

# Organic and Printed Electronics

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# OPE course content and schedule

Dates	Lectures	Lecturers
20.02	<b>Introduction</b>	D. Briand
27.02	<b>Physics of printing I</b>	V. Subramanian
06.03	<b>Physics of printing II</b>	V. Subramanian
13.03	<b>Materials for large area electronics</b>	V. Subramanian
20.03	<b>Thin film transistors fundamentals</b>	V. Subramanian
27.03	<b>Thin film transistors devices &amp; Circuits</b>	V. Subramanian
03.04	<b>Organic light emitting diodes</b>	V. Subramanian
10.04	<b>Solar cells</b>	V. Subramanian
17.04	<b>Flexible and printed sensors</b> 	D. Briand
01.05	<b>Energy storage &amp; Encapsulation</b>	D. Briand
08.05	<b>Integration &amp; Smart Systems</b>	D. Briand
15.05	<b>Sustainable electronics</b>	D. Briand
22.05	<b>Case study</b>	D. Briand

## LESSON 08 – FLEXIBLE AND PRINTED SENSORS

*Dr. Danick Briand*

Reference book 2<sup>nd</sup> ed. on OPE: Chapter 9

## Objectives

- Identify most common sensors implemented using printing: principle, materials, processes

## Content

- Printed sensors: operating principle, materials and processing
  - Physical sensors
  - Chemical sensors

## What is a sensor?

**“A sensor is a system able to respond to a stimulus (heat, movement, moisture...) and provide a measurable response (usually consisting of an electric signal).**

**Such response is used as for measurement or operating a control.”**

*Smart sensor systems*, G.C.M. Meijer (John Wiley and Sons, 2008) ISBN: 0470866918.

## Classification of sensors according to the nature of the input signal\*:

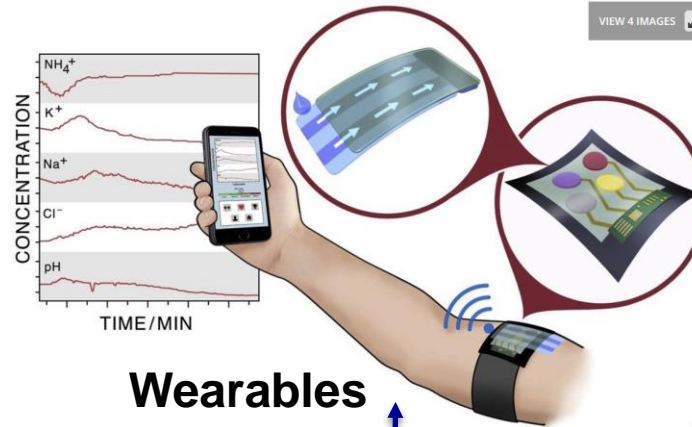
- **physical sensors: able to detect physical signals (heat, electromagnetic signals, mechanical signals...).**
- **chemical sensors: able to detect specific chemical species.**

*\* A Sensor Classification Scheme*, R. M. White, IEEE TRANSACTIONS ON ULTRASONICS, FERROELECTRICS, AND FREQUENCY CONTROL, VOL. 34, NO. 2, 1987.

# Domains of application



Smart Packaging

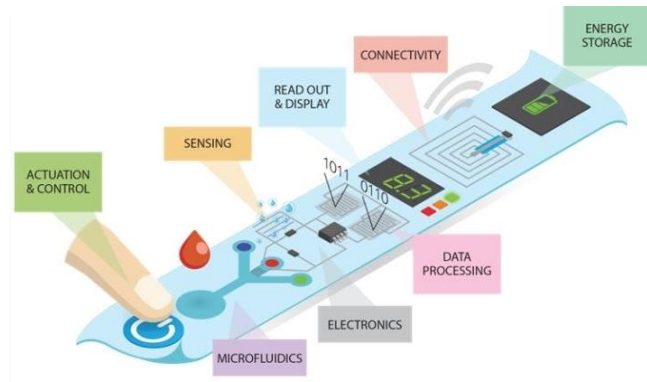


Wearables



Human Interface /  
Consumer Electronics

## Printed sensors & microsystems



Point-of-Care Diagnostics



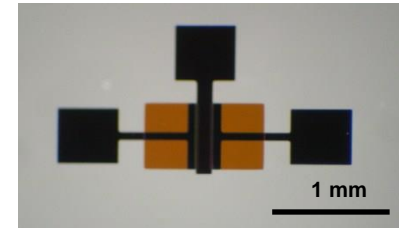
Environmental /  
Agriculture Sensors



Internet of Things

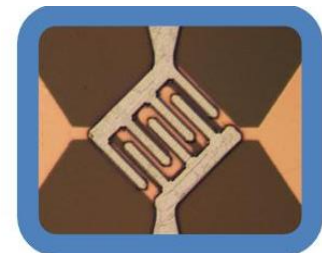
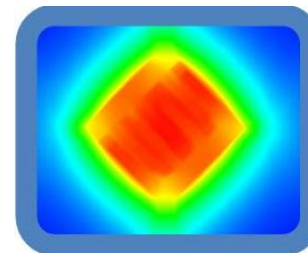
- **Transducing principles**

- Capacitive
- Resistive
- Field-effect
- Electrochemical
- Optical
- Thermal



- **Potential transducers**

- Capacitor, resistor
- OLED, Photodetector
- Diode, Transistor
- Heater
- Resonator ?



- **Main market: printed strip tests for glucose sensing**
- **Strain gauge, Pressure / Touch sensors**
- **Photodetectors / Radiation sensors**
- **Temperature & Humidity**
- **Recording electrodes (EEG, ECG, EMG...)**
- **Electrochemical sensors (ions, metabolites...)**

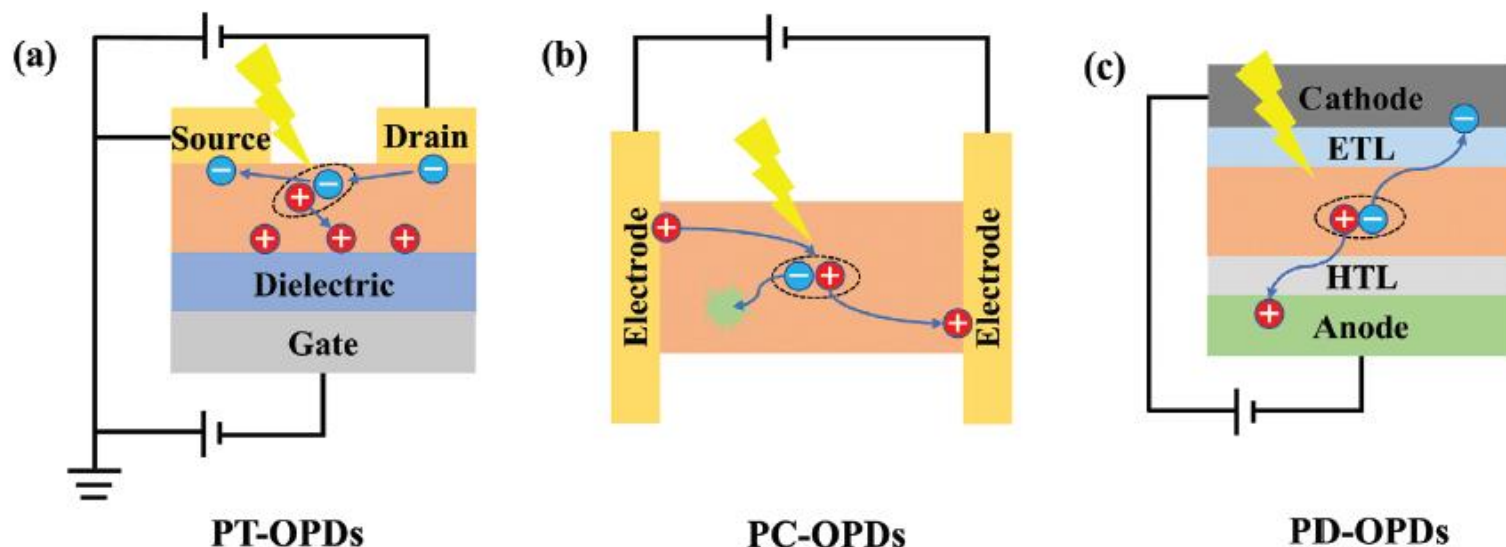
**Other types at the R&D level with a vision of printed devices**

- **Biosensors**
- **Gas**
- **3D printed**

**Physical sensors using mechanical moving parts such as accelerometers, resonators have been tried out, with no real success.**



## Architectures for Organic Photodetectors (OPDs)



- **Phototransistors (PT)**: an additional photoconductive gain can be realized by using the three-terminal structure and applying an additional electrical bias
- **Photoconductor (PC)**: simple structure to implement, very high EQE possible by photomultiplication effect (PM), limited in performances like low S/N ratio in some cases
- **Photodiodes (PD)**: extraordinary property in photosensitivity and photoresponsivity, but lower EQE due to inevitable charge recombination

## Organic Photodiodes

Development of Organic Semiconductor Photodetectors:  
From Mechanism to Applications. *Adv. Optical Mater.* 2019, 7, 1800522  
DOI: 10.1002/adom.201800522

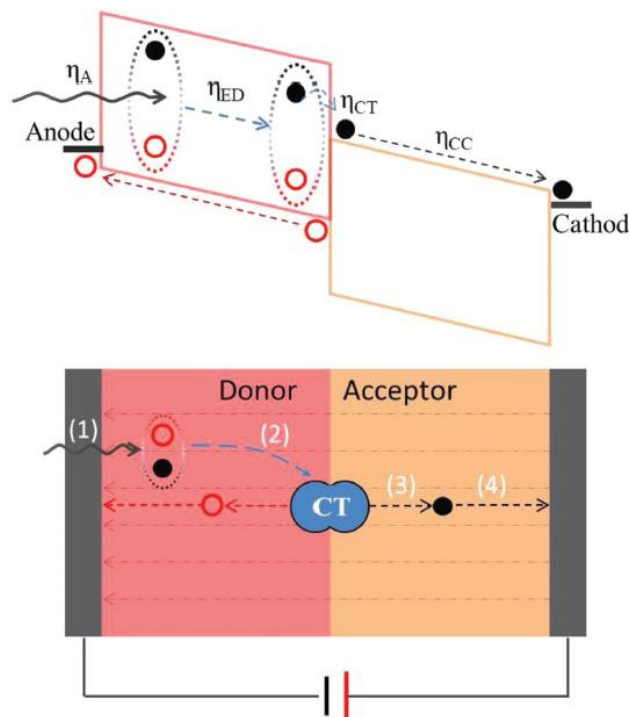


Figure 1. Working principle of OPDs.

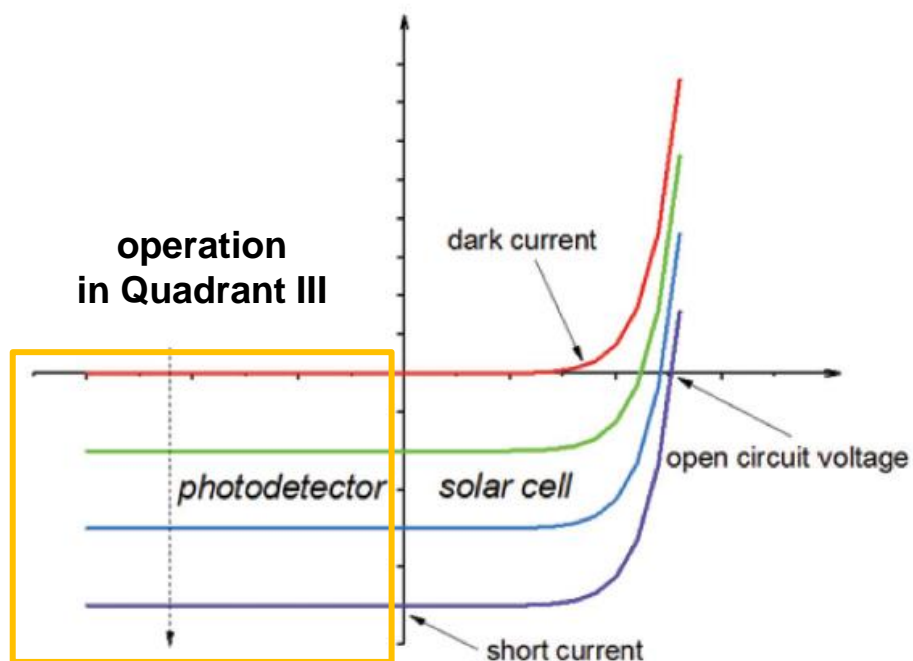
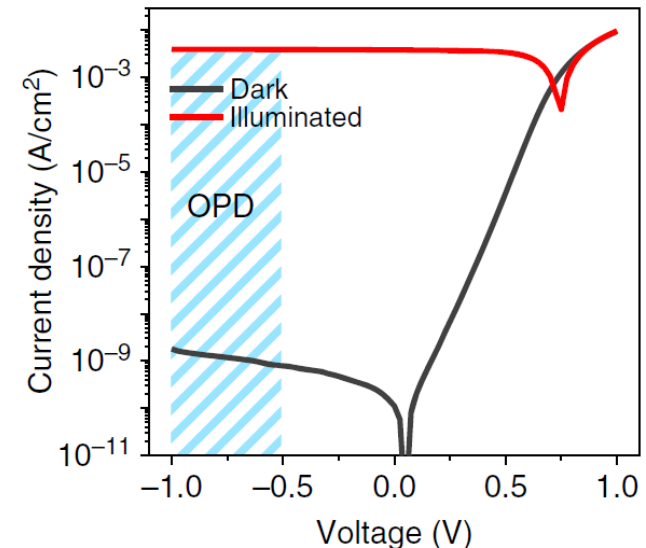
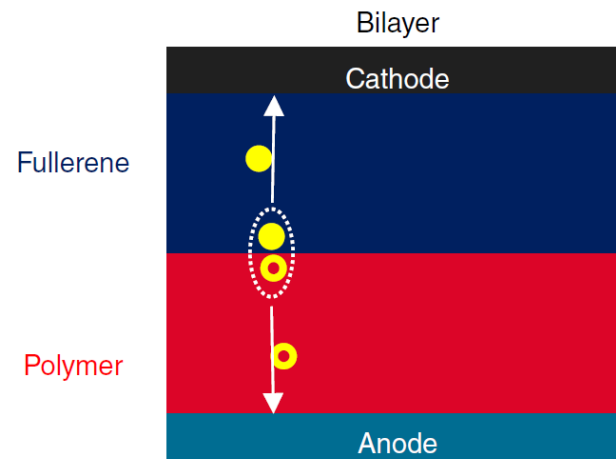
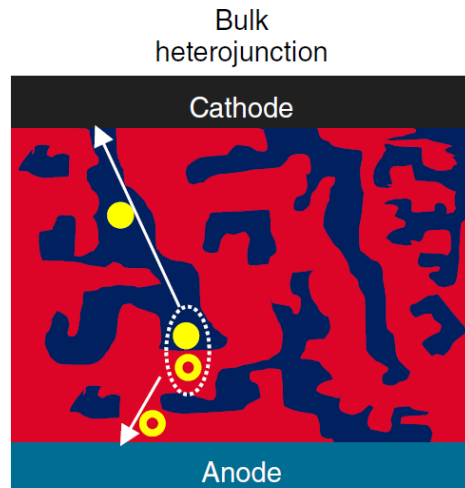


Figure 2. Relationship between the current and voltage of organic photodetectors and organic solar cells in a Cartesian coordinate system.

