INTELLIGENT PAPERS

Abstract

The main purpose of this study was to collect basic information about the electronic paper, *i.e.* "intelligent paper". This term is genarally used to describe different types of paper based or paper-like products, which have properties common to papers added with new values in forms of electronics. Intelligent papers include different electronic components and circuits applied or printed onto the flexible substrate. Fast and cheap roll-to-roll manufacturing processes with existing printing technologies could allow mass production of low cost electronics for several applications.

To understand versatile requirements and functions of the electronics used in intelligent papers, it was given some basic information about the electronic components itself and the materials to manufacture these components. In addition, it was surpricing to notice that there are only limited data available on electronics using paper-based products as a substrate. Despite this, there are many signs showing that real intelligent papers will be reality in the near future.

Preface

This Master´s Thesis was carried out in the Laboratory of Applied Chemistry, University of Jyväskylä The material for this literature review was mainly collected during the academic year 2005 and its writing was made in spring 2006. The starting-kick for the study came from CP Kelco (formely Noviant) Äänekoski, Finland. I will thank Ms Anu Moilanen and Mr Jukka Lehtovuori form CP Kelco for the idea and their support during the first steps in this new area.

My deepest gratitude belongs to the supervisors, Professor Raimo Alén and Dr. Riikka Reitzer for their guiding and advice in preparing the literature review.

Along with the persons mentioned above, I owe thanks to the relatives and friends, but above the all, to my loveing wife Anne, whose support has been extraordinary during the process. Thank you for believing in me!

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Elja Kallberg

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List of Abbreviations

ABPA	=	aminobutyl-phosphonic acid
ACN	=	2-propenenitrile (acrylonitrile)
AFM	=	atomic force microscope
AIBN	=	2,2'-azobisisobutyronitrile
Alq_3	=	aluminium tris-8-hydroxyquinoline
AM	=	active matrix
AMFPD	=	active matrix flat panel display
BCP	=	9-dimethyl-4,7-diphenyl-1,10-phenanthroline
BJT	=	bipolar junction transistor
bpy	=	2,2'-bipyridine
C-545P	=	10-(2-benzothiazolyl)-1,3,3,7,7-pentamethyl-2,3,6,7-tetrahydro-1H,5H,11H-benzo[l]-pyrano[6,7,8-ij]-quinolizin-11-one
C-545T	=	10-(2-benzothiazolyl)-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H,11H-benzo[l]-pyrano[6,7,8-ij]-quinolizin-11-one
CL	=	colloidal lithography
CMOS	=	complementary metal-oxide semiconductor
CMS	=	core / multishell (nanowire)
CNT	=	carbon nanotube
CNTFET	=	carbon nanotube FET
CP	=	conducting / conductive polymer
CRT	=	cathode-ray tube
CuPc	=	copper phthalocyanine
DBSA	=	dodecylbenzenesulphonic acid
DIQA	=	N,N'-di-isoamyl quinacridone
DNA	=	deoxyribonucleic acid
dpi	=	dots per inch
DPN	=	dip-pen nanolithography
DWCNT	=	double-walled CNT
(E)	=	emeraldine, a partially oxidised and partially reduced form of PANI
EB	=	emeraldine base PANI
EC	=	electrochromic
EDOP	=	3,4-ethylenedioxypyrrole
EDOT	=	3,4-ethylenedioxythiophene
EL	=	electroluminescent
EML	=	emissive layer
EPD	=	electronic paper display
ETL	=	electron transport layer
F8T2	=	poly(9,9'-dioctyl-fluorene-co-bithiophene)

FE (SEM)	= field emission (SEM)
FET	= field-effective transistor
FPD	= flat-panel display
HCSA	= 10- camphorsulphonic acid
HOMO	= highest occupied molecular orbital
HPC	= hardness polycarbonate
HRP	= horseradish peroxidase
HSA	= human serum albumin
HTL	= hole transport layer
IBM	= International Business Machines Corporation
IC	= inregrated circuit (a microchip, a chip)
ICP	= intrinsically conducting polymers
IGFET	= insulated gate FET
ITO	= indium tin oxide
JFET	= junction FET
(L)	= leucoemeraldine, a highly reduced form of PANI
LCD	= liquid crystal display
LEC	= light-emitting electrochemical cell
LED	= light-emitting diode
LUMO	= lowest unoccupied molecular orbital
LWE	= low weight
MEH-PPV	= poly[2-methoxy-5(2'-ethylhexyloxy)-1,4-phenylene vinylene]
MIM	= metal–insulator–metal
MIMIC	= micromolding in capillary
MIT	= the Massachuttes Institute of Technology
MOSFET	= metal oxide semiconductor FET
MSC	= molecular semiconductor
MWCNT	= multiwalled CNT
nIL	= nanoimprint lithography
NMP	= N-methylpyrrolidone
NPB	= 4,4'-bis(*N*-1-naphthyl-*N*-phenylamino)biphenyl
NW	= nanowire
NW-FET	= nanowire-based field effect transistor
OFET	= organic field-effective transistor
O-I	= organic-inorganic
OLED	= organic LED
OTFT	= organic thin-film transistor
(P)	= pernigraniline, a completely oxidised form of PANI
P2VP	= poly(2-vinylpiridine)
P3HT	= poly(3-hexylthiophene)

PA	=	polyamide
PAI	=	polyamide-imide
PANI	=	polyaniline
PARC	=	Palo Alto Research Center (Xerox Corporation)
PAT	=	poly(alkylthiophene)
PC	=	personal computer
PCA	=	polycyanine
PDA	=	personal digital assistant
PEDOT	=	poly(3,4-ethylenedioxythiophene)
PEO	=	polyethylene oxide
PES	=	polyether sulphone
PET	=	polyethylene terephthalate
PFO	=	poly(9,9-dioctylfluorene)
Ph_2Bq	=	organoboron quinolate
PL	=	photoluminescence
PLED	=	polymer LED
PMMA	=	polymethylmethacrylate
PN	=	p-n or PN junction (in diodes)
POMA	=	poly(*o*-methoxyaniline)
PPS	=	polyphenylene sulfide
PPV	=	poly(1,4-phenylene-vinylene)
PPY	=	polypyrrole
PQT-12	=	poly(3,3'''-didodecylquarterthiophene)
PS	=	polystyrene
PSS	=	polystyrenesulphonate
PSSA	=	poly(styrenesulphonic acid)
PT34bT	=	poly(thieno[3,4-*b*]thiophene)
PTAA	=	poly(3-thiopheneacetic acid)
PTCBI	=	3,4,9,10-perylenetetracarboxylic bisbenzimidazole
PVC	=	polyvinyl chloride
PVP	=	polyvinylephenyle
PWB	=	printed wiring board
RFID	=	radio-frequency identification tag
rms	=	root-mean-square
RR	=	regioregular
R_S	=	sheet resistivity, $\Omega/\square$
SAM	=	a self-assembled monolayer
SAS	=	self-assembled superlattice
s-CNT	=	semiconductor carbon nanotube
SEM	=	a scanning electron microscope

SiNW		= silicon nanowire
SMOLED		= a small molecular organic LED
SNCT		= single-nanocrystal transistors
SPM		= scanning probe microscope
STM		= scanning tunnelling microscope
SWCNT		= single-walled CNT
TCBQ		= tetrachloro-1,4-benzoquinone
TEM		= transmission electron microscope
tFMmC		= α,α,α-trifluoromethyl-m-cresol
TFT		= thin-film transistor
T_g		= a glass transition temperature, °C
TMB		= trimethylboron
TPD		= 1,4-bis(phenyl-m-tolylamino)biphenyl
TTFT		= transparent TFT
USA		= the United States of America
UV		= ultraviolet
VLS		= vaporliquid-solid (growth technique)
WORM		= write-once read-many-times (memory)
α6T		= sexithiophene
μCP		= microcontact printing
1D		= one-dimensional
2D		= two-dimensional
A		= electrode's area
C		= capacitance
d		= film thickness
ε_o		= the permittivity of free space, equals to 8,8541878176 x 10^{-12} F/m
ε_r		= relative dielectric constant (κ)
κ		= relative dielectric constant is used instead of ε_r
σ		= conductivity (κ) or (γ), S/cm
μ		= charge carrier mobility, (field-effect mobility) cm^2/(V·s)

1 What are the "Intelligent Papers"?

We live in rapidly changing world nowadays. Our society is more and more dependent on the various technological revolutions around us. One of the main leaps has been the globalisation of information and information technology. The new chapter in information media started in 15th Century in Germany, when Johann Gutenberg conceives of the idea for movable type printing press. In his workshop, he brought together much older, well-known, technologies of paper, oil-based ink and winepress to print books. In 1452, Gutenberg's Bible became the first book published in volume. Since that, storing, transmitting and presenting information have been an important endeavour in human communications. The latest advances in digital media such as computers and the Internet have increased the amount of information in our every day's life. Presenting information, data and images have an important role in our information society. Despite the use of different forms of electronic display-screens including for example, television, computer, mobile phone, personal digital assistant (PDA), electronic book, the most popular display medium is still a printed page on paper made of cellulose /1/. Therefore, there is a great driving force to develop and manufacture the electronic display media that is being to match the essential qualities of paper.

In this work, the term "intelligent paper" was used to describe different types of paper based or paper-like products, which have properties common to paper added with new values in forms of electronics. Intelligent papers include different electronic components and circuits applied or printed onto the flexible substrate. Fast and cheap roll-to-roll manufacturing processes with existing printing technologies could allow mass production of low cost electronics for several applications.

As mentioned above a printed page is the most popular display media, therefore there is a great interest either to upgrade paper's display properties to meet new requirements for information media or to create new display-types having paper's display benefits. This area forms an intelligent paper category called "paper-like displays". This is a term for active display used for visual and imaging applications consisting of electronic paper or ink and digital paper or ink. There will be many

different applications for products using these methods. Giving here some examples like reusable paper substrate in rewritable printing applications, simple display applications, an updatable visual display of information on tags, labels, tickets and smart cards. Other applications could be; simple indicator labels for environmental sensing, timer labels / lifetime indicator labels for packaging applications, document protection and security, voltage and state-of-charge indicator labels for batteries, disposable electric meters /2/.

Short history of intelligent papers

The idea of intelligent papers goes back to 1970's to the dawning of personal computing (PC). After the rise of data computing, electronic media has taken a great role in information transport and put pressure to invent more compact and readable display-solutions to transfer information from a computer. The liquid crystal display (LCD) technology (first used in electronic calculators in 1973 by Sharp) beat a bulky and heavy cathode-ray tube (CRT) display technology. The LCD technology soon extended over a wide range of displays, and became the dominant flat panel display technology. After that, display developers set a new goal; electronic display media that would match the paper's displaying properties, in other words, paper-like display-type intelligent paper.

Paper has a remarkable list of specifications /2/: it is cheap, light, portable, flexible, foldable but still durable enough for most daily applications. It can be annotated, bound and filed away for later references. Its weight, colour, texture and general condition give an indication of its provenance. Its size and shape have evolved into a number of form factors to suit the different needs for portability, readability and ease of handling. It also offers high-resolution images with good contrast and brightness. It has high and even reflectivity, and it can be read from a wide range of angles and lighting conditions. Its readability and viewability are excellent. It needs no batteries of electricity and stores the images indefinitely. Despite all of this, paper's main shortcoming is the fact that it is a passive carrier of information.

To combine advantages from both paper and electronic media has led to the paper-like displays. The beginnings towards the goal is the first electronic paper, also called Gyricon, which was invented in 1970's by Nick Sheridon and patented /3/ at Xerox

Palo Alto Research Center (PARC) in the USA. It was technically challenging and Gyricon was almost forgotten until, in 1990's Joe Jacobson invented the competing technology, E-Ink, at the Massachuttes Institute of Technology (MIT). Based on electronic paper display (EPD) technologies research at the MIT Media Lab, E Ink Corporation was founded in 1997. In addition, in 1999 company unveiled its first product using electronic ink; "Immedia" large-area displays. Since that development and commercialising of intelligent papers has moved on by leaps /4/.

The first "electronic reusable paper"; SmartPaper™ by Gyricon Media Inc. (later renamed Gyricon LLC) was launched in 2000 /5-7/. Moreover, some years later in 2004 the first consumer application of an EPD module, the "LIBRI'e", the first-generation Electronic Paper Display in Sony's e-Book reader from merged companies: Philips, Sony and E Ink saw daylight. These both are commercialised display technologies that are thin, flexible and portable like paper but can be connected to a network and reused thousands of times. There is a wide range of applications that intelligent paper is aimed to or can be utilized for, notably in mobile electronic applications.

With the paper-like display getting closer to the paper properties, some suggesting that the electronic information displays may replace the printed-paper page. Now there is not a substantial threat from the electronic sector on paper industry, because there are still many technical challenges on the sector of developing display properties; weight, robustness, energy consumption, display readability and viewability, etc. Still major obstacle is to find the cost-efficient manufacturing technologies. Nevertheless, even traditional paper is not going to dissaper anywhere, it would be wise for paper industry, especially in publishing related sector to look for new opportunities to balance future threats from the electronic sector.

2 Intelligent Papers and Basic Electronic Components

The leading idea of intelligent paper is to increase paper's information content. By embedding optoelectrical, optical, and electrical functionalities into a paper its character as a passive carrier of information can be extend. For these purposes, a great bounce of elements like displays, photodetectors, light sources, solar cells, battery elements, diffractive optical elements, lightguides are required /8/. Of course, there are certain requirements for electronics needed, but still they are composed of electric circuits made from different electrical components. These fundamental building elements, such as resistors, capacitors, transistors and diodes by connecting to each other in different ways, practically form all the electronics. Even the latest state-of-the-art integrated circuits (IC), commonly known as microchips or chips, are nothing more than very advanced electric circuits /9/. This chapter introduces these circuit-building elements.

2.1 Resistor and Capacitor

Resistors and capacitors are so called passive circuit elements /10/. A resistor is a two-terminal component that resists an electric current by producing a potential difference, obeying the Ohm's Law, between its terminals. Resistors are used to control and modify the currents. A capacitor is instead a two-terminal component that store electric charge and electric potential energy. Both have several applications in electronic technology.

Two main active (or reactive) components are:
1. a diode and
2. a transistor.

2.2 Diode

A diode is the simplest and the oldest semiconductor device. Its history goes back to 1874 when the German scientist Karl Ferdinand Braun found one-way conduction in metal sulphide crystals /11/. Although discovering the important operation principle of

crystal diodes; there was not any practical application for the effect at the time. Many years later that rectifying property of a semiconductor material composed of the galenite; lead sulphide (PbS), crystal was adapted to create the "cat's whisker" crystal radio detector. In those days, these first semiconductor devices were called rectifiers, because radio receivers required a device called a rectifier to detect signals.

There is another route leading to the first diode /11,12/: namely the English physicist John Fleming. He fitted two electrodes to an experimental filament light bulb, building so vacuum tube where electrons flowed from the negatively charged cathode to the positively charged anode. This invention of the thermionic valve or *Fleming's Valve* in 1904 was a vacuum-tube diode, the first of devices, which were to be a mainstay of electronics well into the solid-state era. William Henry Eccles coined the term diode in 1919 from Greek origins; di means "two", and ode means "path".

Most modern diodes are based on two different semiconductor layers. One is a p-type doped (having a density of mobile holes in excess of that of conduction electrons) and another is n-type doped (having more conduction electrons than mobile holes) semiconducting layer. (More about semiconductivity is discussed in Chapter 3.2) The point where the two layers connect is known as the p-n or PN junction and such the diode is called a p-n diode. In a p-n diode, conventional electric current can flow from the p-type side to the n-type side, but not in the opposite direction. If using the terminology of the vacuum-tube diode, the p-type layer is known as the anode and the n-type layer is known as the cathode /13/.

Besides a normal p-n diode there are several different types of diodes; like a Zener diode, an avalanche diode, a photodiode, a Schottky diode and probably the most well known and most easily identified, a light-emitting diode, LED /13/. The LED emits visible light when electrons cross the p-n junction and therefore it has great application potential in active panel displays, hence in intelligent papers.

2.3 Transistor

The transistor is considered one of the greatest inventions in modern history, as revolutionary as the Gutenberg's printing press, an automobile or a telephone /14/. Doctors John Bardeen, Walter Brattain and William Shockley discovered the transistor effect and developed the first device, in 1947, at Bell Laboratories, in the USA. In addition, they were awarded the Nobel Prize in physics in 1956 for their researches on semiconductors and their discovery of the transistor effect.

A transistor is a three-terminal, solid-state semiconductor device which allows a variable current, from an external source, to flow between two of its terminals depending on the voltage (which creates an electrical field through the transistor); in field-effect transistors (FETs) or current; in bipolar junction transistors (BJTs) applied to the third terminal. In other words, a voltage or a current led to the input terminal increases the conductivity of a semiconducting layer between the other two terminals and hence controls current flow through those terminals.

Transistors have two basic applications /9/: 1) modulation of an electronic current and 2) switching. The current modulation ability makes transistors to be the fundamental building blocks for basic analytical circuits, such as amplifiers.
Switching is of the utmost importance in computer operations, which are based on millions and millions of extremely fast on / off decisions. Therefore, the transistor is the key active component in practically all modern electronics; it is an integral component of an integrated circuits.

The field-effect transistors are more common in modern electronics than bipolar junction transistors /9/; the inorganic FETs have dominated the mainstream microelectronics industry. Because the FET uses either electrons or holes for conduction it is sometimes called a unipolar transistor. The terminals of the FET are named source (S), gate (G) and drain (D) (Figure 1).
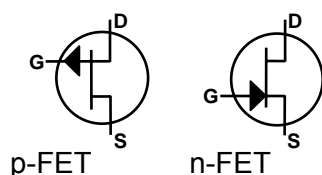

p-FET   n-FET

Figure 1. FET symbols; source (S), gate (G) and drain (D).

According the semiconducting properties, there are two types of FETs /9/: p-FET or sometimes called P-channel FET (a hole conducting type, *i.e.* having a density of mobile holes in excess of that of conduction electrons) and n-FET, N-channel FET (a electron conducting type, *i.e.* having more conduction electrons than mobile holes). In a p-FET, when a negative charge is placed on the gate and the applied voltage exceeds a certain threshold then a hole current flows through it. Similarly, for an n-FET, an electron current flows when a positive charge is on the gate and the voltage exceeds the threshold. These FETs are divided also into two main categories; junction FET (JFET) and insulated gate FET (IGFET). More common name for the IGFET is however MOSFET, a metal-oxide-semiconductor FET. Traditional MOSFETs are made on silicon (Si) wafers and use the bulk-silicon as the active, current-carrying layer. Such semiconducting components are far too big and rigid for the electronics on flexible substrates.

The answer for intelligent paper is a special transistor type: the thin-film transistor, TFT. As the transistor's name describes, its active current-carrying layer, is not bulk-silicon, but a thin film (Figure 2).
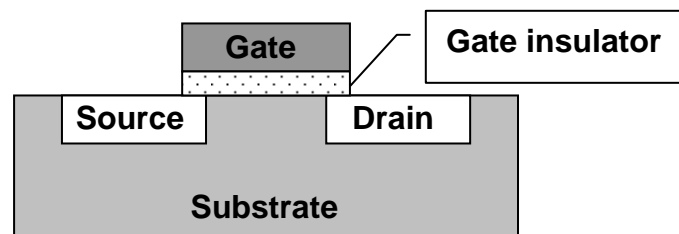

Figure 2. A schematic drawing about a thin-film transistor.

The TFTs could be manufactured form several inorganic or organic materials and have been basic elements for flat-panel displays (FPDs) since their discovery /15/. The term TFT is broadly abused to describe the whole display-systems; instead of its nature to be a FPD component.

The following Chapter 3 leads into the world of materials and structures of components for flexible and printed electronics, especially displays.

3   Materials of Electronic Components

Development of FPD technologies has been a driving force to the development of micro- and especially nanoscale components and materials to meet the new requirements to manufacture smaller components /16,17/. Although traditional silicon transistors have made great strides under the Moore's Law in terms of cost and size, there is a growing effort to develop organic electronics so that ambient intelligence can be universally applicable everywhere at the right cost point. Furthermore, the fabrication of organic TFTs will allow flexible large-area electronic devices to be developed. These devices are affordable, flexible, lightweight and shock resistant, in other words have properties that are necessary for large, economic, high-resolution displays, wearable computers and paper displays.

Polymer electronics can take the cost advantage of an in-line roll-to-roll manufacturing process based around existing techniques like ink-jet printing and device stamping processes /16,18/. Polymers can act as semiconductors if they have the right chemical structure. The working transistors have already been produced from organic polymers; despite that organic semiconductor has the relatively low mobility of the electrons and holes. Now, organic thin-film transistors, OTFTs cannot rival the performance of FETs based on single-crystalline inorganic semiconductors, such as Si, Ge and GaAs, which have charge carrier mobility; μ ($cm^2/(V·s)$) of three or more orders of magnitude higher. However, they are already good enough for applications such as a transistor drive backplane for flexible displays.

Because of organic, polymeric, electronics would be the most promising candidates for intelligent paper electronics, this chapter will concentrate to the organic based semiconductor components /18/: organic field-effective transistors, OFETs (or OTFT) and organic light-emitting diodes OLEDs (and polymer LEDs; PLEDs). Figure 3 shows two common device configurations used in OTFTs. Top-contact device, where source and drain electrodes are set onto the organic semiconducting layer and bottom-contact (sometimes called as bottom gate) device, where the organic semiconductor layer is deposited onto the gate insulator and the source and drain electrodes.
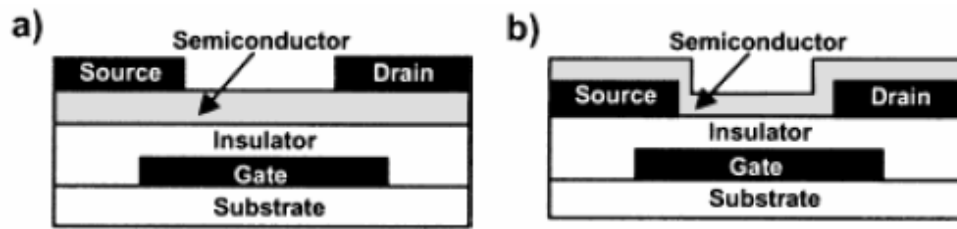
Figure 3. The schematic cross-section of OTFT device configurations /18/: a) Top-contact device, with source and drain electrodes onto the organic semiconducting layer and b) Bottom-contact device, with the organic semiconductor deposited onto the gate insulator and the source and drain electrodes.

As could be seen from Figure 3, there are three functional materials required for fabrication of an organic / polymeric semiconducting component /18/:

1. conductor (electrodes),
2. dielectric (insulator) and
3. semiconductor (active).

Materials are categorised by their conductivity (σ) (sometimes (κ) or (γ) are also used) /10/.

