

# Micropatterning and casting PEDOT-PSS /DMSO layers

Benoît Charlot, Gilbert Sassine, Alexandra Garraud, Alain Giani, Philippe Combette

IES Institut d'Electronique du Sud CNRS Université Montpellier II  
Place E. Bataillon, 34095 Montpellier - France



# *Outline*

Introduction

PEDOT:PSS deposition

Soft lithography techniques

    Casting

    Stamping

Shadow masking

Lithography techniques

    Lift off

    Protection layer

Applications

Conclusions

# Introduction

**PEDOT:PSS is a blend of polymers :**

**PSS :** polystyrene sodium sulfonate

**PEDOT :** poly(3,4-ethylenedioxythiophene)

- **Conductive polymer, flexible transparent when deposited in thin film layer**

- **low temperature , low cost process**

- **Often use in organic solar cells**

- **Candidate for the replacement of ITO**

- **Organic electronics, large area display**

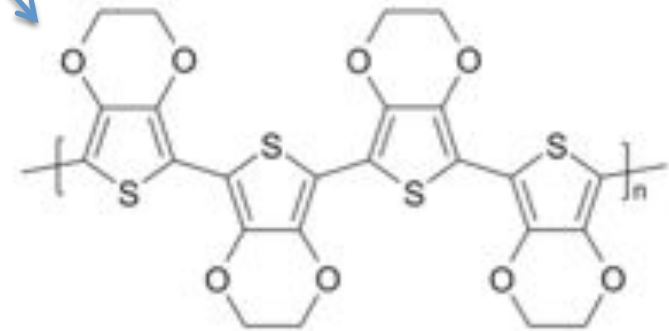
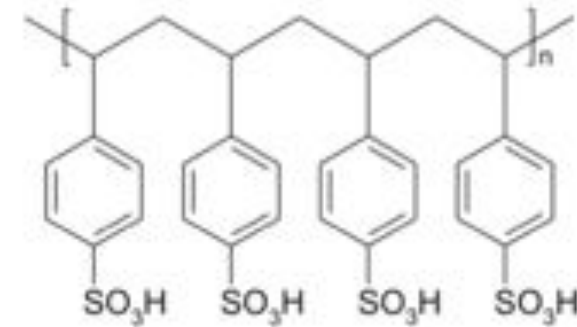
**But :**

- **low charge carrier mobility**

- **Sensitive to moisture, water and UV**

**Issues of patterning**

Ink-jet printing, vapor deposition through shadow masks, soft and hard imprint lithography, and photolithography



$$R=5.10^{-3} \text{ ohm.cm}^{-1}$$

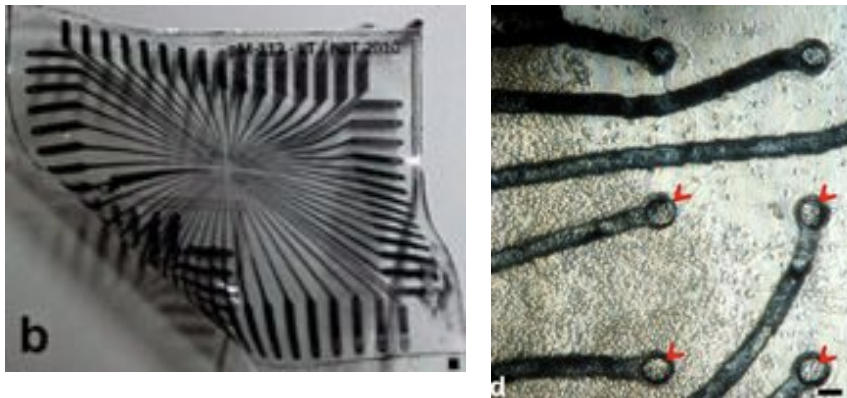
Work function 5.2 eV

# Bioelectrode

PEDOT-PSS is a candidate material for bioelectrode  
Improvement of the neural tissue-electrode interface  
and lifetime of implants

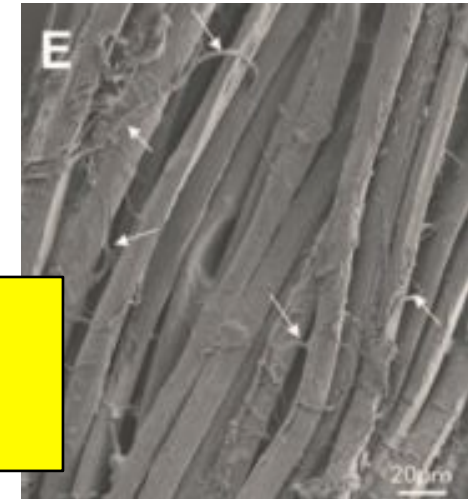
- highly electroconductive
- hydrophilic and biocompatible
- Softness

Microelectrode arrays for the capture of cardiac and neuronal signals



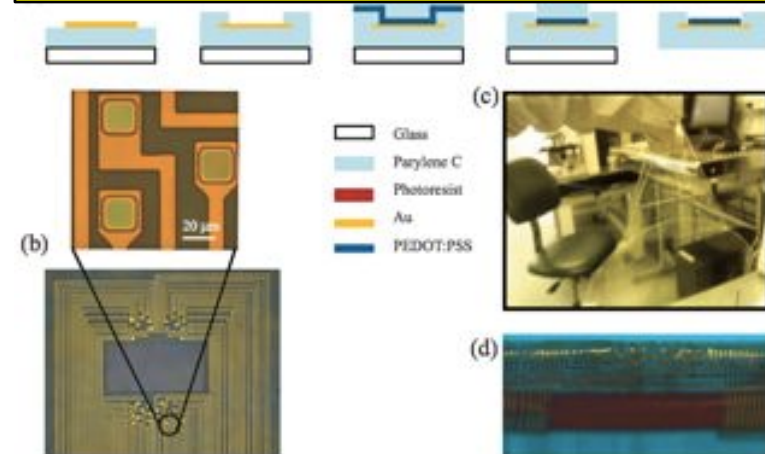
A. Blau et al. Biomaterials  
Volume 32, Issue 7, March 2011