- 1) the generation of excitons from photon absorption;
- 2) the diffusion of the generated excitons to the interface between the donor and acceptor to produce charge transfer excitons;
- 3) the separation of charge transfer excitons into free charges at donor/acceptor interface;
- 4) the collection of free charges at the electrodes.

## Organic Photodiodes

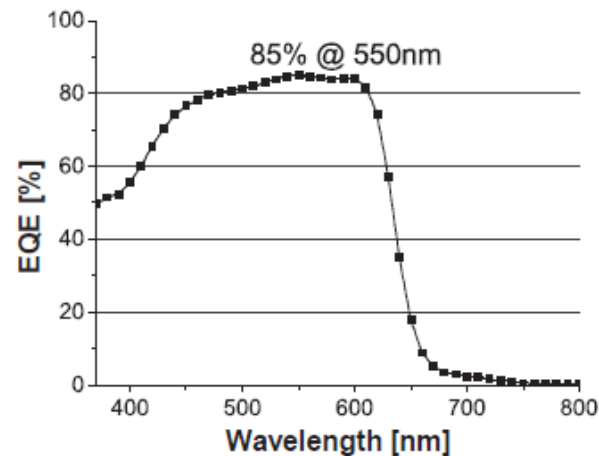
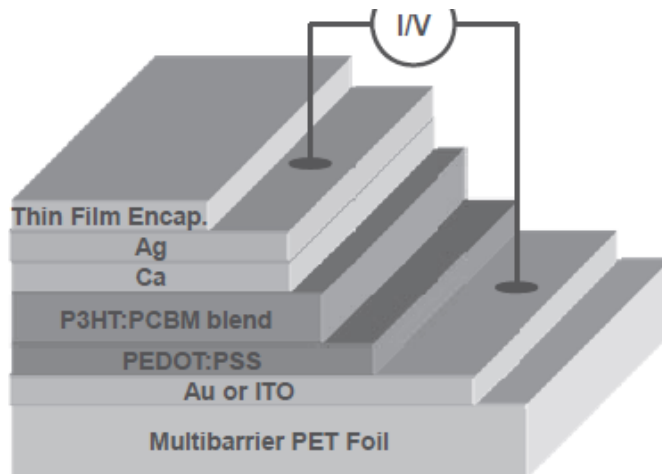
$$\text{EQE}(\lambda) = \frac{hc}{q\lambda} \times \frac{I_{\text{ph}}}{\phi_{\text{opt}}}$$



- Bulk heterojunction for higher exciton heterojunction efficiency;
- Reversely biased for charge collection;
- $I$ - $V$  curves are typically shown in log scale, in order to visualize both the dark and illuminated current;
- At this reverse bias, the photocurrent is in principle directly proportional to the incident light flux.

Solution-Processable Components for Organic Electronic Devices -  
2019 - Ulanski – Chapter 10: Solution-Processed Organic Photodiodes

- Screen / inkjet printed organic heterojunctions (photodiodes)
  - Large area image sensors
  - Touchless pads / screens
  - X-ray detectors
  - Detectors for titer plates

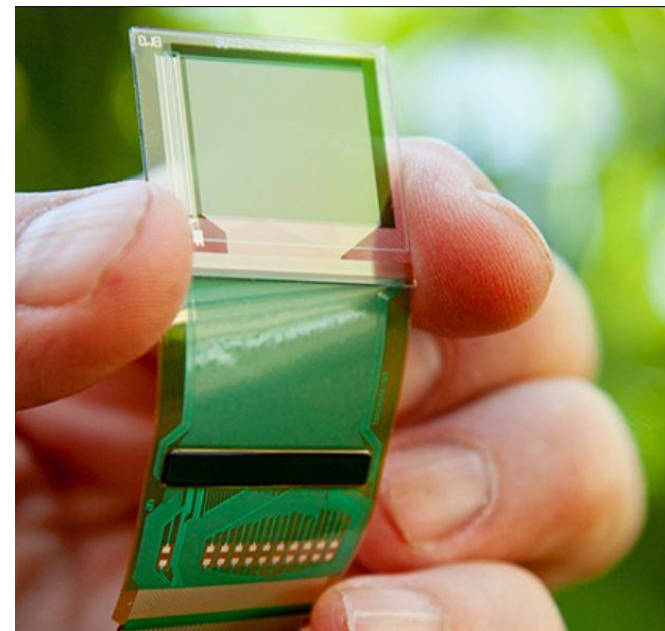
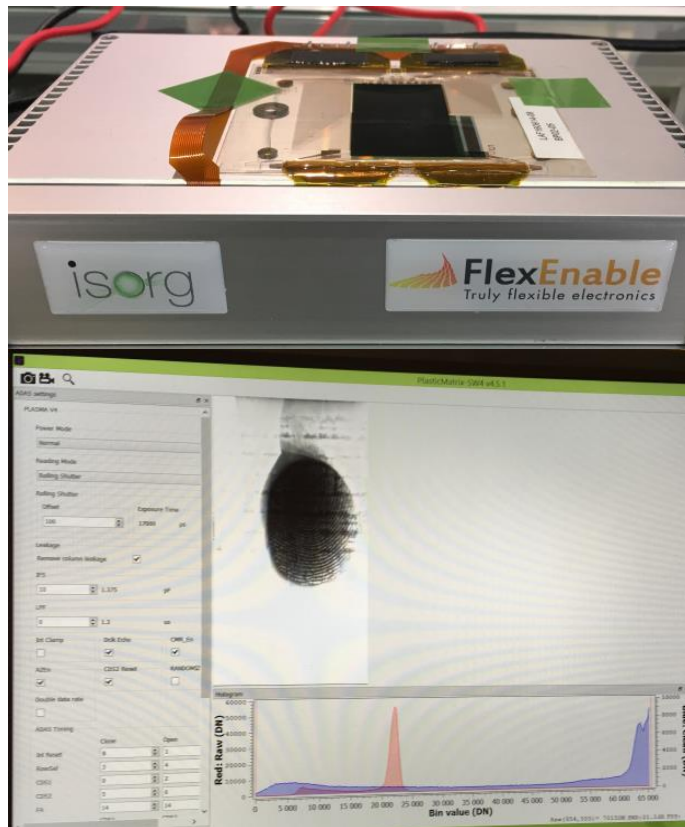


From Siemens

External Quantum Efficiency (EQE) is the ratio of the number of charge carriers collected by the photodetector to the number of photons of a given energy

# Photodetector finger print sensors

- **Finger print and vein sensor from ISORG (France)**
  - 500 DPI photodiodes on OTFTs backplane for matrix addressing
  - 300 um thick
  - Can be printed on top of foil, glass, CMOS chips

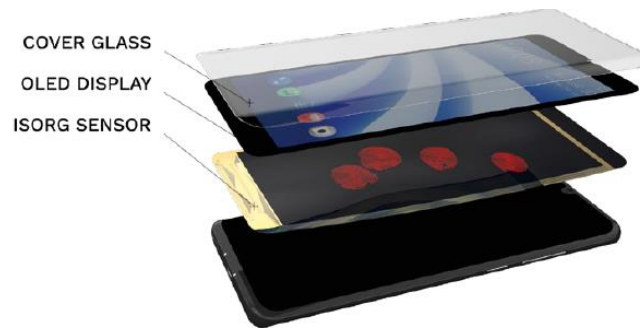


<https://www.youtube.com/watch?v=jLoMWWYDVH4>

<https://www.youtube.com/watch?v=XTuFrKBJHTA>

# Photodetector finger print sensors

- Multi-finger size design. From 1 to 4 fingers
- Work indoor and outdoor condition
- Better performance in humidity than capacitive sensor

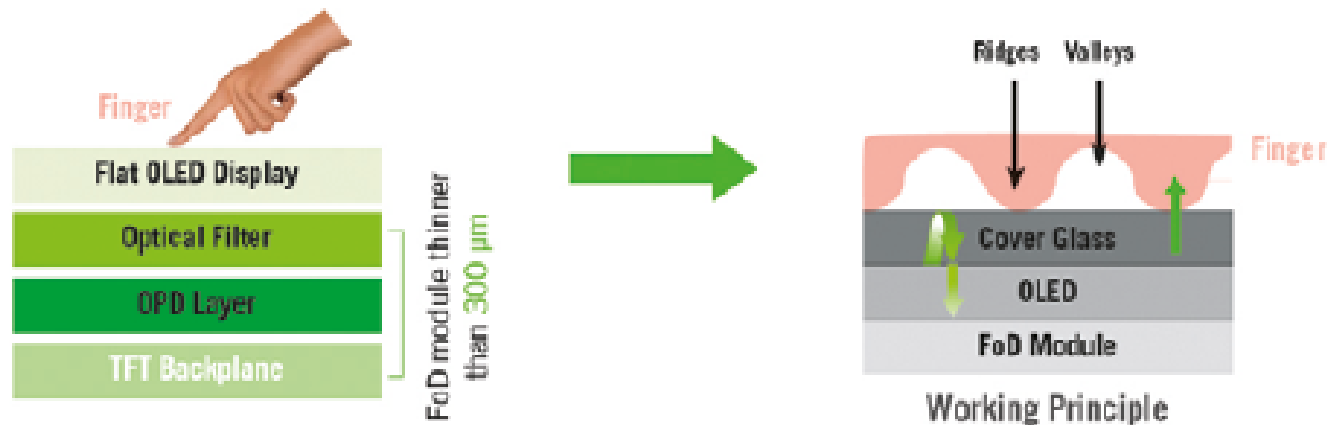


## Finger on Display (FoD) from ISORG

Display light is:

- Absorbed by the ridges
- Reflected on the valleys location

## FoD Module Stack Structure





# Pressure sensor

- **Screen printed Force Sensing Resistor (FSR)** composite with a conductive (i.e. carbon or metallic nanostructures) and a non-conductive component (i.e. silicones, polyurethanes).
- As deposited, only a few conductive traces across the conductive particles (Fig. 2a) exist, allowing current to pass through the otherwise non-conductive polymer. This leads to an internal electrical resistivity of an unloaded sensor of multiple kilo to mega ohms.
- Through the application of a force (Fig. 2b), the layer compresses and an increasing number of conductive paths emerge. The specific resistivity of the FSR drops and thus the resistance of the device, which correlates to the applied force.

Conduction channel thanks to a percolation path between the conductive particles (few % in loading)

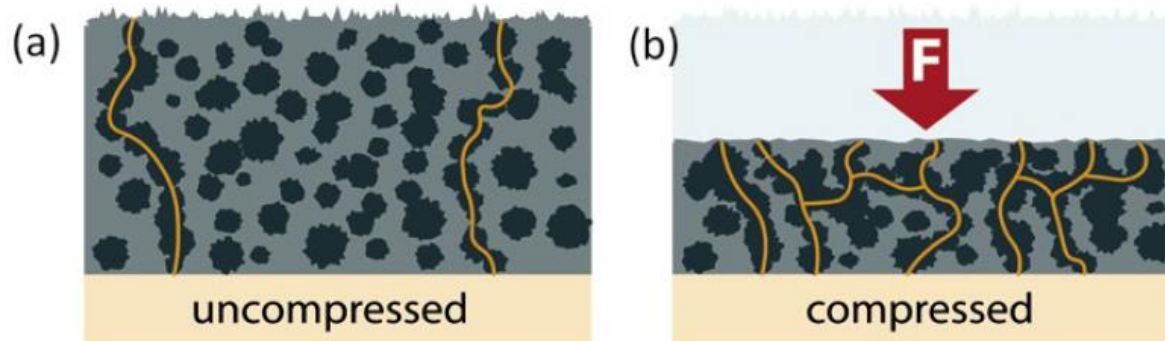
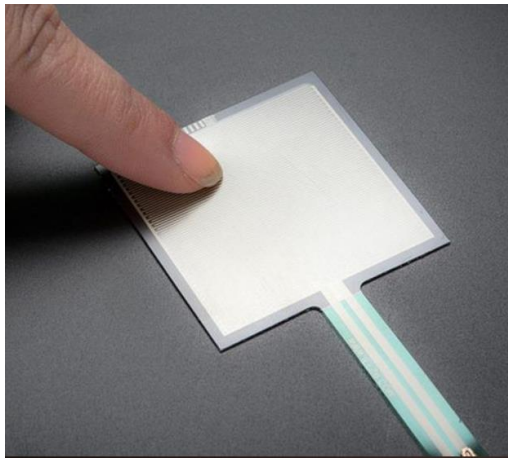


Fig. 2: Working principle of an FSR pressure sensor (a) in the uncompressed situation and (b) in the compressed situation. Black regions are conductive particles and grey regions are non-conductive compounds. Yellow traces are conductive paths bridging the entire material.

# Pressure sensor

- The force-resistance correlation can be tuned by different mixing ratios of the conductive (few %) and insulating compounds and with that, also the characteristics of the sensors, regarding their actuation force (lowest detectable force), and measurement range (lowest to highest measurable force).
- The size of a single FSR sensor varies from less than  $1\text{mm}^2$  up to several centimeters squared. By combining multiple sensors on one substrate, a sensor matrix, which allows for spatially resolved force or weight measurements, can be built.