The materials selected can vary significantly because of organic devices and circuits are fabricated using different manufacturing technologies sensitivity /19,20/. For example, the latest advances in printing technology, like high resolution ink-jet printing, has proven to be an enabling step in the development of plastic electronic devices by processing the conducting polymer from solution to manufacture diodes, LEDs and thin-film transistors (Figure 4). In addition, the selection of conductor and dielectric materials is also dependent on the compatibility to organic semiconductors. The organic semiconductors are developed and optimised based on electrical performances, processing properties and environmental.
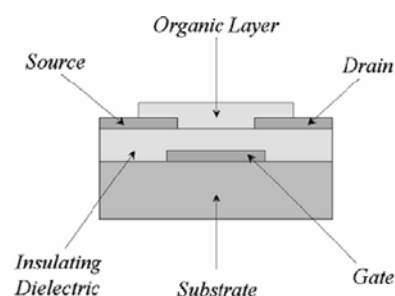

Figure 4. A schematic cross section of a typical printed organic transistor /19/. As the gate electrode is in contact with the substrate; transistor is a bottom-contact device.

3.1 Conductors

In electronics, conductors are needed mainly to produce electrodes, pixel pads, conductive lines and tracks for electrical devices. Materials considered good conductors, as inorganic copper (Cu) and iron (Fe), have σ-values of 10^6 - 10^8 S/cm.

3.1.1 Metallic Conductors

Nobel metal conductors

Noble metals, such as gold (Au), silver (Ag) and platinum (Pt), are commonly used as conductors for organic transistor /19/. They have high conductivity and are environmentally stable. An advantage is operational stability because the minimal process control is required to fabricate flawless thin metal films for device electrodes, which ensure low contact resistance at the source–drain and semiconductor interfaces. The main disadvantage is that processing requires high temperature and high vacuum.

Gold nanoparticles have been successfully explored as a low-temperature, high-conductivity alternative but the high cost of gold may negate its merits /21/. Liquid-processed silver materials accordingly represent an appealing approach if both the high conductivity and low-temperature processing requirements can be met.

Metal oxide conductors

There is a great amount of conducting metal oxides, which can be used as primary oxides to produce electrodes, such as indium oxide, titanium oxide, cadmium oxide, gallium indium oxide, niobium pentoxide and tin oxide /22/. The most commonly known metal oxide used as electrode is transparent indium tin oxide (ITO). In addition to a primary oxide, the electrodes may include a secondary metal oxide such as an oxide of cerium, titanium, zirconium, hafnium and / or tantalum. Grace *et al.* /22/ have listed other possible transparent conductive oxides like ZnO_2, Zn_2SnO_4, Cd_2SnO_4, $Zn_2In_2O_5$, $MgIn_2O_4$, Ga_2O_3, In_2O_3 and TaO_3. Even metal electrodes on plastic film have the advantage of higher conductivity than ITO electrodes, still ITO has advantage to be transparent, which is very important for display applications.

3.1.2 Conductive / Conducting Polymers (CP)

While rapid strides have recently been achieved in designing solution processable semiconductors for printed electronics, little progress has been made in printable conductive materials (inks) for similar solution-processing techniques, like spin coating, ink-jet and graphic arts printing, despite their importance as electrodes, pixel pads, conductive lines and tracks in enabling low-cost electronics /19-21/. Conducting polymers offered, however, the promise of achieving a new generation of polymers: materials which exhibit the electrical and optical properties of metals or semiconductors and which retain the attractive mechanical properties and processing advantages of polymers.

Conjugated polymers have the electronic configuration suitable for CPs; the chemical bonding leads to one unpaired electron (the π-electron) per carbon atom /20/. Moreover, π-bonding leads to electron delocalization along the backbone of the polymer, which provides the "highway" for charge mobility along the backbone of the polymer chain. The electronic structure in conducting polymers is determined by the chain symmetry (*i.e.* the number and kind of atoms within the repeat unit), with the result that such polymers can exhibit semiconducting or even metallic properties.

Active history of conjugated CPs dates back to 1980 when A. Heeger and A. MacDiarmid reported of metallic properties in chemically doped polyacetylene. Despite the processing advantages of polymers, in 1987, there were only five known CPs: polyacetylene, polyparaphenylene, polypyrrole, polythiophene and polyaniline. In addition, even as late as 1990 none of those was a stable metallic polymer, which could be processed in the metallic form as industrial products required /20,23-26/. Doctors Heeger, MacDiarmid and H. Shirakawa solved this major outstanding problem first with polyaniline (PANI) in 1991. For this discovery, they were awarded the Nobel Prize for Chemistry in 2000. This work also paved the way to a wide range of conducting polymers, from insulators via semiconductors to metallic-like materials. From literature could be found other names for these CPs: like intrinsically conducting polymers (ICP) or synthetic metals.

In following is considered on some of commercially available CPs /20,27/: polystyrenesulphonate doped poly(3,4-ethylenedioxythiophene) (PEDOT/PSS), dodecylbenzenesulphonic acid doped polypyrrole (PPY/DBSA) and polyaniline (PANI) have properties that may be exploited in applications such as sensors, energy storage, solar cells, LEDs, light-emitting electrochemical cells (LECs) and transistors. The key to such broad applications lies in the adequate combination of chemical structure and doping process, which is related to the polymer oxidation state. Doping introduces carriers into the electronic structure and forms the ability of those charge carriers to move along the π-bonded highway. CPs can be doped n-type (reduced) or p-type (oxidised) to a relatively high density of charge carriers, since every repeat unit is a potential oxidation-reduction (redox) site.

Polyaniline (PAn, PANI)

PANI is the electroactive polymer obtained by either chemical or electrochemical oxidation of aniline /28/. The term "polyaniline" as commonly employed today, refers to a class of polymers consisting of 1000 or more *p*-phenyleneimine units repeated. PANI has three distinct oxidation states as follows (Figure 5) /29,30/:

1. the completely oxidised poly(*p*-phenylene) iminoquinone form; referred usually pernigraniline (P), has all its nitrogens in the form of imine groups with sp^2 hybridization, and thus has the lowest reduction potential (*i.e.* electron accepting)

2. the highly reduced form; leucoemeraldine (L), has all nitrogens in the form of a secondary amine with sp^3 hybridization, and has the lowest oxidation potential of the three states (*i.e.* electron donating), therefore a good reducing agent;

3. the partially oxidised and partially reduced form; emeraldine (E), has a mixture of amine and imine groups and partially delocalised nitrogen 2p electrons (50 % sp^2 + 50 % sp^3 hybridization). Emeraldine was found to be the most conductive among the PANI oxidation states.

Oxidized polyaniline (pernigraniline, (P))

Polyaniline as purchased (emeraldine, (E))

Heating
in TCBQ

Heating
in N-methylpyrrolidone
(NMP)
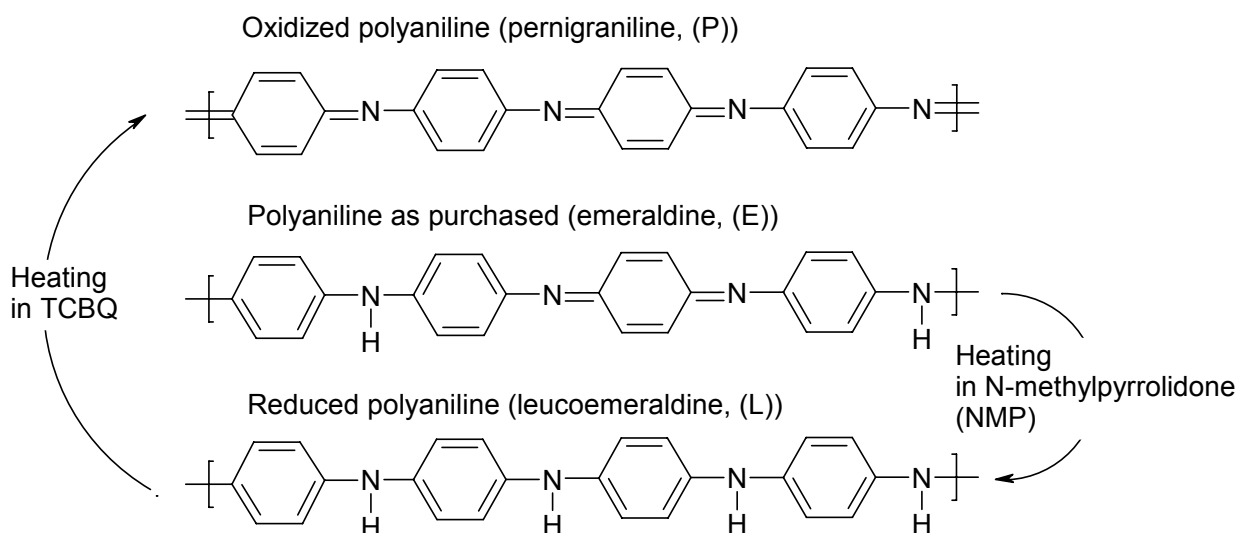
Reduced polyaniline (leucoemeraldine, (L))

Figure 5. Structure of the three oxidation states of polyaniline (PANI) /30/.

Compared to other conducting polymers, PANI has the unique character /28/: it can be reversibly doped and undoped based on simple acid / base chemistry. In acid or doped (E) salt form, polyaniline is conductive, and in the (E) base or undoped form, it is insulating. These two forms can be reversibly interconverted by the application of acid or base as shown in Figure 6.
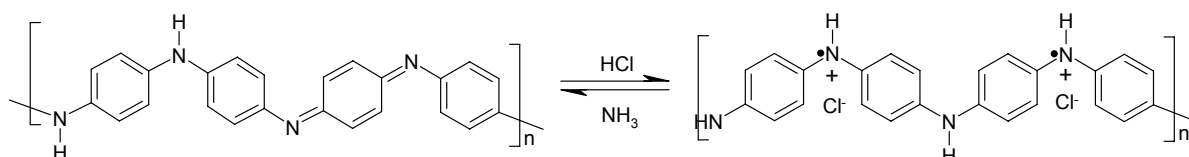

Figure 6. PANI is unique in that it can be reversibly doped and undoped on the basis of simple acid / base chemistry /28/.

There is a great variety of PANI materials modified by different dopants. Tan *et al.* /31/ have studied several PANIs used as hole conductors in organic devices: material compositions and conductivities are listed in Table 1 and the chemical structures are given in Figure 7.

Table 1. PANIs used as hole conductors in organic devices /31/: material compositions and conductivities

PANIs	components	σ (S/cm)
EB	emeraldine base in *N*-methylpyrrolidinone	$\sim 10^{-7}$
ES$_1$	mixture of EB and ES$_4$	$\sim 10^{-3}$
ES$_2$	4-dodecylbenzenesulphonic acid doped polyaniline in chloroform	3.5
ES$_3$	mixture of ES$_2$ and ES$_4$	131
ES$_4$	10-camphorsulphonic acid doped PANI in *m*-cresol	297

a)

b)

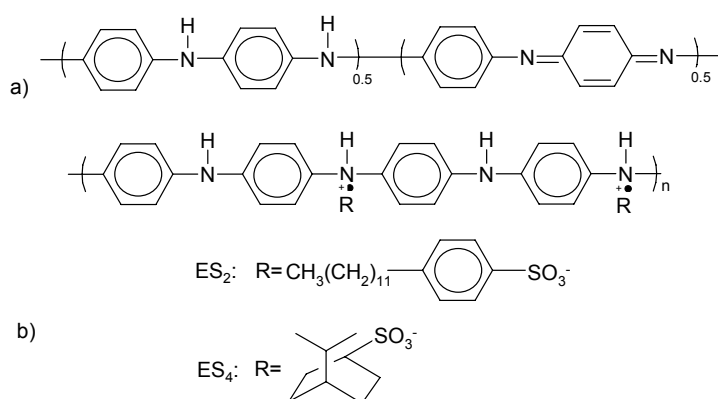ES$_2$: R = CH$_3$(CH$_2$)$_{11}$ —〈〉— SO$_3^-$

ES$_4$: R =

Figure 7. Chemical Structures of PANIs: (a) EB (b) ES$_2$ and ES$_4$ /31/.

Another interesting report is from Ma *et al.* /28/ in 2004. They have studied fabrication of PANI nanowires on thermally oxidised Si surfaces by use of DNA as templates. The principle of the nanowire fabrication method is sketched in Figure 8.
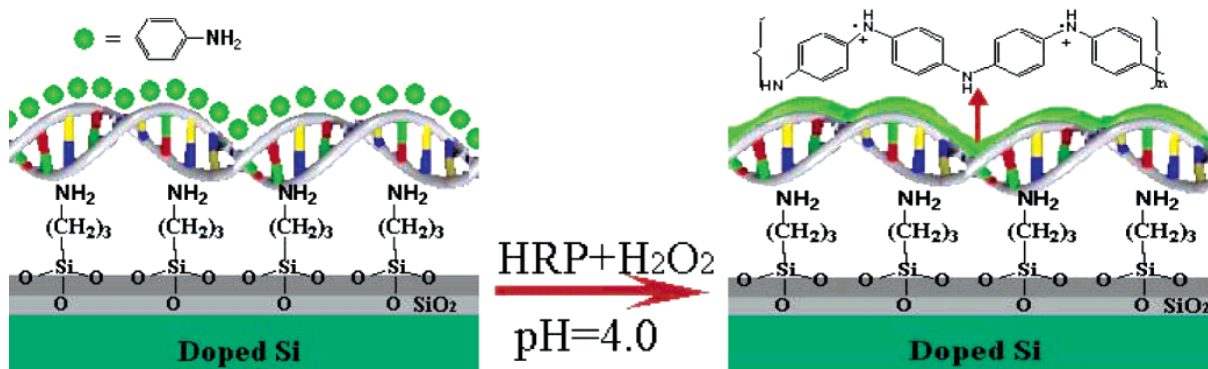
Figure 8. Fabrication of a polyaniline nanowire immobilised on a Si surface with stretched double-stranded DNA as a guiding template /28/.

In the beginning, double-stranded λ-DNA is stretched, aligned and immobilised on a thermally oxidised Si-chip. Then the DNA templates are incubated in protonated aniline monomer solution to emulsify and organise the aniline monomers along the

DNA chains /28/. Finally, the aligned monomers are polymerised enzymatically by adding horseradish peroxidase (HRP) and H_2O_2 successively to form polyaniline-DNA nanowires. The conductivity of the PANI nanowires is very sensitive to the proton doping-undoping process, suggesting that the nanowires could be used for sensitive chemical sensor applications.

Other typical conductive polymers

Monomers containing thiophene or pyrrole groups could be polymerised to form a great variety of redox-active, electrode-confined films by different oxidation methods /26,32/. One method is to polymerise the monomer in the presence of a water soluble polyelectrolyte such as poly(styrenesulphonic acid) (PSSA). In this case, PSS^- (Figure 11d) acts as the charge compensating dopant for the oxidised conjugated polymer and renders the resulting complex a colloidal dispersion, as these polymers are water-soluble. By using this template approach 3,4-ethylenedioxythiophene (EDOT) have been polymerised to yield a processable polymer: polystyrenesulphonate doped poly(3,4-ethylenedioxythiophene) (PEDOT/PSS), which is widely used CP.

Thomas *et al.* /32/ have reported several variations of EDOT as well as 3,4-ethylenedioxypyrrole (EDOP) monomers and their polymerisations. In following Figure 9 is shown a matrix describing routes to afford six monomers (6-11) from aromatic acetonitriles (1 and 2) condensed with aromatic carboxyaldehydes (3, 4 and 5) with KO*t*Bu in ethanol. Figure 10 shows electrical properties of the polymers which have been composed of monomers.
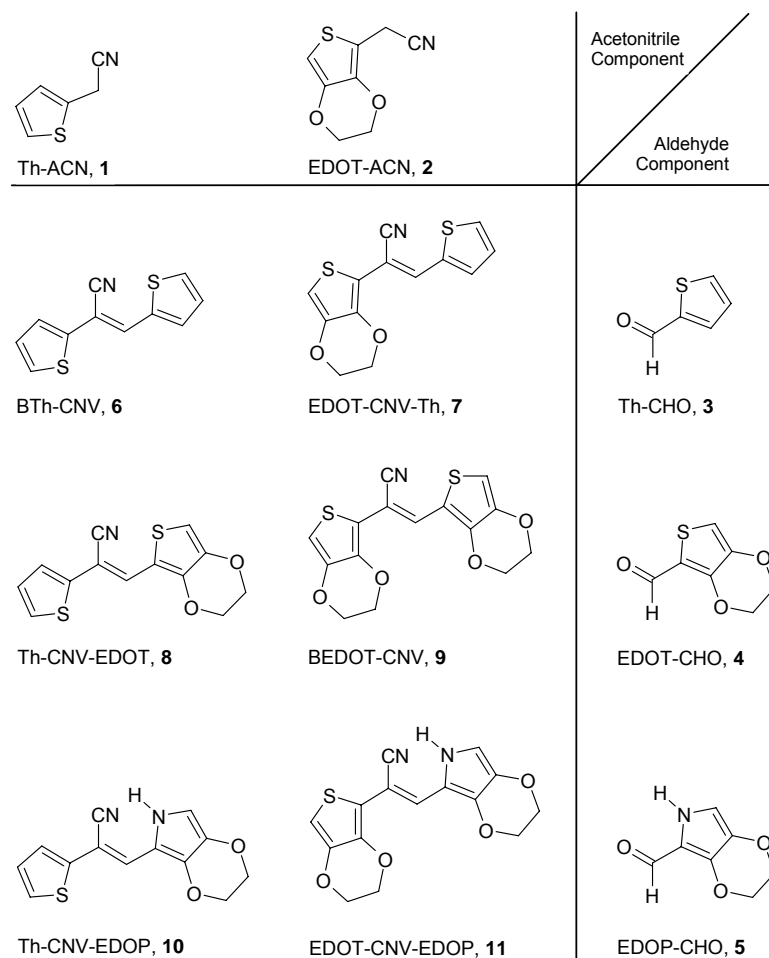
Figure 9. Aromatic acetonitriles (1 and 2) are condensed with aromatic carboxaldehydes (3, 4 and 5) with KOtBu in ethanol to afford six monomers /32/.
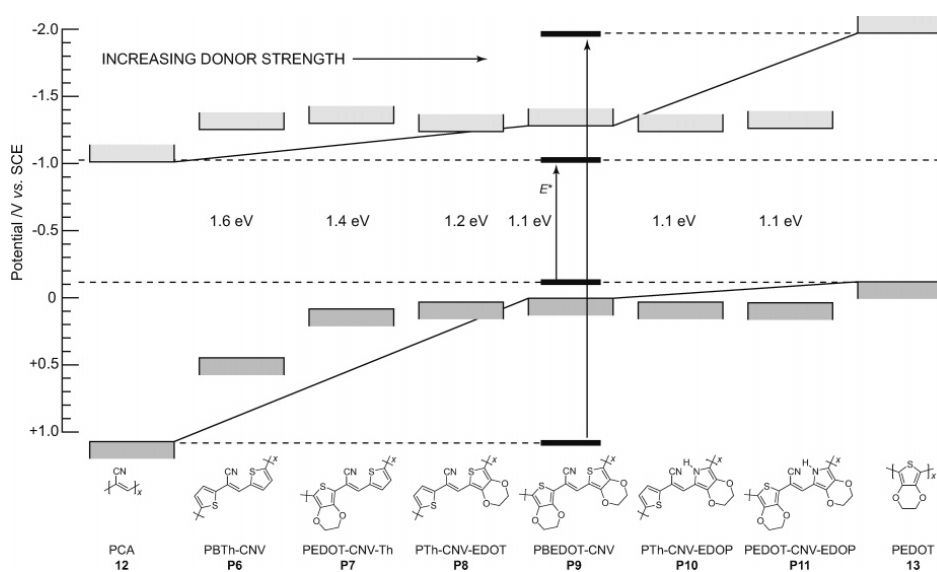

Figure 10. Approximate levels of frontier bands for pure acceptor (PCA) through pure donor (PEDOT), showing the effect of increasing donor strength in a donor-acceptor-donor configuration /32/.

Roussel *et al.* /25/ have investigated conductivities (σ) and sheet resistivities (R_S) on glass and plastic substrates of different type of electrodes made of CPs (Table 2). Two differently doped PANIs, (PPY/DBSA) and (PEDOT/PSS) were used as electrodes. To produce electrodes these doped synthetic metals were dissolved in various organic solvents:

1. The emeraldine (E) base PANI:
   a. was dissolved in N-methylpyrrolidone (NMP) doped with HCl vapour and then named (PANI(HCl), NMP),
   b. was dissolved in 10- camphorsulphonic acid (HCSA) doped with in *α,α,α*-trifluoromethyl-*m*-cresol (tFM*m*C) and named (PANI(HCSA), tFM*m*C)
   c. chloroform ($CHCl_3$) was used as solvent instead of tFM*m*C, named (PANI(HCSA), $CHCl_3$).
2. Polypyrrole (PPY) doped with dodecylbenzene sulphonic acid (DBSA) was stirred in $CHCl_3$ resulting CP mixture named (PPY(DBSA),$CHCl_3$).
3. Polystyrenesulphonate-doped polyethylenedioxythiophene dispersed in an aqueous solution (PEDOT(PSS), H_2O) /25/.

Table 2. Conductivity (σ) and sheet resistivity (R_S) values of the various types of conducting electrodes /25/. (l) is the average thickness of the conductive layer as estimated by a scanning electron microscope (SEM)

Type of electrode	Substrate	l (nm)	σ (S/cm)	R_s (Ω/□)
ITO	glass	800	10^4	100
PANI(HCSA), tFM*m*C	glass	180	122	$1.2 \cdot 10^3$
PANI(HCSA), tFM*m*C	plastic	420	2.2	$66.1 \cdot 10^3$
PANI(HCl), NMP	glass	440	0.2	$139.1 \cdot 10^3$
PANI(HCSA), $CHCl_3$	glass	clusters	-	-
PEDOT(PSS), H_2O	plastic	1000	1.6	$637.3 \cdot 10^3$
PPY(DBSA), $CHCl_3$	glass	70	2.6	$150.7 \cdot 10^3$
PPY(DBSA), $CHCl_3$	plastic	100	0.9	$344.5 \cdot 10^3$

The results shows that electrodes, with given thickness (l), made of PEDOT(PSS) films present the best transmittance properties, followed by PANI(HCSA) then PPY(DBSA) films. Roussel *et al.* /25/ have been surprised that the nature of the substrate (glass or plastic) of the CP layers played an important role on the

conductivity and sheet resistivity: electrical conductivity decreases when a plastic substrate is used. This decrease in σ (increase in R_S) has been related to significant morphological changes of the CP coating on a plastic substrate.