silk thread  
coated with  
PEDOT-PSS



Shingo Tsukada et al. Plos One  
Volume 7, Issue 4, April 2012

Highly Conformable Conducting  
Polymer Electrodes or In Vivo  
Recordings



D. Khodagholy et al. Adv. Mater.  
2011, 23, H268–H272

# PEDOT:PSS deposition

Spincoating

3000 rpm Th=100nm

and drying on hotplate 125°C

Wetting issue can be solved by adding IPA

Mean Resistivity PEDOT:PSS only :  
 $R=6 \Omega \cdot \text{cm}^{-1}$

Additives for increasing conductivity

Ethylène glycol  $\text{C}_2\text{H}_6\text{O}_2$

Glycerol  $\text{C}_3\text{H}_8\text{O}_3$

Sorbitol  $\text{C}_6\text{H}_{14}\text{O}_6$

**Dimethyl Sulfoxide DMSO**  $\text{C}_2\text{H}_6\text{OS}$

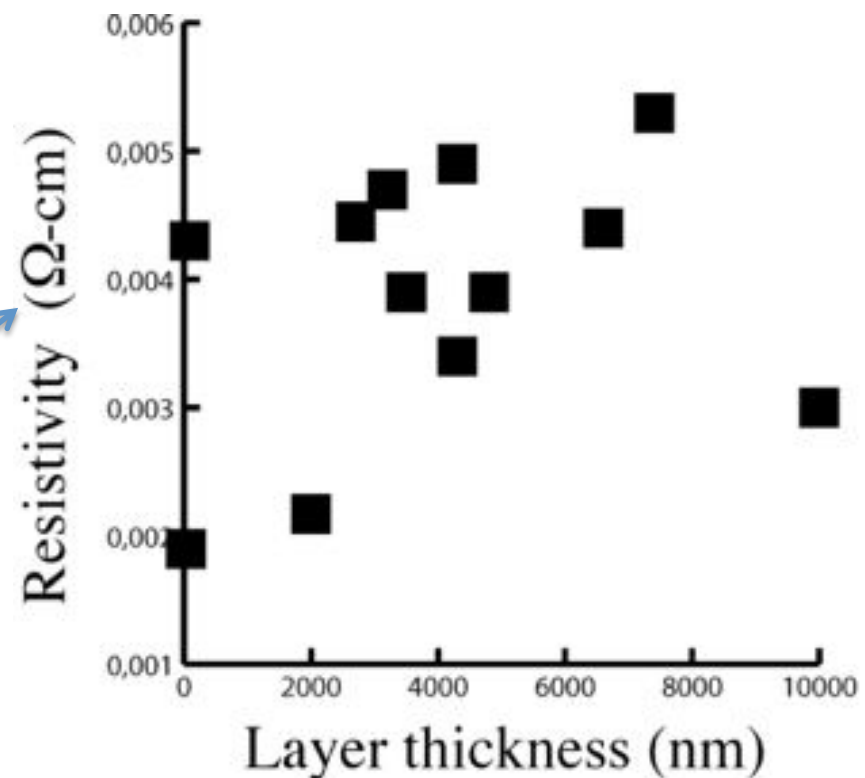
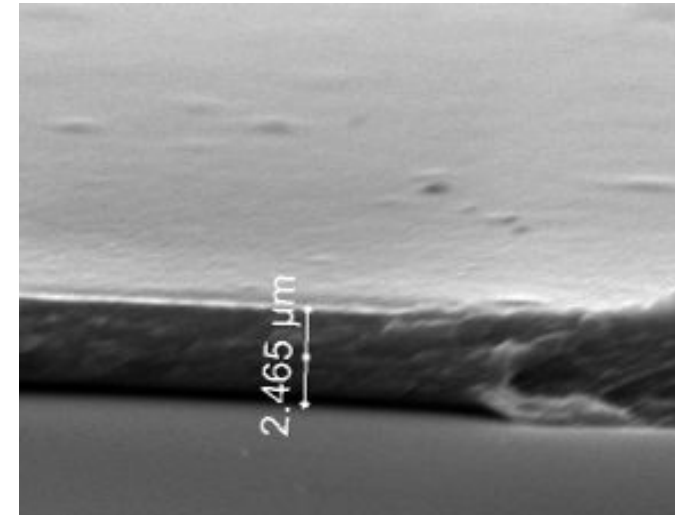
Erythritol  $\text{C}_4\text{H}_{10}\text{O}_4$

Mean Resistivity PEDOT:PSS / DMSO

$R=5.10^{-3} \Omega \cdot \text{cm}^{-1}$

Mean Resistivity PEDOT:PSS / EG

$R=6.10^{-3} \Omega \cdot \text{cm}^{-1}$



# Casting in PDMS

Goal : obtaining deformable electrodes in PDMS for large deformations  
Direct metalization Problems : Inclusion / deposition of metals in PDMS  
adhesion problems / cracks