**Square Force-Sensitive Resistor, Adafruit sold on Distrelec**

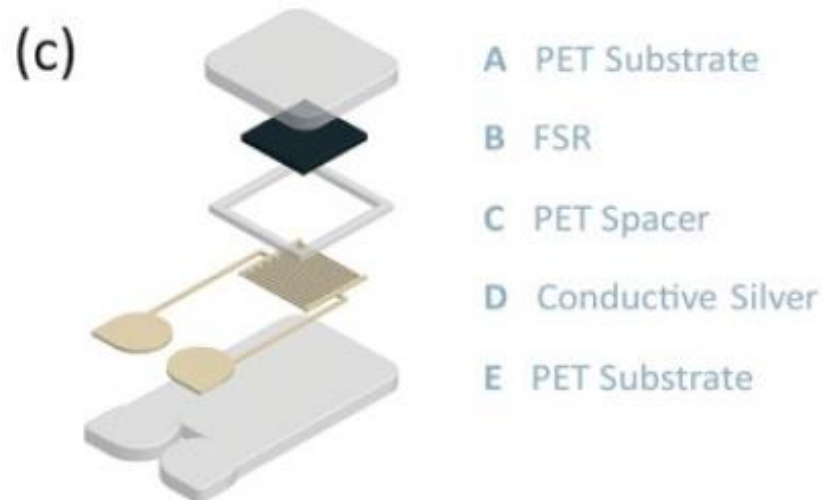


**Kytronix MS9711 large area FSR matrix array sensor has 576 force sensing nodes by using 24 columns and 24 rows and is designed for true force and multi-touch detection.**



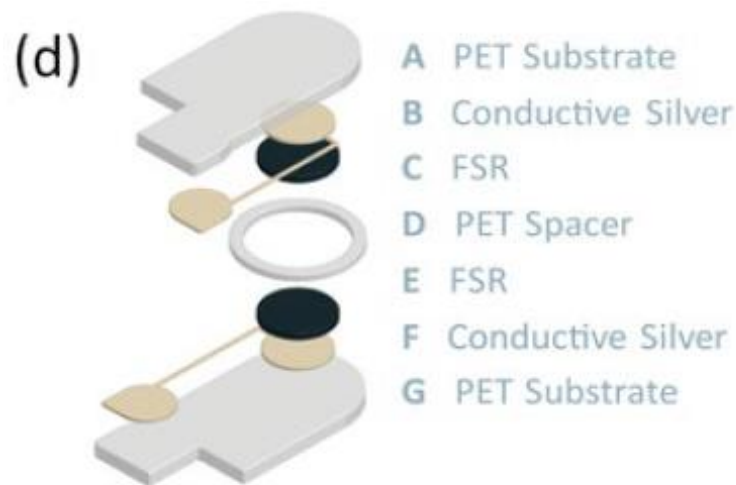
# Pressure sensor

- FSR sensors are manufactured in two basic configurations: namely the shunt-mode (Fig. c) and thru-mode (Fig. d).
- A shunt-mode sensor** consists of a bottom substrate with interdigitated electrodes made from printed, conductive silver ink, and a top substrate with a printed FSR layer.
- By applying a force, the FSR material shortens the silver electrodes, which allows a current to flow.
- Shunt-mode sensors have a large dynamic range and are typically used for less sensitive applications.



# Pressure sensor

- In a **thru-mode sensor** (Fig. 2d), the silver electrodes are printed onto both substrates over the entire area of the final sensor. In a second processing step, the FSR is printed on top of the silver electrodes.
- Thru-mode sensors are more responsive to small forces compared to shunt-mode sensors.
- With electrodes physically separated on two opposing substrates, the risk of electrical shorts between the electrodes is eliminated and sensor sizes of less than 1x1mm are possible.



# Pressure sensors

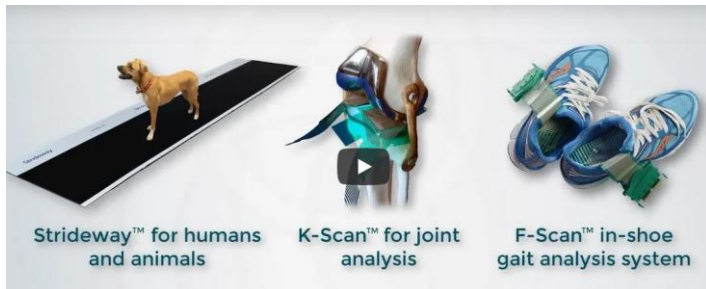
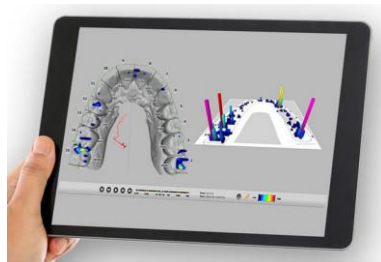
- Some applications



Photo courtesy of Bonbouton



Seat occupancy detection and screen printed car seat heaters from IEE sensing

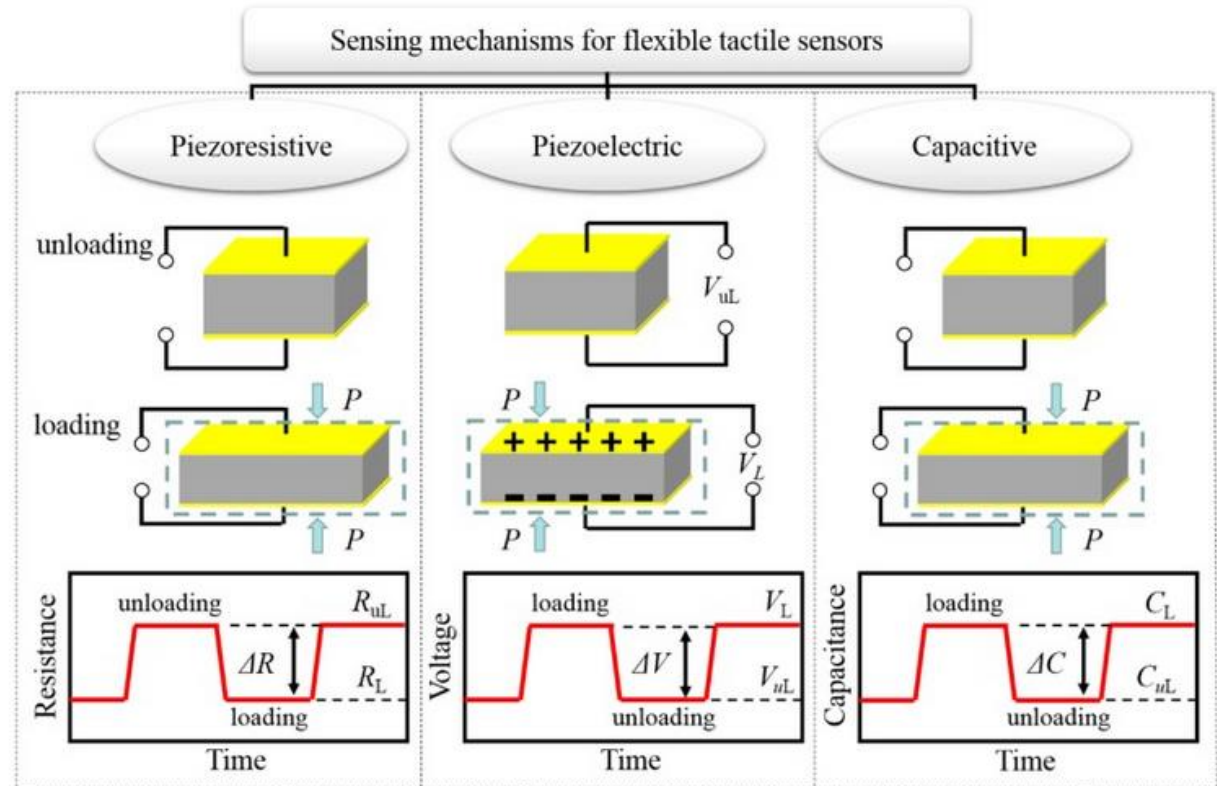
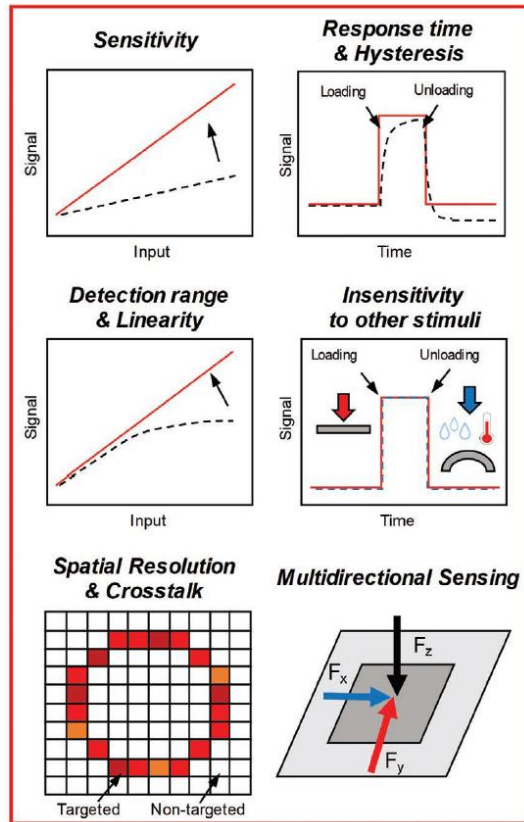


Tekscan dentistry occlusion system + biomechanics sensors



Fig. 3: The showcase of InnovationLab demonstrates the diverse applications of printed electronics with the example of printed pressure-sensor arrays.  
(a) Floor mat for motion detection,  
(b) smart shelves,  
(c) digital occlusion control OccluSense, by Bausch  
(d) smart bed

## Characteristics and sensing mechanisms



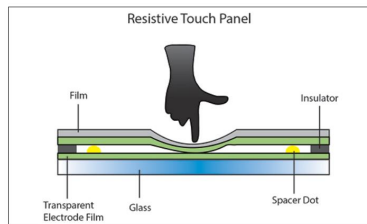
*Adv. Mater.* **2021**, 2005902, DOI: 10.1002/adma.202005902

3D Printing Technologies for Flexible Tactile Sensors toward Wearable Electronics and Electronic Skin, *Polymers* **2018**, 10(6), 629;

# Touch sensors

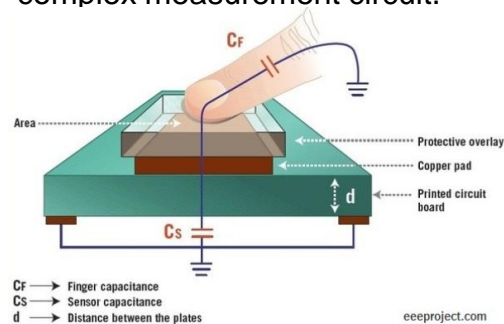
## Resistive

- Transduction of external pressure into a change in electrical resistance.
- Resistive sensors rely on the change in contact resistance.
- Resistive tactile sensors comprise active materials sandwiched between two opposing electrodes or stacked on a pair of in-plane electrodes.
- When pressure is applied, the contacts between conductive materials in a porous matrix or the contact area between the conductive materials and electrodes increases, thereby considerably decreasing the resistance.
- Resistive tactile sensors have advantages such as high sensitivity, simple device structure, and a facile fabrication process.
- However, high power consumption is regarded as drawbacks.



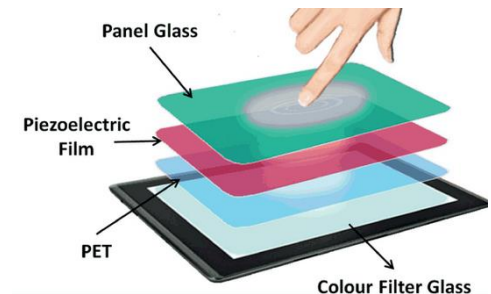
## Capacitive

- Common mechanisms used in tactile sensing for normal and shear forces.
- Typically fabricated by sandwiching a dielectric layer or leaving a gap between two parallel electrodes.
- The capacitance of tactile sensors can be changed under pressure owing to the geometrical changes.
- Dielectric layers: various elastomers with a low modulus, PDMS, polyurethane, and Ecoflex have been explored.
- Capacitive tactile sensors exhibit low power consumption, temperature independence, and stability against long-term signal drift.
- However, highly susceptible to electromagnetic interference and complex measurement circuit.



## Piezoelectric

- Piezoelectric sensors typically consist of two parallel electrodes and a piezoelectric material between them.
- External pressure causes the piezoelectric material to deform.
- The deformation results in a change in the dipole density, which leads to a voltage generation.
- Tactile sensors based on PVDF and its composite provide mechanical flexibility, ease of fabrication, and low cost of PVDF.
- Piezoelectric tactile sensors exhibit high sensitivity and excellent dynamic response
- In contrast, the detection of static pressure is limited because the piezoelectric effect occurs only when the applied stimuli change.