Other conducting polymers like poly(3-thiopheneacetic acid) (PTAA) with poly(*o*-methoxyaniline) (POMA), group of poly(alkylthiophenes) (PATs) and poly(thieno[3,4-*b*]thiophene) (PT34bT) (Figure 11) are promising and studied conjugated polymers too /26,33,34/.
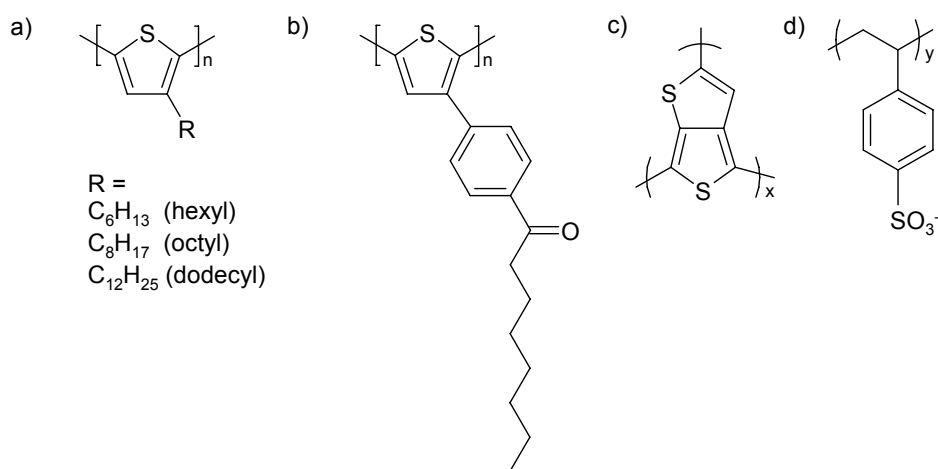

R =
C_6H_{13} (hexyl)
C_8H_{17} (octyl)
$C_{12}H_{25}$ (dodecyl)

Figure 11. The chemical structures of (a) poly(alkylthiophenes) (PATs), (b) poly(oxyoctylphenylthiophene), (c) poly(thieno[3,4-*b*]thiophene) (PT34bT) and (d) poly(styrene sulphonate) (PSS⁻) /26,33/.

Polymer electrolytes

Polymer electrolytes are another group of conducting polymers /27/. They are formed from polymer oxides, for example polyethylene oxide (PEO) consisting salts dissolved in polymers. They have potential applications in all-solid-state devices, such as rechargeable batteries and flexible displays. The crystalline complex's molecular structure is $PEO_6:LiXF_6$ (X = P, As, Sb) or some of the XF_6^- anions can be replaced with the isovalent $N(SO_2CF_3)_2^-$ (bis(trifluoromethanesulphonyl)imide ions.

Conducting nanoparticles

Li *et al.* /21/ have studied and published results about the stabilised silver nanoparticles that can be transformed at relatively low temperatures to highly conductive elements suitable for low-cost printed electronics. The one phase reaction

they developed is relatively fast, gives high yield and uses relatively inexpensive starting materials. In Figure 12 is shown the principle of the reaction and schematic drawing of a bottom-contact OTFT (built on n-doped silicon wafer with a poly(3,3'''-didodecylquarterthiophene), PQT-12 semiconductor layer and the source/drain electrodes printed from silver-nanoparticles, NanoAg-R, used to validate nanoparticles usefulness as conductive elements of the source/drain electrodes. With printed NanoAg-C16 electrodes, OTFT properties were similar to those using vacuum-deposited silver electrodes.
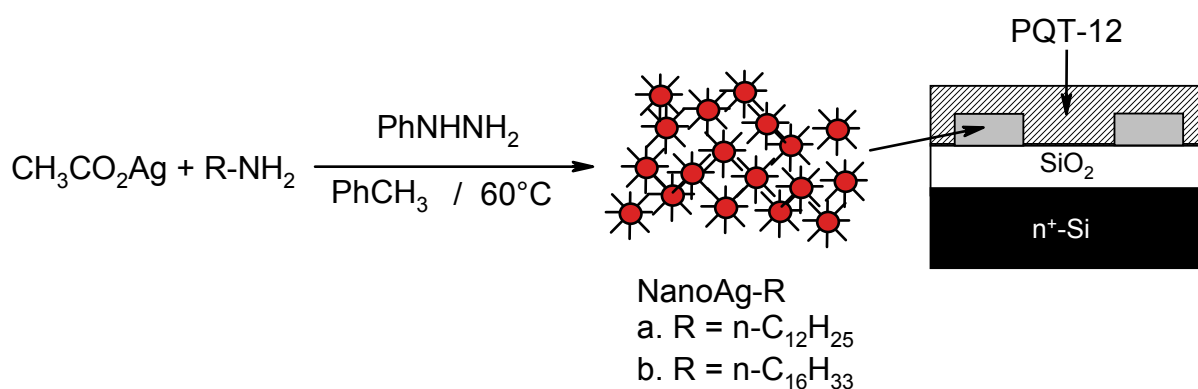

$$CH_3CO_2Ag + R\text{-}NH_2 \xrightarrow[\text{PhCH}_3 \ / \ 60°C]{\text{PhNHNH}_2}$$

NanoAg-R
a. R = n-$C_{12}H_{25}$
b. R = n-$C_{16}H_{33}$

Figure 12. The principle of the reaction to form NanoAg-R particles and a schematic drawing of an OTFT used to validate nanoparticles usefulness as conductive elements of the source / drain electrodes /21/.

3.2 Semiconductors

This chapter concentrates on organic semiconductors, which are very interesting materials, as they, on one hand, show good semiconductor properties, and, on the other hand, have the mechanical properties of polymers. Due to these reasons, the perspective of printed and flexible electronics seems now very close and they have a great potential for several applications such as in intelligent papers.

Since their proof of concept in 1986, organic semiconducting devices have progressed in recent years to a point where their carrier (electron or hole) mobility µ (cm^2/(V·s)), environmental stability, and advancements in p- and n-type organic semiconductor materials have resulted in reports of device operation suitable for many low-functionality, low-cost products (Figure 13) /19/.
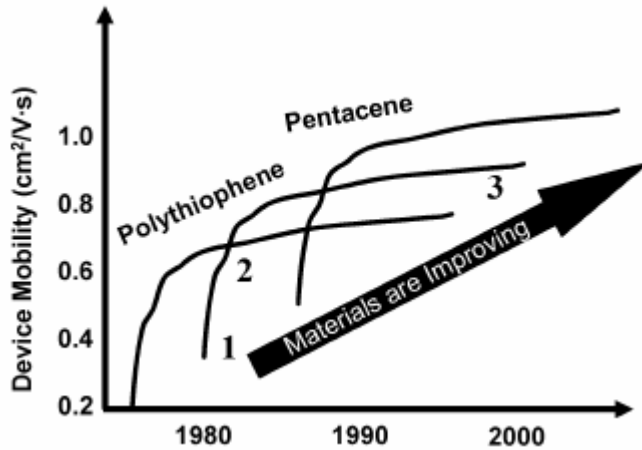
Figure 13. Organic semiconductor development maturity trend /19/: 1 discovery, 2 process management, 3 saturation.

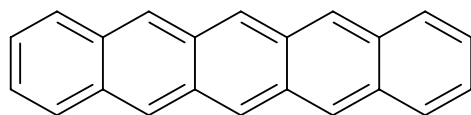Organic semiconductor materials primarily consist of carbon, hydrogen and oxygen. Four classes of organic semiconductors have been used in OFET applications:

1. "small" molecules based on heteroaromatic rings,
2. conjugated polymers,
3. hybrid organic–inorganic structures and
4. molecular semiconductors, such as nanotube-based semiconductors /19/.

3.2.1 Small Molecule Organic Semiconductors

Small molecule organic semiconductors have a unique character /19/: the ability to form high-quality polycrystalline organic films to achieve high mobility field-effect device.

Pentacene (Figure 14) is the most extensively studied small molecule organic semiconductor material, due to its commercial availability and relatively well-understood processing techniques /19/. The reported field-effect mobility (µ) of vacuum-deposited pentacene-based thin-film transistors has been regularly quoted in the range of 0.5–1.5 $cm^2/(V·s)$, which is comparable to devices using α-Si as the semiconductor material. Despite this there are two main concerns in using pentacene to build organic circuits are: 1) stability to environmental oxygen and 2) insolubility in almost all organic solvents.

Pentacene

Figure 14. Molecular structure of pentacene.

Other small molecule organic semiconductors such as sexithiophene (α6T) and α,ω-dialkyl-sexithiophene have also been systematically studied The difficulty of synthesis and poor environmental sensitivity of these small molecule systems have restricted their potential use in product applications /19/.

3.2.2 Conjugated Polymer Organic Semiconductors

Polymeric semiconductors exhibit structural stability, tuneable electrical properties and solubility, which are achieved by designing and shaping polymer chain structures. The conjugation-chain length and rotational freedom determine the semiconductor polymer functionality and environmental sensitivity, while the alkyl side chains determine polymer solubility.

Polythiophenes

In Figure 15 is shown two examples of organic semiconductor chemical structures of regioregular polymers; poly(3-hexylthiophene) P3HT and poly(9,9'-dioctyl-fluorene-co-bithiophene) F8T2. Thin-film transistors based on solution processable regioregular P3HT has reported to have field-effect mobility (µ) values on the order of 10^{-5} to 10^{-3} cm^2/(V·s), depending on process conditions (for example, in air or oxygen-free environments). Another relatively air-stable material F8T2 has µ-values of 0.01–0.02 cm^2/(V·s). The most recent individuals in the conjugated regioregular polythiophene family is poly(3,3-dialkyl-quaterthiophene)s. They have advances like enhanced oxygen resistance, solution processability and self-assembly of the layer. The average µ-value for device is 0.07–0.12 cm^2/(V·s) under ambient conditions /19/.
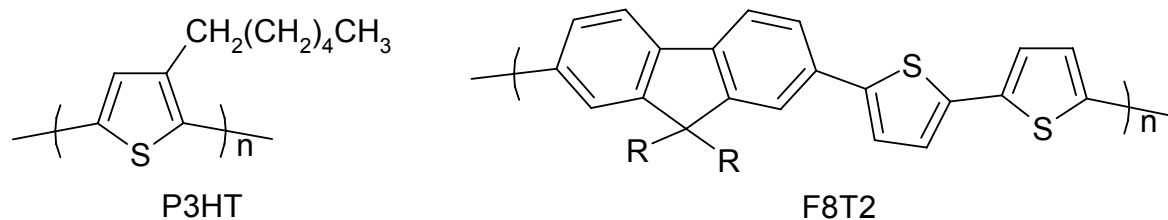
Figure 15. Two examples of conjugated polymer semiconductor chemical structures poly(3-hexylthiophene) P3HT and poly(9,9'-dioctyl-fluorene-co-bithiophene) F8T2 /19/.

3.2.3 Hybrid Organic–Inorganic (O-I) Semiconductors

Hybrid organic–inorganic (O–I) materials with different level of macro- or microscopic organisation, both natural and man-made, have long been known as structural components of biological origin, adobe, leather, reinforced plastic /35,36/. In recent years an increasing number of papers and patents have appeared dealing with bulk and more sophisticated, micro- or nanostructured O–I hybrid materials, focused on the specific application. Such interest arises from the several unique features of these materials, which is often related to the increasingly important role played by the interfacial forces and by the chemistry of surface molecular layers as the size of the dispersed phase decreases.

The O–I core–shell nanoparticles can be useful precursors of hollow spheres with well-defined size and composition, which can be further employed for surface modification /35,36/. Moreover, through the precise control of processing parameters, various other material shapes like powders, fibres, monoliths and thin films can be achieved. Thin films have been most attracting for optoelectronic applications due to the ease coating fabrication and the optical transparency of oxide materials. As an example, the film formation of polystyrene/poly(2-vinylpiridine) (PS/P2VP) hybrid nanoparticles with controlled diameter (20–200 nm) can be deposited as ordered mono or multilayers on a wide variety of substrates. These hybrid materials have been realised by incorporating organic functionalities and inorganic material network either via doping or via covalent bonding of organic groups and inorganic backbone to form organometallics.

3.2.4 Molecular Semiconductors

Developing methods that allow the materials surface-chemistry to be controlled on the 1–100 nm length scale is a fundamental and exciting challenge in nanoscience and nanotechnology /37,38/. That opens new possibilities to develop molecular electronics, even single-molecule and single-electron devices. This challenge has motivated numerous researchers since the invention of the scanning tunnelling microscope (STM) and its descendents (including atomic force microscopy (AFM) and scanning probe microscope (SPM)). With help of those technologies methods to oxidise, scrape, or etch nanostructures onto surfaces has been developed.

Molecular semiconductors (MSCs) are finding increasing interest, because of their potential use in electronic circuit elements: memory devices, FETs, LEDs and solar cells /37,38/. A few MSCs, such as naphthalene diimides and phthalocyanines have been doped to metallic levels, while the vast and potentially useful semiconducting range, between the intrinsic material and the molecular metal, remains virtually unexplored. Gregg *et al.* /39/ have described a method for doping molecular semiconductors in which the dopant forms an integral part of the semiconductor lattice and does not contain any mobile ionic species. PEDOT/PSS, is an example of a metallically conducting polymer that, in principle, does not require mobile ions and therefore could form stable junctions with n-type organic materials. Thus, it should be possible to synthesise mobile-ion-free polymers with covalently bound counterions that are doped to semiconducting levels.

Besides using organic molecules, such as conjugated oligomers and aromatic molecules, in molecular semiconducting devices, it has been demonstrated recently molecular single-electron devices, including room temperature transistors, using carbon nanotubes attached to nanoscale metal electrodes. As well core-shell CdSe/ZnS semiconductor nanocrystals are exhibiting unique size-dependent optical properties, which make them ideal candidates for applications in various fields such as the design of new optical devices /37,40/. Other nanomaterials such as carbon nanotubes, as well as nanomaterial-based devices, are described later in Chapter 4.3.1.

3.3 Dielectrics (Insulators)

Dielectric materials known also, as insulators are substances that can sustain an electric field and thus have a very low electrical conductivity. That property of the material is described by the (relative) dielectric constant ε_r (often in the English literature, the abbreviation κ is used instead of ε_r. In proper microelectronics slang one than talks of "low κ materials" when on actually means, "low kappa" or "low epsilon relative"). Dielectric constant can be calculated from following equation (1) /9,10,13/.

$$\kappa = \frac{Cd}{\varepsilon_0 A} \qquad (1)$$

where C is capacitance, d is film thickness, ε_o is the permittivity of free space and A is electrodes area /41/.

The dielectric is one of the most critical, but sometimes underappreciated, materials for organic transistor performance /10,19/. The higher dielectric capacitance would permit greater charge injection into the semiconductor layer of a thin-film transistor and thereby permitting the device to operate at lower voltage. Dielectric films require the following properties: low trapping density at the surface, low surface roughness, low impurity concentration, and compatibility with organic semiconductors. Two categories of dielectrics are commonly used in transistors (as well in organic transistors too): 1) inorganic and 2) organic.

3.3.1 Inorganic Dielectrics

Commonly used gate dielectric materials for both traditional silicon based, as well as organic based transistors are inorganic dielectrics /19/; silicon dioxide (SiO_2) and silicon nitride (SiN_x). The well-known dielectric characteristics and the mature manufacturing processes are capable of depositing a pinhole-free gate dielectric layer with a thickness <100 nm. However, these materials are not solution processable dielectrics, which have prompted researchers to investigate organic processable dielectrics.

3.3.2 Organic Dielectrics

As known saturated polymers, polymers in which all of the four valence electrons of carbon are used up in covalent bonds are insulators such as polyvinylpyrrolidone (PVP) and polymethylmethacrylate (PMMA) /19,20/. It is important to note that the performance of organic devices using solution processable organic dielectrics depend significantly on the semiconductor material used and quality of dielectric deposition process. In addition, the interfaces between the dielectric, substrate, and organic semiconductor have a profound effect on device performance for example pentacene crystalline film formation was shown to be very sensitive to dielectric surface roughness.

3.3.3 Hybrid Organic–Inorganic (O-I) Dielectrics

The fact that easily processable polymers have typically low κ-values: polystyrene PS (κ = 2.6) or PMMA (κ = 3.12) has led to the development of new structures for flexible and printable high κ-value dielectrics. Maliakal *et al.* /41/ have reported a new high κ, flexible gate dielectric material TiO_2-PS using a core-shell nanoparticle architecture with titanium dioxide as the high capacitance core, and polystyrene as the shell (Figure 16) /41/.
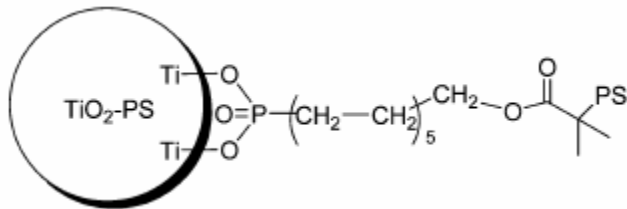

Figure 16. Molecular structure of flexible gate dielectric material TiO_2-PS using a core-shell nanoparticle architecture with titanium dioxide as the high capacitance core, and polystyrene as the shell /41/.

4 Manufacturing Intelligent Papers

Embedding of optoelectrical, optical, and electrical functionalities into low-cost products like product packages and printed matter can be used to increase their information content /8,42/. Additionally, the price of the components for low-end products and disposable sensors has to be in cent scale or preferably below that. Therefore, new, cost-effective, and volume scale capable manufacturing techniques are required. The conventional roll-to-roll manufacturing techniques such as gravure printing have been difficult to use because high temperature process of silicon based TFTs (α-Si:H and poly-Si TFT) limited the use of plastic substrate. Recent developments of liquid-phase processable electrical and optical polymeric, inorganic and hybrid material inks together with biocompatible materials have made it possible to fabricate functional components by conventional roll-to-roll manufacturing process on flexible paper and plastic like substrates.

4.1 Components

4.1.1 Organic Field-Effective Transistor, OFET

There has been fast progress in the field of OFETs and their applications such as integrated circuits and organic transistor controlled LEDs. Often the FETs are prepared using inorganic substrates and electrodes, although its final use is envisioned in all-organic applications. As the organic semiconductor materials are improved, the interest in making all-organic electronic components has grown. From the manufacturing point of view, it is desirable to use solution processable polymers, inks, which allow low-cost fabrication by roll-to-roll printing processes. Another important fact is that transistors made completely from plastic are very flexible; they can keep on working even when the substrate is bent through angles of 90 ° /43,44/.

Bäcklund *et al.* /44/ have reported manufacturing method for all-polymer solution processable FETs starting from the hybrid silicon based device and substituting the inorganic parts one by one with polymeric materials ending up with a solution processable all-polymer FET. The fabrication of solution processable organic FETs is

demanding, and it is important that the different solvents and materials are compatible so that the various layers in the FET structure do not dissolve, mix or crack during device fabrication. All the organic polymer materials Bäcklund *et al.* /44/ used in their work: regioregular poly(3-hexylthiophene) (RR-P3HT) (*cf.* Figure 15) for semiconducting material, PMMA for the gate dielectric (insulator), PEDOT/PSS for the gate electrode, polyethylene terephtalate (PET) for flexible substrate and PANI for the source and drain electrodes, were commercially available and used as received. In following Figure 17 is shown steps to the all-polymer FET.
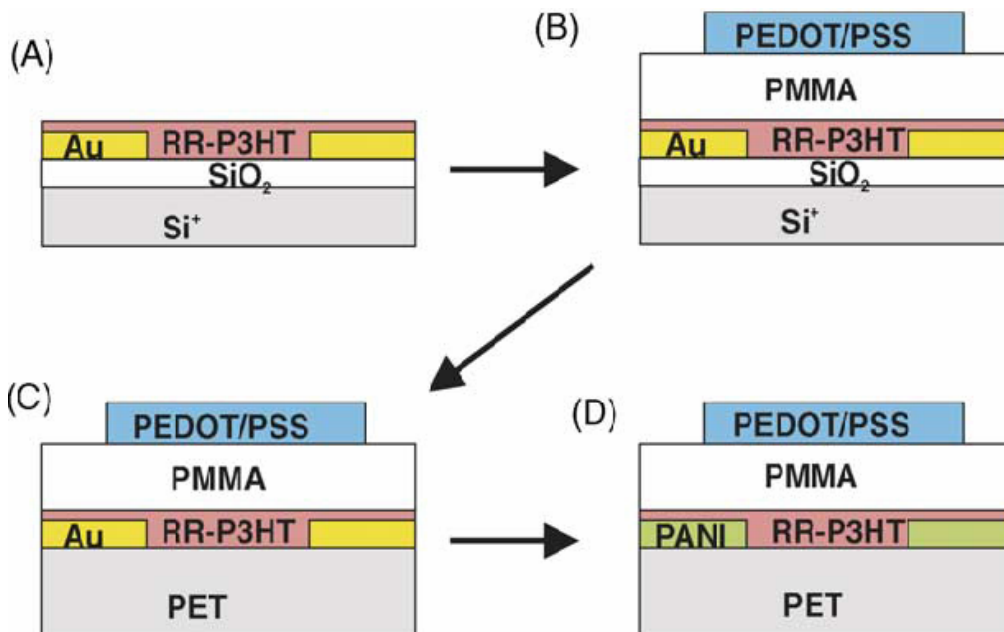

Figure 17. Device (A) was fabricated with only an organic semiconductor and (B) is the same as (A) with an additional organic insulator layer and a gate electrode on top /44/. Device (C) is similar to (B), with the silicon substrate replaced with a PET film. The all-polymer device (D) is of the same device structure as (C), using PANI as the source and drain electrode material.

The whole manufacturing process of all-polymer TFT as Bäcklund *et al.* /44/ did it is shown in Appendix 1.

4.1.2 Organic Light Emitting Diode, OLED and Polymer LED, PLED

A light emitting diode (LED) is a semiconductor device that emits incoherent narrow-spectrum light when electrically biased in the forward direction. This effect is a form of electroluminescence. Electroluminescent (EL) materials have attracted significant attention ever since the development of the first thin-film hetero-junction organic light emitting diode (OLED) in 1987 by Tang and Van Slyke /45/ and some years later polymeric light-emitting diodes (PLED) by Burroughes *et al.* /46/ due to their great potential application in flat panel displays. The recent fabrication of LEDs from conjugated polymers demonstrates the technological potential of this class of electronic materials practical for display technologies due to distinctive attractions such as low materials costs, self-emission, efficient and broad variety of colour tunability chemically during synthesis, compatibility with complementary metal-oxide semiconductor (CMOS) technology, and amenability to large-scale production /47/.