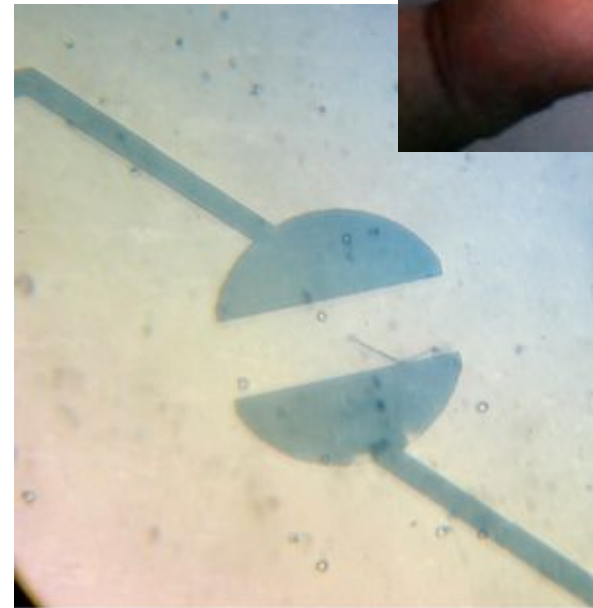
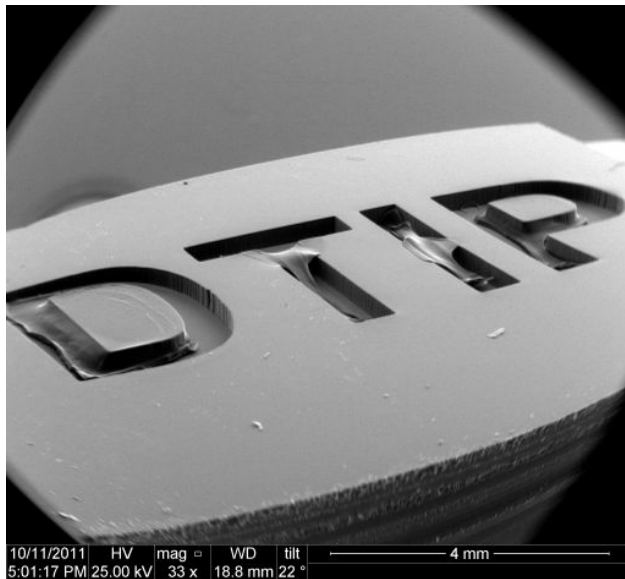
## Cristallization of PEDOT:PSS in PDMS grooves

Hydrophilisation : Oxygen Plasma

Filling, squeegee: scrapping with a glass blade

Hot plate cristallization

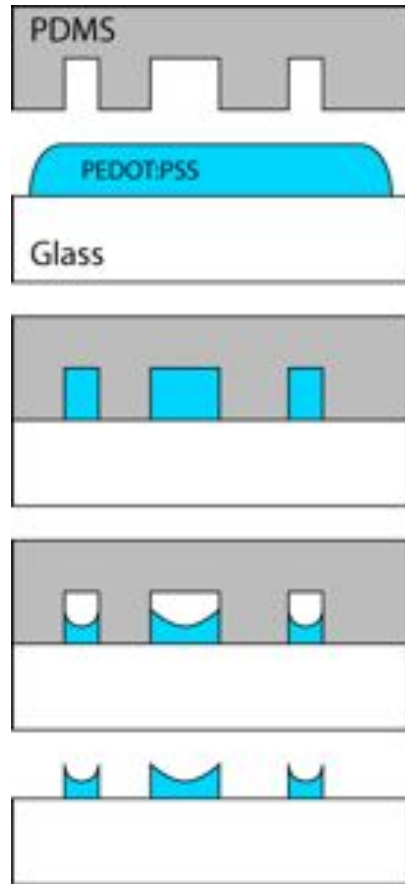
Repeat...



**Wettability issues in PDMS, volume diminution during cristallization**

# Casting from PDMS

Deposition of PEDOT:PSS patterns from a PDMS scaffold

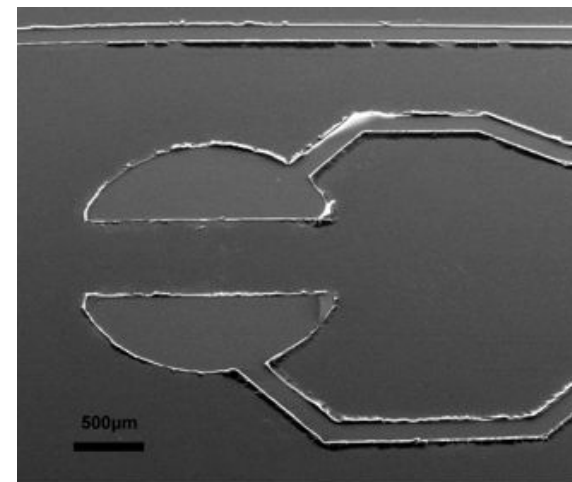
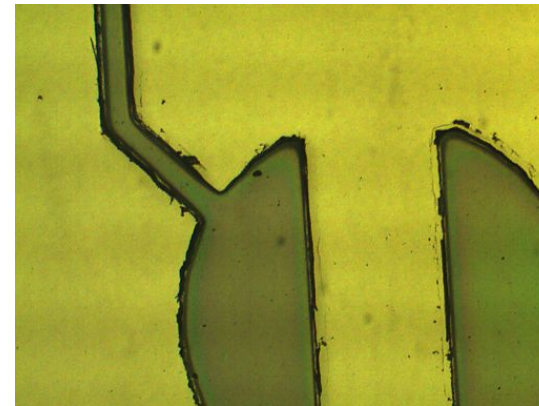
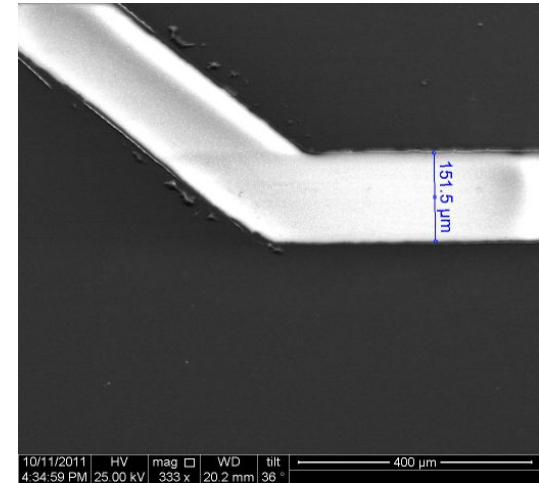


