric.

2.7 Insulators

As explained before, insulators are a class of materials with very large bandgap and very low electrical conductivity. In this work, insulators are used in the device structures as a matrix to hold the silicon particles and form a semiconducting film. A material with a very low conductivity is needed for this purpose, otherwise the conductivity of the material used as matrix dominates in the film resulting in a conductive film rather than a semiconducting one.

2.7.1 SU-8

SU-8 is a commercially available polymer commonly used as photoresist. It is soluble in several organic solvents and can be cross-linked by exposing to UV light. The viscosity of SU-8 can be tuned to make it compatible with printing techniques.

2.7.2 Nano-Fibrillated Cellulose

Paper based materials are mainly synthesized from wood, and can be used in printed and/or flexible electronics because of their particular properties such as low cost and large volume production compatibility, and being environmental friendly [3]. Nano-fibrillated cellulose (NFC) is refined from paper pulp and consists of thin fibers with large aspect ratio that compose the inner structure of wood fibers. The fibers that are typically about one micrometer long with 5-15 nm diameter, are hydrophilic and can be dispersed in water to form a viscous gel [72].
A self-standing, semitransparent, and mechanically strong film can be fabricated by casting and drying an NFC aqueous dispersion.
3 Devices

The working principles of the electronic devices and components designed or used in this work are briefly explained in this chapter.

3.1 Diode

Diodes are two terminal electronic components that conduct or block the electrical current depending on the polarity of the applied electric field. The characteristic current response of a diode in respect to the applied voltage together with the symbol used for diodes in electrical circuits are shown in Figure 3-1. Under forward bias (positive voltage in the figure), the diode is conductive and under reverse bias (negative voltage in the figure) it is practically insulating. This is due to the energy barrier on the path of charge carriers in the reverse direction. Most diodes are composed of two materials with different energy levels, forming a junction. The charge carriers face a high energy barrier in the reverse direction and therefore the current is blocked. In the forward direction, there is a small or no energy barrier and thus the device conducts the electric current.
There are different kinds of diodes such as PIN, Schottky, Shockley, Zener etc. In Schottky diodes, a metal-semiconductor Schottky contact causes the energy barrier in the path of the charge carriers. As described in section 2.4, the charges at a Schottky junction redistribute due to the energy level difference between the two materials in the junction. This charge redistribution results in the formation of a potential difference, $V_{bi}$; that is the difference between the work functions of the two materials at the junction. If an input potential higher than the built-in potential ($V_{bi}$) is applied to the junction, the charges can surmount the energy barrier and an electrical current is established through the device (see Figure 3-1). The current in a Schottky diode is a combination of tunneling and thermionic emission charge transfer and can be expressed as [2]:

\[
I = I_0 \left[ \exp \left( \frac{qV}{nkT} \right) - 1 \right]
\]

where $k$ is the Boltzmann’s constant, $q$ is the electronic charge, $V$ is the applied potential minus the built-in potential of the junction, $T$ is the temperature, and $n$ is the ideality factor. The saturation current, $I_0$ is a parameter dependent on temperature, barrier height, and surface area. The ideality factor; $n$; is 1 for a diode with only thermionic emission mechanism and becomes larger as tunneling mechanism starts. There are several other charge transfer mechanisms that can contribute to the current in a diode and in reality, the diode current is a combination of different charge transfer mechanisms. In this case, the current-voltage relation is a superposition of the currents due to different mechanisms, with coefficients indicating the contribution of each mechanism in the total current [2].
Diodes are used in several circuits such as rectifiers, voltage multipliers and charge pumps for radio frequency (RF) electronics and energy harvesting applications. Schottky diodes are preferable in most of the RF and high frequency applications due to their high speed. They are widely used as frequency multipliers in RF circuits due to their non-linearity and high speed [73]. Ultra-high frequency rectifiers have also been demonstrated for RF energy harvesting applications [74, 75].

3.2 Electrochemical devices based on PEDOT

The devices discussed in this section are based on tuning the electrical and optical properties of PEDOT through an electrochemical process. As explained in section 2.5, PEDOT is an organic semiconductor with a bandgap that is variable according to its oxidation state. By tuning the bandgap, other properties of PEDOT such as color and conductivity can be adjusted.

3.2.1 Electrochromic Display (ECD)

PEDOT:PSS ECDs are based on the electrochromic properties of PEDOT:PSS polymer blend [76]. As explained in section 2.5, a PEDOT thin film has a dark blue color in its reduced (un-doped) state while it is transparent in its oxidized (doped) state. The oxidation state of the doped PEDOT can be changed via applying an electric field through an electrolyte.