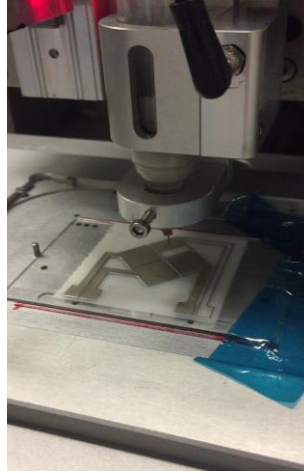
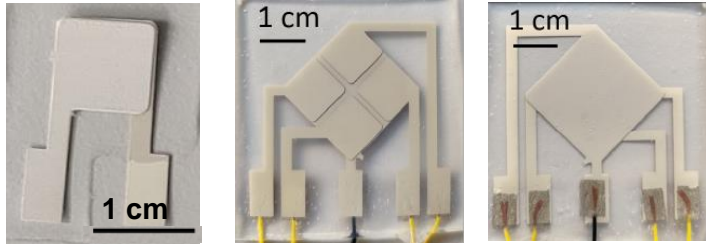




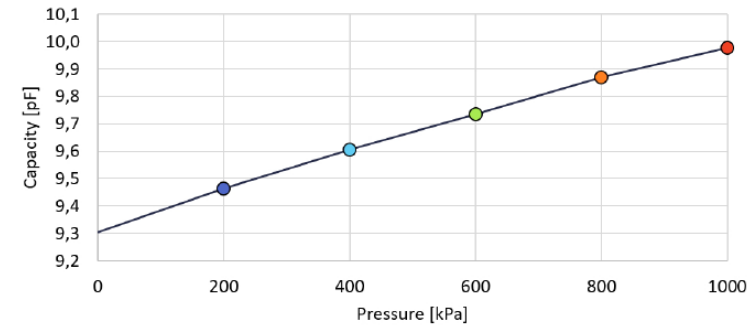
# Printed touch sensors

## Capacitive + piezoelectric sensors

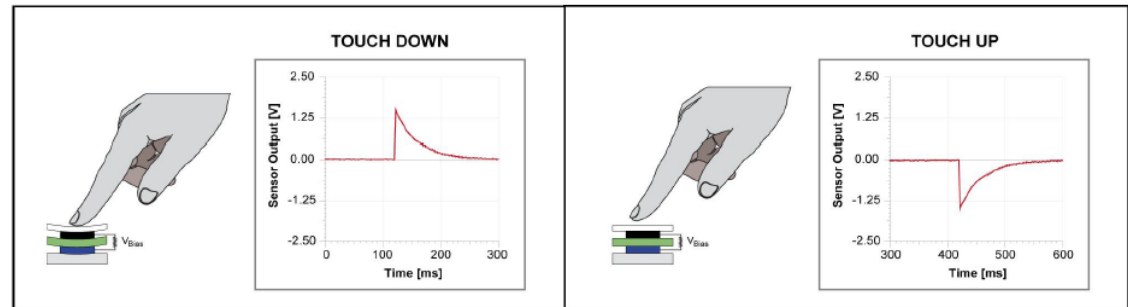
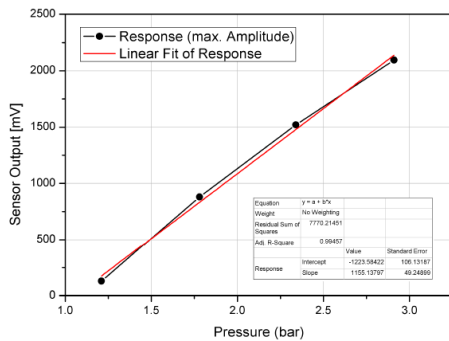
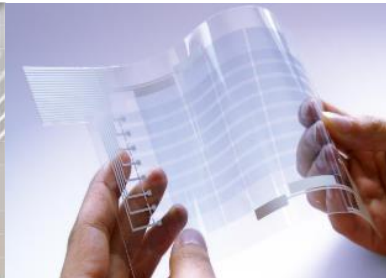
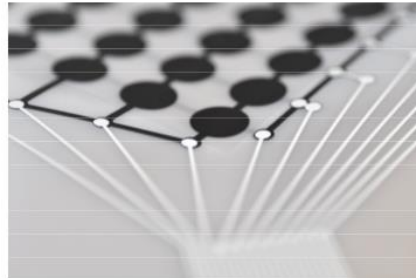
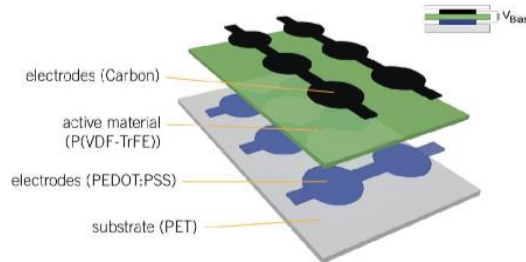
D-SENSE SFA project, D. Briand EPFL-LMTS



- Normal and shear force capacitive sensors
- 3D-printed by Direct Ink Writing (DIW)
- Parallel plate silver electrodes with silicone composites dielectric film and substrate

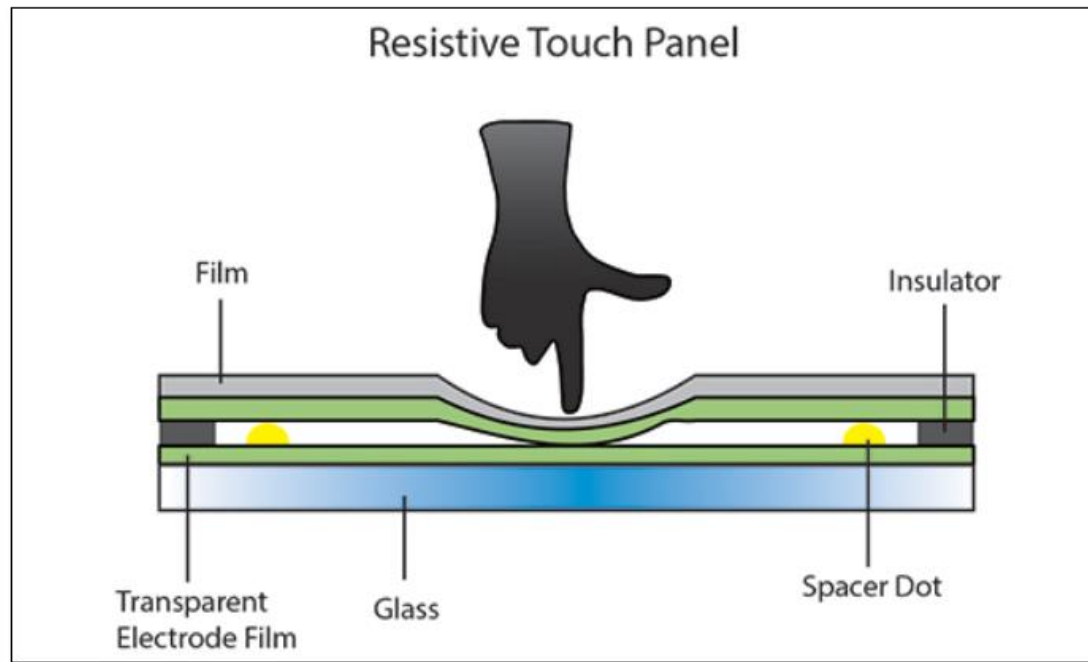


Pyzo Flex® screen printed piezoelectric sensors, JRF Austria



# Resistive touch panel

- They work by combining two conductive electrode layers separated by very small transparent insulation spacers also known as spacer dots.
- When pressure is applied from a finger or stylus it brings the two layers into contact (*See Figure below*).
- This results in a drop in voltage at the contact point which is then detected by a controller.



# Touch sensor from PolyIC

- PolyTC® films can be used for resistive as well as for capacitive touch sensors and touch controls



## Advantages and Features of PolyTC® Touch Screens

- Thin and flexible on PET substrates
- High optical transparency due to transparent substrate
- High and individually adjustable electrical conductivity due to metallic circuits (metal mesh)
- Mass production in a roll-to-roll process
- Individually customizable layout and sensor systems possible

From PolyIC in Germany



## Roll to roll production

- ❑ Typical substrate PET
- ❑ Substrate thickness 50 $\mu$ m
- ❑ Web length up to 5 km
- ❑ Web width 0.65m
- ❑ Layout width up to 0.6m
- ❑ Web speed > 30m/min

## Multi-layer setup for touch sensor applications

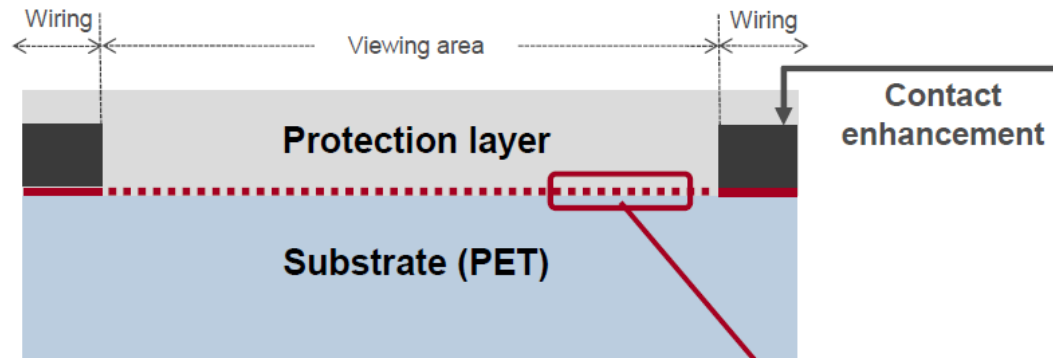
- ❑ PolyTC® metal layer thickness: < 100nm
- ❑ Thickness of additional layers: 50nm up to several  $\mu$ m
- ❑ Minimum structures size: ~ 10 $\mu$ m ➡ **Gravure printed**



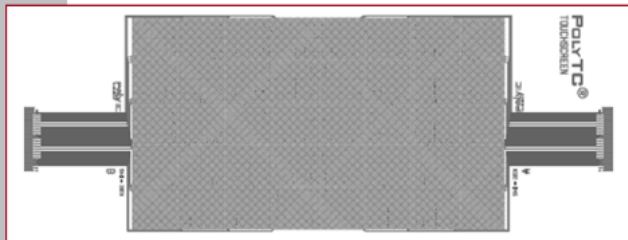
# Touch sensor from PolyIC

A **resistive touchscreen** panel comprises two thin, transparent electrically resistive layers facing each other and separated by a thin space. One layer has conductive tracks with 90° of rotation compared to the other (form a grid). A voltage is applied to one layer, and sensed by the other. When an object, such as a fingertip or stylus tip, presses down onto the outer surface, the two layers touch to become connected at that point, resulting in a current flow. The point of contact is identified by detecting this change in voltage.

## High quality multilayer setup for R2R printed touch sensors

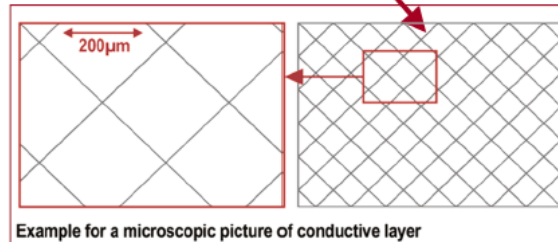


Individual layout including tail, traces and contact enhancement possible



© PolyIC 2013

PolyTC®  
Metal layer with min. 10µm resolution



Narrow silver lines provide good transparency

11

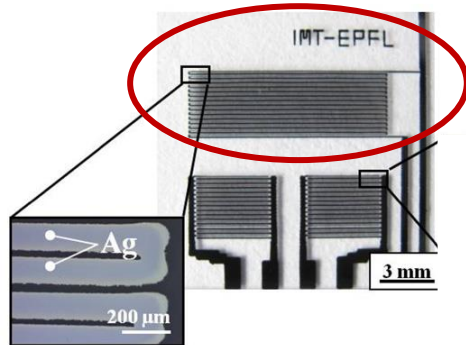
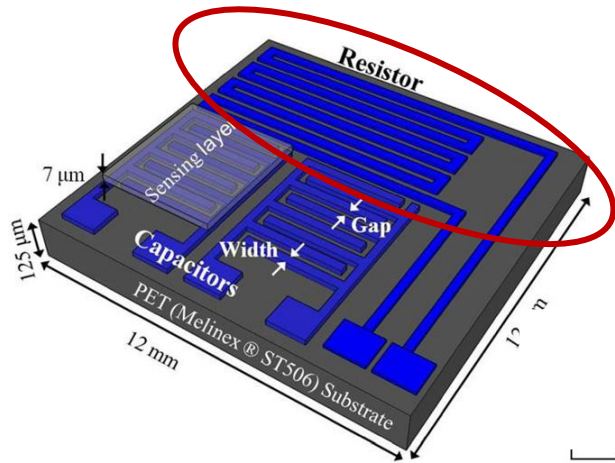
# Touch sensor from PolyIC



Property	Typical value
Substrate	PET (typically 50µm)
Overall sensor thickness	~ 50µm – 75µm (depending on layer setup; customized)
PolyTC® conductive material	Metal mesh (Ag or Cu)
Resolution of metallic structures	~ 10µm
Width of wiring	~ 50µm
Sensor layout	Customized
Form of delivery	Single sensors or transparent conductive film on roll

Specifications	Typical Values
<b>Electrical</b>	
Conductivity	20 – 100 Ω/sq (depending on transparency)
Connector pitch	0.5 – 1.0mm
Point accuracy	0.4mm (Layout optimized; as a result of high conductivity)
Linearity (@9mm Finger)	1.5mm (compared to 2.4mm for ITO sensors)
Multi-touch capability	> 5 fingers possible
<b>Optical*</b>	
Transparency	80% - 90%
Haze	1.80% +/- 0.10%

## Inkjet-printed resistors for temperature measurements

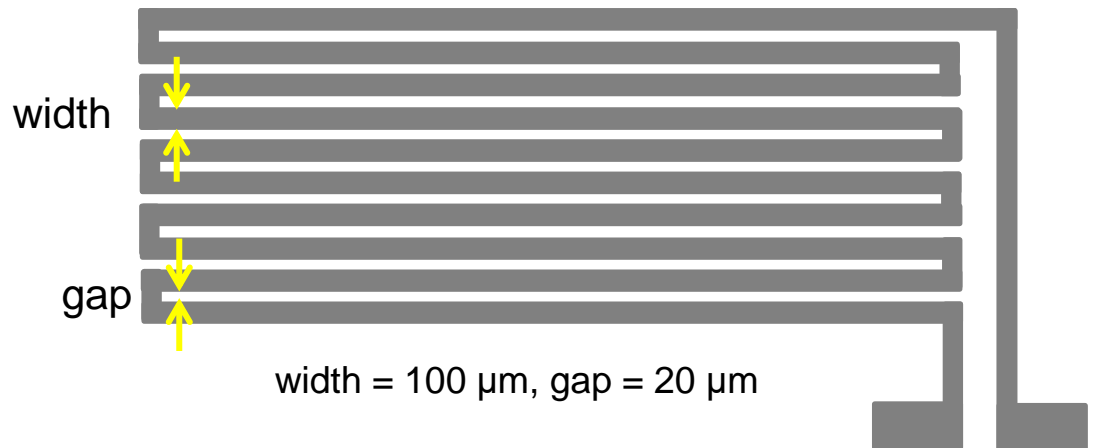


**Substrate: PET films 125  $\mu\text{m}$**

- Meander-shaped metallic resistor

**Deposition techniques:**

- inkjet-printing of Ag
- electrodeposition of Ni with higher **temperature coefficient of resistance (TCR)**;

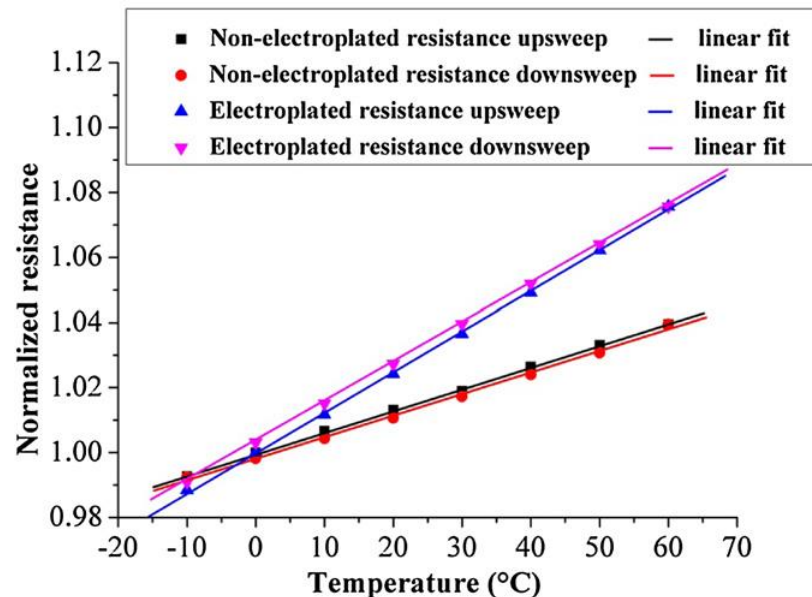


F. Molina-Lopez et al., "Large area compatible fabrication and encapsulation of inkjet-printed humidity sensors on flexible foils with integrated thermal compensation," J. Micromech. Microeng. 23 (2013) 025012 (11pp)

# Temperature sensor

**Sensing mechanism: variation of metal resistivity  $\rho$  (and therefore, of the electrical resistance  $R$ ) as a function of temperature, according to the following law:**

$$R(T) = R_0 [1 + \alpha(T - T_0)]$$



Linear variation of electrical resistance as a function of temperature.