Liquid PEDOT:PSS droplet

Pressing

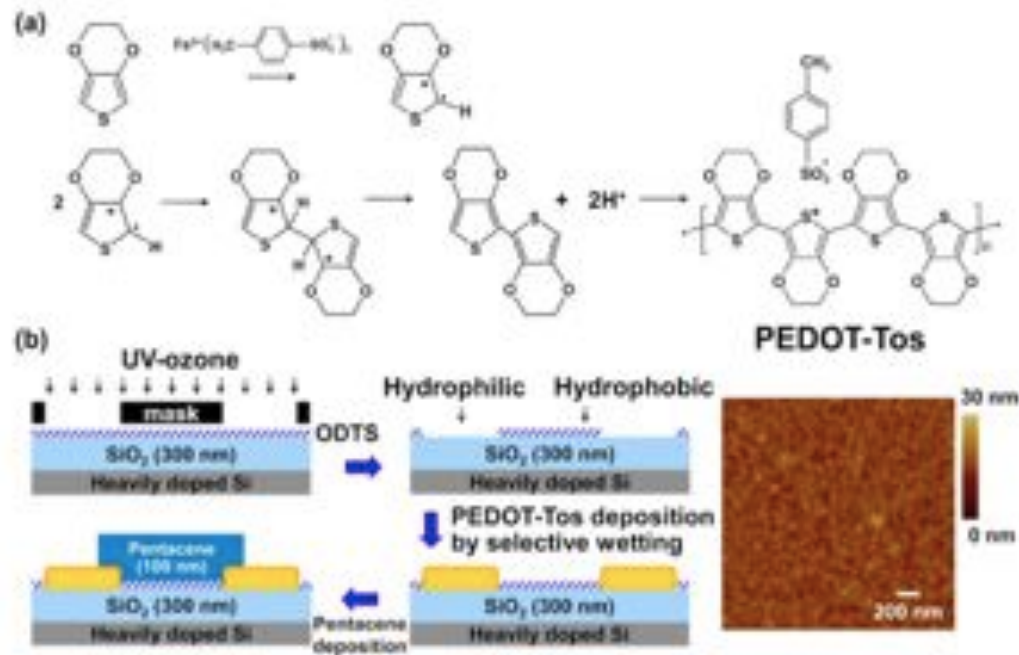
Hot plate cristallization

Residues cleaning :  
Reactive ion etching



# ***PEDOT:PSS selective deposition***

Selective deposition of PEDOT:PSS using hydrophobic surfaces

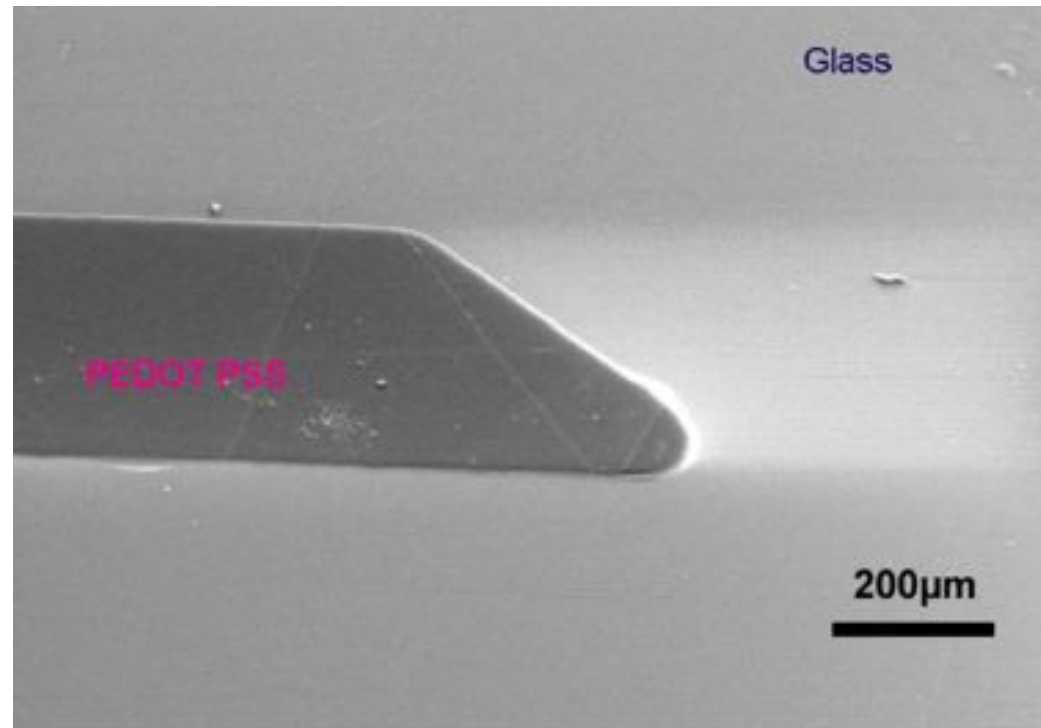
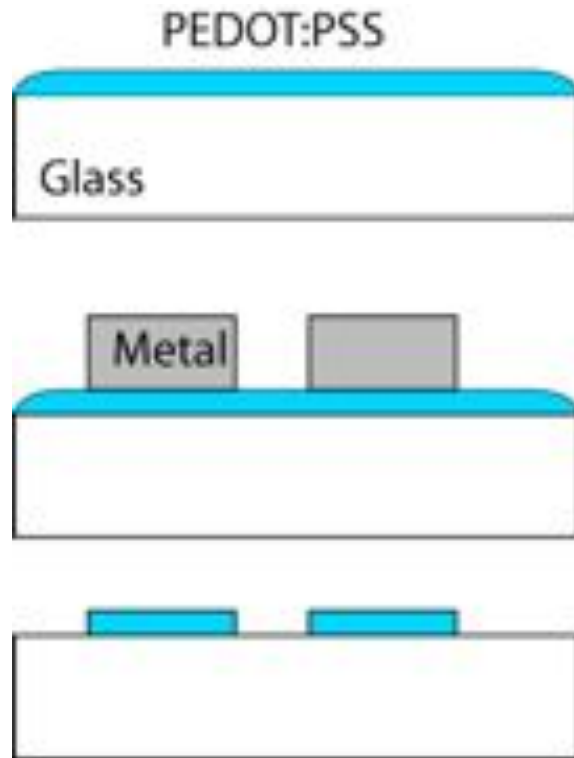