![Figure 3-2 Structure of a simple PEDOT:PSS ECD.](image)

A simple PEDOT:PSS ECD structure is schematically shown in Figure 3-2. Since the conductivity of PEDOT is high enough to be used as an electrode, it can also be used as the bottom electrode of the ECD. Therefore, all the layers of the device can be deposited on a flexible substrate to produce an all-organic flexible display [76-78]. PEDOT:PSS ECDs are commercially available [79, 80].
3.2.2 Organic Electrochemical Transistor (OECT)

Transistors are three terminal devices where the conductivity of a channel connecting two of the terminals (drain and source) is altered by the voltage applied to the third terminal (gate). The tuning of the channel resistance occurs via different mechanisms depending on the type of the transistor. In an organic electrochemical transistor (OECT), the channel conductivity varies according to the oxidation state of the channel [81-84].

The structure of a PEDOT:PSS OECT is schematically shown in Figure 3-3(a). PEDOT:PSS is a p-type semiconductor and therefore the charge carriers in the channel are holes and the OECT with PEDOT channel is a p-channel transistor. Without applying a gate voltage, the channel is conductive since the PEDOT chains are doped by PSS. By applying a positive gate voltage, the cations in the electrolyte move into the polymer and de-dope PEDOT. Consequently, the conductivity of the channel decreases. This type of transistor where the channel is initially conductive and by applying the gate voltage the channel becomes more resistive is called a depletion type transistor.

The output and transfer curves are used for basic characterization of transistors. The transfer curve shows the effect of the gate voltage bias on the channel current for a constant $V_{sd}$ while the output curve shows how the drain-source bias changes the channel current in various $V_g$ levels.

The typical transfer curve of a PEDOT:PSS OECT is shown in Figure 3-3(b). A constant voltage of -0.5 V is applied between drain and source. As the gate bias increases from 0 V to positive voltages the PEDOT channel starts becoming reduced. Consequently, the channel conductivity drops and the drain-source current decreases. The transconductance of the transistor, which is defined as the
ratio between the change of the drain-source current and that of the gate voltage \( \frac{\partial I_{ds}}{\partial V_g} \) can be extracted from the transfer curve.

The output characteristics of the transistor are usually plotted for different gate voltage biases (see Figure 3-3(c)). The conductivity and current of the channel are lower for more positive gate biases. With a constant gate bias, the drain-source current increases linearly with the drain voltage at low drain voltages. Once the difference between the drain and the gate voltage reaches a certain value, i.e. the pinch-off voltage \( V_p \), the drain-source current saturates. Saturation occurs due to charge depletion of the channel region closest to the drain contact.[85]. The pinch-off voltage and also the on-off ratio of the transistor, defined as the ratio between the drain-source current in on- and off-states of the transistor, can be extracted from the output curves.

OECTs have been implemented in a variety of the applications such as active matrix displays, logic circuits, and bio-applications [78, 84, 86].

### 3.3 P(VDF-TrFE) Ferroelectric Capacitor

A ferroelectric P(VDF-TrFE) capacitor is composed of a layer of ferroelectric polymer; P(VDF-TrFE); sandwiched between two metal electrodes. One of the advantages of this device is the simple fabrication. Normally a layer of P(VDF-TrFE) is deposited on a metal electrode (e.g. by spin coating) and the second electrode is evaporated on top. In order to increase the crystallinity in the P(VDF-TrFE) film, it should be annealed at around 130 °C after deposition [87].

The electrical current and surface charge of a P(VDF-TrFE) film vs. the applied electric field are shown in Figure 3-4. As long as the applied field is below the coercive field, the current is low and the surface charge density is constant. Once the coercive field is reached, a displacement current is established in the film due to the alignment of the dipoles. Consequently, the polarity of the surface charge is also switched. When all the dipoles are aligned with the field the current decreases again until a coercive field with the opposite polarity is applied. The current-voltage profile of the device shows peaks of the displacement current at the coercive field values (Figure 3-4(a)). In the charge-voltage characteristics of the device, steep changes of the surface charge polarity is observed at coercive field (Figure 3-4(b)).

Ferroelectrics in general are widely used in memory devices [88]. In principle within ferroelectric memory devices, 0 and 1 memory states are assigned to the two polarization states of the ferroelectric material. The readout of the of the
Ferroelectric memory can be either destructive, as in case of ferroelectric capacitors, or non-destructive, as in case of Ferroelectric Field Effect Transistors (FeFETs) [89]. In order to read a ferroelectric capacitor memory cell, an electric field higher than the coercive field is applied to the cell and the current is recorded. The polarization of the film can be determined according to the amplitude of the current [15]. In addition to memory application, P(VDF-TrFE) capacitors can be used in other applications such as energy storage and to induce bistability in other components [90, 91]. In paper IV and V, we have used a P(VDF-TrFE) capacitor to induce non-linearity in electrochromic and electrophoretic display cells and electrochemical transistors.

![Figure 3-4](image_url)

**Figure 3-4** (a) The current of a P(VDF-TrFE) film vs. the applied electric field. The inset illustrates the schematic structure of a P(VDF-TrFE) capacitor. (b) Charge vs. the applied field in a P(VDF-TrFE) capacitor.