The basic cross-section structure of a typical multilayer OLED is shown in Figures 17 and 18 /47,48/. In Figure 18 is shown energy diagram for different material layers too.
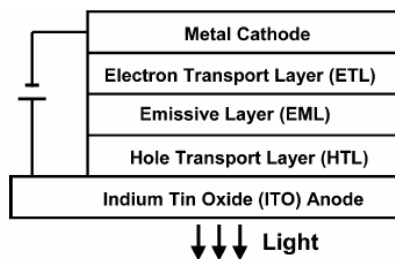

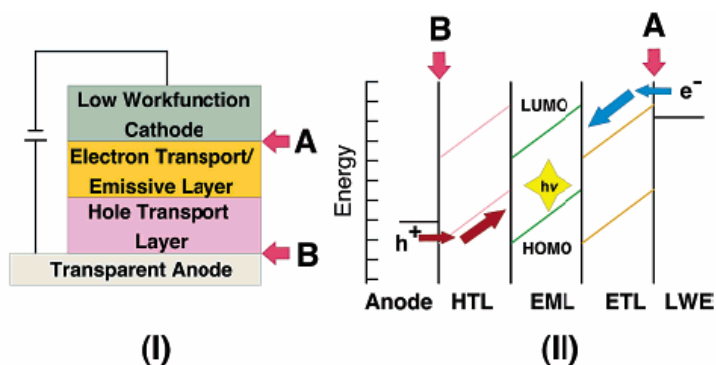*Figure 17.* Cross-section and of a typical multilayer OLED structure /47/.

Figure 18. Cross-section and energy diagram of different layers of a typical multilayer OLED structure /48/.

Sophisticated multilayer structures incorporating specifically tailored hole transport layers (HTLs), emissive layers (EMLs), and electron transport layers (ETLs) sandwiched between the two electrodes. Each layer plays a specific role in producing organic electroluminescence. Some component-materials are listed in following as examples /47-50/ (Figure 19):

Anode materials:

- a transparent conducting oxide, ITO

HTL-materials:

- 1,4-bis(phenyl-*m*-tolylamino)biphenyl, TPD
- 4,4'-bis(*N*-1-naphthyl-*N*-phenylamino)biphenyl, NPB
- PEDOT doped with PSS, PEDOT/PSS

EML-materials:

- aluminium tris-8-hydroxyquinoline, Alq$_3$
- poly(9,9-dioctylfluorene), PFO
- dopant; N,N'-di-isoamyl quinacridone, DIQA

ETL-materials:

- 9-dimethyl-4,7-diphenyl-1,10-phenanthroline, BCP
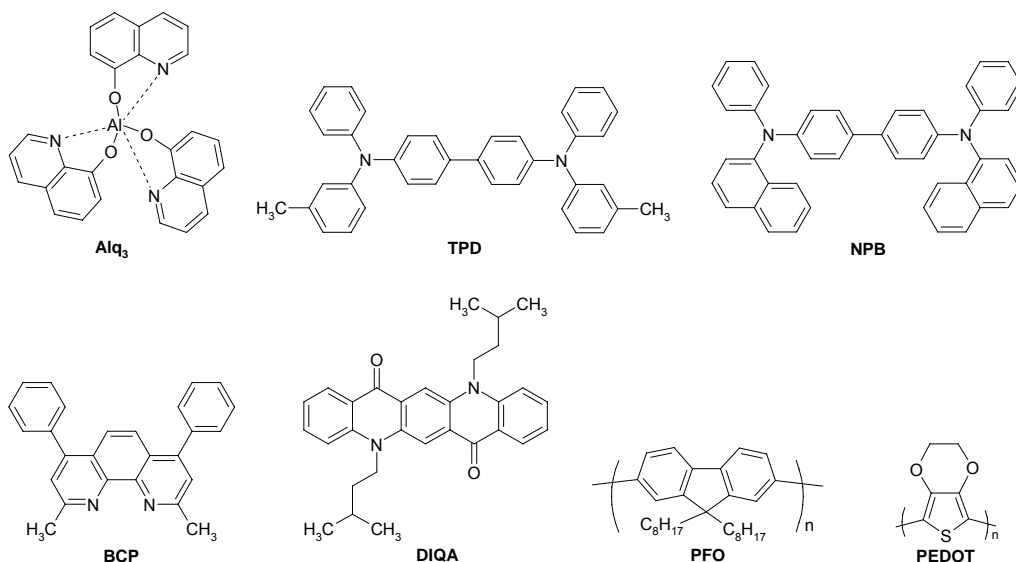- aluminium tris-8-hydroxyquinoline, Alq$_3$

Figure 19. Structural formulas of typical materials for electron transport Alq$_3$ and BCP, hole transport materials TPD, NPB and PEDOT, emissive dopant DIQA and emissive polymer PFO /47,48/.

Gustafsson *et al.* /51/ have reported the fabrication of a fully flexible LED using PET as the substrate, soluble PANI as the hole-injecting electrode, a substituted poly(1,4-phenylene-vinylene) (PPV) as the electroluminescent layer and calcium as the electron-injecting top contact. The structure is mechanically robust and may be sharply bent without failure. The LED is easily visible under room lighting the 'plastic' LED demonstrates that this unique combination of optical, electrical (high power efficiency and low power consumption) and mechanical properties can be used to make novel structures that are compatible with conventional devices /50,51/.

Huang *et al.* /47/ have reported fabrication of an all-OLED device on bare ITO substrate that was treated with solvents and oxygen plasma. The substrates were loaded into a bell jar deposition chamber housed in a nitrogen-filled glove box (Figure 20). A typical deposition procedure is as follows: at vacuum environment a 20 nm layer of NPB was first deposited, followed by 60 nm of Alq_3 doped with 1 % DIQA. Another 20 nm thick layer of BCP was then deposited, followed by thermally evaporating 1 nm thick Li. Finally, a 100 nm thick Al cathode was deposited through a shadow mask. This metallic layer was patterned via a shadow mask.

Figure 20. A humidity- and environmental-controlled glove box (PlasLabs) for OLED manufacturing /38/.

Other promising material candidates for OLED device fabrication through solution processes include the four materials Huang *et al.* /49/ have studied (Figure 21) to make a highly efficient and deep blue light-emitting OLED device. The blue emitting LEDs were a major breakthrough in 1990s by Nakamura *et al.* /52/. Materials had very good solubility in common organic solvents, showed a good thermal stability and high glass transition temperature, T_g (>100 °C) which made them suitable for

solution-processed small molecule blue OLEDs. The highest electroluminescence (EL) efficiency was achieved by using compound, they had named as, Blue C as the emitter.
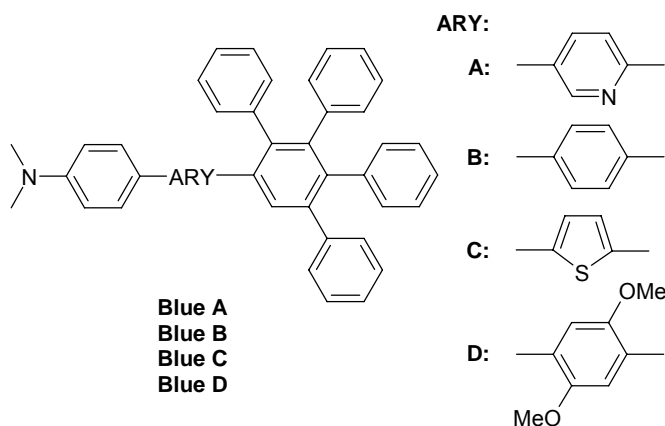

Figure 21. Four materials for highly efficient blue small molecular organic light-emitting diodes (SMOLED) /49/.

Wong *et al.* /53/ have studied EL properties of the terfluorene derivatives with highest thin-film photoluminescence (PL) quantum yields. Devices they have made exhibit pure blue EL similar to PL spectra of terfluorenes. High PL / EL quantum efficiencies in conjunction with carrier transport properties render these terfluorenes /53/: 4aa and 4cc very interesting and promising optoelectronic materials (Figure 22).
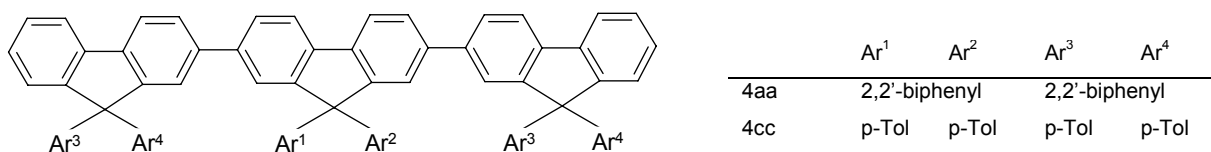

	Ar^1	Ar^2	Ar^3	Ar^4
4aa	2,2'-biphenyl		2,2'-biphenyl	
4cc	p-Tol	p-Tol	p-Tol	p-Tol

Figure 22. Molecular structures for two highly blue emitting terfluorenes 4aa and 4cc /53/.

In addition, Wong *et al.* /54/ have later reported for more efficient OLED device with blue emission characteristic of terfluorene by using a novel molecular doping strategy, in which 4,5-diazafluorene was incorporated as the substitution group of terfluorene to facilitate electron injection from the metal cathode (Figure 23).
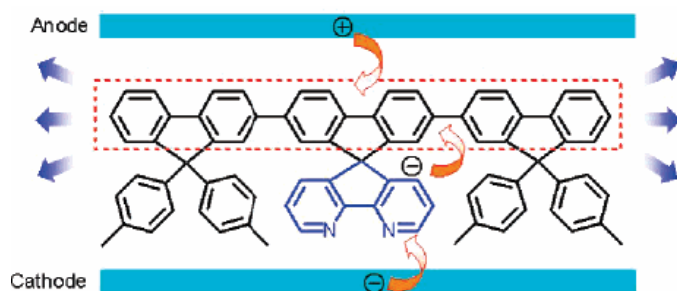
Figure 23. A novel molecular doping scheme to terfluorenes has been established by incorporating 4,5-diazafluorene as the C9 substitution of terfluorenes /54/.

Huang *et al.* /47/ have studied HTL materials to improve the poor thermal stability of TPD (*cf.* Figure 19). HTL materials need to fulfil criteria such as substantial hole mobility, good energy level matching with anodes and EMLs, good thermal properties (stability; T_g), low optical absorption in the visible region, and smooth, amorphous film-forming morphology. They have approached the problem by synthesizing small molecule TPD analogues with higher T_g parameters and / or by incorporating a triarylamine hole transport motif into a polymer chain. They have presented that simple saturated hydrocarbon self-assembled monolayer (SAM) HTLs (Figure 24) which achieve covalent ITO anode-HTL bonding, can function as HTLs and ITO-NPB interlayers.
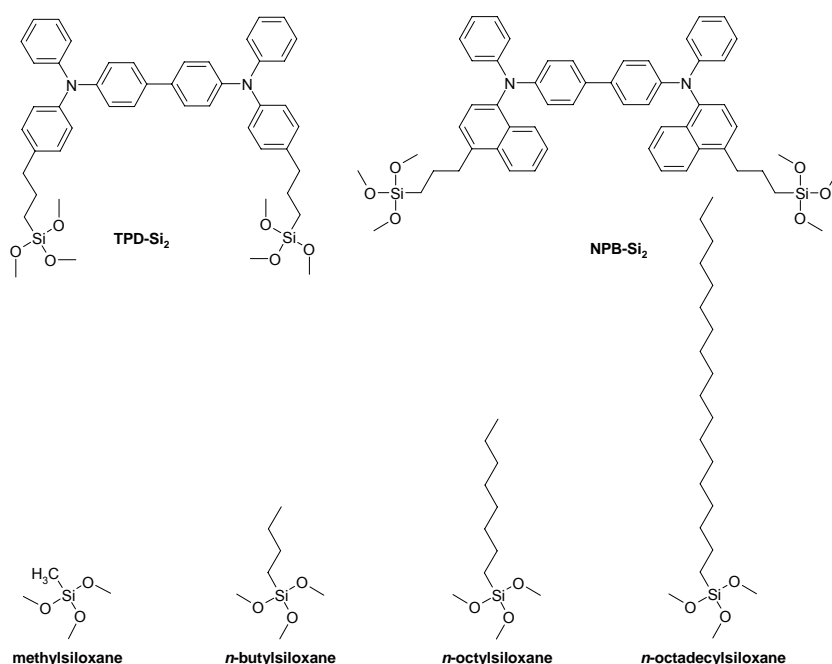

Figure 24. Chemical structures of the organosiloxanes used as SAM HTLs and ITO anode modification layers /47/.

New promising green dopant for OLED have been reported by Lee *et al.* /55/ (Figure 25): 10-(2-benzothiazolyl)-1,3,3,7,7-pentamethyl-2,3,6,7-tetrahydro-1H,5H,11H-benzo[l]-pyrano[6,7,8-ij]-quinolizin-11-one (abbreviated as C-545P), which can be used as a doped green emitter in OLEDs. C-545P notably improves the EL performance over the corresponding C-545T as well as its thermal properties, photo-, and device-stability without affecting its emissive colour.
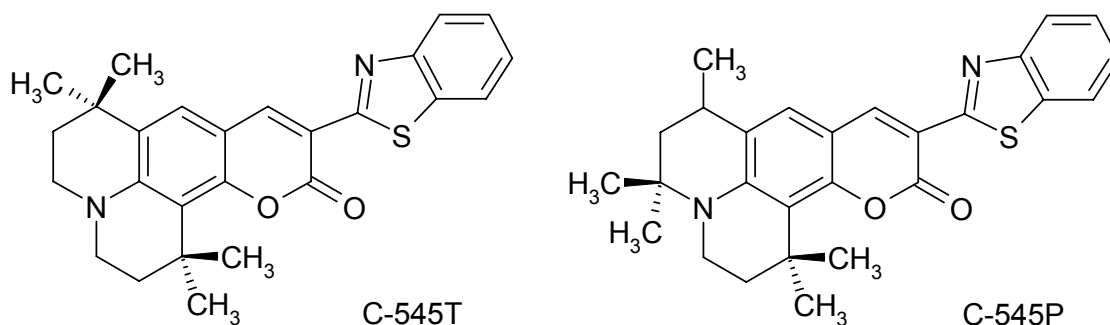

Figure 25. Chemical structure of new promising green dopant for OLEDs: 10-(2-benzothiazolyl)-1,3,3,7,7-pentamethyl-2,3,6,7-tetrahydro-1H,5H,11H-benzo[l]-pyrano[6,7,8-ij]-quinolizin-11-one (abbreviated as C-545P) which has notably improved EL performance compared to the C-545T /55/.

The recent discovery by Qin *et al.* /56/ shows that certain organoboron quinolates such as Ph₂Bq (Figure 26) has efficient luminescence while at the same time providing good stability. Incorporation of the inorganic component into polymer structures provides new possibilities. Boron and aluminium quinolates are promising materials to manufacture low-cost OLEDs by solution processing methods including ink-jet printing techniques. However, only recently have the first reports on the synthesis of Alq₃- and boron quinolate polymers appeared in the literature.
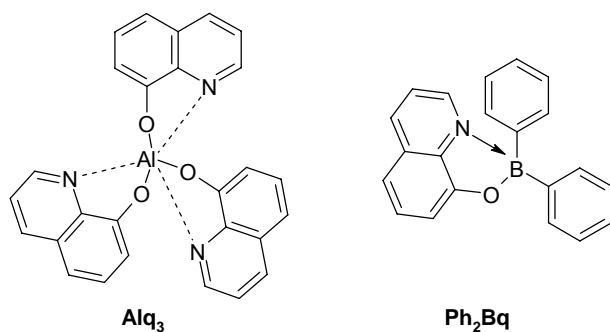

Figure 26. Molecular structure of aluminium quinolate (Alq₃) and organoboron quinolate (Ph₂Bq) /56/.

Kwok *et al.* /57/ have reported the synthesis and photophysical properties of the material for, so far, the most efficient yellow OLEDs. From the materials they studied the robust Pt(II) complex [(F^{t}Bu$_2$O^N^N)-PtCl] emitter, had the highest thermal stability and gave the best OLED.

Polymer Light Emitting Diode, PLED

PLEDs can be considered a subspecies of OLEDs in which the luminescent organic material is a polymer, not for example organic small molecule. The light-emitting layers may be selected from any of a multitude of light-emitting, conjugated organic polymers such as PPV, poly[2-methoxy-5(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV), PANI, poly(thiophene), P3HT, poly(3-octylthiophene), poly(N-vinylcarbazole) /58,59/.

PLEDs have attracted much attention for their applicability to a large-area flatpanel display, its simple and easy processability, low-cost and short time process. However the luminescent properties of the fully conjugated polymer are mainly dependant on its film morphology. Kim *et al.* /59/ have reported MEH-PPV/AIBN (AIBN; 2,2'-azobisisobutyronitrile) PLED devices with nano-porous morphology suppressed the interchain interaction of polymer. They found that in such PLED, the emission from the interchain aggregates and eximers was restrained exceedingly; therefore, colour purity was also greatly improved in PL and EL spectrum. They report also that their method can be applicable to most other luminescent polymer EL devices, because T$_g$ of most conjugated polymers is higher than that of the MEH-PPV (about 75 °C).

4.1.3 Nanoscale Electronic Components

One-dimensional nanostructures, such as nanorods (nanocrystals), nanowires and nanotubes have unique properties due to quantum confinement in two directions and a gradual transition to the classical limit in the third (quantum wires) /60/. They are also playing an important role as components in fabrication of future nanoscale electronic and optronic devices. The use of the Langmuir film and the reaction in it produces a highly ordered 2D array of rods and / or wires of ~1 nm width, with a controlled (nano) distance between the particles, extending over large regions, on the order of a micron.

Nanorods

Physical investigations of individual nanocrystals have received considerable attention because a single nanocrystal represents the miniaturization limit of ensemble-based devices. Gudiksen *et al.* /61/ have fabricated the single-nanocrystal transistors (SNCTs) by first synthesizing rod-shaped CdSe nanocrystals (CdSe nanorods) using a solution-based approach. The nanorods were then deposited from solution onto a silicon wafer coated with 300-nm thick oxide, and individual, isolated nanorods were located to their places. Golden source and drain electrodes contacting individual nanorods were defined using electron-beam lithography and the doped silicon substrate was used as a gate electrode. A scanning electron micrograph of a resulting device is presented in Figure 27a, showing a single nanorod contacted by two gold electrodes with ~30 nm separation.
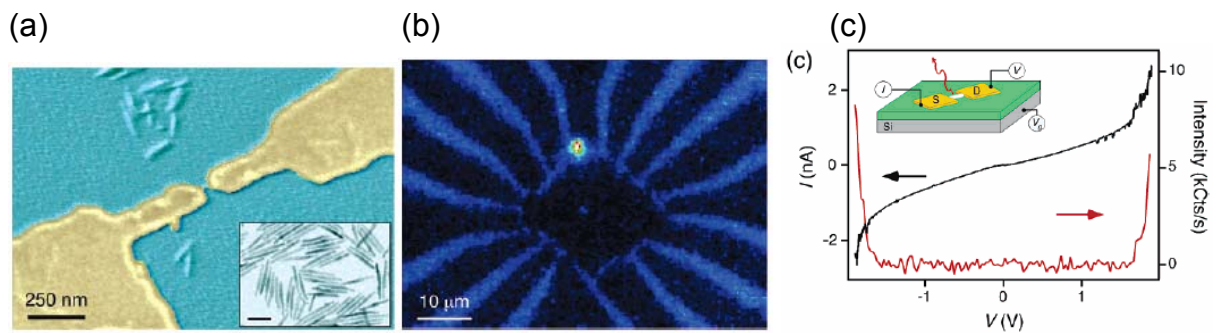
(a)   (b)   (c)

Figure 27. (a) A scanning electron microscope (SEM) image (false colour) of a CdSe-nanorod transistor /61/. The inset shows a transmission electron microscope (TEM) image of the synthesised CdSe nanorods (scale bar is 50 nm). (b) Optical microscope image showing electroluminescence (EL) from a nanorod transistor. (c) Current (*I*) (black) and simultaneously measured EL intensity (red) plotted against bias voltage (*V*) obtained from device. The inset gives a schematic illustration of the transistor geometry, showing source (S) and drain (D) electrodes contacting the nanorod with a back gate.

Acharya and Efrima /60/ have studied ZnS nanorods and their nanoscale surface patterning and derivatisation. They have found that two-dimensional surface pressure in the Langmuir films provides a direct driving force, decreasing the activation energy of a cooperative oriented coalescence of ZnS nanorods into nanowires at near room temperature.

Nanowires

Silicon nanowires (SiNWs) are currently attracting great interest, as these are the most promising building blocks for the "bottom-up" approach to future nanoscale devices. Remarkable developments have taken place in recent years that show applications of SiNWs as logic and memory circuits, as well as biological and chemical sensors. Most exciting are the applications in optical and photonic devices domain that is almost forbidden for bulk silicon. The reason for this versatility of SiNWs lies in the increased number of controllable parameters at the nanoscale as compared to bulk. In the case of SiNWs, the growth direction, thickness, morphology, and the way the surface is pacified (via oxidation or hydrogenation) can be controlled to modify their electronic properties. The ability to reproducibly modulate the carrier type and concentration of the SiNWs during synthesis is important and has to be addressed to facilitate future NW-based device designs.

There are several articles about doping SiNWs /62,63/. The most of these concentrates in p-type dopants during vaporliquid-solid (VLS) growth of single-crystal SiNWs from gas sources such as diborane (B_2H_6) and trimethylboron (TMB). The VLS growth technique uses a metal such as gold (Au) to catalyse the decomposition of the source gas (*e.g.,* silane (SiH_4) or silicon tetrachloride ($SiCl_4$)), which forms a liquid alloy at temperatures greater than the eutectic temperature of the alloy (*i.e.* 363 °C for Au-Si11). Single-crystal SiNWs are then precipitated from the liquid alloy when it becomes supersaturated with silicon. Simultaneous introduction of additional dopant-gases during VLS growth can be used to modify the composition and / or carrier concentration of the SiNWs.

Not only the SiNW-structures are attractive, but also the idea of fabricating nanowire-based field-effect transistors (NW-FETs), that can be employed with flexible substrates and inexpensive processing techniques. For numerous electronic and optoelectronic device applications, the use of semiconducting nanowires offers the attraction of well-controlled device channels without the need for high-resolution lithography. If suitable structures for device and gate dielectric could be realised, then nanowire-based devices would also provide the means to achieve flexible electronic circuits and displays.

As bulk ZnO is a promising material for many electronic applications because of its wide band gap and high exciton binding energy. These unique material properties in addition to the fundamental advantages of quasi-one-dimensionality make ZnO nanowires useful as active channel materials for flexible displays. Indeed ZnO NW-FETs have excellent transparency and mechanical flexibility, which have attracted much interest for manufacturing sensors, transducers, solar cells and optoelectronic devices.