Nickel electroplating on inkjet-printed sensors proved to be an effective means to increase TCR ( $\alpha$ ).

F. Molina-Lopez et al., "Large area compatible fabrication and encapsulation of inkjet-printed humidity sensors on flexible foils with integrated thermal compensation," J. Micromech. Microeng. 23 (2013) 025012 (11pp)



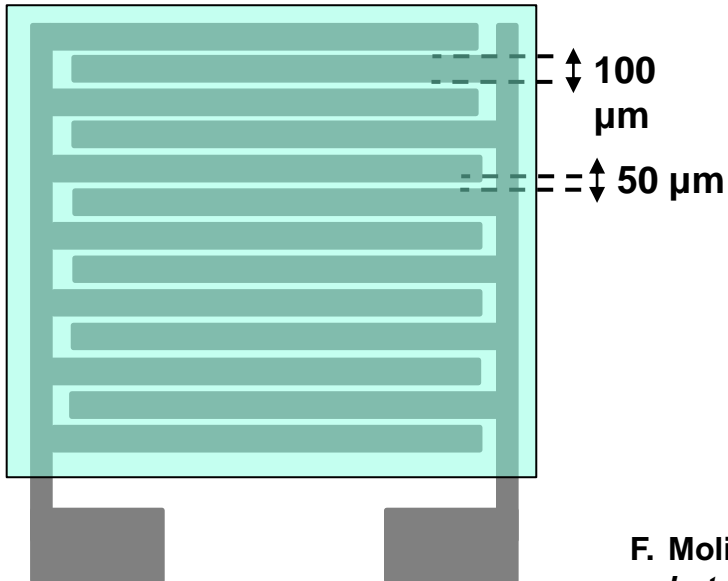
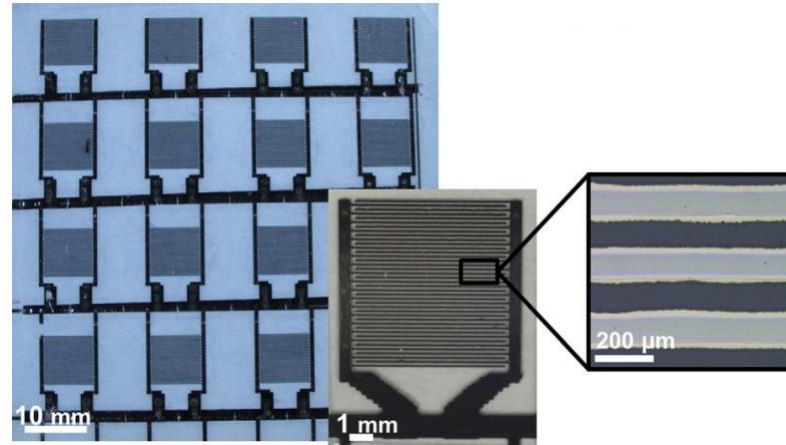
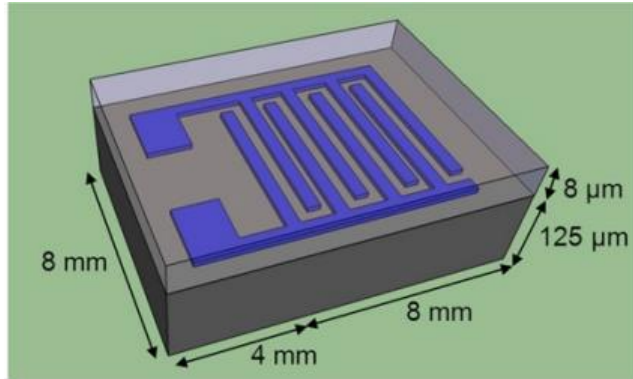
- Screen printed silicon nanoparticle ink on plastic and paper substrates
- Key point is that silicon in the format of nanoparticles does not suffer from oxidation (important for stability over time)
- Negative temperature coefficient
- Single sensor & arrays for temperature distribution mapping

- [illegible]



# Printed humidity sensor

## ■ Inkjet-printed capacitors for humidity measurements



**substrate:** PET films 125 μm

**deposition techniques:**

- inkjet-printing (electrodes +sensing layer);
- electrodeposition of Ni for increase stability;

**inks:**

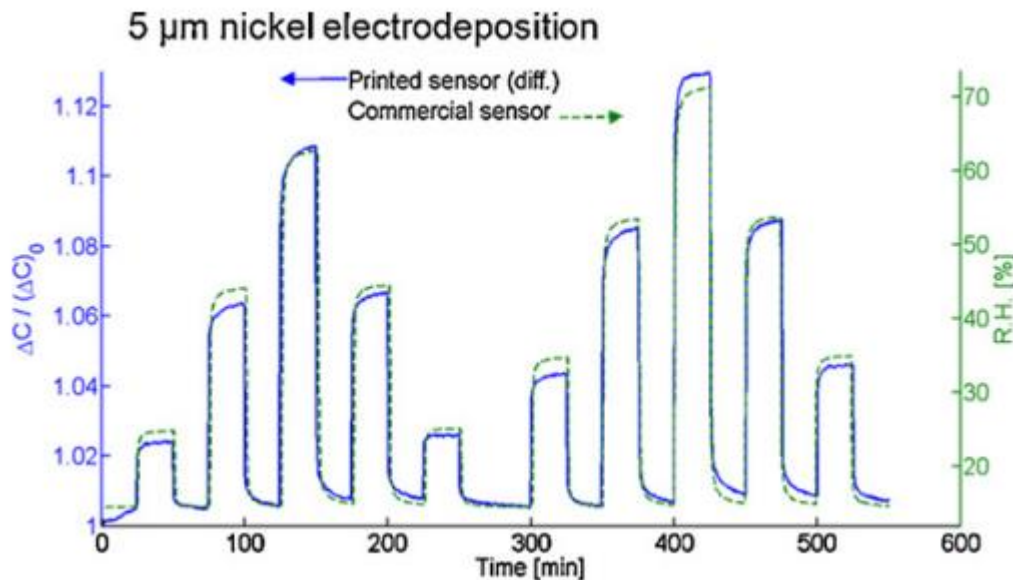
- silver ink (interdigitated electrodes);
- cellulose derivative (CAB, sensing layer).

F. Molina-Lopez et al., "All additive inkjet printed humidity sensors on plastic substrates," *Sensor Actuat. B:Chem*, 166 (2012) 212-222.

# Printed humidity sensor

**Sensing mechanism: variation of dielectric permittivity  $\varepsilon$  and thickness  $t$  (and therefore, of the electrical capacitance  $C$ ) as a function of relative humidity, according to the following law:**

$$C = f(\varepsilon_{CAB}, t_{CAB}, \dots) \rightarrow \Delta C = f(\Delta\varepsilon_{CSB}, \Delta t_{CAB}, \dots)$$



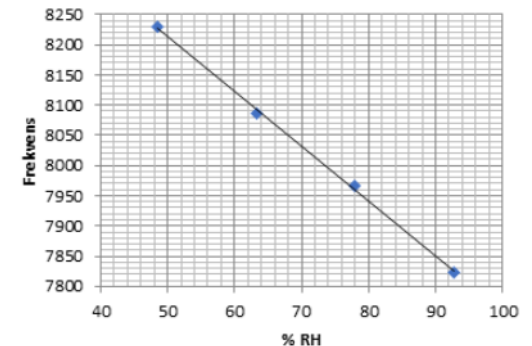
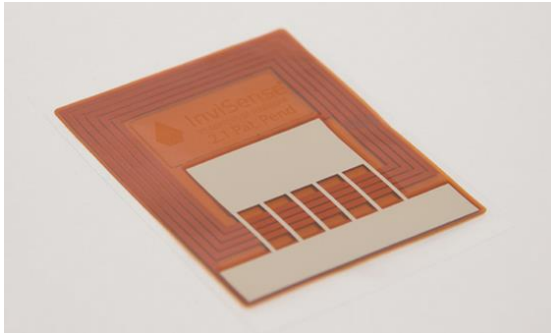
Sensor response towards variations of relative humidity. Inkjet-printed sensor + Ni electroplating compared to a commercial, silicon based sensor.



# Commercial printed humidity sensor

## InviSense moisture sensor

- Silver/copper conductive tracks with embedded  $\text{H}_2\text{O}$  sensitive dielectric on polyimide
- Length: 77mm, Width: 62mm, Thickness: <0.1mm
- RF remotely powered capacitive humidity sensor integrated in a LC chipless circuit (no silicon)
- When the sensor absorb water molecules, it sets itself at a frequency in a given range. With InviSense moisture scanner, the given frequency range is swept and when the sensor and the scanner end up in resonance, we read the relative humidity percentage (RH%) between 20-95% with high accuracy.
- Applications: monitoring of buildings' roof, inside the water proofing layer in a tiled bathroom, drying of structures made of concrete

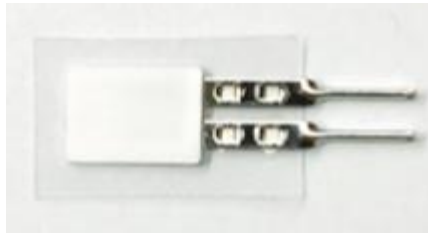


- **Carbon-based nanotechnology** (most likely to be CNTs)



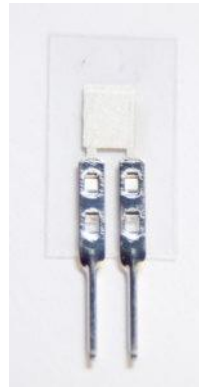
## Flex sensor

- High sensitivity ( $\sim 0.3\%$ ) change in resistance per degree bend
- Gauge factor  $> 15\times$  that of metal strain gauge
- Bi-directional bend sensitivity
- Ultrafast response time to bend ( $< 10$  ms)
- $> 98\%$  linear change in resistance vs. bend angle from  $+180^\circ$  to  $-180^\circ$



## Humidity sensor

- Ultrafast response time ( $\leq 10$  ms)
- Low-power operation ( $< 30$  pW)

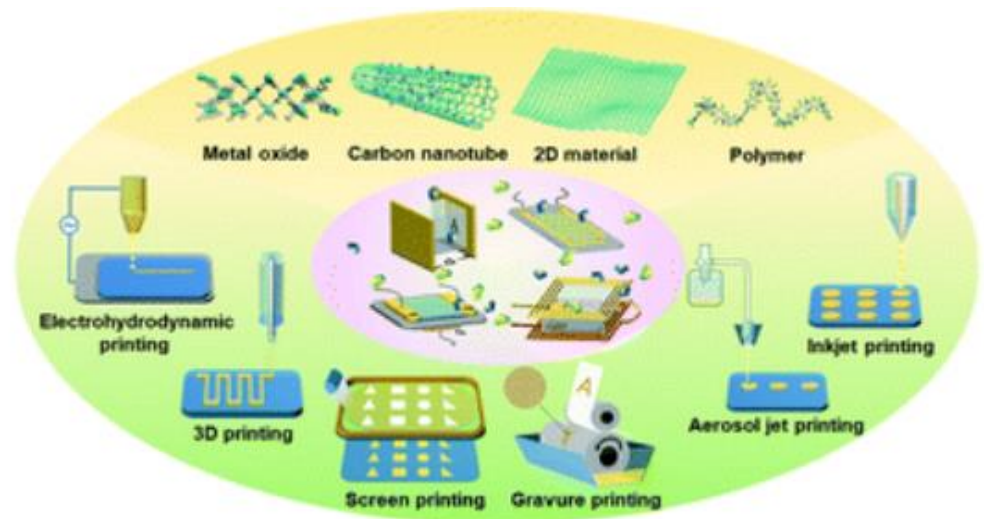


## Temperature sensor

- Ultrafast response time ( $< 250$  ms)
- Low power operation ( $< 30$  pW)
- Hermetically sealed;
- Low drift; high accuracy
- Flexible form factor