### 3.4 Electrophoretic Display

Electrophoretic (EP) displays are a class of displays based on electrophoresis of colloidal suspensions a.k.a. electrophoretic inks. EP inks consist of charged colored particles that can move upon applying voltage [92]. An EP display is made of EP ink encapsulated between a bottom electrode and a transparent top electrode. By applying an electric field to the EP display, the charged particles accumulate on the electrode with the opposite polarity and thereby change the color of the display accordingly.

EP displays have several advantages over traditional display technologies, such as compatibility with flexible electronics, superior optical properties and low power consumption [14, 51-53].
The EP ink used in this work is composed of negatively charged organic-inorganic hybrid particles in an inert blue dyed media. The particles consist of a TiO$_2$@SiO$_2$ core-shell structure as the inner part and are therefore white. Figure 3-5 shows the working principle of an EP pixel incorporating this ink. Without applying any voltage, the cell has a light blue color (Figure 3-5(a)). When a positive voltage is applied to the top electrode the white negatively charged particles accumulate on the top electrode and the cell turns white (Figure 3-5(b)). By applying a negative voltage to the top electrode, the particles are pushed toward the rear electrode and the dark blue color of the media is exposed (Figure 3-5(c)).
4 Methods

This chapter describes the techniques used to fabricate and characterize the devices in this work.

4.1 Thermal Evaporation and Patterning

Deposition of organic or inorganic material within well-defined areas or patterned designs allows complex devices to be fabricated. Within this thesis, patterning includes all the techniques used to deposit a layer of thin film such as metal or polymer on a substrate in a designated area. Generally, the fabrication process of a device starts with depositing the bottom electrodes using a conductive polymer or a metal. Depending on the design of the device, the electrodes might have different shapes and surface area. Thermal evaporation and photolithography are two of the most routinely used deposition and patterning techniques [54, 57].

4.1.1 Thermal Evaporation

Thermal evaporation is commonly used to deposit metal electrodes [54]. In this process, metal pieces are placed in containers in an evaporator (see Figure
and the substrate material is suspended above the metal. The metal is melted and evaporated in vacuum by passing a high current through the container. In vacuum condition, the evaporated particles travel in straight trajectories and settle on the substrate. A shadow mask can be employed in order to create metal patterns instead of a global metal coating. Metals can be deposited and patterned on vacuum compatible materials such as Si, glass, plastic foils, etc. via this method. Although evaporation with shadow mask is a simple and useful technique, the accuracy and resolution of the pattern depends on the thickness of the shadow mask and on how finely it can be cut or patterned. For patterning fine structures with narrow lines or spaces, other techniques such as photolithography must be employed.

4.1.2 Photolithography

Photolithography, which is a commonly used technique for patterning a pre-deposited film, involves a series of steps to create patterns with high resolution and reproducibility [57]. In case of metal film, initially the substrate is cleaned and heated to minimize the amount of particles, dust, or vapor on top of the film. Then the film is coated with a photoresist usually through spin coating and baked in the oven. Exposure of the photoresist layer to UV light follows through a mask with pre-designed patterns. Depending on the type of photoresist, either the UV exposed regions (in case of positive photoresist) or non-exposed regions (in case of negative photoresist) become soluble in a chemical called photoresist developer. In this thesis, positive photoresist is used for patterning. After exposing to UV light, the substrate is washed in the developer to remove the parts of the photoresist that

![Image](image_url)
are exposed and the substrate is ready for etching. In some cases, another baking step is performed to improve the adhesion of the photoresist to substrate.

Etching is the process of removing the parts of the deposited film that are not protected by the photoresist. This process can be done using chemicals that dissolve the film (wet etching) or by exposing it to plasma (dry etching). The last step in photolithography is to remove the photoresist.

4.2 Printing and Coating Techniques

The inventions of paper production and printing techniques have been pivotal in the development and spread of civilization. Printed electronics on flexible substrates including plastic and paper has given new dimension and momentum to this technology. The printing and coating methods used for fabrication of the devices are explained in this section.

4.2.1 Screen Printing

Screen printing is one of the oldest methods of printing in which the pattern to be printed is transferred onto the substrate through a screen. The screen is a mesh of thin wires attached to a frame, on which the image is patterned i.e. the voids of the mesh are blocked according to the image. The screen is placed on top of the substrate and the ink is placed on the screen. A squeegee is used to push the ink through the frame. The ink can pass through the mesh where voids of the mesh are not blocked and thus forms the image on the substrate as shown in Figure 4-2(a).

![Screen printing process](image-url)

**Figure 4-2** (a) The screen printing process. (b) Screen printer.
Both organic and inorganic materials can be printed using this method if embedded in inks with appropriate viscosity for screen printing [28, 29, 32]. However, in the paper I, Si and NbSi$_2$ particles in form of dry powder are successfully printed using screen printing. The screen printer used for fabrication of samples in this thesis is shown in Figure 4-2(b).