Jung Ah Lim et al.  
Appl. Phys. Lett. 95, 233509 (2009)



# Shadow masking

Use of metal shadow mask



Need of a perfect contact between mask and substrate  
Limitation on design (free standing structures and size)  
Magnetic clamping

# Lithography

## Issues

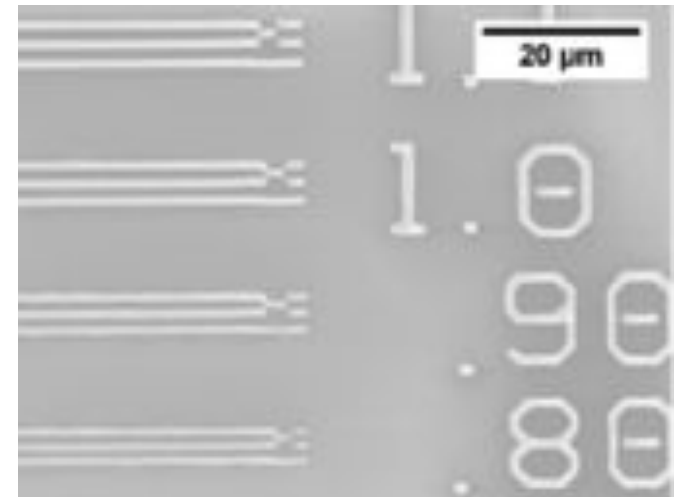
- PEDOT:PSS films are damaged by aqueous solutions, which are standard developers in conventional photolithography
- acid-sensitive photoresists are affected by the acidic PEDOT:PSS.

## 3 solutions :

- Lithography before PEDOT deposition : Lift off
- Protection coating on PEDOT layer

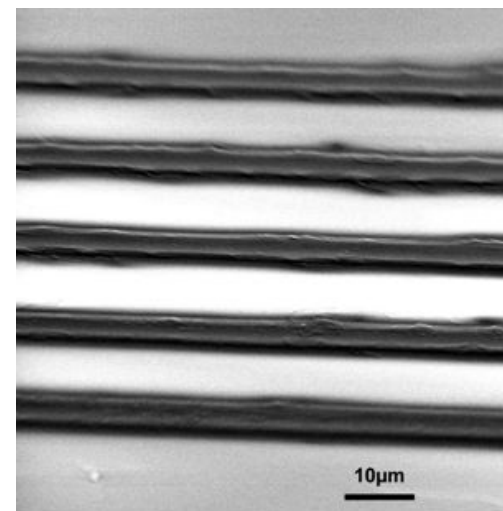
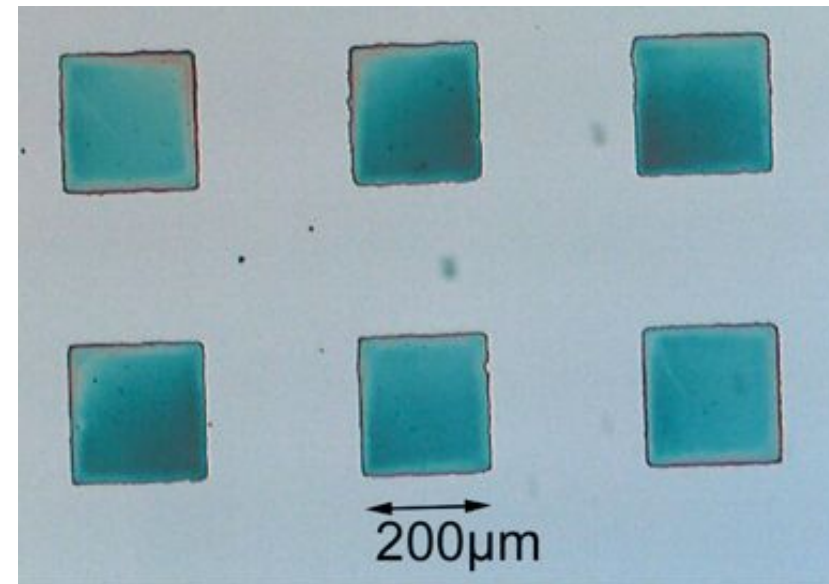
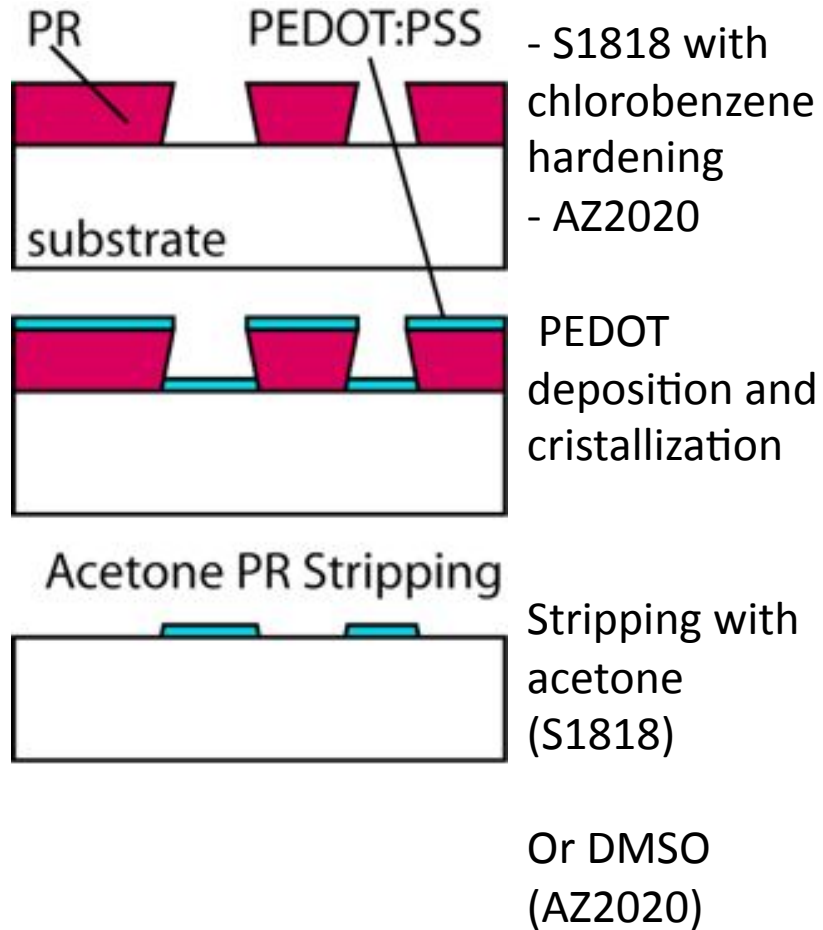
And :