Ju *et al.* /64/ have reported about fabrication of single ZnO NW-FETs. Their report is the first using nanoscopic self-assembled superlattices (SASs) dielectric materials as gate insulators for nanowire devices instead of conventional photolithography fabricated ones. Their device structure is a typical bottom-gate configuration as shown in cross section in Figure 28a. The SAS films, which were used, consist of layer-by-layer self-assembled organic monolayers. "Type III" multilayers as they named those, are composed of the following building blocks (Figure 28b):

(i)   α,ω-difunctionalised hydrocarbon chains that block charge transport due to transverse crosslinking efficiently,

(ii)   highly polarisable stilbazolium layers that stabilise charge carriers in the channel with oriented π-electron dipoles and

(iii)   glassy siloxane polymer layers that planarise the surface and enhance structural robustness by cross-linking and filling pinholes.
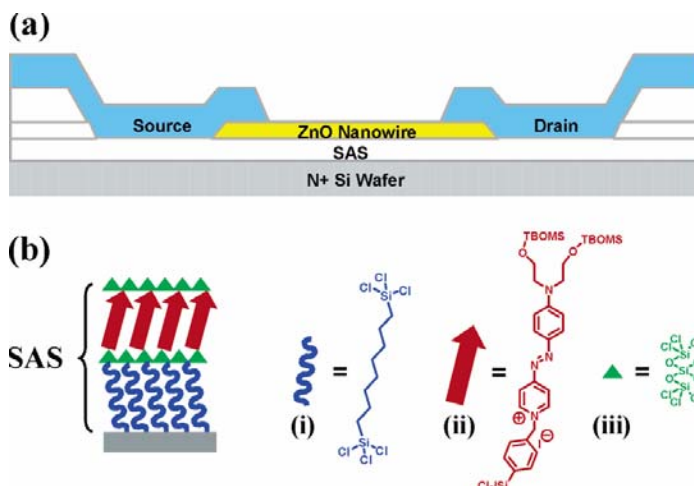

Figure 28. (a) Cross-sectional view of the SAS-based ZnO NW-FET device structure (b) Type-III SAS structure and component building blocks /64/: (i) α,ω-difunctionalised hydrocarbon chain, (ii) stilbazolium π-electron layer, and (iii) octachlorotrisiloxane capping layer.

Individual ZnO nanowires were contacted with source and drain metal patterns, and devices containing single nanowires were imaged using field-emission (FE) SEM (Figure 29). The realization of low voltage, low-leakage, low power consumption devices and the potential compatibility with flexible and / or transparent substrates make the ZnO NW-FET devices excellent candidates for future flexible display and electronics applications /64/.
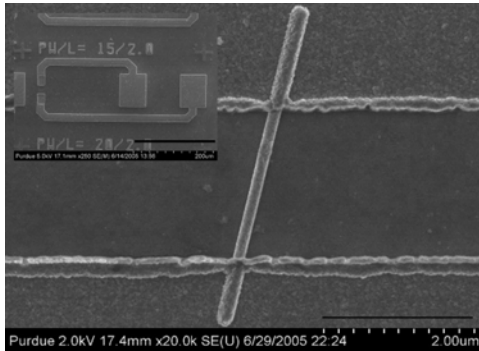

Figure 29. FE-SEM image of a ZnO NW-FET (130 nm diameter; scale bar is 2 μm) /64/. The inset shows a top view of a fabricated device (scale bar is 200 μm).

Qian *et al.* /65/ have reported about very sophisticated type of NWs: the GaN-based core / multishell (CMS) nanowire radial heterostructures. These are multicolor, electrically driven emission "dots", which are integrated into a GaN planar device using crossed NW architecture (Figure 30). In these NW-devices electron/hole, injection occurs directly across the interface between p- and n-type NWs. In other words they have synthesised single-crystal n-GaN/In$_x$Ga$_{1-x}$N/GaN/p-AlGaN/p-GaN CMS NW structures, with well-defined radial modulation of doping, composition and thickness.

Figure 30. Cross-sectional view of a CMS nanowire structure and the corresponding energy band diagram /65/. The dashed line in the band diagram indicates the position of the Fermi level.

The measurements demonstrated that these NWs exhibit well-defined and reliable electrical n-type cores and p-type shells and behave as p-n diodes. Moreover, EL measurements showed that in forward bias the CMS NWs yield intense, colour-tunable and efficient light emission due to radiative recombination in controlled In composition in $In_xGa_{1-x}N$ shells. These electrically driven CMS NWs offer great promises as compact, efficient, reliable building blocks for integrated nanoscale photonic systems, including multicolor LEDs and lasers (Figure 31) /65/.
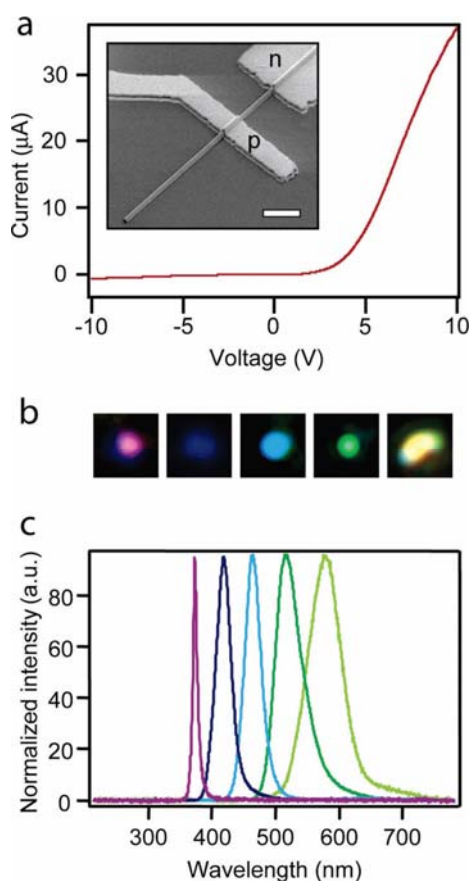

Figure 31. (a) Current versus voltage data recorded on a CMS nanowire device /65/. Inset: field emission SEM image of a representative CMS nanowire device. Scale bar is 2 μm. (b) Optical microscopy images collected from around p-contact of CMS nanowire LEDs in forward bias, showing purple, blue, greenish-blue, green, and yellow emission, respectively. (c) Normalised EL spectra recorded from five representative forward-biased multicolor CMS nanowire LEDs.

Nanotubes

The most widely studied forms of molecular electronics (especially transistors) are based on carbon nanotubes /66/. Carbon nanotubes (CNTs) are macromolecular

systems with unique physical and chemical properties. The small diameter and long length of single-walled carbon nanotubes (SWCNTs) lead to very large aspect ratios that make them almost ideal one-dimensional (1D) systems. Depending on their chirality, CNTs can be metals or semiconductors. The high conductivity and exceptional stability of metallic nanotubes makes them excellent candidates for future use in interconnects. Furthermore, in CNTs, all chemical bonds are satisfied and very strong, leading to extremely high mechanical, thermal and chemical stability. The lack of interface states that need passivation, as in the case of the Si-SiO$_2$ interface, which makes it easier to integrate the CNTs with high κ-dielectrics, and thus provides a greater flexibility to the fabrication process. Recent advances in the solubilization of CNTs have made possible the application of liquid-phase chemistry and chemical spectroscopy in the modification and characterization of the structure of CNTs, which can help achieve the self-assembly of CNT circuits. To a great extent, the future of nanotube electronics is now in the hands of the chemists.

Double-walled carbon nanotubes are needed in a pure, highly crystalline form before features such as their electronic properties, thermal transport and mechanical behaviour can be investigated. Endo *et al.* /67/ have fabricated a paper-like material that consists of hexagonally packed bundles of clean, coaxial double-walled carbon nanotubes (DWCNTs). These DWCNTs consist of two concentric grapheme cylinders, a structure that is intermediate between single-walled (SWCNTs) and multiwalled carbon nanotubes (MWCNTs). Because DWCNTs may have striking new electronic and mechanical properties predicted to be superior to those of both their single- and multiwalled relatives.

Endo *et al.* /67/ have described that this material should be useful in the fabrication of nanocomposites, field emission sources, nanotube bi-cables and electronic devices. It is possible that DWCNTs will eventually replace SWCNTs or MWCNTs in various applications because their mechanical properties, thermal conductivity and structural stability are likely to be superior owing to their coaxial structure (Figure 32).
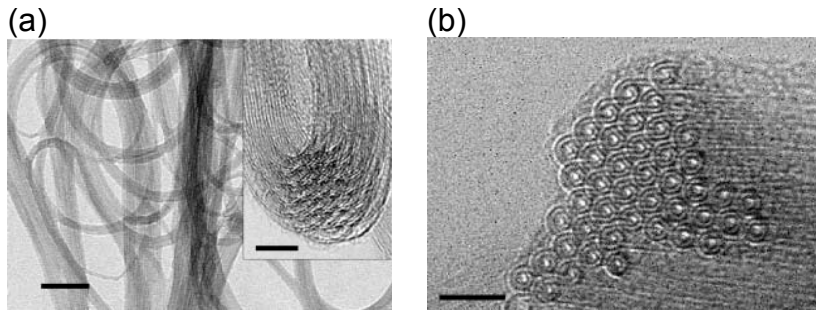
(a) (b)

Figure 32. Pure and clean DWCNTs /67/: (a) low-magnification TEM graph of DWCNT paper, showing bundles of CNT (scale bar 50 nm), insert: a single bundle; note the material's resistance to bending (scale bar 5 nm). (b) High-resolution TEM image of a bundle, showing the perfect hexagonal packing structure in both cross-section and side view (scale bar 5 nm).

Carbon Nanotube Field Effect Transistor (CNTFET)

The basic FET structure involves two metal electrodes; source and drain connected by a semiconducting channel. In conventional devices, the channel is made of Si, however, in carbon nanotube FETs, CNTFETs, the channel is formed by a semiconductor carbon nanotube (s-CNT) (Figure 33). CNTFETs have excellent operating characteristics that are as good as or even better than state-of-the-art silicon devices. In addition, the single atomic layer thin channel of a CNTFET leads to an extreme sensitivity to its environment. According Odom *et al.* /66/ and Klinke *et al.* /30/, CNT-based transistors have recently seen significant advances in terms of understanding their interaction with the environment and their performance limits, despite this the performance of CNTFETs is not yet fully optimised, and improvements are expected soon.
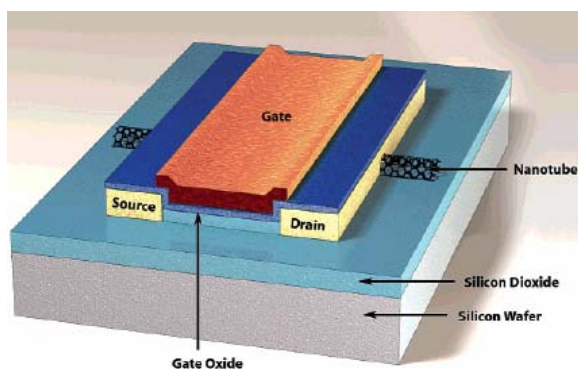

Figure 33. A schematic drawing of a top-gated CNTFET /66/.

In modern computer logic, complementary circuits composed of both n- and p-type FETs have a performance that is far superior to that of the older circuits based on combinations of resistors and transistors of only one type /66/. Thus, to develop nanotube complementary logic circuits, it is needed to find a way of preparing both types of CNTFETs. However, when CNTFETs are made from as-grown CNTs, without any further processing, the resulting transistors are invariably p-type.

Odom *et al.* /66/ and Klinke *et al.* /30/ have reported about the manufacturing of both p- and n-type CNTFETs.

To manufacture p- and n-type CNTFWTs (Figure 34) Odom *et al.* /66/ have positioned a SWCNT (in Figure 34, blue line crossing the FETs) over the gold electrodes (yellow stripes) to produce two p-type CNTFETs in series. The device was then covered by a PMMA resist (transparent blue), and a window was opened by e-beam lithography to expose part of the nanotube. Potassium (K) was then deposited through this window to produce an n-CNTFET, while another CNTFET remained p-type.

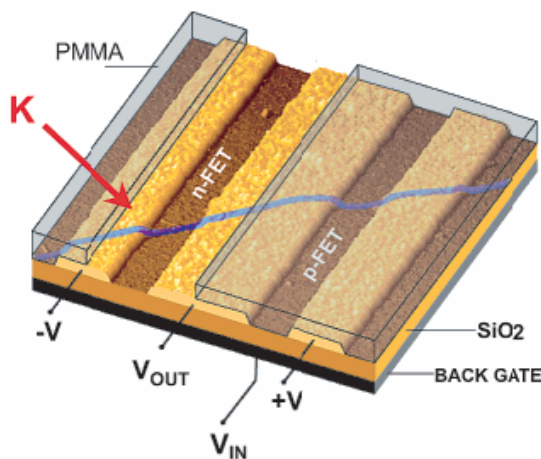Figure 34. An AFM image showing the design and manufacturing of n- and p-type CNTFETs /66/. A SWCNT (blue line) is positioned over the gold electrodes to produce two p-type CNTFETs in series. The device is covered by a resist (PMMA), and a window is opened by e-beam lithography to expose part of the nanotube. Potassium (K) deposited through this window produces an n-CNTFET, but the other CNTFET remains p-type.

Klinke *et al.* /30/ demonstrated the use of the amine-containing monomers (like aminobutyl-phosphonic acid, ABPA, $(H_2N(CH_2)_4PO(OH)_2)$ as dopants to convert p-type CNTFETs to n-type devices. They also manipulated the CNTFETs charge transfer process by accessing different oxidation states of polymeric PANI (*cf.* Figure 5): amine groups of PANI (L) were capable of transferring electrons to CNTFETs and therefore converted pristine p-type FETs to n-type. The more oxidised imine groups in PANI (P) behaved as electron acceptors and converted the doped n-FETs back to p-type.

From these components (p- and n-CNTFETs), it is possible to produce complementary integrated circuits. Complementary transistor are superior to other types, because; they consume less power, can have higher gain, are immune to fluctuations in the characteristics of the FET, and are easier to implement in integrated circuits. Figure 35 shows the schematic representation of a circuit: a complementary transistor-inverter based on two CNTFETs /66/.
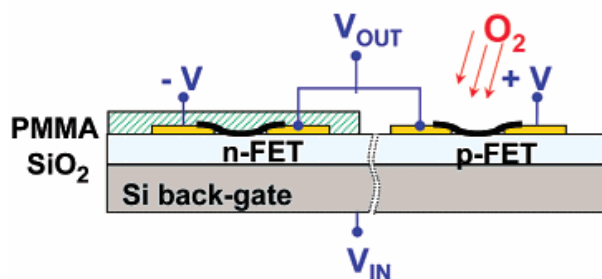

Figure 35. Schematic representation of the complementary circuit /66/: a voltage inverter using two CNTFETs.

Moreover the IBM team has been working with perovskites /43/, *i.e.* inorganic molecules that are linked together to form an extended layered framework. Dimitrakopoulos and Malenfant /18/ have produced perovskites from tin iodide, which has respectable carrier mobility, with phenethyl-ammonium. The composite material self-assembled to form multiple sheets of octahedral tin iodide molecules, in between organic layers was sandwiched. Perovskites could be fashioned into both p- and n-type semiconductors and so to use in low-cost complementary logic circuits.

Other nanoscale electrical devices

An electron transport through semiconductor and metallic nanoscale structures, molecular monolayers, and single molecules connected to external electrodes are important for miniaturisation of electronic devices. In many cases, the manufacturing of such devices need ultrahigh vacuum and / or cryogenic working conditions. Albrecht *et al.* /68/ have introduce a single molecule device concept based on a class of robust redox active transition metal (Os(II)/(III)) complexes inserted between the working electrode and tip in an electrochemical scanning tunneling microscope. This configuration resembles a single-molecule transistor, where the reference electrode corresponds to the gate electrode. It operates at room temperature in an aqueous *i.e.* a highly polar condensed medium, environment. Transistor-like current features were found for a class of Os(II)/(III) complexes with osmium as the central ion and bpy (2,2'-bipyridine) as ligands, suitable for combination with single-crystal Au(111) and Pt(111) electrodes (Figure 36). Albrecht *et al.* /68/ have focused molecules: $[Os(bpy)_2(p2p)_2]^{2+/3+}$ and $[Os(bpy)_2(p0p)Cl]^{+/2+}$, inserted between the substrate and tip in a three-electrode electrochemical scanning tunnelling microscope (in situ STM).

Figure 36. The *in situ* STM images of the two Os(II)/(III) complexes /68/: on left $[Os(bpy)_2(p2p)_2]^{2+/3+}$ on a Au(111) surface and on right $[Os(bpy)_2(p0p)Cl]^{+/2+}$ on a Pt(111) surface.

According Albrecht *et al.* /68/, aqueous electrochemistry can be extended to solid matrices such as anhydrous proton conductors, solid electrolytes, and conducting polymers. The liquid state environment used in their study is not prohibitive for real molecular-scale technology based on these systems.

It is well known that surface charges induce electrostatic ion screening and electrokinetic effects such as electro-osmosis, electrophoresis, streaming potentials,

and streaming currents in micro / nanofluidic channels. Daiguji *et al.* /69/ have studied nanofluid channels, which could be basis of a nanofluidic bipolar transistor. In microfluidic channels, analogous to MOSFETs, electrokinetically pumped liquid flow rates can be controlled by modifying the surface potential inside a microfluidic channel by using a gate electrode. In contrast, in nanofluidic channels, the surface charges have larger effects on the flow of ions as opposed to the flow of liquids. By modifying the surface charge density locally at the middle part of a channel, leads to the basis of a nanofluidic current-potential characteristics for two nanofluidic devices: a nanofluidic diode and a nanofluidic bipolar transistor.

4.2 Substrates

Substrates are critical components of electronic paper /22,26,70/, because they enable the devices to be lightweight, mechanically flexible and rugged. A flexible substrate may enable fabrication of electronics by a roll-to-roll process, with various operations formed while the flexible substrate is still part of a web of material. In flat-panel displays, glass has been used as substrate, because light must be able to pass through the substrate material to reach the viewer. Glass is, however, not flexible enough for electronic paper applications, so other materials are needed. There are certain organic, polymeric substrates, which are flexible while being transparent and are therefore useful.

4.2.1 PlasticFilm

The back substrate may be made of an optically transparent thermoplastic polymeric material. From patents /22/ it could be found a great list of possibly suitable materials, such as polycarbonate, polyvinyl chloride (PVC), PS, PMMA, PET, polyurethane polyimide, polyester, polyether sulphone (PES), polyethylene naphthalate, polybutylene terephthalate, polyphenylene sulphide (PPS), polypropylene, aramid, polyamide-imide (PAI), polyimide, polyetherimide, acrylonitrile butadiene styrene and cyclic polyolefin polymers. Also some commercially available, suitable products have been listed /22,70,71/: hardness polycarbonate (HPC) films from Teijin Limited, of Osaka, Japan include (HA 120) and (HT 200), PET films are available from DuPont (Mylar), which is heat stabilised and has T_g of 78 °C. and a

prosessing temperature of up to 120 °C. Even, there are suitable materials available, some problems with polymeric substrates still occur /22/: the difficulty of aligning such substrates properly, when using roll-to-roll formation processes. In addition, polymeric substrates often require organic or inorganic coatings with high barrier properties, to prevent ingress of moisture, oxygen, and / or other contaminants into the substrates.

4.2.2 Paper and Packaging Board

Even the whole idea of intelligent papers relay on paper or paper-like products, from best knowledge of author, there is just one report using real paper or board as substrate for flexible electronics. Lamprecht *et al.* /72/ have reported about the fabrication of organic photodiodes deposited on ordinary newspaper ("Die Zeit") sheets. Compared to the other flexible substrates newspaper is a quite complicated substrate for electronic devices, mainly because of poor mechanical and chemical stability and a very rough surface.

To minimize effects of mechanical instabilities Lamprecht *et al.* /72/ have mounted newspaper substrates onto glass sheet, but only for the time of the fabrication process. To improve newspaper-substrate's poor chemical stability and to reduce its water absorbtivity, the entire substrate was coated with Parylene C, which is known to provide a quite effective chemical and moisture barrier with good mechanical and dielectric strength values. Profilometer-measurements yielded a Parylene thickness of about 6.1 µm.

Lamprecht *et al.* /72/ have found out that the bare newspaper substrate's surface roughness was too high for fabricating thin photodiodes (<100 nm). A surface roughness should be in the order of only a few nanometers referring to surface areas in the micrometer range. In Figure 37a is shown a SEM image of the newspaper substrate. Cellulose fibers and bundles with dimensions in the 50 µm range can be seen clearly and that was why a smoothing layer was needed to form thin continuous layers of the active materials.
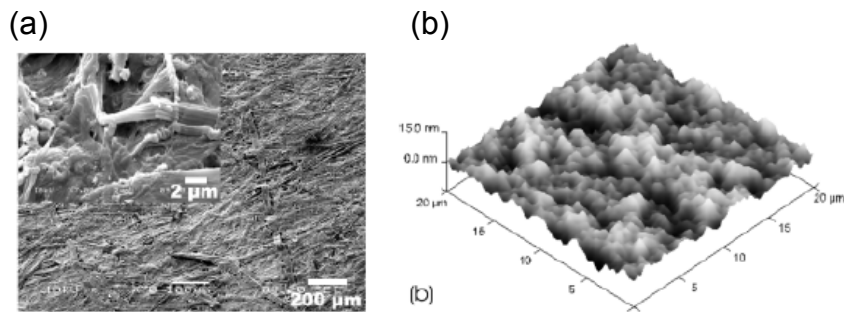
(a)   (b)

Figure 37. (a) SEM image of a newspaper surface (coated with a 30 nm Au layer to improve image quality) /72/. (b) AFM surface topography of the ORMOCER layer spincoated on the Parylene coated newspaper.

For smoothing the surface Lamprecht *et al.* /72/ have spincoated newspaper substrate with an ORMOCER material (Ormoclad B66). The ORMOCER was chosen as it features perfect surface planarisation and is a quite inert. It is a silicate based inorganic–organic hybrid polymer material (*cf.* Chapter 3.3.3), which combines the good properties of inorganic structures (*e.g.*, increased mechanical and thermal stability) with those of conventional polymers (*e.g.*, easy processing at low temperatures). Profilometer-measurements delivered a thickness of the ORMOCER layer of about 100 µm. In Figure 37(b) is shown an AFM plot of the newspaper surface spincoated with the ORMOCER, which indicates a root-mean-square (rms) roughness of the surface less than 3 nm. This perfect flattening leads to a smooth surface that proves to be particularly suitable as undercoating and base layer for organic electronic devices.