4.2.2 Inkjet Printing

Inkjet printing is a digital printing technique in which the pattern is formed by propelling droplets of the ink onto the substrate. In continuous inkjet method, introduced by William Thomson in 1867 for the first time [93], a high pressure pump pushes the ink from the reservoir creating a continuous flow of the ink droplets out of the reservoir. The droplets are then charged and directed towards the substrate according to the image.

![Inkjet printer diagram](image)

Figure 4-3 (a) The principle of piezoelectric DOD inkjet printing. (b) A 16-nozzle desktop inkjet printer.

In piezoelectric drop on demand (DOD) inkjet printing, the image data is translated into voltage pulses to a piezoelectric crystal connected to the ink channel. With each voltage pulse, the piezoelectric crystal pushes one ink droplet out of the nozzle to form the image on the substrate [94]. The operating principle of the DOD inkjet printing and the 16-nozzle inkjet printer used in this thesis are illustrated in Figure 4-3.

4.2.3 Spin Coating

Spin coating is a commonly used method for depositing a film on a substrate from solution [57]. Spin coater, is in principle a spinning disc, on which the substrate can be fixed, usually by applying vacuum through perforated holes. The
solution containing the material to be deposited is applied on the substrate. The spin coater then rotates the substrate with a certain speed causing the solution to spread on the surface due to the centrifugal force. Generally, the spinning starts with a few seconds of low speed spinning to disperse the solution over the substrate surface, followed by a second spinning step with higher spin rate to obtain the desired film thickness. The important parameters to adjust to obtain a film with homogenous thickness and good quality are the viscosity of the solution, the spin rate, and the spinning duration.

4.3 Electrical Characterization

When an electrical device or component is designed and fabricated, the most fundamental measurement to perform is the electrical characterization. For instance, in the case of diodes, threshold voltage, forward current, leakage current, rectification ratio and the resistance in on-stage are among the primary properties of the device to characterize.

The topic “electrical characterization” includes a huge variety of different measurements depending on the type and application of the device. For example, the resistance can be measured by simply applying a DC voltage and measuring the current in some cases. However, if more accurate information about the impedance of the device is needed, a DC measurement would not suffice since impedance is a frequency dependent parameter. In such cases, cyclic voltammetry or impedance spectroscopy may be more suitable. The electrical characterization techniques used in this work are explained briefly in the following sections.

4.3.1 DC Measurements

DC measurement is one of the most primary electrical characterization techniques. It basically includes applying a DC voltage to the device and measuring the current or vice versa. DC in principle means a signal with a constant level; however, measurements including signals with multiple levels applied with long intervals, slow amplitude sweeps etc. are commonly referred to as DC measurements as well. Although DC measurements are among the simplest characterization methods, several device parameters and material properties can be extracted from the results.

Most of the DC measurements in this thesis are performed using a semiconductor parameter analyzer (Figure 4-4(a)). This device has several source
measure units (SMUs) through which the electrical current or voltage can be applied and/or measured. The SMUs are usually connected to the device through probes in a probe station (Figure 4-4(b)).

Figure 4-4 (a) A semiconductor parameter analyzer. (b) A probe station. (c) A cryogenic probe station.

In some cases, the device parameters are extracted from the behavior of the device at different temperatures. A cryogenic probe station can be used for this type of measurement. Cryogenic probe station is a relatively small vacuum chamber containing a stage to place the sample and several probes to connect the sample to the measurement equipment (Figure 4-4(c)). The stage is connected to a temperature control unit that can adjust the temperature. The measurements are usually performed in several temperature steps under vacuum to make sure the stage and the sample are at the same temperature.

4.3.2 High Frequency Measurements

For devices designed for high frequency applications, the device behavior should be characterized in a range of frequencies. As the signal frequency increases to a few tens of megahertz and up, the wavelength becomes comparable to the size of the circuit implying that the voltage and current are no longer spatially uniform through the circuit [95]. The signals should be analyzed as propagating waves that are partially reflected back and forth between any two connections in the circuit.
In this case, transmission line theory should be used to study the behavior of the circuit rather than directly applying Kirchhoff laws [96].

![Figure 4-5](image)

(a) The signal generator and the oscilloscope. (b) A pair of ACPs connected to the 50 Ω cables through the connectors, probing a device.