From Brewer Science

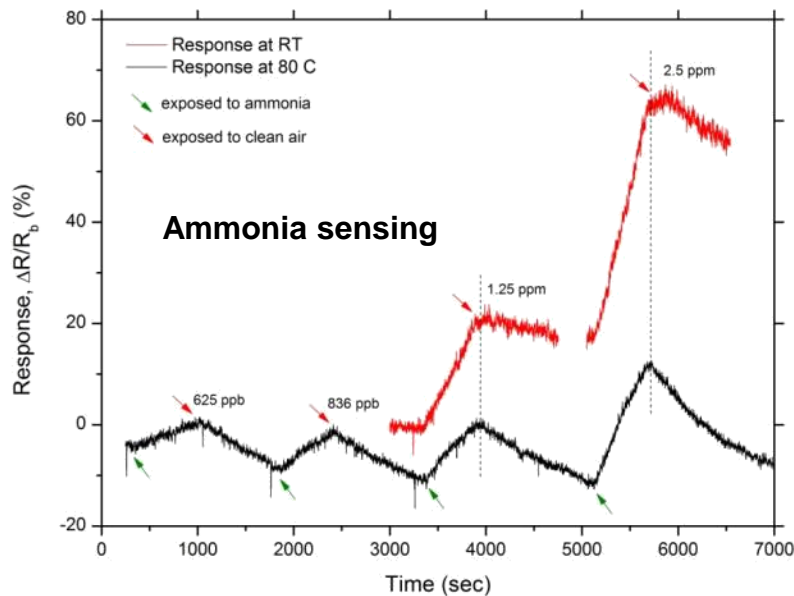
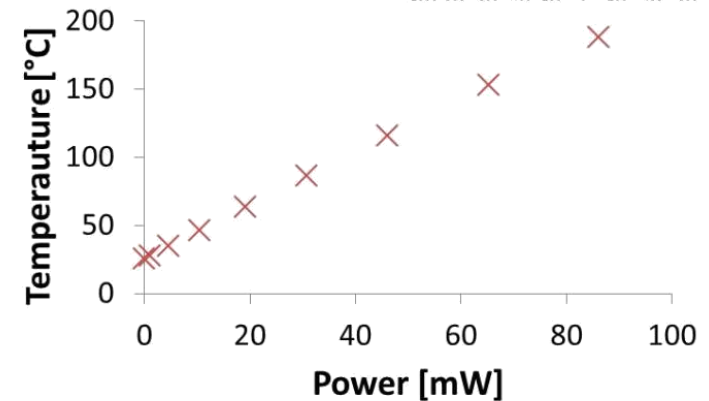
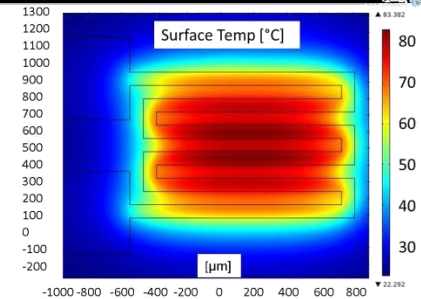
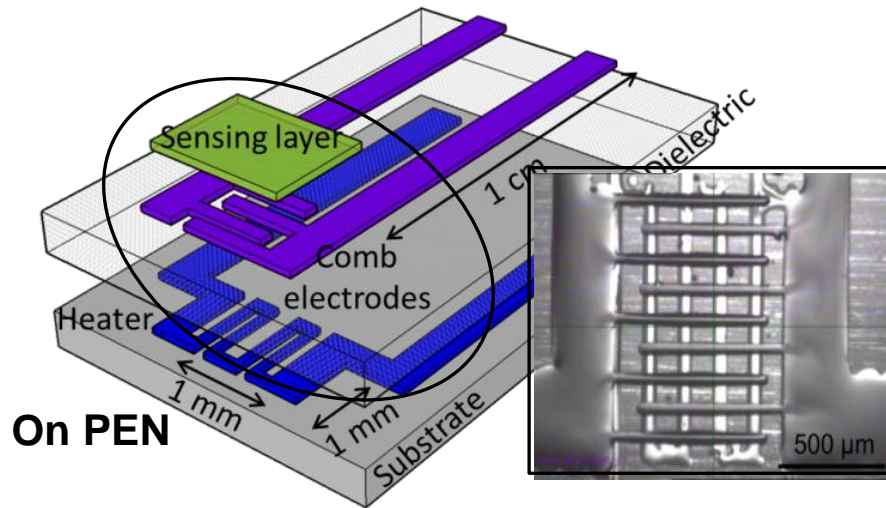
- **Polymeric, metal-oxide, carbon (CNT/graphene) gas sensitive layers**
  - Printed using mainly inkjet over printed metallic electrodes, allowing the digital formation of multi-sensor array
  - Change of resistance when interacting with the surrounding gases
  - These sensors are not gas selective with interference of humidity
  - For enhanced sensitivity, selectivity: functionalisation, composites formulation, doping



Review on Printed gas sensors: *Chem. Soc. Rev.*, 2020 49, 1756

# Chemoresistive hotplate gas sensor

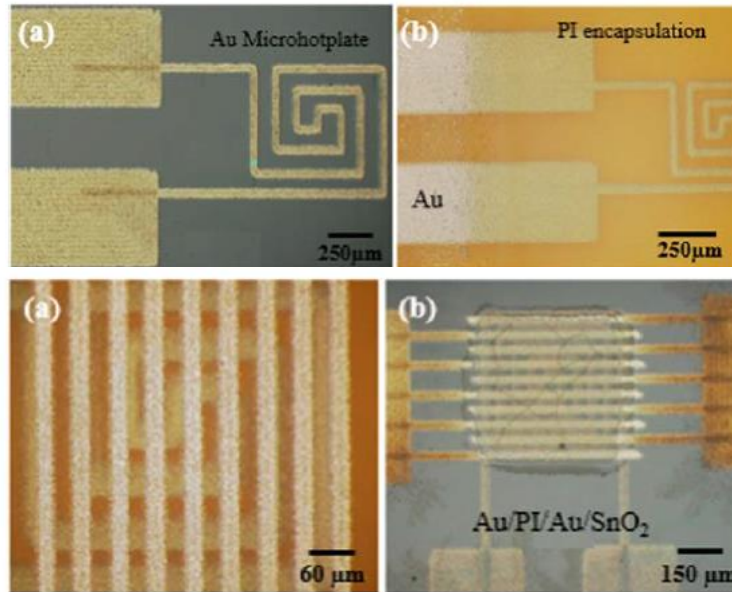
## Polyaniline sensing layer (PANI)



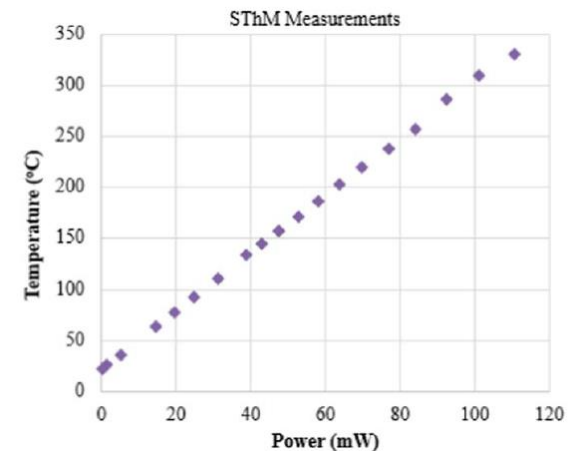
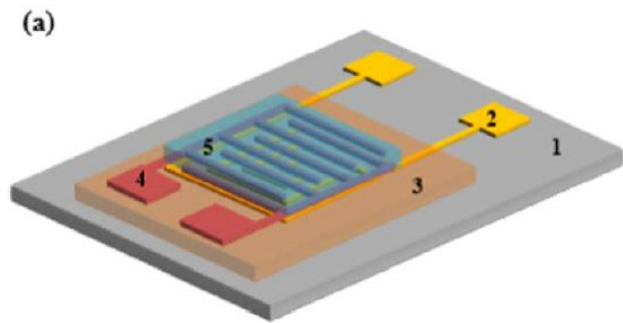
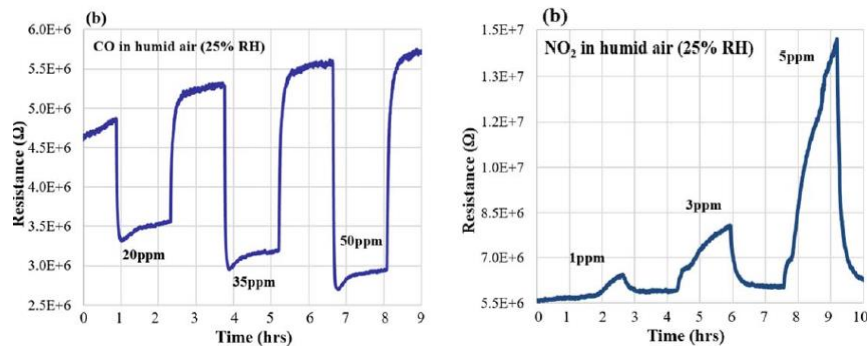
- Inkjet printed Ag + Ni (heater) / Au (electrodes) electroplated on top of Ag
- Ag alone not stable enough: oxidation, ions migration
- 30 mW power consumption at 100°C
- Heating for reversibility of the sensing signal

# Chemoresistive hotplate gas sensor

## Tin dioxide nanoparticles sensing layer



### CO and NO<sub>x</sub> sensing



- Aerosol jet printing of narrow heaters and electrodes
- Temperature resistant Polyimide substrate and inkjet printed dielectric
- Inkjet printing of SnO<sub>2</sub> sensing layer
- Operating up to 200-300°C



## Materials and working principles

- At elevated temperatures (typically  $>150^{\circ}\text{C}$ ), metal oxides become more conductive due to the increased carrier concentration; and in the presence of air, highly reactive oxygen molecules can exchange electrons with the metal oxide and stay adsorbed in the form of oxygen anions, such as  $\text{O}_2^-$ ,  $\text{O}^-$  and  $\text{O}^{2-}$ .
- Reducing and oxidising gases can interact with the metal-oxide surface, trapping or releasing electrons, modulating the depletion zone (no charge carriers) at the surface of the grains in the material, resulting in a change of resistivity/resistance
- Operation temperature: 150 to  $400^{\circ}\text{C}$
- Doping with catalytic metals (Pd, Pt, Au...) to modify sensitivity / selectivity profiles

Table 5 Selected list of preferred metal oxides for applications in specific gases<sup>144</sup>

Detected gas	Metal oxides preferable for application
Reducing gases (CO, H <sub>2</sub> , CH <sub>4</sub> )	SnO <sub>2</sub> ; Cr <sub>2-x</sub> Ti <sub>x</sub> O <sub>3+z</sub> ; Ga <sub>2</sub> O <sub>3</sub> ; In <sub>2</sub> O <sub>3</sub>
Oxidizing gases (O <sub>3</sub> , NO <sub>x</sub> , Cl <sub>2</sub> )	In <sub>2</sub> O <sub>3</sub> ; WO <sub>3</sub> ; ZnO; TiO <sub>2</sub>
H <sub>2</sub> S, SO <sub>2</sub>	SnO <sub>2</sub> /CuO; SnO <sub>2</sub> /Ag <sub>2</sub> O
NH <sub>3</sub>	WO <sub>3</sub> ; MoO <sub>3</sub> ; In <sub>2</sub> O <sub>3</sub>
CO <sub>2</sub>	SnO <sub>2</sub> /La <sub>2</sub> O <sub>3</sub> ; Al <sub>2</sub> O <sub>3</sub> /V <sub>2</sub> O <sub>5</sub>
Alcohol	La <sub>2</sub> O <sub>3</sub> /In <sub>2</sub> O <sub>3</sub> ; La <sub>2</sub> O <sub>3</sub> /SnO <sub>2</sub> ; In <sub>2</sub> O <sub>3</sub> /Fe <sub>2</sub> O <sub>3</sub>
Oxygen	Ga <sub>2</sub> O <sub>3</sub> , SrTiO <sub>3</sub> , SrTiFeO <sub>3</sub> ; TiO <sub>2</sub> ; Nb <sub>2</sub> O <sub>5</sub> ; ZnO

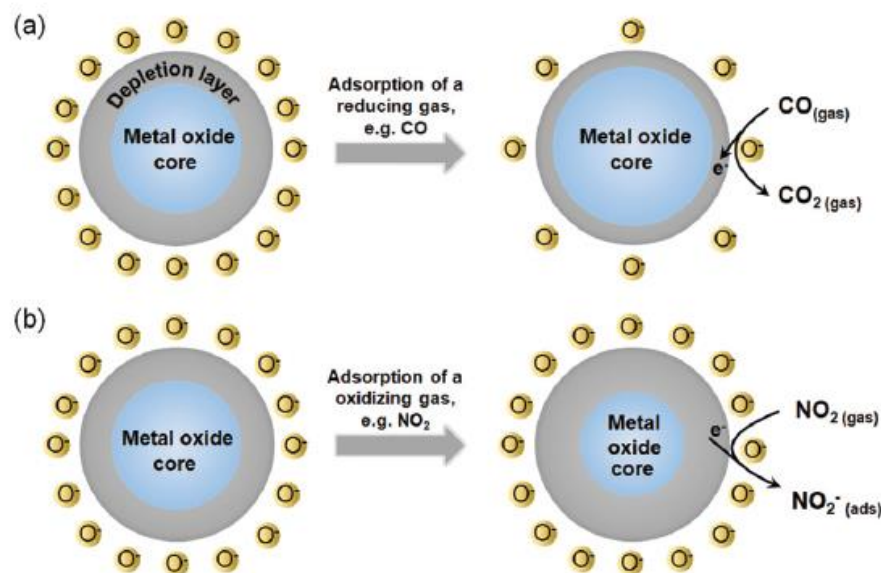


Fig. 6 Schematic illustration of the change of depletion layer of an n-type semiconducting metal oxide with surface adsorbed oxygen anions in response to (a) a reducing gas and (b) an oxidizing gas.

# Electrochemical ion sensors

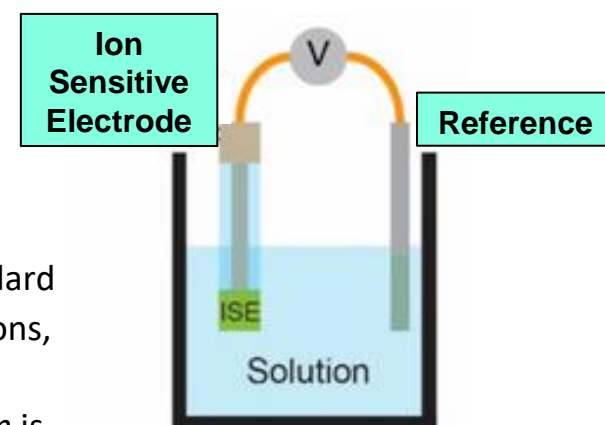
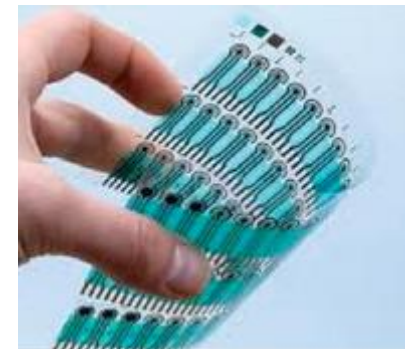
- Based on the potentiometric sensing principle

- Potentiometric sensors measure the potential difference between two electrodes under the conditions of no current flow. The measured potential may then be used to determine the analytical quantity of interest, generally the concentration of some component of the solution.
- The signal of a general potentiometric sensor is based on the **Nernst equation**. This equation predicts a linear dependence of the sensor response,  $E$ , on the logarithm of a function of the activity of the ion in solution:

$$E = E^{\circ} + \frac{RT}{nF} \ln[a_i]$$

At equilibrium, sensitivity defined by the slope at **59.2/z mV** at 298 K, where  $z$  is the charge of the analyte ion.