In Figure 38 is shown a schematic representation of the photodiode on newspaper substrate Lamprecht *et al.* /72/. More about the organic photodiodes on newspaper is discussed in Chapter 5.4.3.
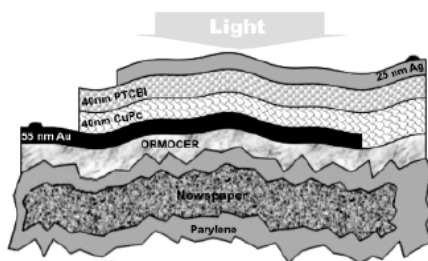

Figure 38. A schematic representation of the photodiode on newspaper substrate Lamprecht *et al.* /72/. Parylene is a chemical and moisture barrier layer, ORMOCER

layer is for surface planarisation, Ag and Au forms electrodes, the active layers: CuPc layer is copper phthalocyanine (p-type organic semiconductor) and PTCBI layer is perylene tetracarboxylic bisbenzimidazole (n-type organic semiconductor).

There is another article considered to be in this gategory: using paper as a substrate. Shah and Brown /1/ have reported a successful development of a dynamic display on cellulose. They refer their work to be the first significant effort to achieve an electronic display using bacterial cellulose. More about the display itself is discussed in Chapter 5.1.5.

While modern digital display media are good for streaming video and visual text data, people still prefer to print articles on paper rather than reading them on a computer screen. That is mainly so, because the following properties associated with paper makes it the best medium for reading information:

1. high reflectivity and contrast,
2. flexibility,
3. light weight and ease of portability and
4. low cost and wide viewing angles.

In contrast, computer screens suffer from disadvantages such as:

1. low reflectivity,
2. high emissivity,
3. high cost,
4. high power consumption and
5. bulkiness.

In addition, the display screens are hard on the eyes and prolonged use is difficult. Therefore, many recent efforts concentrated on achieving an electronic display screen, which combines the desired optical properties of paper with the dynamic capability of conventional digital screens, *i.e.* intelligent papers /1/.

It is worth of telling here something more about the paper Shah and Brown /1/ have studied. As commonly known, paper consists of cellulose derived from plant cell walls, which is the largest source of cellulose for paper. However, the cellulose derived from plant cell walls is not in the most pure form. Traditional paper contains

also a mixture of lignin and hemicelluloses. A cellulose that is much more pure is the cellulose synthesised by bacteria, *Acetobacter xylinum*. Shah and Brown /1/ used in their experiment various strains of Acetobacter, some with very special mechanisms for spinning cellulose, like *Acetobacter xylinum* strain ATCC 53582. The optical micrograph in Figure 39 shows various cells of *Acetobacter xylinum* spinning cellulose from glucose-rich medium.

Figure 39. Optical micrograph showing *Acetobacter xylinum* cells spinning cellulose nanostructures /1/. The dark lines are the cellulose fibrils.

Shah and Brown /1/ have reported unique properties of this kind of cellulose and its several advantages over traditional paper: unique microfibrillar nanostructure (Figure 40), complete purity, higher dimensional stability, greater mechanical strength and in dry-state, extraordinarily high absorptivity. This cellulose can so be manipulated to absorb external materials to impart functionalities. At the same time, it retains the desired optical properties of paper in its dry state; and it is biodegradable, renewable and selfassembled during biosynthesis.
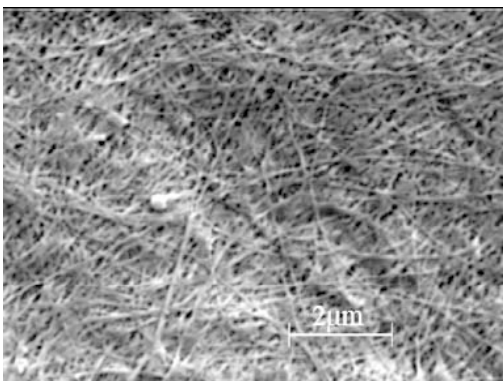

Figure 40. A SEM micrograph (5000 times magnified) showing the woven nanostructure of microbial cellulose (scale bar is 2 µm) /1/.

4.3 Printing Methods and Intelligent Papers

The use of low-cost manufacturing techniques such as those used in graphic arts printing processes promise to enable the manufacturing of cheap flexible electronic products /19,22,73/. Traditional silicon based semiconductor fabrication consists of many complex and process parameter sensitive manufacturing technologies: photolithography, chemical- and physical vapour deposition and electroplating. Many of these processes are performed in clean rooms and require high-vacuum environments. Recent advances of organic materials demonstrating attractive optoelectronic and semiconducting properties combined with low-cost manufacturing technologies; including printed wiring board (PWB) fabrication processes used in the microelectronics industry and printing technologies used in the graphics arts printing industry may lead to a revolution in the electronics industry. The use of hybrid manufacturing processes such as inline use of ink-jet printing and photolithography could be the key for producing flexible electronics. In Figure 41 is presented manufacturing technologies used in traditional silicon semiconductor and graphic arts printing industries and the feature sizes of the fabricated structures.

Figure 41. Manufacturing technologies and capabilities used in silicon semiconductor and graphic arts printing industries /19/.

In the beginning of the organic semiconductor studies, a combination of vacuum deposition and solution processes was used to fabricate OTFTs. More recently the use of graphic arts printing technologies, such as screen printing and ink-jet printing, and different lithographic printing methods including soft-lithoraphy, (also called microcontact printing (µCP)), have been the main methods for manufacturing solution-processable organic semiconductors /19,29/.

4.3.1 Screenprinting

There are certain advantages for using screenprinting techniques /70/: the printing matrial's surface does neither have to be printed under pressure, unlike etching or lithography, nor it does not have to be planar. In micro- and nanoelectronics manufacturing industries, screenprinting technologies are used mostly to deposit planar working electrodes and dielectrics to circuit boards and components like OTFTs. In addition, screenprinting is used also to fabricate molding structures for micromolding in capillar (MIMIC) –techniques. Karyakin *et al.* /29/ have reported succesfull screen-printing of carbon electrodes to OTFT from two types of commercial carbon inks.

4.3.2 Ink-Jet Printing (Noncontact Printing)

Ink-jet printing is a noncontact reprographic technique that takes digital data from a computer representing an image or character, and reproduces it onto a substrate using ink drops /74,75/. In recent years, the applications of the technology have been successfully extended from its traditional areas in electronics and micro engineering. Ink-jet printing has the advantage of simplicity, low cost, flexibility, and maturity. Ink-jet printing is considered one of the most promising methods for controlled deposition of polymers and functional materials especially in relation to the fabrication of polymer-based electronics parts from organic semiconductor inks. Such a microscopic patterning technique (ink-jet) is needed, because such devices cannot be prepared by conventional spin coating.

Printing submicrometer structures with ink-jet have some limitations /74,75/: minimum spacing at which dots can be printed without coalescence of the droplets on the surface is at present about 125 µm. Confinement of the droplets, either mechanically or by surface energy patterning, will be necessary to produce smaller regular arrays. As ink-jet printing requires low viscosities (typically 1-10 mPa s), polymeric materials can only be deposited from dilute solution. Ink-jet printers can deliver as little as 8 pL/droplet, or as much as 95 pL/droplet. The droplet sizes vary according to the temperature gradient applied, the frequency of the current pulse, and the sample viscosity /75/. It is interesting to note that, by using dilute solutions, structures can be

created smaller than the diameter of the nozzle. This may be a potential strategy for the ink-jet printing of defined submicrometer structures. Figure 42a shows a dot array (the average dot diameter 29 µm) that was obtained by printing a rectangular array of single, acetophenone-based droplets at a mutual distance of 150 µm on a perfluorinated surface. Figure 42b displays a corresponding cross-section.
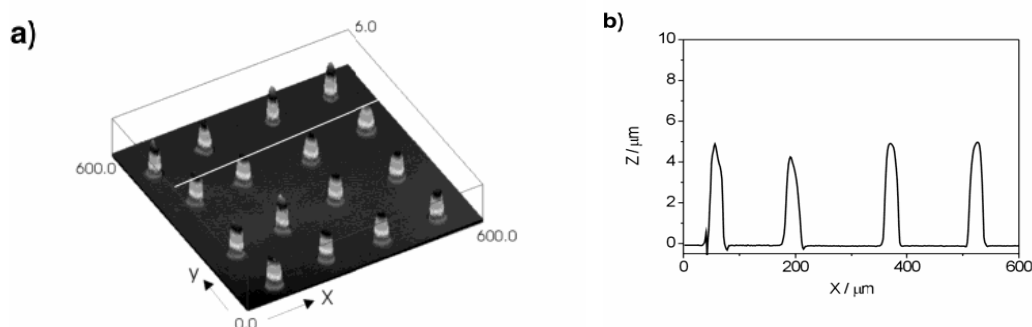

Figure 42. (a) Array of polymer dots printed at a mutual distance of 150 µm, formed by droplets of a 1 wt-% solution of polystyrene in acetophenone /74/. The typical size of the dots shown here is 29 ± 2 µm, which is smaller than the nozzle diameter; (b) cross-section in the x- direction, corresponding to the line in Figure 42a.

Until now, it has been reported several different ink-jet printed organic or polymeric devices, such as a all-polymer FETs with channel length of 500 nm fabricated by surface-energy-assisted ink-jet printing /76/, multicolour PLED displays. However, the potential of ink-jet printing is huge and goes far beyond what has been realized until now. Future areas of application may include the fabrication of sensors, polymer-based solar cells, or microfluidics devices, all based on polymers as matrix or functional materials, however by now ink-jet is too slow method for larger scale mass production.

4.3.3 Contact Printing and Lithography Printing

In the context of miniaturization in microelectronics, nanometer-scale device fabrication has become a serious technological challenge. Traditional contact printing, including lithography printing, methods have been stretched to micro- and nanoscale electronics manufacturing /38,70,77/. There have been developed a great variety of fabrication techniques such as photolithography, soft lithography (i.e microcontact printing, µCP), nanoimprint lithography (nIL), colloidal lithography (CL)

and scanning-probe microscopy lithography techniques: dip-pen nanolithography (DPN) techniques, as well as laser interference lithography, electron-beam and ion-beam lithography and X-ray lithography. These methods have been used for patterning nanoscale 2D surfaces for printed electronics.

Photolithography

The "etching with light" technique is used to make integrated circuits. In this technique, a layer of silicon or other semiconductor is covered by a protective oxide layer, which in turn is covered by a polymer that reacts to light. A mask outlining desired circuits is laid on top, and then the masked polymer is exposed to light. The light chemically changes the exposed areas of the polymer. Chemicals are then applied to wash away the exposed polymer and the oxide underneath. The remaining polymer is washed away with other chemicals, leaving the layer of oxide in the form of the mask and the layer of silicon exposed in the pattern of the desired circuits. The exposed silicon is then doped, or chemically altered, to become more electrically conductive. This forms the transistors and logic gates of the chip /22/.

Soft lithography / microcontact printing (µCP)

A more sophisticated printing approach for achieving higher resolution, higher performance organic circuits is the use of microcontact printing (µCP) technology (also called soft lithography, µ-lithography) /19,70,73/. Since the technique has been established in 1990's it has been videly used to fabricate organic devices and circuitry. Microcontact printing closely resembles flexographic printing, and thus a roll-to-roll manufacturing format using microcontact printing can be envisioned for printing intelligent papers. Li *et al.* /21/ have reported microcontact printing to fabricate TFT -electrodes from silver nanoparticles. Lampert /78/ and Kosc /5/ have made cholesteric liquid-crystal flakes by soft lithography. These flakes can be microencapsulated to form flexible reflective displays, for example, for intelligent paper applications.

Nanoimprint lithography (nIL)

A key benefit of nanoimprint lithography is its sheer simplicity. It creates patterns by mechanical deformation of imprint resist and subsequent processes /38/. The imprint resist is typically a monomer or polymer formulation that is cured by heat or UV-light during the imprinting. There is no need for complex optics, high-energy radiation sources or finely tailored photoresists designed for both resolution and sensitivity at a given wavelength. Another key benefit is its low cost because of the simplified requirements of the technology. One very important benefit is that nIL offers higher resolution than for example µCP does. Since large areas can be imprinted in one-step, this is also a high-throughput technique. The key concerns for nanoimprint lithography are, due to the direct contact involved: overlay, defects and template patterning. Figure 43 shows different caracters of printing methods.

Figure 43. Comparison of various lithographic tools /38/.

The vast majority of these lithographic techniques requires elaborate and expensive instrumentation and is inherently single-ink processes /38,79/. Although these techniques based on a "top-down approach" are useful in pattern fabrication, cost and process considerations limit their usefulness. Self-assembly techniques that use chemical or physical driving forces based on a "bottom-up approach" are an alternative; these techniques allow simple control of the pattern size and low-cost parallel processes.

Choi *et al.* /80/ have reported a versatile and useful technique in the field of nanopattern fabrication; colloidal lithography (CL) combined with reactive ion (plasma) etching. They have used method to fabricate polymeric nanofibrillar surfaces and patterned structures using colloidal single layers and double layers. These resulting structures of nonspherical building blocks can be used as templates or masks for micro- or nanoscale 2D particle arrays, which are important in applications of stamps for µCP, carbon nanotube arrays etc. CL has the advantage of being an inexpensive, inherently parallel, high-throughput nanofabrication technique.

Scanning probe microscopy lithography

Scanning probe microscopy (SPM) has been shown to be powerful in nanometerscale materials and devices engineering. By using scanning probe lithography it is possible to reach a resolution that may exceed the standard of other lithography processes.

Dip-Pen Nanolithography (DPN)

Dip-pen nanolithography (DPN) is a direct-write SPM-based lithography tool for fabricating nanostructures on a range of surfaces /38/. In DPN, an AFM-tip is used to deliver chemical reagents directly to nanoscopic regions of a target substrate (Figure 44). As perhaps the only lithographic technique that offers high resolution and registration with direct-write printing capabilities (*cf.* Figure 43), distinguishes DPN from any alternative lithographic method and makes it a promising, powerful, production tool for patterning soft organic nanostructures in the lithographic mask fabrication and semiconductor industry.
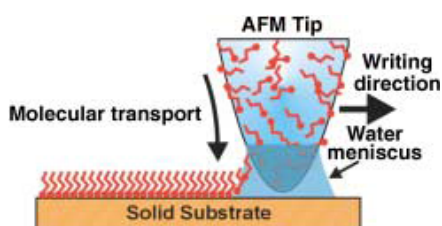

Figure 44. A schematic representation of the DPN process. There is a water meniscus between the AFM tip which is coated with "ink" molecules and the solid substrate /38/.

Well-defined conducting polymer nanowires have been created on semiconducting and insulating surfaces with DPN /28,38,81-83/. DPN is compatible with many types of ink, from small organic molecules to organic polymers, and from colloidal particles to metal ions and solids.

Maynor *et al.* /81/ have described the DPN manufacturing of GaN nanowire heterostructures by a local electrochemical reaction between an n-type GaN nanowire and a tip-applied KOH "ink" to produce gallium nitride/gallium oxide heterostructures (Figure 45).
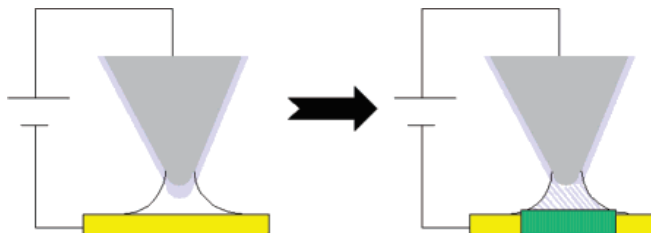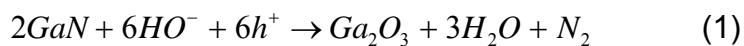

Figure 45. A schematic drawing of the DPN modification of GaN nanowires /81/. The AFM tip is coated with KOH "ink" (light gray) and engaged with the GaN nanowire (yellow). During modification of the NW, KOH diffuses from the tip to the NW surface and electrochemically reacts with the nanowire to produce a gallium oxide heterostructure (green).

The electrochemical reaction, a two- step dissolution mechanism, between GaN and KOH is described by Nowak *et al.* /84/: In the first step, the semiconductor is oxidised (the anodic oxidation of semiconductors requires holes (h^+) in the valence band of the solid):

$$2GaN + 6HO^- + 6h^+ \rightarrow Ga_2O_3 + 3H_2O + N_2 \qquad (1)$$

while the oxide can be chemically dissolved in the second step:

$$Ga_2O_3 + 6HO^- \rightarrow 2GaO_3^{3-} + 3H_2O \qquad (2)$$

In addition to the modification of GaN, this modification scheme could be applicable for other semiconductor nanowires such as CdS or InP /81/. This DPN modification

scheme provides a convenient means to deliver chemicals to specific locations on an existing nanostruture to perform chemical and structural modification. Kim and Lee /85/ have discovered that forcing Ag-nanoparticles by DPN in physical contact with organic films can induce a photolytic reduction of the organic moiety simply by irradiating it with a visible laser under ambient conditions. This indicates that Ag nanoparticles can act as moderate photoelectron emitters. The fabrication of such patterned monolayers on engineered substrates is essential for the development of molecule-based optoelectronic and biomimetic devices and sensors. Despite this, at the moment, the DPN-method's disadvantage is that due to the slow nature of the SPM technique, method cannot be used for high-throughput applications.

As could be seen, several printing methods have been studid for printing low-cost, flexible (organic) electronics. The best results until now have been reached by combining different processes; printing methods with other fabrication technologies like spin coating.

In following Chapter 5 is described some applications which already uses flexible electronics and thus are steps towards real intelligent papers. Applications include large-area electronically driven products; such as switching devices for active matrix flat panel displays (AMFPDs) (large-area flexible displays) /16-19,78,86/. Additionally, sensors, low-end smart cards, and radio-frequency identification tags (RFIDs) consisting of organic integrated circuits have been proposed. As well as an organic electronic memory, completely flexible and transparent TFTs (TTFTs), an all-polymer integrated circuits and printed, uncased thin, flexible energy cells on a polymer film substrate have been demonstrated.

5   Applications for Printed Electronics

5.1   Flat-Panel Display, FPD and Flexible Display

As mentioned earlier it is desirable to manufacture lightweight, large area FPDs for use in many applications, like in portable devices such as computers, electronic books and PDAs. The flexible panel displays may be made by roll-to-roll processes, with various fabrication operations formed while the flexible substrate is still part of a web of material. Such a low-cost mass-production processes will able to reduce display prices and so will allow the use of displays in new, low-end applications. There is a great variety of display-types, such as liquid crystal displays (LCDs), electroluminescent displays (ELDs); devices made of OLEDs and PLEDs, electrophoretic ink-containing electronic paper displays etc. /22/.

5.1.1 Active Matrix Backplane Circuits

Despite differencies, all displays consisting pixels need one similar component; the backplane drive circuit, to control pixels. The active matrix (AM) backplane circuit consists of a square array of suitably interconnected p-channel transistors. The AM backplane structures, formed from flexible TFTs (*cf.* Chapter 4.1.1) are typically suitable for low-cost paper-like displays. In Figure 46 is shown one example of the flexible AM backplane circuit layout. That particular backplane is designed to drive 256 (16x16) pixels. On the left in Figure 46: green areas are indicating gate and yellow source / drain levels of TFTs, which are driving each pixel. On the right is layout of pixel electrodes and pinout connections. These electrodes are bonded to a sheet that connects to pixels on one side and to the backplane circuit on the other /17,70/.
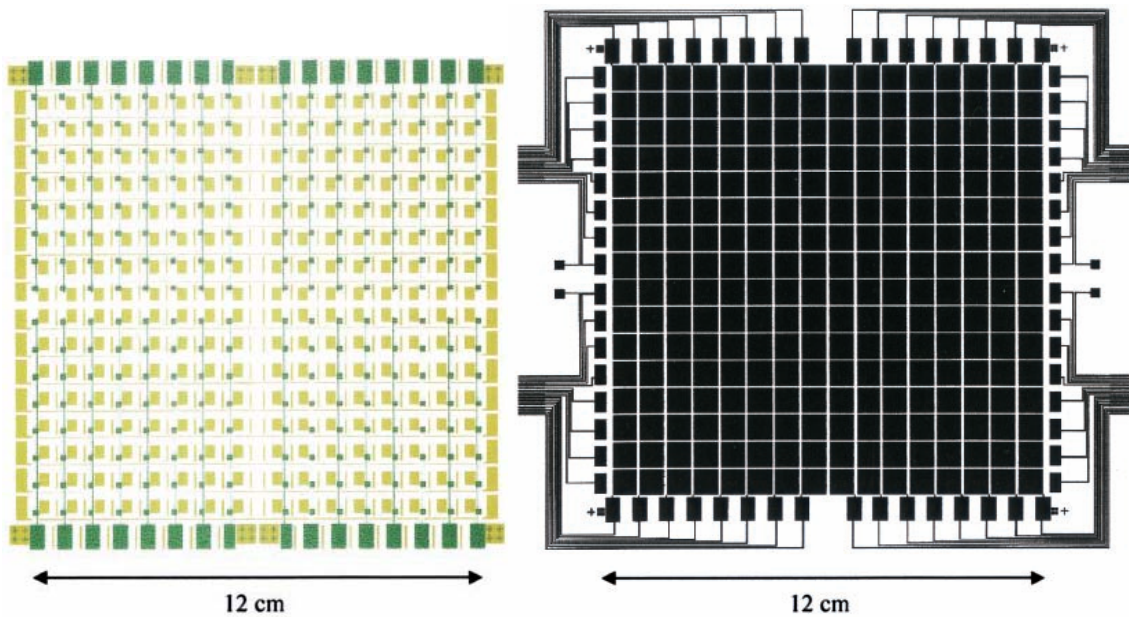
Figure 46. On the left: Layout of gate (green) and source / drain (yellow) levels of an active matrix backplane circuit for a display sheet with 256 pixels /70/. On the right: Layout of pixel electrodes and pinout connections. The electrodes are bonded to a sheet that connects to the display sheet on one side and to the backplane circuit on the other.

The Figure 47 shows an image of printed, flexible, plastic AM backplane circuit, and in inset; a micrograph of its TFT /70/.

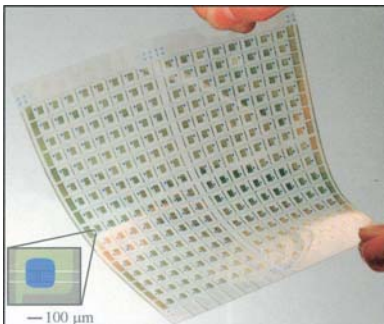*Figure 47*. An image of a plastic active matrix backplane circuit. The Inset shows an optical micrograph of a typical transistor /70/.

Among many others Comiskey *et al.* /4/ have reported about an all printed metal–insulator–metal (MIM) TFT structure capable of forming the active matrix for high-pixel-count sheets, while maintaining the ease of fabrication and low-cost structure provided by the ink material itself.