In terms of measurements, special equipment designed for the desired bandwidth should be used otherwise a considerable part of the signal might vanish along the cables and connectors even before it reaches the device under test (DUT). In this thesis, two ultra-high frequency diodes are designed and their bandwidth is measured using a setup suited for the measurements in the frequencies between 10 MHz and 6 GHz. The setup, which is intended to check the frequency range within which the diodes are still able to rectify the input signal, consists of a signal generator, cables, connectors, Air Coplanar Probes (ACPs) and an oscilloscope (see Figure 4-5). The signal generator can generate single harmonic signals up to 6 GHz. The ACPs are special probes designed for and commonly used in Radio Frequency (RF) measurements. The signal generator, cables and connectors all have the standard 50 Ω input/output impedance to assure the optimum signal transfer and minimum loss. The input signal is transferred from the signal generator to the diode using cables, connectors and an ACP. The diode rectifies the signal and produces a DC signal, which is transferred to the oscilloscope again using the ACP, cables and connectors. The frequency of the input signal is varied between 10 MHz to 6 GHz and the output DC level is recorded. The output level is later plotted vs. the input frequency to identify the bandwidth of the diode. Although all of the components and equipment in the measurement setup have the standard 50 Ω input/output impedance, there are still a lot of signal reflections in the circuit during the measurement. The reason is that the impedance of the DUT is not
matched with the rest of the circuit. As a result, the plot of output voltage vs. frequency has many ripples making it difficult to estimate the bandwidth. An impedance matching network is needed in order to resolve this problem. However, designing a matching network for the whole frequency range of the measurement and especially for a non-linear device is very complicated. The approach we have taken in this work is to connect simple matching networks at the parts of the circuit where the highest reflections are expected, to attenuate the reflected signal. The measurement is repeated with several setups where these matching networks are slightly altered. Each of these setups diminishes the reflections and therefore the ripples in the voltage-frequency plot in a part of the frequency range. The response of the circuit and the bandwidth are estimated by averaging the results of the measurements collected using different set-ups.

4.3.3 Impedance Spectroscopy

The impedance of a material or a device is a frequency dependent complex number defined as the ratio between voltage and current:

\[ Z = \frac{V}{I} \]

In case of liquids, impedance spectroscopy is usually performed on a cell with two metal electrodes containing the material to be characterized. A voltage with a relatively small amplitude is applied to the electrodes of the cell, in a range of frequencies, and the current is recorded in each frequency step. The current of the cell depends on the geometry and dimensions of the cell, properties of the material and the electrodes and the interaction between them. One of the common approaches to analyze the measurement results of impedance spectroscopy is to find an electrical equivalent circuit for the cell, which describes certain parameters such as the conductivity of the material and the double layer capacitance formed on the electrodes.

The impedance is usually expressed using its phase and magnitude:

\[ Z = |Z|e^{2\pi if\Phi_z} = |Z| \times [\cos(2\pi f\Phi_z) + i \sin(2\pi f\Phi_z)] \]

where |Z| is the magnitude and \( \Phi_z \) is the phase of Z and \( f \) is the frequency. Three basic elements in electrical circuits are resistors, capacitors, and inductors. The phase of the impedance is the phase shift between voltage and current. If the phase of the impedance is zero, i.e. voltage and current are in phase, the impedance becomes a frequency independent, real value a.k.a. resistor (R). In case of the
capacitor (C) and inductor (L), the phase of the current has -90° and 90° shift compared to voltage respectively. A very useful tool in analyzing impedance data is Nyquist plot, in which negative of the imaginary part of the impedance is plotted vs. the real part in a frequency band [97]. Nyquist plot is convenient in essence that the elements in an electrical circuit have signatures in the plot that can be easily recognized.

![Diagram](image)

Figure 4-6 (a) A capacitor, a series RC, a three-element and a four-element circuit commonly used as equivalent circuit in modelling of impedance spectroscopy data. (b) The Nyquist plot of the elements and circuits in (a).

The Nyquist plot of a capacitor, a series RC and two simple circuits commonly used as the cell equivalent circuits in impedance spectroscopy are shown in Figure 4-6. A capacitor (number 1 in Figure 4-6) has a very high impedance in low frequencies (open circuit at DC) that reaches zero (short circuit) in high frequencies. A series RC (number 2 in Figure 4-6) has the same shape of a single capacitance but with a shift equal to the resistance, in the real axis. A half cycle Nyquist is the typical signature of a parallel RC, with the diameter of R. Connecting a resistor in series to the parallel RC, gives the Nyquist a shift equal to the resistance in real axis (number 3 Figure 4-6).

Analysis of the impedance spectroscopy data usually starts with choosing an appropriate model (equivalent electrical circuit) for the cell followed by estimating
and optimization of the model parameters. Figure 4-7(a) shows the Nyquist plot of the electrophoretic display cell used in paper V (stars). A half cycle shifted in real axis is the characteristic of a parallel RC in series with resistance. The tail in the low frequencies indicates that the cell can be modelled better by adding another series capacitance as shown in Figure 4-6 (number 4). The cell itself has two double layer capacitances forming on the electrodes (C_{dl}) in series with a resistance (R_I) representing the resistivity of the media. The two series double layer capacitances can be represented as one capacitor in the model (two C in series is replaced by C/2). Another parameter that should be considered is the parallel plate capacitance of the cell in between the two electrodes (C_p). The resistance of the cables and connectors used to connect the cell to the impedance spectrometer can be modelled as another resistor (R_s) in series with the impedance of the cell. This four-element circuit illustrated in Figure 4-7(b) can therefore well explain the cell parameters and behavior.

Figure 4-7 (a) The Nyquist plot of the experimental data (stars) and the model (solid line). (b) The equivalent circuit used for modeling the data. (c) The real and imaginary part of the impedance vs. the frequency for the experimental data (stars) and the model (solid line).