- Specific photoresists Developed with hydrofluoroethers



P. G. Taylor et al. Adv. Mater. 2009,  
21, 2314–2317

# Lithography : Lift off



U-shape structures

# Lithography with protection : Parylene

Example : use of Parylene-C as protective layer

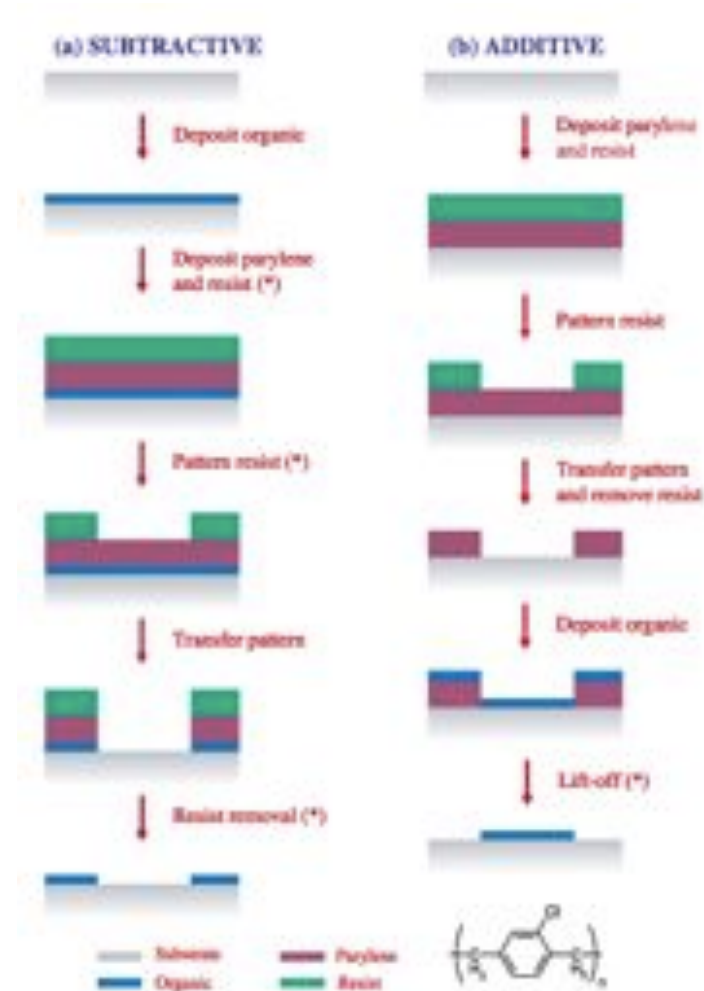
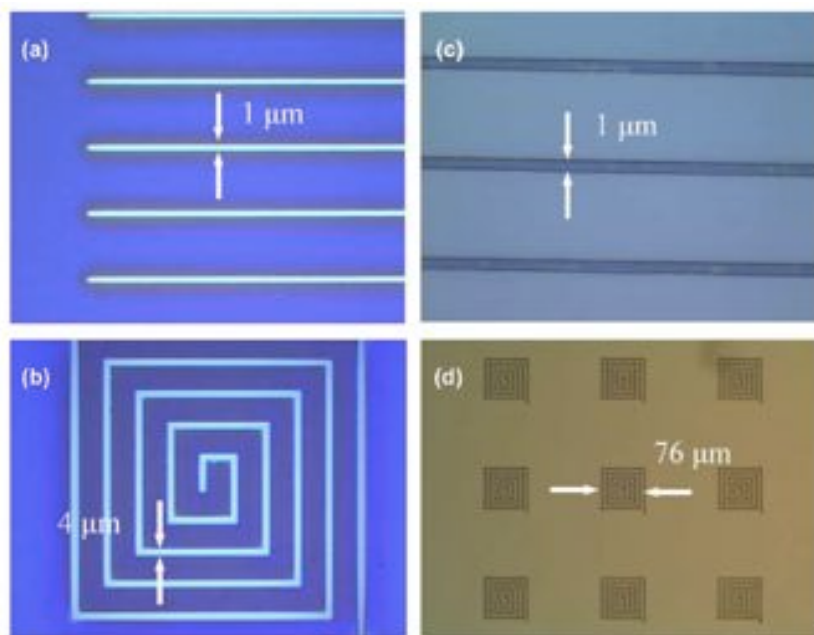
PEDOTS:PSS thin layer