5.1.2 Electrochromic Display, ECD

There are some reports about developments of a high viewing angle, paper-like electrochromic displays ECD for electronic papers /78/. As the name describes, in ECDs, electrochromic material (ink) forms simple, electronically addressable and dynamically switchable pixels which light absorption could be reversibly switch by using applied voltages.

As shortly mentioned in Chapter 4.2.2 Shah and Brown /1/ have demonstrated the concept and a prototype of a ECD, based on the printed page consisting of a static coloured dye fused with cellulose. In following this real paper-like display is described more in detail.

Real Paper-like Display

The key idea for Shah and Brown /1/ has been literally "ink-on-paper" appearance, *i.e.* to integrate an electronic dye into the nanostructure of the microbial cellulose. Due to the nanostructured nature and paper-like optical properties, microbial cellulose has been used instead of commercial paper for creating devices.

In their work ink formed electronically addressable and dynamically switchable simple pixels, which light absorption could be reversibly switch from the ON to the OFF state by using applied voltages. The pixel size was controlled by the minimum addressing resolution of back-plane drive circuits (*cf.* Figure 47) /1/.

Even it is possible to synthesise very thin microbial cellulose membranes (ca. 700 nm), Shah and Brown /1/ synthesised a microbial cellulose paper with thickness of around 100 μm, which is close to standard commercial paper in appearance and properties. Then microbial cellulose membranes were impregnated throughout with various solution-processed dopant conductors to improve their conductivities.

The next step in the manufacturing process was embedding a suitable electrochromic (EC) dye. The EC dyes are materials, which undergo completely switchable optical changes, by the mechanism of a reversible redox reaction, upon the application of an electric charge. These two states of the material, which exhibit

changes in absorption levels, leading to different colours in ambient light, co-exist in same physical conditions and both are thermodynamically stable. The dye Shah and Brown /1/ have chosen underwent the following redox reaction:

$$State\ A\ (colourless) + e^- \leftrightarrow State\ B\ (dark\ blue\ state)$$

Hence, the working idea of the device is the creation of dark state, *State B*, when a potential is applied /1/. That state can maintain its status without additional supplied power, and once a reverse potential is supplied, the colourless *State A* dominates. This means that once an image / text is displayed on such the electronic display screen; it is retained even after the power is turned off. Therefore, a full-scale multi-pixel device is a bistable display. The display can be read as a dark state of dye versus the white state of the microbial cellulose paper (since the dye *State A* is colourless, the white paper state is read). A composite bacterial cellulose sheet that is conductive and has an electronic dye integrated forms the basic electronic paper unit.

Shah and Brown /1/ integrated the microbial cellulose membrane in three ways to form full-size devices for tests:

1. The membrane was sandwiched between two transparent electrode plates. In this case an inflexible electronic screen was manufactured having an electrode plate in front and an electrode plate on a glass-circuit at the back, similar to a conventional LCD arrangement, despite that: there is a continuous film of conductive bacterial cellulose across the whole device. This has enhanced optical properties, compared with current devices.
2. The membrane was layered over the top of in-plane bottom circuitry (two parallel electrode plates, both on the bottom side). This device can be integrated to have microbial cellulose membrane across the top. In addition, it do have a much greater paper-like appearance and feel than any other current device.

In both these devices, pixel-level colour change-testing has been done and the following optical micrographs obtained (Figure 48) /1/:
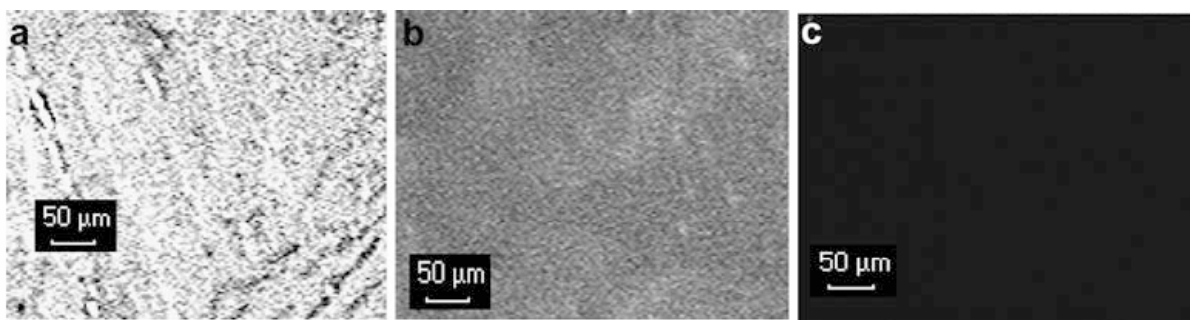
Figure 48. Pixel-level color changes from the in-plane device recorded at a) *t* = 0 s, b) *t* = 0.25 s and c) *t* = 0.45 s /1/.

As can be seen, the switching rate is about 450 ms. A contrast ratio of about 15 is achievable between the two states of dye (Figures 48a and 48c). The reflectivity in the completely clear state is paper-like.

In addition, the power consumption of this device was low and the coloured state of dye was retained for approximately 15 min after the power was turned off /1/. The refresh rate was lower than that video-rate requires for, but for applications such e-books, e-papers and switchable wallpapers, refresh rate is sufficient. The optical properties of the device were much superior compared with current technologies.
Another test of the membrane application; an "etch-a-sketch", was done /1/. In this application the electronic paper can be used as a medium for writing text, which can be stored and erased with an opposite voltage, by using a moving pen-shaped top electrode. The dye changes colour at the point where the electrode touches it (Figure 49). Then, this is automatically erased by an opposite potential from the bottom electrode that clears the whole device.

Figure 49. In an "etch-a-sketch" application, the electronic paper is used as a medium for writing text, which can be stored and erased with an opposite voltage, by using a moving pen-shaped top electrode /1/.

These recent developments and successful demonstrations of electronically switchable ink display in a true cellulose paper matrix by Shah and Brown /1/, hopefully will sooner or later become common form of a new revolutionary electronic paper. This method could be said to be the basics of intelligent papers. Such a products could be used in larger surfaces, such as wallpapers, electronic billboards, art and photographic displays on walls and even displays on textiles. Such devices can also take the full form of a rewritable paper, highly adaptable medium for effective communication and education, which can be used in several applications from dynamic writable maps in the hands of soldiers till learning- and writing tools for children, for example. Only imagination makes limits for usage.

5.1.3 Electrophoretic Display, EPD

Function of the electrophoretic displays (EPDs) is based on the motion of charged particles in a colloid under the influence of an applied electric field /87/. Because of that, the name: charged particle display is sometimes used. Electrophoretic displays are reflective and nonemissive, and thus have significantly lower power consumption than a LCD. They can be combined with flexible substrates.

At the time the leading EPD- technologies, in the market are based on microbeads. These beads are typically about 100 μm or less in diameter and have differently coloured particles and / or liquid inside the microcapsules. The color of these displays can be made to switch between two states of microbeads upon the application of an electric field. Microbead-based displays possess intrinsic bistability, and have demonstrated high contrast and reflectivity. These features of EPD result in an ink-on-paper look.

Gyricon, Twisting Ball

In the Xerox PARC's Gyricon construction, the beads are contained in an oil-filled cavity, and beads are free to rotate within those cavities. The beads are bichromal hemispheres of two contrasting colours (for exampe black / red and white), and charged so they exhibit an electrical dipole. When voltage is applied to the surface of the sheet, the beads rotate to present one coloured side to the viewer. Millions of the

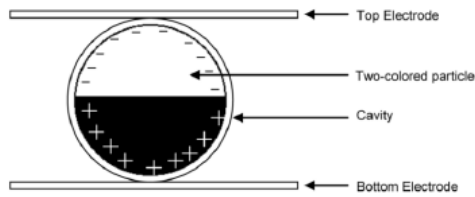encapsulated beads are sandwiched between two flexible sheets, each containing electrodes (Figure 50).

Figure 50. A Gyricon bead containing two colours /19/. The bead is suspended in a cavity filled with oil.

In December 31st in 2005, Xerox Corporation announced to terminate the operations of Gyricon LLC and to refocus its efforts in electronic paper technology through licensing of the underlying intellectual property /88/.

E Ink, Micro Encapsulation Particles

Electronic ink or E-ink is an invention from the MIT Media Lab /6,19/. E-ink consists of microcapsules in which pigment particles are encapsulated together with a fluid. In one embodiment, pigment chips of one colour are contained in a liquid dye of a contrasting colour. In another embodiment, E-ink consists of positively charged white and negatively charged black particles suspended in a clear fluid carrier medium. This suspension is encapsulated within a microcapsule (Figure 51). When a positive electric field is applied, the black microcapsules appear near the top and the white microcapsules are pulled to the bottom.
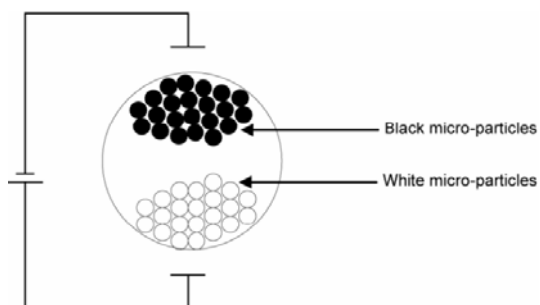

Figure 51. Schematic illustration of an embodiment of an E-ink microencapsulated electrophoretic bead /19/.

Comiskey *et al.* /4/ have reported about synthesisation of two different type of electrophoretic inks by microencapsulating droplets of an electrophoretic dispersion in individual microcapsules with diameters in the range of 30–300 μm by using following processes:

1. The internal phase of the microcapsules was composed of a mixed dispersion of black and white microparticles in a dielectric fluid /4/. To obtain white microparticles, they atomised a suspension of rutile titanium dioxide in molten low-molecular-weight polyethylene. A similar process was used to prepare black microparticles with an inorganic black pigment. The resulting particles were sieved to obtain a dry powder with an average diameter of 5 μm. These microparticles were then dispersed in a mixture of tetrachloroethylene and an aliphatic hydrocarbon (they did not specify that), which is specific-gravity-matched to the manufactured particles. In the case where the particles are designed with charges of opposite sign, they are prevented from coagulation by providing a physical polymeric adsorbed layer on the surface of each particle, which provides strong inter-particle repulsive forces.

2. A single particle system (white microparticles) dispersed in a dyed (Oil Blue N) dielectric fluid was prepared. This suspension was then emulsified into an aqueous phase and microencapsulated by means of an *in situ* polycondensation of urea and formaldehyde. This process produced discrete mechanically strong and optically clear microcapsules. The microcapsules are optionally filtered to obtain a desired size range, and are subsequently washed and dried.

An E-ink display can be made by depositing the microcapsules onto a plastic film, followed by laminating it to a second layer containing the AM backplane that controls the microcapsules.

Comiskey *et al.* /4/ have also manufactured a system of microencapsulated charged microparticles, in which particles were migrated towards the viewer by means of an externally applied electric field. They prepared microcapsules consisting white particle in dye, dispersed them in an ultraviolet-curable urethane and subsequently coated onto a transparent conductive ITO film on polyester. Bottom electrodes were printed from a silver-doped polymeric ink and then applied to the display layer. By

using differently structured top electrodes they were able to fractionally address single microcapsules, yielding an addressable resolution of ~600 dots per inch (dpi), till up to ~1200 dpi.

In Figure 52 it is shown a series of microphotographs, at different magnifications, in which the letter 'k' has been electronically addressed in the electronic ink, with a mean capsule size of 40 ± 10 µm yielding a capsule resolution of ~600 dpi.
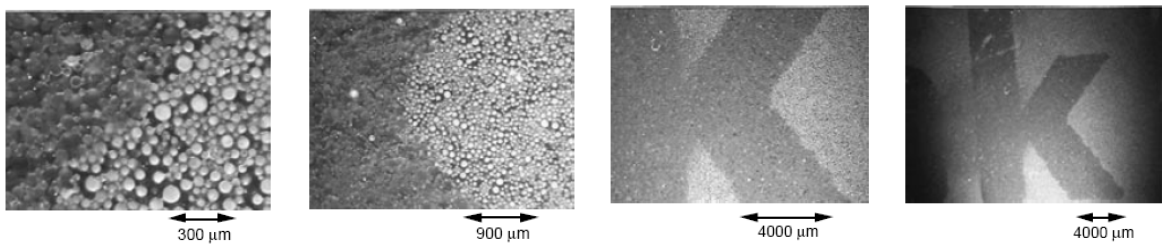

Figure 52. Photomicrographs of 200 µm-thick film of "white particles in dye"-type electronic ink with a capsule diameter of 40 ± 10 µm /4/. The electronically addressed letter "k" is blue, other areas are white.

In addition, Comiskey *et al.* /4/ have measured contrast ratios of 7:1 with 35 % reflectance and a near-lambertian viewing characteristic. With the same method, they measured newspaper at 5:1 contrast and 55 % reflectance.

Rogers *et al.* /70/ have studied and made a prototype of a flexible E-ink display, using printed, flexible AM backplane circuit (*cf.* Figure 47) to drive its pixels. The total thickness of a completed sheet of electronic paper was ≈1 mm. Its contrast ratio was significantly better than that of newsprint (>10:1). The switching-time from one image to another is ≈1 s and display had operated on small battery packs, which had lifetimes of several months of continuous use. Figure 53 shows displaying images that demonstrate that all of the 64 pixels are functioning well, even while being flexed; the bending did not affect its performance.

Figure 53. A sheet of electronic paper displaying images while being mechanically flexed. Bending does not alter the performance of the display /70/.

The example of real flexible display with E-ink is reported by Chen *et al.* /15/. The display they have made on a stainless steel substrate, was less than 0.3 mm thick, had rather high pixel density ((160 x 240) pixels) and resolution; 96 dpi, and could be bent to a radius of curvature of 1.5 cm without any degradation in contrast (Figure 54).

In addition, display's white state reflectance was 43 % and contrast ratio 8.5:1. The ink-switching speed is 250 ms, which is sufficient for electronic paper; despite this, a reduction to 15 ms would be required for video-rate switching. Chen *et al.* /15/ have also suggested that electronic ink combined with flexible AM backplanes will provide a viable pathway to electronic paper, intelligent paper, and wearable computer screens.

Figure 54. An example of a flexible active-matrix electronic-ink display /15/. (a) Operating principle of electronic ink: the relative movement of negatively charged black and positively charged white particles inside their microcapsules is controlled by the direction of the applied voltage. (b) A backplane TFT measured *in situ* under compressive stress. The transistor is bent to three different radii of curvature: green, 2.0 cm (0.19 % strain); blue, 1.3 cm (0.29 % strain); and red, 1.0 cm (0.38 % strain). The TFT has identical characteristics when measured without bending (black curve) and at a radius of curvature of 2.0 cm; degradation is minimal even at 1.0 cm. The results were similar under tensile stress. (c) Text image shown on a bent display whose resolution is 96 dpi.

In addition, there are several other types of electrophoretic displays based on charged particles. Kosc /5/ has listed in her article following methods:

- SiPix Inc. has developed their product the Microcup, a process in which the particle suspension is deposited into 80-160 μm wide compartments embossed into a resin substrate. The compartment-structure of the Microcup substrate allows full colour display producing, in which each Microcup can act as an individual pixel consisting particles suspended into red, green or blue fluid.

- Japanese Bridgestone Corp. has announced the Quick Response Liquid Powder Display (QR-LPD) technique to produce EPDs. This technique consists of black and white opposite charged particles contain in air, in substrates ribbed structure compartments. Particle-powder is chemically treatened so that it does not pile up, but act like liquid, spreading all over. The lack of fluid increases the switching speed and so reduces response time.

- In the University of British Columbia, in the USA, has been developed a charged liquid electro-active response (CLEAR) display technology. The CLEAR technology is based on electrophoretic motion of particles to produce reflection state and absorptive state of ambient light via total internal reflection.

5.1.4 Electroluminescent Display (OLED, PLED)

Another type of flexible display is electroluminescent display, the display that emits light to be seen by the viewer, in other words, EL-display is an emissive type display. These 'plastic' displays are based on either OLED- or PLED devices (*cf.* Chapter 4.1.2). Even such emissive non-bistable displays do not meet one important criterion of electronic paper, namely the persistent display of information with zero power consumption, despite this, recent results in ink-jetting of electroluminescent doped polymer films for organic light-emitting structures for flexible displays, have lately garnered a lot of media attention /4,16,58,78/.

For example, Song and Ryn /89/ have fabricated a panel consisting of an array of OTFTs and OLEDs in order to demonstrate the possible application of OTFTs to flexible active matrix OLED (AMOLED). The panel was composed of 64 × 64 pixels on 4-squareinch-size PET substrate in which each pixel had one green OLED integrated with one OTFT. They have successfully demonstrated that panel displayed

some letters and pictures by emitting green light, which was controlled by the gate voltage of OTFT. This was a successful step toward electronic paper.

5.1.5 Liquid Crystal Display, LCD

New LCD technologies with bistable properties such as cholestric liquid crystals (Ch-LCs) and ferroelectric liquid crystals (FLCs) are examples of state-of-the-art technologies currently under development. Compared to traditional refreshed LCDs, bistable displays consume less than a hundredth of the power /2,90/.

Cholesteric liquid crystal (Ch-LC) displays are normally reflective, so no backlight is needed and can function without the use of polarizing films or a colour filter /22,58,78/. Cholesteric liquid crystal is sometimes called "chiral nematic" because Ch-LC is normally obtained by adding chiral agents to host nematic liquid crystals. Cholesteric liquid crystals may be used to provide bistable and zero field multistable liquid crystal displays (FMLCDs) that do not require a continuous driving circuit to maintain a display image, thereby significantly reducing power consumption. In addition Ch-LC displays have excellent sunlight readability, the ability to display various gray scales and fast switching operation; 30 milliseconds per frame.

Ferroelectric liquid crystals (FLCs) use liquid crystal substances that have chiral molecules /58,78/. The spiral nature of these molecules allows the microsecond switching response time that makes FLCs suitable for advanced displays. Surface-stabilised ferroelectric liquid crystals (SSFLCs) apply controlled pressure using a glass plate, suppressing the spiral of the molecules to make the switching even more rapid.

Polymer-dispersed liquid crystal (PDLC) displays are potential for FPDs and flexible switchable windows /25,78/. PDLC commonly consists of micron-sized liquid crystal droplets dispersed in a polymer matrix. The scattering power of the film can be modulated by an electric field, which aligns the liquid crystal molecules in the droplets bringing the film from a highly scattering state to transparency. PDLCs can be sandwiched between two plastic substrates coated with conductive polymer layers to form all-organic displays. PDLC displays are promising devices for paper-like

displays for electronic books, and other applications, which require flexibility, lightness, and low-power consumption.

Polymer cholesteric liquid crystal (PCLC) –flake display technology has been developed in University of Rochester /5/. The device function relays on the interfacial polarization of at the flake-fluid boundary induces a dipole moment upon which the applied electric field acts, reorienting flakes from a bright reflective state to a dark state.

5.2 Organic Electronic Memory

Even organic devices are revolutionizing the field of electronics by providing extremely inexpensive, lightweight and capable ubiquitous components that are printed onto flexible substrates, an organic electronic memory, has not received much attention. Moller *et al.* /91/ have reported architecture for a write-once read-many-times (WORM) memory, based on the hybrid integration of an organic electrochromic polymer with an inorganic thin-film silicon diode deposited onto a flexible metal foil substrate. The WORM memory pixel exploits a mechanism of current-controlled, thermally activated un-doping of a two-component electrochromic conducting polymer PEDOT/PSS, layered onto the surface of a thin-film Si p–i–n diode deposited onto a stainless steel substrate (Figure 55), conducting polymer layered across the full Si surface.
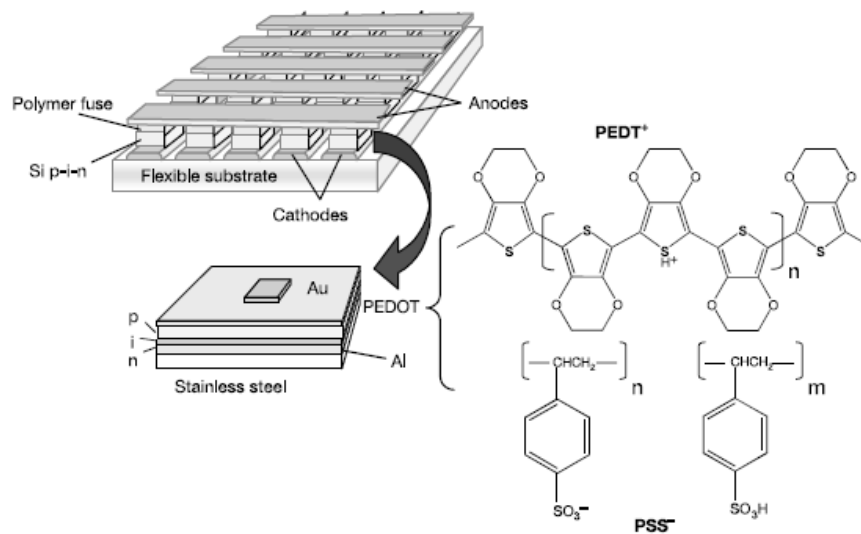
Figure 55. Generalized architecture of the WORM memory, and the materials used in its implementation /91/. Top, schematic view of a hybrid organic / inorganic semiconductor WORM memory. Bottom, diagram of the WORM memory element, employing an Al cathode coated flexible stainless steel substrate. On the right is shown the chemical structure of the PEDOT/PSS, used as the fuse material in the WORM memory element.

After testing the WORM memory element, Moller *et al.* /91/ have discovered that reliability, irreversibility and reproducibility of the switching process were essential to a practical memory array. Ultralow-cost and small (the area that WORM cell occupies is only $4F^2$ (where F < 500 nm)) WORM memories have widespread uses in varied applications, such as the rapid, archival storage of video images, where the vulnerability to breakage and the relatively high cost associated with slow and power-hungry magnetic or optical disk drives are not acceptable.

5.3 Intelligent Packaging

A fast growing applications area for flexible, low-cost electronics, intelligent papers, is intelligent packaging. By intelligent packaging new functional characteristics can be created to the customer packages, in order to add the value of package itself. This means, for example, that personalised and fresh announcements, advertments and consumer informations can be as an integrated part of a package. Also very new kinds of systems for the optimisation of the delivery chain can be developed, like

coding and detection systems for logistics and anti-thefts. Brand protection, safety and features ensuring authenticity are important features of intelligent packages too. In near future the packaging will thus be much more multifunctional, informative and demand-oriented than they are today.