Some parameters of a model can easily be determined. In this case, for example, the series resistance (R_s) and the ink resistivity (R_I) can be easily determined by the lateral distance of the left most point of the half cycle to the center and the diameter of the half cycle respectively. Other parameters such as C_{dl} and C_p in this circuit are more complicated to determine. Several methods can be
found in the literature to select a proper model and estimate the model parameters [98-101]. In this case, the model parameters are determined according to a method Yezer et al. suggested for a similar system [98].

As illustrated in Figure 4-7, the experimental data and the model are in good agreement; however, they do not perfectly match. This is a very usual case dictated by the fact that the behavior of a cell can seldom be modelled with ideal elements with 0 and ±90° phases. It is possible to choose a more complicated circuit to start with and obtain a better match between the model and the experimental data through data fitting algorithms. However, the accuracy and the reliability of the model for explaining the behavior of cell is questionable with a complicated model with several variables. In general, it is preferable to find the simplest equivalent circuit that matches the data and explains the behavior of the cell, and depending on the case, some mismatch between the data and the model is acceptable.

4.4 Surface Morphology and Chemical Composition Characterization

Surface morphology and chemical composition characterization include techniques to investigate the sample at the macroscopic, microscopic and atomic scales. These techniques examine the composition, internal and crystal structure, chemical state and bonding, impurities and density of the sample among many other properties.

![Figure 4-8](image)

(a) Relative intensity (b) SEM

Figure 4-8 The results of a spectroscopy technique (XPS) in (a) and a microscopy technique (SEM) in (b).
Microscopy and spectroscopy are two important physical characterization techniques. The results of the spectroscopy techniques are graphs showing the measurement results vs. the input. The microscopy techniques deliver images of the sample (see Figure 4-8). Light Optical Microscopy (LOM) and Scanning Electron Microscopy (SEM) are among common microscopy techniques and X-ray photoelectron spectroscopy (XPS) is one of the frequently used spectroscopy methods. The basics of the microscopy, spectroscopy and other physical characterization techniques used in this work are explained in the following sections.

4.4.1 Light Optical Microscopy (LOM)

The human eye can distinguish objects with 100 µm gap in between from a close distance [102]. For observing smaller features, image magnification is necessary. Optical microscopes are the oldest microscopy equipment humans have employed to this end. The principle is simple; transparent optical lenses are used to magnify the reflected or transmitted image of an object [103]. Optical microscopes can magnify an object up to 2000 times. The primary problem with the image quality of optical microscope is the shallow depth of field. Depth of field is the range of distances from the lens where the object appears sharp in the image. The depth of field decreases as the magnification increases, as a result, the specimens with some roughness or inhomogeneous profile are difficult to observe with an LOM.

4.4.2 Scanning Electron Microscopy (SEM)

SEM is a surface sensitive microscopy technique where the information about the specimen is extracted from the interaction between the surface of the specimen and an electron beam that scans it. Excitation of the surface with an electron might cause the ejection of electrons or photons (Auger, secondary electron, backscattered electron, X-ray, etc.). These electrons or photons are collected by detectors and converted into electric current. The current strength defines the brightness of each pixel of the image that is created by the scanning process. The fundamental components of SEM include an electron gun, column, and the detector in a vacuum chamber (see Figure 4-9). The electron gun produces the electron beam directed to the specimen. The beam passes through electromagnetic lenses in the column to form an electron spot with a certain diameter on the specimen.
The detector then collects the photons or electrons ejected from the specimen as the result of the electron excitation [103].

![Figure 4-9 Scanning Electron Microscope (SEM)](image)

Different detectors are utilized to detect different types of ejected electrons or photons. The most common type of the ejected particles detected using SEM, is the secondary electron, which is ejected from a depth of up to 50 Å from the surface of the specimen. The secondary electrons can be used to obtain information about the topology and profile of the specimen. SEM has a better magnification and depth of field compared to the LOM. However only vacuum compatible specimens can be studied using this technique. Another limitation is the difficulty to capture a good image from an insulating specimen since the electrons electrostatically charge the specimen. This problem can sometimes be resolved by depositing a layer of metal (metal evaporation for example) on the specimen to electrically ground it. A secondary electron image captured from Si particles using SEM is illustrated in Figure 4-8(b).

### 4.4.3 X-ray Photoelectron Spectroscopy (XPS)

XPS is a surface sensitive spectroscopy technique used to obtain information about chemical composition, chemical bonds, and the electronic band structure of the sample. The surface of the sample is excited using an x-ray beam causing the electrons to be ejected from atoms within the sample [103]. The kinetic energy of these ejected electrons depends on the energy states they occupied in their original atom. This means that each of the electrons ejected from the sample can be tracked
back to a certain energy level in the atomic structure of a certain element. Shifted energy levels of elements occur when the atom has one or more chemical bonds. The energy shift depends on the type and number of bonds that the original atom had when the electron was ejected. Therefore, the chemical bonds that the atom has with other elements can also be identified according to this energy shift.