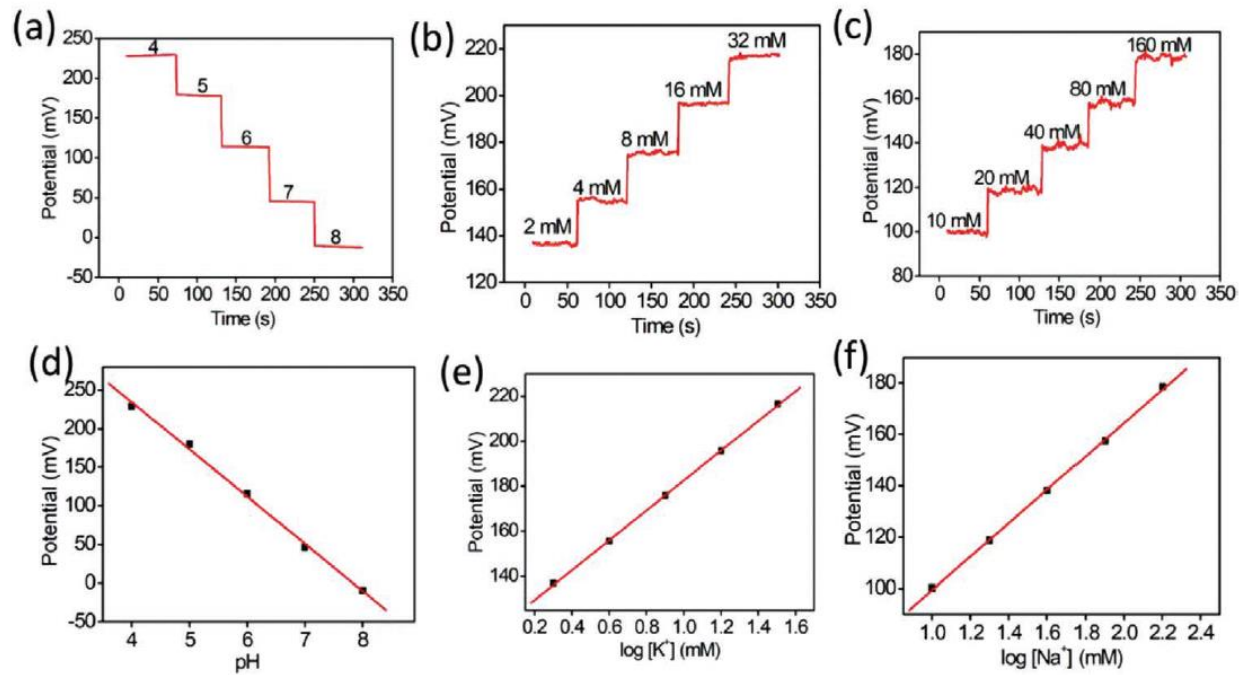
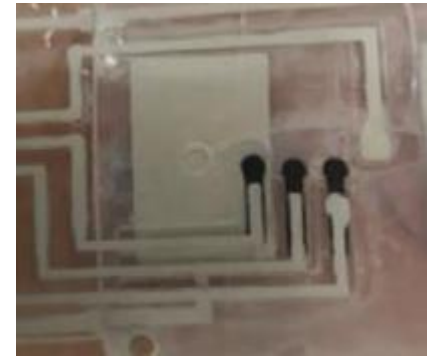
where  $E$  is the potential (V),  $R$  is the gas coefficient (8.314 J/K),  $E^{\circ}$  is the standard potential,  $F$  is the faraday constant (96,500 C/mol),  $n$  is the number of electrons, and  $a_i$  is the activity of the principal ion.  $E$  is the potential difference for the electrochemical cell composed of the ion-selective and reference electrode;  $n$  is the charge numbers of the primary ion



# Electrochemical ion sensors

- Based on the potentiometric sensing principle

- Screen printed carbon electrodes coated with Ion Selective Membranes (ISM) for the detection of pH,  $K^+$  and  $Na^+$  ions
- Ions diffusing into ISM (because of gradient concentration) generate the potential difference
- Screen printed Ag/AgCl reference electrode (far right)
- On PET with integrated microfluidics for sweat analysis (dehydration)



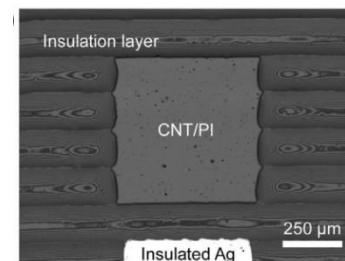
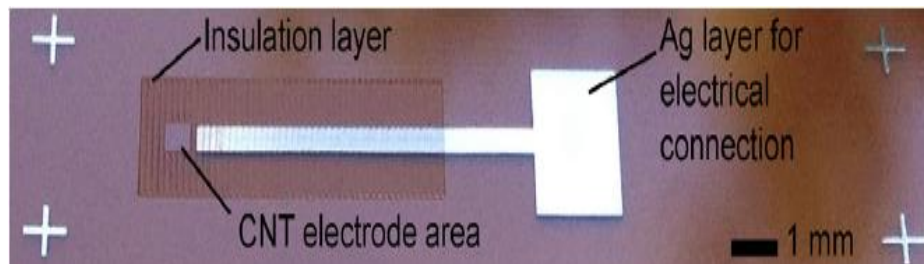
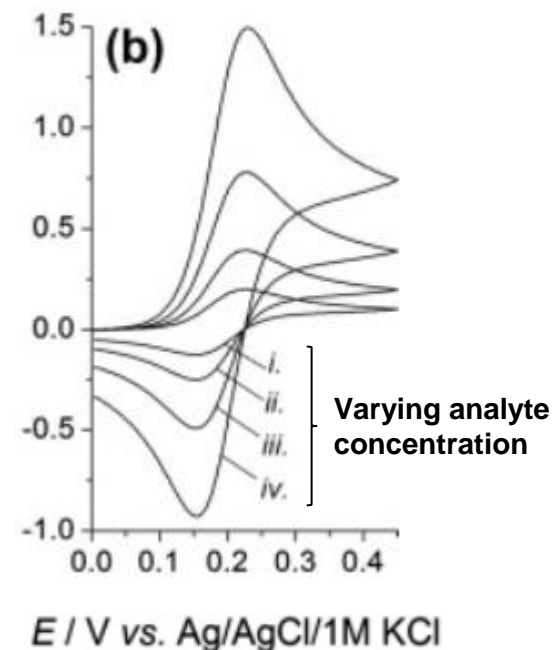
**Figure 2.** Open-circuit potential (OCP) response of a)  $H^+$  sensor, b)  $K^+$  sensor, c)  $Na^+$  sensor, and calibration curve for d)  $H^+$  sensor, e)  $K^+$  sensor, and f)  $Na^+$  sensor in their respective ionic solutions.



# Printed electrochemical blood sensor

- Inkjet-printed sensor fabricated on Kapton flexible sheets for the detection of antioxidants, such as uric acid, glutathione in biological samples
- Electrode is fabricated by inkjet-printing a silver nanoparticles-based ink
- The sensor's active area is realised by inkjet-printing on the top of the silver electrode a DWCNTs dispersion.
- A final UV-curable insulating layer is inkjet-printed all around the active area and on the top of silver electrode

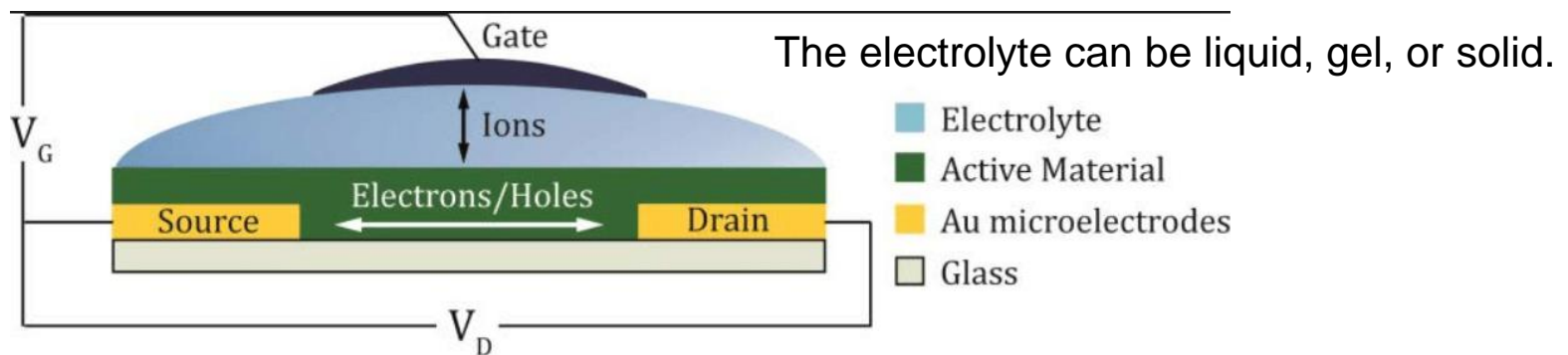
## Cyclic voltammetry



Lesch, A. et al. (2014). Large scale inkjet-printing of carbon nanotubes electrodes for antioxidant assays in blood bags, *J. Electroanal. Chem.*, 717-718, pp. 61-68.

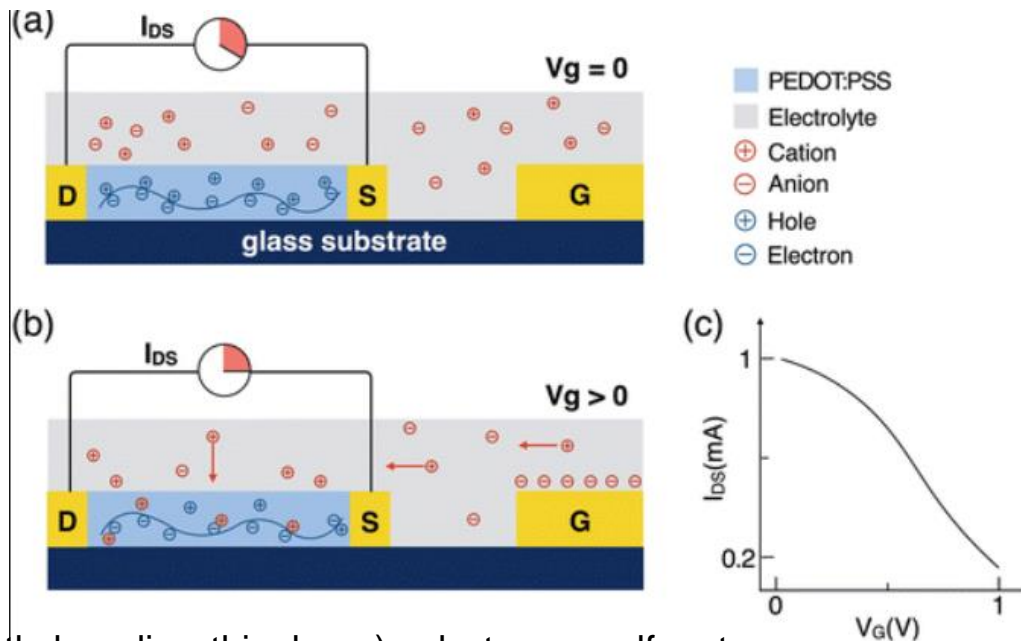
# Organic electrochemical transistors (OECT)

- Transistor in which the drain current is controlled by the injection of ions from an electrolyte into a semiconductor / conductor channel
- Semiconductor film usually made of a conjugated polymer, which is in direct contact with an electrolyte
- When a voltage is applied to the gate, ions from the electrolyte are injected in the channel and change the electronic charge density, and hence the drain current
- When the gate voltage is removed, the injected ions return to the electrolyte and the drain current goes back to its original value.
- Operate with a small gate voltage (  $< 1\text{V}$ ), high transconductance because of bulk coupling between ionic and electronic charge, but are slow (diffusion of ions).