Parylene

Photoresist

Reactive ion etching of Parylene and PEDOT

**Peeling** of parylene (weak adhesion)



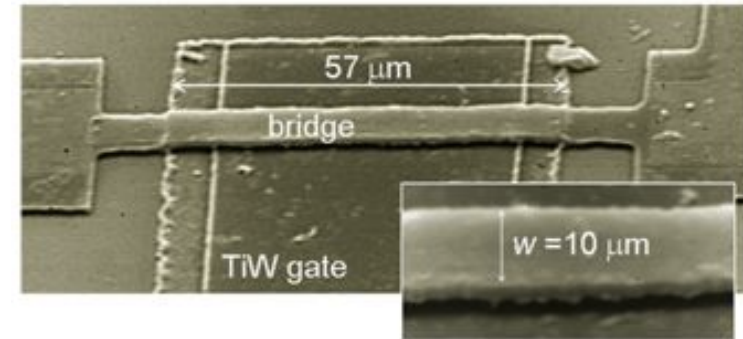
J.A. DeFranco et Al. Organic Electronics 7, 22–28

**Peeling Parylene limits the shape of patterns : continuous structures**

# Lithography with protection : Aluminum

Blend of  
PEDOT:PSS  
IPA  
PMMA

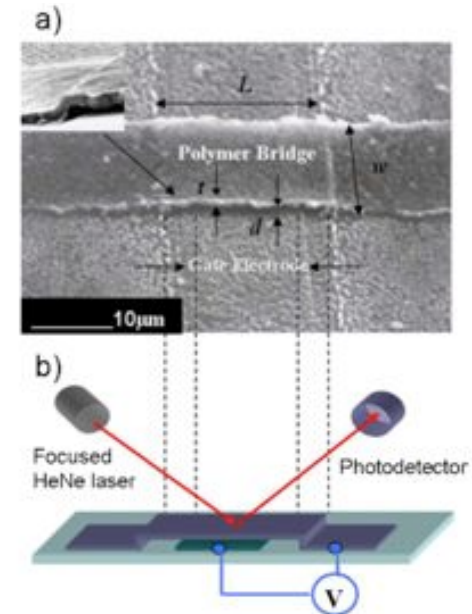
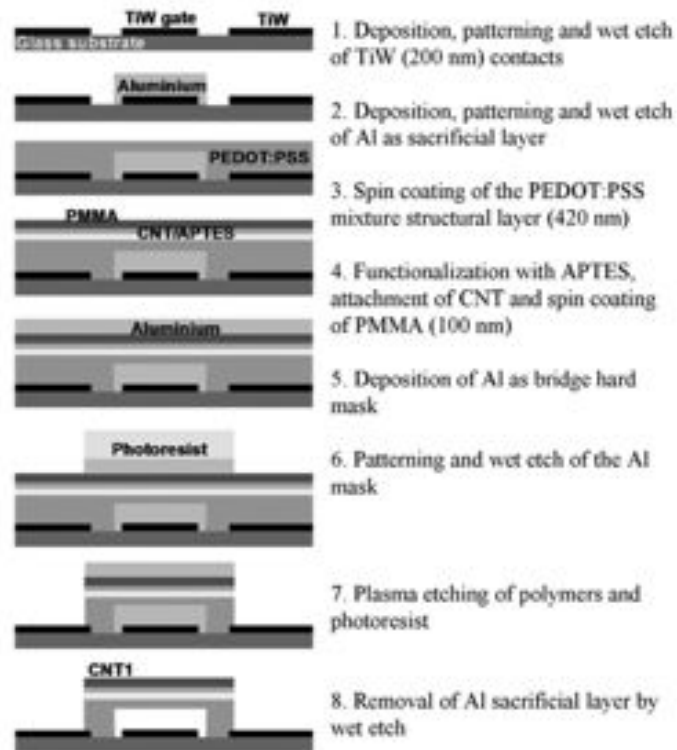
Virginia Chu and Joao Conde,  
INESC MN, Lisboa, Portugal



And addition of CNTs attached by  
surface functionalisation

Use of Aluminium for both  
Hard mask for etching and  
Sacrificial layer

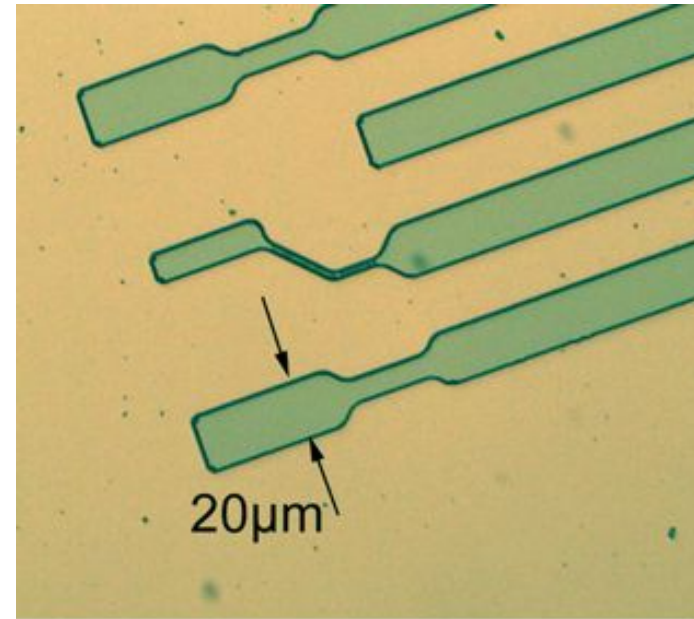
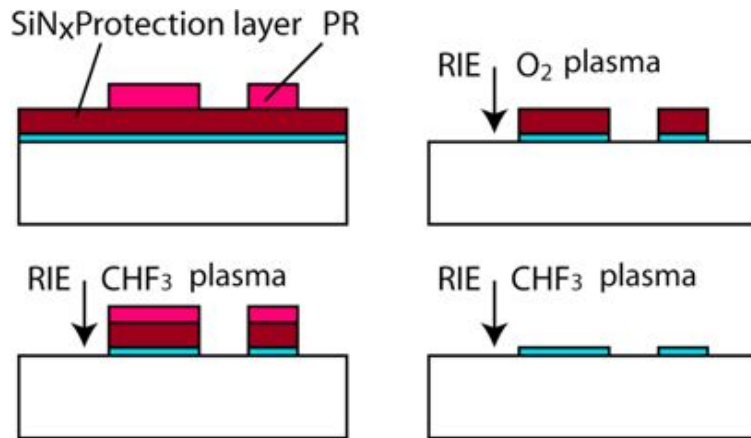
Wet etching of Aluminium  
compatible with PEDOT:PSS  
compound