In an XPS spectrum, the percentage of the electrons collected with different energies is plotted as a function of the electron’s energy. An XPS spectrum from the surface of a sample consisting of Si particles in an SU-8 binder is illustrated in Figure 4-8(a). The presence of Si, O and SiO₂ is detected in the spectrum. By further analysis of the results, the oxide thickness was also calculated to be about 3 nm [33, 104].

4.4.4 Profilometry

Information about the profile of a sample such as thickness and roughness can be obtained using profilometers. Profilometers can be divided into two classes, contact and non-contact. In contact profilometers, the tip of a stylus is brought into contact with the surface of the sample and scanned across a certain distance of the surface with a predefined force collecting the profile information. Non-contact profilometers utilize other methods such as interferometry and confocal microscopy to provide the profile information of a sample. In interferometry for example, the profile information is extracted by comparing two originally identical beams of light; one reflected from the sample and the other reflected from a reference mirror.

Figure 4-10 (a) A contact profilometer (Dektak). (b) A non-contact optical profilometer.
Figure 4-10 shows a contact profilometer (Dektak) and a non-contact optical profilometers (Sensofar PLu neox). In general, optical profilometry is not a proper method for transparent samples which do not reflect much of the incoming light, while contact profilometry can be problematic with sticky or soft samples where the stylus can get stuck in or go through the sample.

4.5 Production of Micro-Particles (μPs)

In this thesis, NbSi$_2$ and Si micro-particles (μPs) have been used to produce printed and/or flexible ultra-high frequency diodes. A multi-step process is followed for production and characterization of these particles.

For Si, the process starts with breaking a Si wafer in small pieces using a hammer. NbSi$_2$ is purchased in powder form; however, further milling is needed to achieve a desirable fine powder. The material (Si pieces or NbSi$_2$ powder) is placed into grinding jars together with the grinding balls in a RETSCH PM 100 Planetary Ball Mill. The jars are subjected to planetary rotation movement inside the ball mill. The balls in the jars move around under the centrifugal force and crush the material inside the jar into fine pieces. The RETSCH PM 100 Planetary Ball Mill and its schematic working principle are shown in Figure 4-11.

(a) RETSCH PM 100 Planetary Ball Mill. (b) The schematic working principle of the ball mill.

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The powder obtained from ball milling is mixed in acetone and left to settle in a sedimentation tube for a certain period of time according to the targeted particle size range. Naturally, the larger particles settle quicker at the bottom of the tube since they are heavier. The sedimentation time can be calculated according to the density of the particles; so that particles larger than a threshold are settled at the bottom of the tube and the ones smaller than the threshold remain floating in the media. A big portion of the particles with sizes larger than the targeted range can be separated through sedimentation. As for the particles much smaller than the targeted range, a centrifuge step in acetone can be applied. The suspension of the particles in acetone is placed in an MSE Mistral (see Figure 4-12(a)) and centrifuged for 10 minutes with 1000 RPM and the small particles that have remained floating in acetone after the centrifuge are discarded. The sedimentation and centrifugation methods are suitable for obtaining particles of sizes smaller than 20 µm. For sorting and collecting of relatively bigger particles, sieves can be used instead. Figure 4-12(b) shows a Retch sieve shaker where the sieves with different mesh sizes can be fixed in. The shaker can be programmed to shake the sieves with different amplitudes, time durations and intervals. By choosing the right mesh sizes, the particles larger or smaller than the desired range can be filtered away.

![Figure 4-12 (a) An MSE Mistral centrifuge. (b) A Retch sieve machine.](image)

After preparing the particles, a size distribution analysis can be performed by taking microscopy images and using different image processing techniques. In this
work, the online image processing tool; SIMAGIS live; is used to identify particle size distribution and average size.

4.6 Synthesis of the Electrophoretic Ink

The synthesis of the electrophoretic (EP) ink is performed in several steps starting with the synthesis of micro-initiators. The PLA$_{23}$-SG1 micro-initiators are synthesized in a process similar to that reported in a work from Charbonnier et al [105]. Blocbuilder® and lauryl acrylate are mixed in toluene, stirred, and heated. The micro-initiator is then dispersed in methanol and dried overnight at 50°C in vacuum.

TiO$_2$@SiO$_2$ core-shell particles are synthesized following the Stöber process [106]. TiO$_2$, deionized water, ethanol and ammonium hydroxide are mixed together and stirred in a sonicator. Then, Tetraethyl orthosilicate (TEOS) is added and the solution is stirred. The particles are carefully cleaned by repeated centrifugations in ethanol and then dried in a vacuum oven at 50°C for one night. Silanization of TiO$_2$@SiO$_2$ particles surface is performed with OTS coupling agents leading to TiO$_2$@SiO$_2$-OTS.