# Organic electrochemical transistors (OECT)

- Most common OECTs are based on PEDOT:PSS, and work in the depletion mode.
- PEDOT is doped p-type by the sulfonate anions of the PSS (the dopant) and hence exhibits a high (hole) conductivity.
- In the absence of a gate voltage, the drain current will be high and the transistor will be in the ON state.
- When a positive voltage is applied to the gate, cations from the electrolyte are injected into the PEDOT:PSS, where they compensate the sulfonate anions. This leads to dedoping of the PEDOT:PSS, and the transistor reaches its OFF state

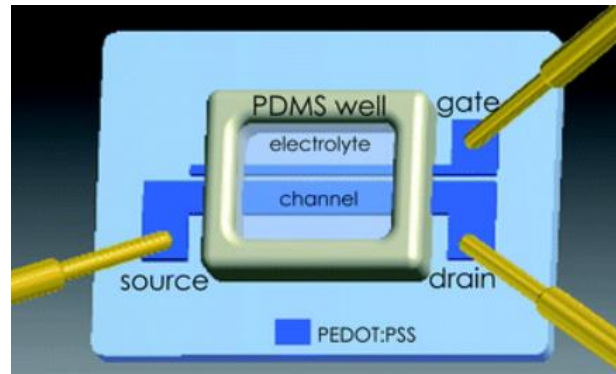


PEDOT:PSS : poly(3,4-ethylenedioxythiophene) polystyrene sulfonate

# Organic electrochemical transistors as sensors

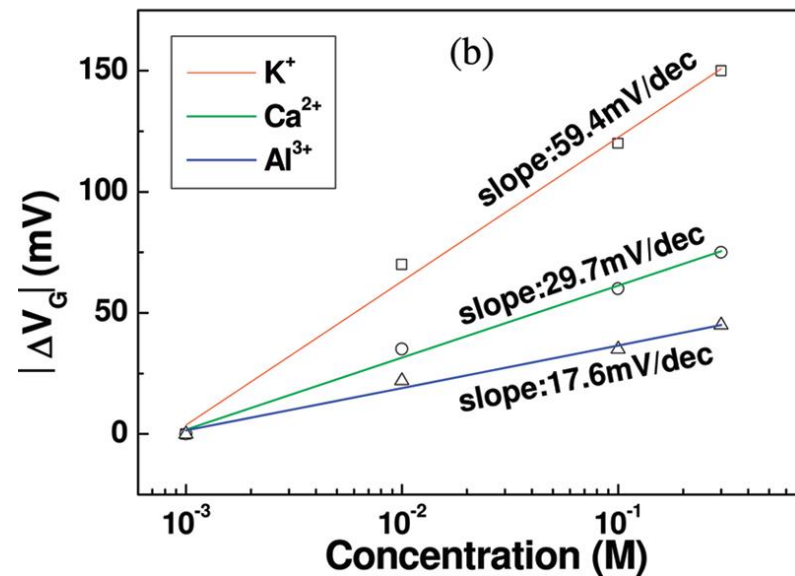
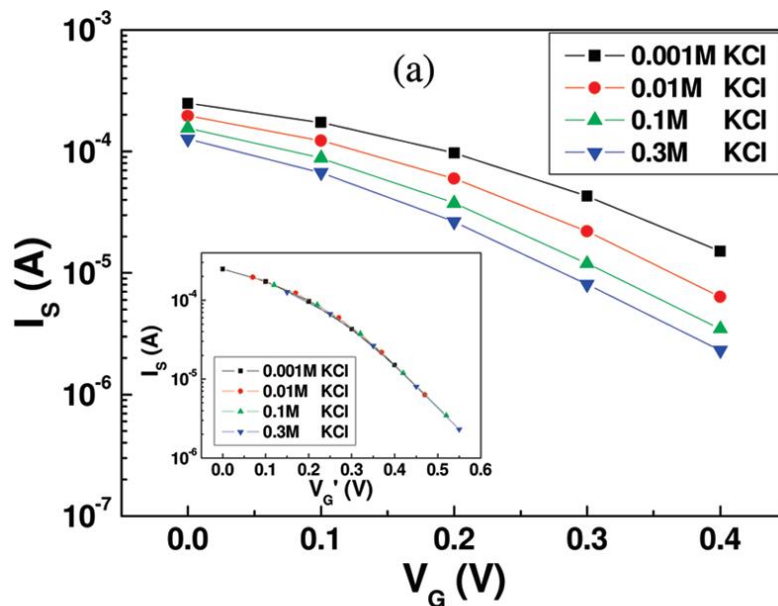
- OECT can be used as ion, chemical and bio (with functionalisation) sensors

pH  
Ions  
Glucose  
Lactate

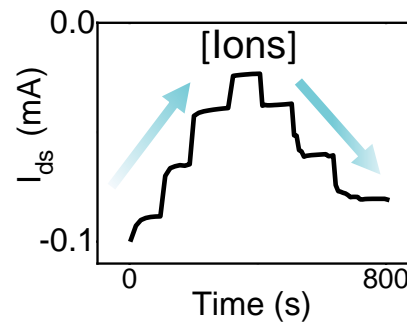
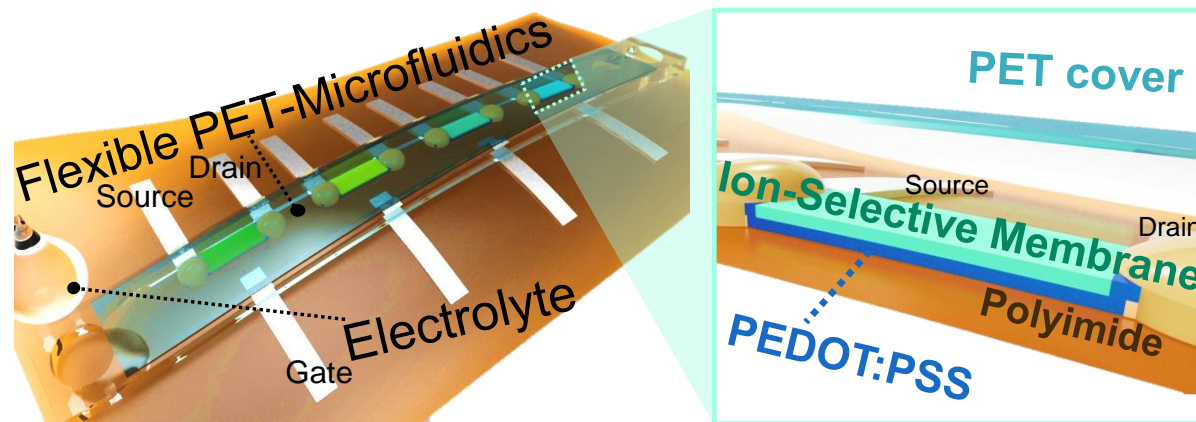


DNA  
Virus  
Bacteria  
...

Peng Lin et al, ACS Applied Materials and Surfaces, vol 2(6) 1637–1641 • 2010

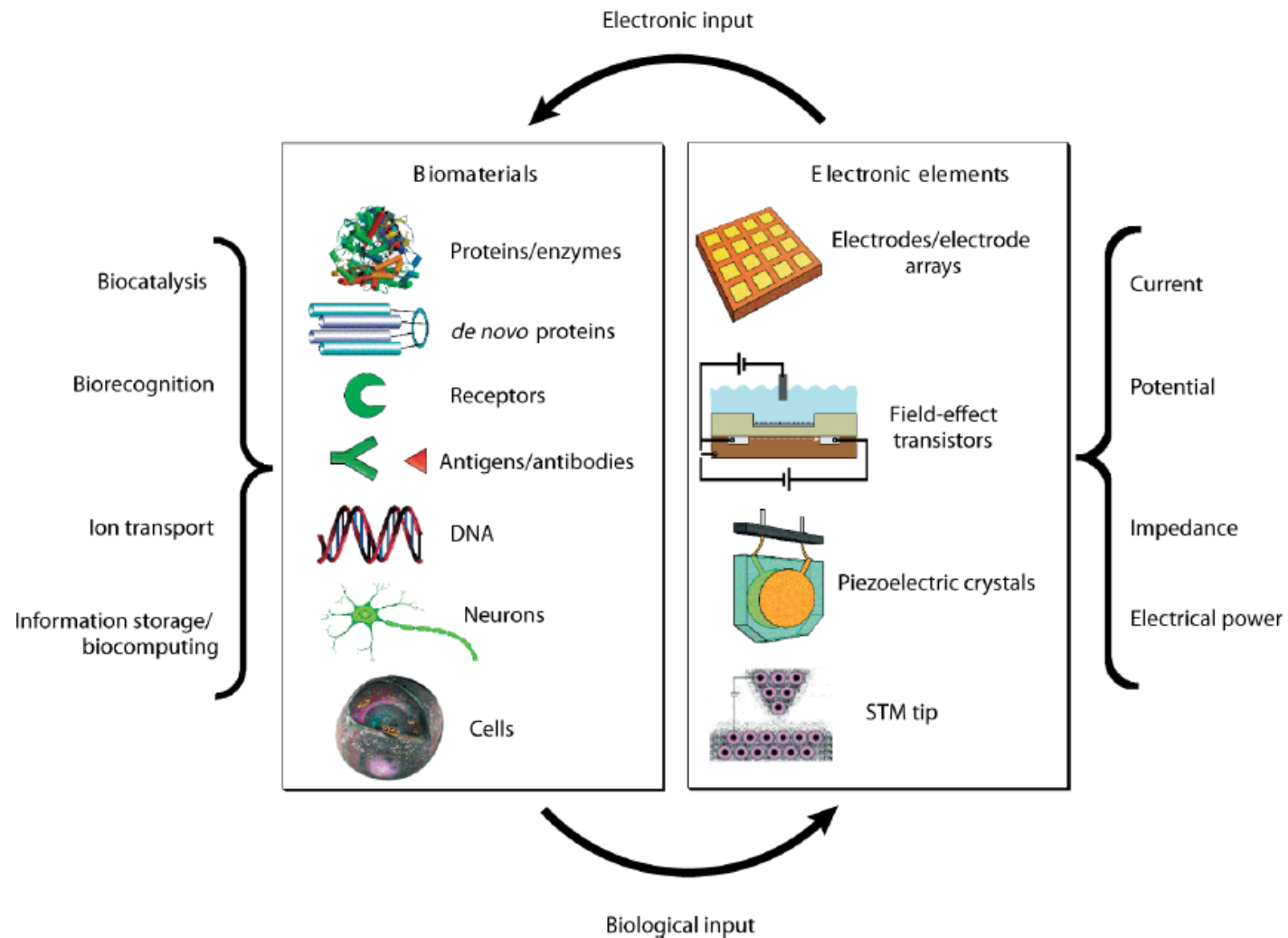


# OECTs array for multi-ion detection



Use of different ISMs for multi-ion sensing in real-time, achieving higher selectivity

# Bioelectronics: Coupling biology with electronics



I. Willner, E. Katz, *Bioelectronics*, 2005



## Opportunities

- Ease of processing → low cost fabrication, disposable devices
- Tunability of electronic properties → tailored to fit applications
- Integration with biological systems → improved selectivity in sensors
- Ionic conductivity → electrical interfacing with neurons
- Ideal surfaces/interfaces → high sensitivity, low noise
- Mechanical props. similar to tissue → improved implant stability

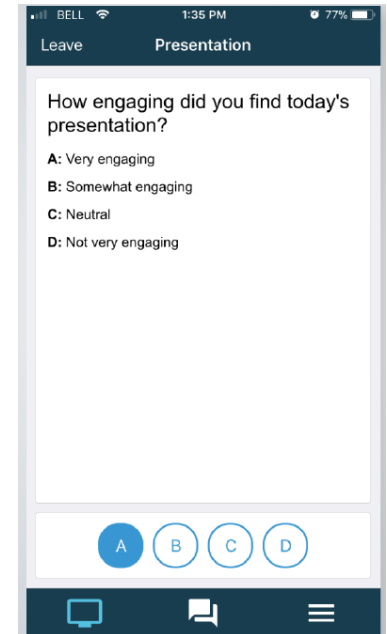
**Organic and printed electronic technologies are an enabler for the fabrication of bioelectronic probes and sensors**

# Some questions

- ❑ List the different types of flexible and printed sensors: physical & chemical
- ❑ Describe the design and operating principle of a given sensor, the materials involved, their processing, and the sensing mechanism
- ❑ Maturity of the technologies: R&D under development vs. Commercial products

## Utilisation du logiciel PointSolutions (anciennement TurningPoint Cloud)

- Sur Téléphones et tablettes = app ou web
- ou sur ordinateurs = web
  - Rester anonyme (comme invité)
  - Depuis un téléphone portable, les données sont envoyées sur leur serveur
  - Des garanties ont été offertes à l'EPFL concernant la protection des données
  - La protection des données n'est pas garantie si vous vous identifiez personnellement sur l'application/site web



- Smart phones

- iPhone
- Android



Download and install the App  
*“PointSolutions”*



- Laptops / Tablets

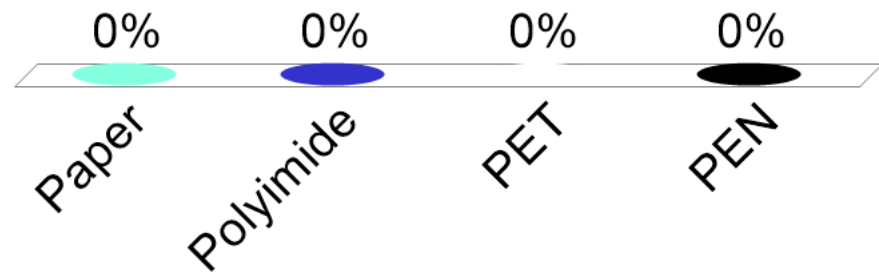
- <https://ttpoll.eu>

- Join session – micro505

- If asked – Enter anonymously (**not your real name**)

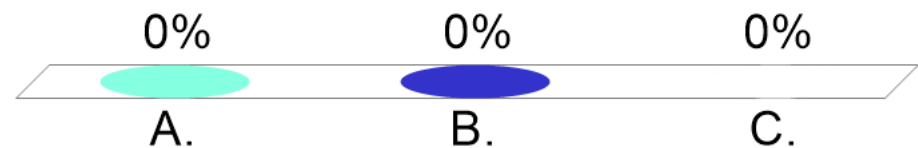
## Q1: Which substrate is the most temperature resistant ?

- A. Paper
- B. Polyimide
- C. PET
- D. PEN



## Q2: In Force Sensing Resistor, which mode is the most sensitive ?

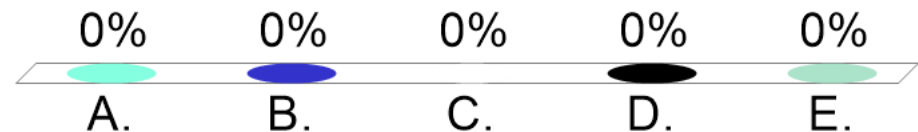
- A. Shunt mode
- B. True mode
- C. Both have the same sensitivity





### Q3: In capacitive humidity sensors, which effects are involved ?

- A. Transfer of electrons
- B. Swelling (change of dimensions)
- C. Change of permittivity
- D. Change of permittivity and swelling
- E. Electrochemical reactions



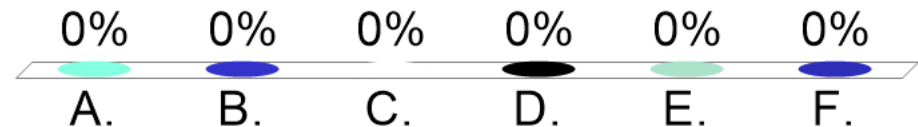
## Q4: Which transducing principle is commonly used in chipless sensing ?

- A. Resistive
- B. Inductive
- C. Capacitive
- D. Field-effect



## Q6: In OECTs and not in OTFTs, we can find:

- A. Organic conducting polymer
- B. Electrolyte
- C. Field-effect principle
- D. Bulk accumulation
- E. Ionic and electronic conduction
- F. Higher transconductance



## Q5: Sensing mechanism in chemiresistive metal-oxide gas sensors

For n-type metal oxide semiconductor:

- A. Oxidizing gas causes an increase of resistance because of smaller depletion layer
- B. Oxidizing gas causes a decrease of resistance because of smaller depletion layer
- C. Reducing gas causes a decrease of resistance because of smaller depletion layer
- D. Reducing gas causes an increase of resistance because of smaller depletion layer