5.3.1 Radio Frequency Identification, RFID, Tags and Stickers

Recently, many publications have presented the compelling cost savings that are achievable when implementing asset tagging networks along the supply chain /16,19,92/. One such technology is radio frequency identification, RFID, which is a generic term for technologies that use electromagnetic coupling in the RF to transmit signals for automatic identification of individual items, and can be a non-line of sight replacement in many circumstances for the ubiquitous bar code. The enablers for larger use of RFID are flexible electronics, especially printed organic semiconductor materials and manufacturing platforms. Several companies like 3M Corp., ORFID Corp., Philips and PowerPaper Ltd. have announced their products in this space. The RFID system consists of a tag, made up of a microchip with an antenna (Figure 56a) and a reader with an antenna (Figure 56b).
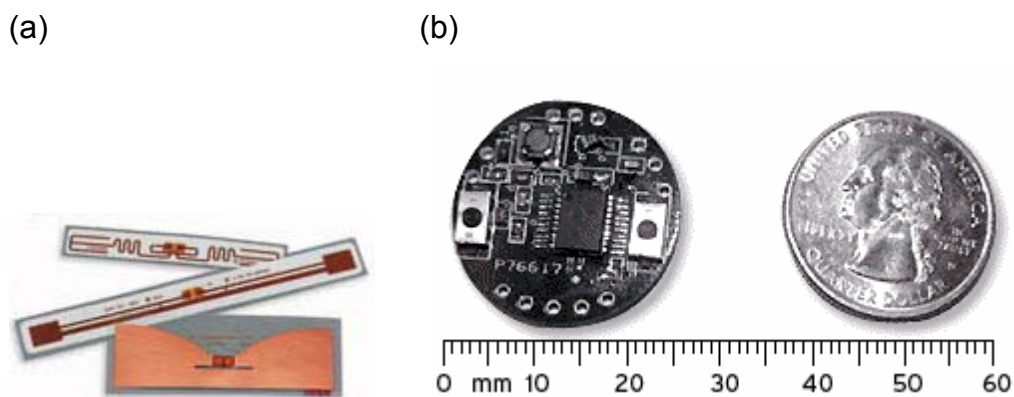
(a)   (b)

Figure 56. (a) Examples of flexible RFID passive tags. (b) "SkyeTek" mini RFID reader /16/.

In case of passive RFID tags, the reader sends out electromagnetic waves that form a magnetic field that couples with the antenna on the RFID tag, which draws power from this electromagnetic field and uses it to drive the microchip's circuits. The chip

then modulates the waves that the tag sends back to the reader and the reader converts the new waves into digital data /16/. The active RFID tags have a powersource on their own (*cf.* Chapter 5.4.1).

In Figure 57 it is shown a prototype of Philips' anti-theft sticker, which is based on integrated plastic circuit. Those anti-theft stickers are already in use for retail goods.
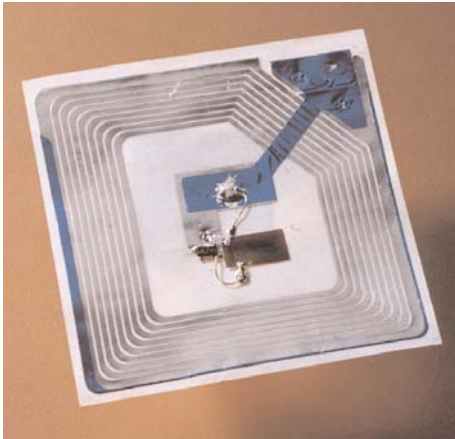

Figure 57. A prototype of Philips' anti-theft sticker based on integrated plastic circuit developed by de Leeuw and his colleagues at Philips /43/.

5.3.2 Customer Communicating Stickers and Packages

A key sector that will benefit intelligent packaging will be supermarkets with retail applications including in-store advertising and promotions, electronic shelf labels, electronic billboards. Intelligent packaging including electronic paper displays would be dynamic, which allows personalised and fresh announcements, advertisments and consumer informations and update-changes almost instantaneously at the touch of a button.

In near future visions, consumer (intelligent) packages can sence and tell its state, condition, suitable storing, for example environment, give user help and tips, recipes and recommendations for use, just to mention some. In this area it has been seen a huge development and spin-up of new allies between packaging, printing and advertisement as well component manufacture companies.

5.4 Flexible Power Sources

5.4.1 Flexible Energy Cells

An Israeli company: PowerPaper Ltd., has developed a technology that enables the mass production of low-cost, thin and flexible energy cells /16,92/. Its core technology is an innovative process that enables the printing of uncased, thin, flexible energy cells on a polymer film substrate, by means of a simple mass-printing technology and proprietary inks. The cells are composed of zinc and manganese dioxide. The cathode and anode layers are fabricated from proprietary ink-like materials so that the combination of the two creates a 1.5 V battery that can be printed on to virtually any substrate, including speciality papers.

One example of commercial products combining printable electronics and novel battery technique, is PowerPaper's PowerID[TM], a smart, active RFID label, that is thin and flexible, and contains a micro-power source, integrated circuit and antenna (*cf.* Chapter 5.3.1) /16/.

5.4.2 Flexible Dye-Sensitised Solar Cell (DSSC)

The dye-sensitised solar cell (DSSC) based on the nanoporous TiO_2 electrode is of great interest since its discovery, in 1991, by O'Regan and Grätzel /93/. Such a DSSCs are relatively low cost and have a reasonably high efficiency compared with the conventional Si or GaAs cell /31,94/. It is proved that solid hole conductors, such as inorganic p-type semiconductors (CuI and CuSCN) and amorphous organic hole conducting materials are promising materials to replace liquid electrolytes in DSSCs. Recently, many researchs are focusing on conducting polymers, for example, polythiophene, polypyrrole, PPV, PANI and their derivatives for fabrication of DSSCs. They are inexpensive and can be tailored chemically to fit a wide range of purposes. Conducting polymers with large band gap, sufficient conductivity, homogeneous surface, and small size of clusters are desirable as a hole conductor in DSSCs. With polymeric materials, it will be easier to maufacture DSSCs by roll-to-roll processes on flexible substrates (Figure 58).
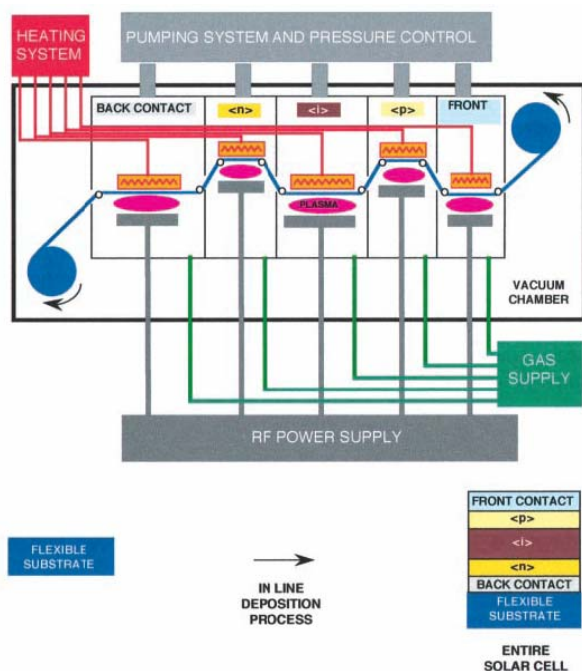
Figure 58. A principle of roll-to-roll deposition process for the deposition of amorphous silicon solar cells on flexible substrates (here, stainless steel) /94/.

5.4.3 Flexible Organic Photodiodes

As shortly mentioned in Chapter 4.2.2, Lamprecht *et al.* /72/ have reported about the fabrication of organic photodiodes deposited on ordinary newspaper sheets. The organic photodiodes they fabricated, were classical Tang -type pn-heterojunction devices /45,72/: consisting of p-type conducting copper phthalocyanine (CuPc) and n-type perylene tetracarboxylic bisbenzimidazole (PTCBI) (Figure 59). These photodiodes can be used as powersources in some optoelectronic applications.

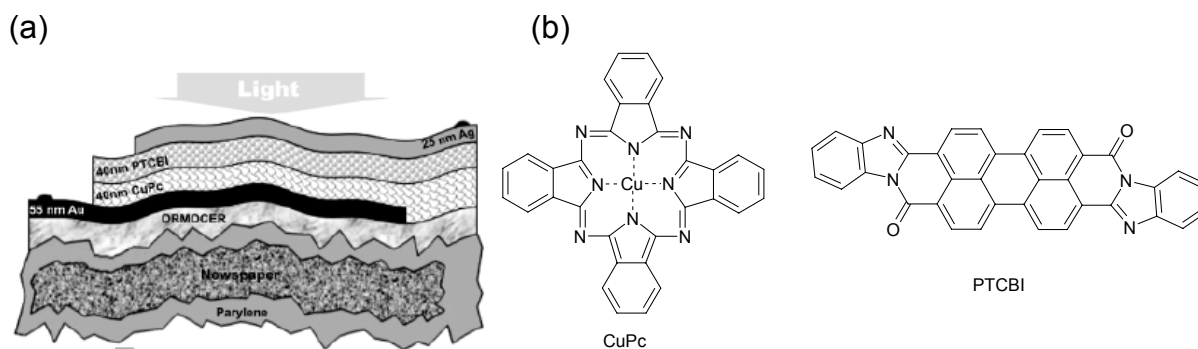(a)   (b)

Figure 59. (a) A schematic representation of the two layer photodiode configuration /72/. (b) The chemical structures of copper phthalocyanine CuPc (p-type organic semiconductor) and 3,4,9,10-perylenetetracarboxylic bisbenzimidazole PTCBI (n-type organic semiconductor).

The organic charge generating layers were sandwiched between two different metal electrodes /72/: a 55 nm thick gold (Au) bottom electrode and a semitransparent silver (Ag) top electrode with a thickness of 25 nm. The deposition of the organic as well as the metal layers was done by room-temperature vacuum sublimation in a tectra vacuum system. For reproducible growth conditions, the organic source materials were sublimed from effusion cells. The cell temperature Lamprecht *et al.* /72/ have used, was 425 °C for CuPc and 460 °C for PTCBI, corresponding to growth rates of 0.4 nm/s for CuPc and 0.8 nm/s for PTCBI. Both organic layers were evaporated without breaking the vacuum and the substrates were rotated during the.

Lamprecht *et al.* /72/ have used conventional shadow masks for all the structuring of layers. In the last process step, the semitransparent silver electrode was evaporated with a low evaporation rate, less than 0.05 nm/s, in order to avoid short-circuiting of the cells. By using a special mask, five stripes of silver were prepared to give five identical photodiodes on each newspaper substrate. The area of the Ag electrode of 10 mm^2 was determined the active device area. The completed devices were not packaged in an inert atmosphere as oxygen and moisture only weakly affect their performance. These Tang -type photodiodes show a good stability at ambient conditions and exhibit large photocurrents of the order of mA / cm^2.

The work Lamprecht *et al.* /72/ have done, demonstrates that organic electronic devices can be fabricated on a wide range of substrates, especially onto challenging paper substrates, which will lead to the real intelligent papers.

5.5 Future Application Visions

Yet it is too early to announce the eventual scope of the plastic electronics - intelligent papers – revolution /16/. Some guidelines can still be predicted: miniature low cost processors with integrated sensors and wireless communications connectivity, attaching information to everyday objects, the intelligent identification and localisation of these objects including wearable electronics, and ubiquitous inexpensive flexible displays.

For sensor applications, the conductivity of CPs can be controlled chemically, making CP nanowires also promising for ultrasensitive, trace-level biological and chemical nanosensors /28/.

In the area of medical sensors Hofmann *et al.* /95/ have reported the use of a thin-film OLED as an excitation source for microscale fluorescence detection as a first step towards a fully disposable stand-alone diagnostic microchip for determination of urinary human serum albumin (HSA). The OLED is simple to fabricate on flexible substrates, and is cheap enough to manufacture for disposable use.

Wearable electronics, which are using fabric as device substrate or wiring electronics into textiles has recently achieved increased visibility. Consequently, E-textiles will have the revolutionary ability to sense, act, store, emit and move while leveraging an existing low-cost textile manufacturing infrastructure. At the same time, systems based on flexible and smart technologies conformable to the human body will help to improve the autonomy and the quality of life of people. The use of "intelligent" materials, as such textiles, will allow the design and production of a new generation of garments with distributed sensors and electronic functions. The integration of electronic and electromechanical systems onto substrates, which are not only flexible, but also ideally conformable to the human body, represents a breakthrough in various areas of application and opens new ways in man–machine interface technology. Some visions for use, as a jacket with an embedded music player, or a jacket with sensors that monitor critical body health parameters, are beginning to be promoted by companies such as Infineon and Philips /17,19/.

Bonfiglio *et al.* /86/ have reported about the ideal candidate for realising a textile transistor: a completely flexible structure assembled starting from a transparent insulating film. In fact, the whole procedure they used, was much like TFT structure shown in Figure 60, were realised without inserting a substrate whose mechanical properties limit the flexibility of the whole structure. So the substrate can be added to the structure only after its assembly, therefore allow employing unconventional substrates as paper, three-dimensional surfaces, and textiles.
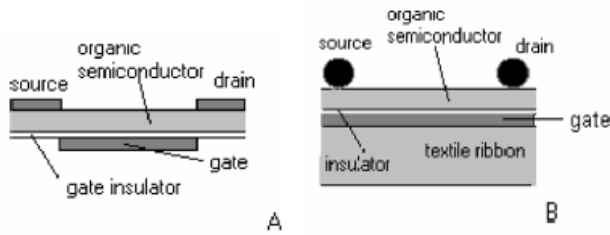
Figure 60. (a) General scheme of a top contact thin-film transistor /86/. (b) Structure adopted for the device on a textile ribbon. The gate is the metal layer deposited on the insulating film and glued to the textile ribbon. Source and drain are metal (gold) wires that cross the ribbon in fixed positions.

Bonfiglio *et al.* /86/ have gone even further; they have performed transistors made of single yarns. One of those TFTs was based on organic semiconductors, where source and drain are simply ohmic contact formed by a metal on the organic semiconductor while the channel between source and drain is formed through a charge accumulation induced by the gate (Figure 61).

Applications of such an array would mainly lie in the sensing field where external interferences partially change the electrical characteristics of the textile since polymer transistor are rather sensitive to geometrical, temperature or even light variations. In order to establish a self-contained device within the textile, piecewise conductivity and nonconductivity of threads are necessary avoiding shorts, multiple excitations of transistor gates and unwanted parallel connection of transistors.
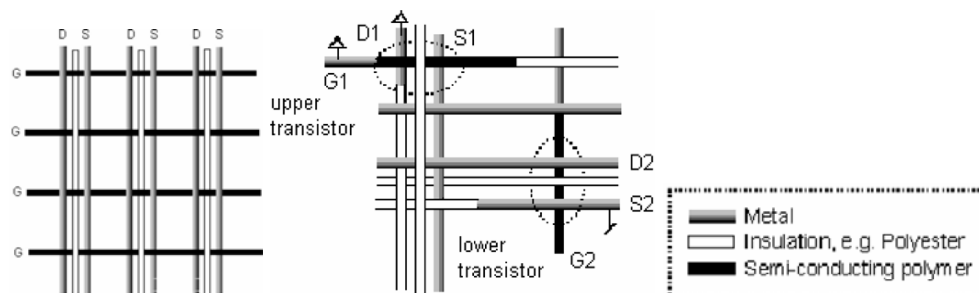

Figure 61. On the left: Transistor array structure. G and S represent textile ribbons with the gate contact and the organic semiconductor. On the right: Example of a ring oscillator structure. This structure implies the implementation of different conductivity properties (insulating, metal and semiconductor) on the same yarn /86/.

Flexible, paper like display applications will include, in addition, simple smart cards, greeting cards, interactive posters, ultra-large screens for sports stadiums and public information, dynamic displays electronic and changeable signs, watches, calculators, smart phones, video phones, displays for television sets and laptops, video displays, etc. (Figure 62) /2,17,96/. Further, when combined with transparent TFTs display functions can be integrated even for example on the windscreens of cars.
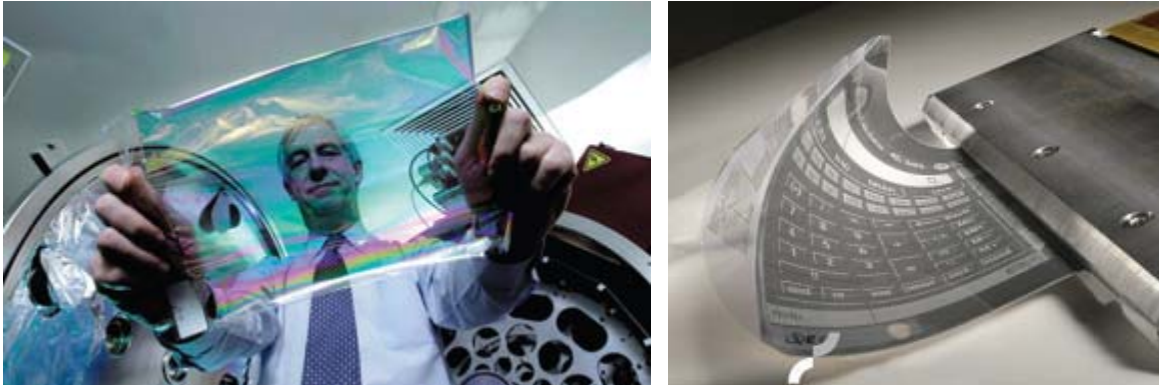

Figure 62. Paper-thin, flexible films can be used to generate images electronically and thus could spawn roll-up television and computer monitors /16,96/.

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7 List of Appendix

1. Bäcklund et al. /44/ manufacturing of all-polymer TFT

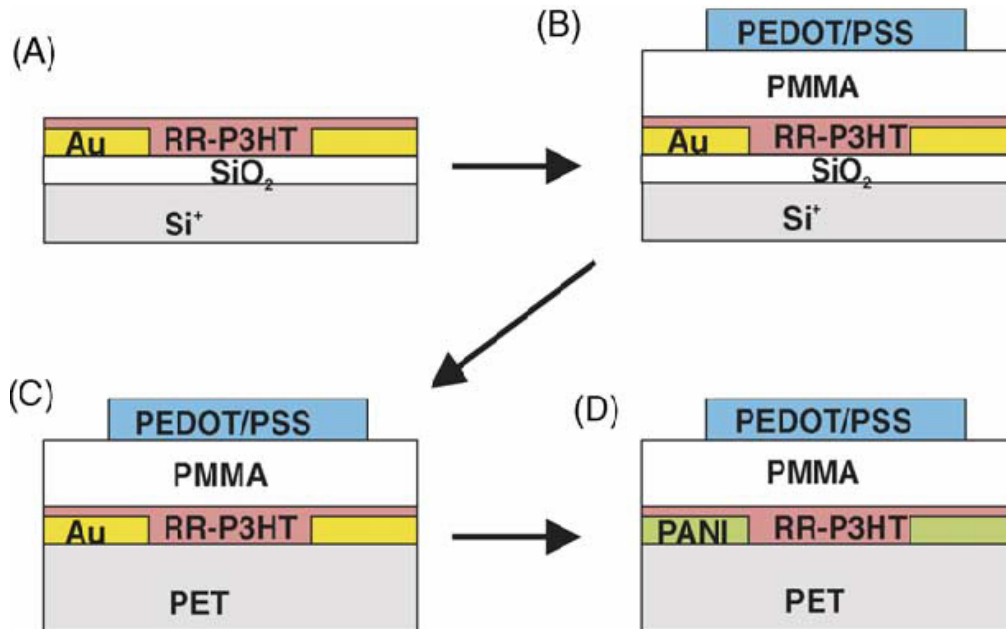## Bäcklund et al. /44/ manufacturing of all-polymer TFT:

Figure 1. Device A was fabricated with only an organic semiconductor and B is the same as A with an additional organic insulator layer and a gate electrode on top /44/. Device C is similar to B, with the silicon substrate replaced with a PET film. The all-polymer device D is of the same device structure as C, using PANI as the source and drain electrode material.

The standard organic field-effect transistor (OFET) structure is an inorganic substrate with an inorganic insulator using metal source–drain electrodes. In this study the starting point was a doped silicon substrate with a 300 nm silicon dioxide layer and patterned gold source and drain electrodes. The silicon dioxide surface was treated with hexamethyldisilazane (HMDS) to modify the surface energy, and the contact angle on HMDS treated silicon dioxide was larger than 90°. It has been shown that the HMDS treatment improves the insulator–semiconductor interface leading to higher field-effect mobility and also improved device stability. The performance of device A serves as a reference to the performance of the devices using polymer insulators, substrates and electrodes. Device B uses the inorganic doped silicon with

silicon dioxide (Si$^+$/SiO$_2$) as substrate, with the FET employing an organic insulator, poly(methyl methacrylate) (PMMA), and a gate of poly(3,4-ethylenedioxythiophene) poly(styrenesulphonate) (PEDOT:PSS). The substrate material was substituted to a flexible poly(ethylene terephthalate) (PET) film for device C with vacuum evaporated gold source–drain electrodes. The source and drain electrodes of the final all-polymer FET, device D, were patterned from polyaniline films on PET substrates. The active material, RR-P3HT, was spin-coated at 1000 rpm for devices A, B, and D but device C was spincoated at 2000 rpm in a dry nitrogen atmosphere from a 2 mg / ml p-xylene solution, and dried at 70 °C for 20 min on a hotplate to remove residual solvent from the film. The organic insulator, PMMA, was spin cast at 2000 rpm in a dry nitrogen atmosphere from a 50 mg/ml ethyl acetate solution and dried on a hotplate at 70 °C for 20 min. Both the RR-P3HT and the PMMA solutions were filtered with a 0.2 µm filter after dissolving the material. Devices A and C have gold source and drain electrodes vacuum evaporated using a shadow mask to define the transistor channel. Device B has predefined interdigitated gold source–drain electrodes on a doped silicon substrate with SiO$_2$ insulator. The organic gate electrode was made with top gate geometry in air from a water dispersion of PEDOT:PSS, after the surface of PMMA was briefly treated with oxygen plasma to make it hydrophilic. Devices were reintroduced into the nitrogen atmosphere after fabricating the gate electrode, and further annealed in order to remove the moisture from the structure after which the device was measured. UV lithography process parameters are:

1. Spin coating electrically conducting PANI (3000 rpm) and curing of the spin-coated PANI films at 120 ºC for 15 min.

2. Spin coating the adhesion promoter HMDS (1500 rpm, 35 s) and spin-coating the positive photoresist (AZ5214E) layer (4000 rpm, 35 s) and curing of the resist (90 ºC, 20 min).

3. Exposure with UV-light through the shadow mask (275 W, 13 s).

4. Development (AZ351 mixed 1:3 deionised water) of the resist (45 s at room temperature).

5. Etching the deprotonated PANI (reactive ion etching (RIE) 30 s, O$_2$).

Removal of resist by flushing with isopropanol and water.