The next step in the process is Nitroxide Mediated Radical Polymerization via dispersion polymerization of TiO$_2$@SiO$_2$-OTS/Poly(AA-co-LA$_{23}$) (PEDG5), starting with solubilizing TiO$_2$@SiO$_2$-OTS and stabilizer in Isopar G. This solution is mixed using an ultrasound bath and ultrasound probe and then degassed by nitrogen bubbling. During the nitrogen bubbling, the monomers, macro-initiators and the charge control agent, DOD$_3$N, are mixed in Isopar G and added into the solution. Finally, the mixture is heated at 120°C under mechanical stirring (375 rpm). Once the reaction is complete, the particle dispersion is cooled down and purified by three cycles of centrifugation and re-dispersion in Isopar G.

For the electrophoretic display application 8.8 wt% of negatively charged PEDG5 particles and 0.13 wt% blue dyed oil are mixed into Isopar G solutions to obtain an electrophoretic ink with white/blue states.
5 Conclusion and Outlook

Two categories of non-linear devices are investigated in this thesis. Flexible UHF diodes are produced and their energy harvesting application is demonstrated. Organic ferroelectric capacitors are also studied and implemented for inducing non-linearity and addressability in several devices. In this section, the outlook of this work is discussed after a brief summary of the findings on each category of the non-linear devices.

5.1 GHz Diodes

Novel printing- and lamination-based methods are developed for production of flexible silicon diodes with GHz operational range. Using the printing-based method, an all-printed flexible diode is produced with GHz operational frequency for the first time. Micrometer-sized Si powder embedded in a polymer matrix is employed as the semiconducting layer in this diode. The diode is coupled with and antenna and a printed display in a simple flexible circuit to demonstrate the energy harvesting application of the diode in GHz range. We show that the diode can rectify the signal received through the antenna from a mobile phone working in the GSM band, and produce a DC to turn on the printed display.
A lamination-based method for producing flexible silicon diodes is further developed where the properties of the device such as threshold voltage, current density, rectification factor, and operational frequency are improved. A flexible semiconducting composite film consisting of Si micro-particles, glycerol, and nano-fibrillated cellulose is produced and used as the semiconducting layer of the diode. This is the first time the environmentally friendly material, cellulose, is used as the binder for Si particles to produce a self-standing semiconducting film, which can be utilized as the semiconducting layer in a UHF device.

Diodes are fundamental semiconductor devices employed in a variety of electrical circuits. In this thesis, the power harvesting application of the diode is demonstrated using a single diode in a so-called half wave rectifier scheme. In a design composed of four diodes, this scheme can be improved to a full wave rectifier, which eliminates a smaller portion of the input signal compared to the half wave rectifier and therefore produces a DC with higher level and consequently higher power. More advanced AC to DC convertors such as voltage multipliers and clamps can also be implemented using a combination of diodes and capacitors.

One of the main applications of the Schottky diodes is in mixers and frequency multipliers, where the non-linear property of the diode is used to generate output signals with a combination or multiples of the frequencies of the input signals. This application of the Schottky diode can also be easily demonstrated using the flexible diodes developed in this work.

Logic gates are among other simple circuits that can be implemented using a combination of diodes in future work.

5.2 Ferroelectric Capacitors

A simple model for understanding the polarization mechanism of the organic ferroelectric P(VDF-TrFE), stacked together with an electrolyte, is developed and verified by comparing the simulation results of the model with the experimental data recorded from P(VDF-TrFE) capacitor structures. These structures are used to induce non-linearity and passive addressability in an electrophoretic display and electrochemical devices.

We show that the ferroelectric polarization can induce ion displacement within a polyelectrolyte layer placed in contact with the conducting polymer PEDOT:PSS and consequently alter its doping level. The resulting bistable hysteresis is successfully implemented in organic electrochromic PEDOT:PSS display cells and electrochemical transistors to introduce addressability and memory functionality.
In another approach intended for designing flexible displays, a P(VDF-TrFE) capacitor is employed to induce non-linearity and addressability in an electrophoretic display cell. The electrophoretic cell is characterized using impedance spectroscopy and modelled to determine the double layer capacitance formed on the electrodes. We demonstrate that by depositing a P(VDF-TrFE) capacitor with suitable surface area, the polarization of the ferroelectric can be matched with the surface charge of the display cell and hence bistable switching behavior is induced in the cell. The so gained bistability makes the implementation of the electrophoretic display technology in a passive matrix scheme viable.

The application of ferroelectric capacitors in inducing non-linearity, bistable switching and memory functionality is demonstrated in this work. As a future outlook, the developed devices can be incorporated in flexible addressable matrices. A flexible electrochemical memory matrix can also be implemented utilizing the bistable PEDOT:PSS transistors with P(VDF-TrFE) gate. Flexible passive matrix displays can also be produced by incorporating the bistable electrochemical PEDOT:PSS or electrophoretic display cells into a matrix.
References


Publications

The articles associated with this thesis have been removed for copyright reasons. For more details about these see:
http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-127014