P. M. Sousa, APPLIED  
PHYSICS LETTERS 99,  
044104 (2011)

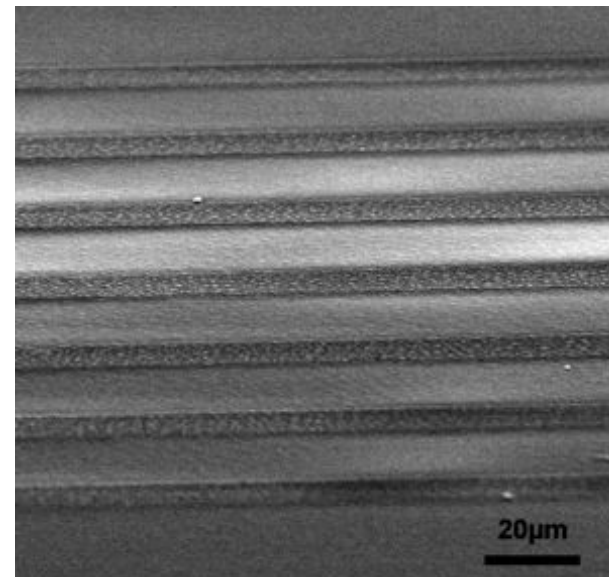
# Lithography with protection : $\text{Si}_3\text{N}_4$

## Silicon Nitride protection layer



PEDOT:PSS deposition  
SiN<sub>x</sub> **PECVD** deposition (**200°C**) 100nm  
Lithography  
RIE selective etching  
CHF<sub>3</sub> for SiN<sub>x</sub>  
O<sub>2</sub> for PEDOT:PSS

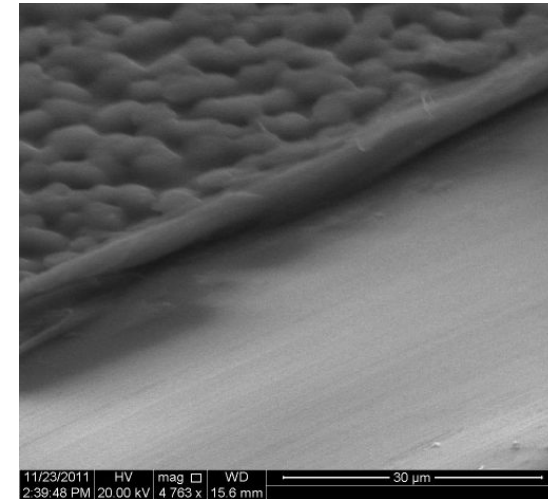
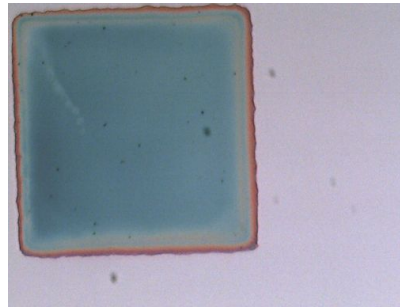
Flat profile, but requires precise etching control



# *Applications*

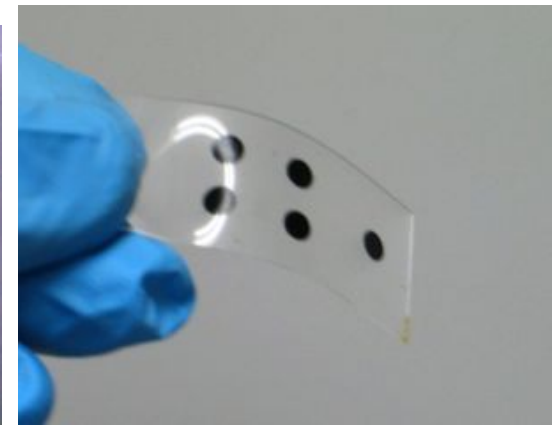
**Electrodes for all polymer pyroelectric sensor**

**Carbon Nanotube interface with PEDOT:PSS**



PEDOT / PVDF / PEDOT

**Deformable electrodes for tactile sensor**  
(graphite PDMS force sensor)



**BioElectrodes for electrophysiology**

# ***Conclusions***

**PEDOT:PSS is an interesting material for implementation of deformable electrodes in several applications**

**Patterning techniques includes**

- Soft lithography**
- standard lithography / RIE etching with process adaptation**

**Potential use in bioelectrodes for neuro interface**

**Further work :**

**Effect of RIE on polymer, degradation?**

**Best gases for etching  $\text{CHF}_3$ ?  $\text{CF}_4$ ?  $\text{O}_2$**