

Bioelectronics and Neuromorphic Computing with Organic Electrochemical Transistors – 3rd Lecture

Lecture Summer Term 2026

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4. Processing of Organic Electrochemical Devices

4.1. Lithography

4.2. Printing, Vacuum Deposition

4.3. Vertical Device Structures

4.4. Scaling of Volumetric Devices

4. Processing of Organic Electrochemical Devices

Introduction

- **Electrochemical devices can cover lateral dimensions from $< 1\mu\text{m}$ to $> 1\text{mm}$ depending on the application**
 - High frequency operation ($>1\text{kHz}$) requires usually small devices ($<10\mu\text{m}$)
 - Biomarker sensors usually do not need to be fast ($>1\text{mm}$)
 - different device dimensions require different patterning techniques
- **Electrochemical devices are volumetric devices and at the border between thin-film and thick-film devices**
 - OMIEC has often very high conductivity → very thin devices needed to limit power consumption ($<10\text{nm}$)
 - Electrolytes are often poorly conductive → thick layers needed to get sufficient conductance ($>20\mu\text{m}$)

4. Processing of Organic Electrochemical Devices

Introduction

- **Parameters relevant to decide on the processing techniques**
 - **Device performance**
 - Transconductance/ on/off ratio, threshold voltage, cut-off frequency
 - Circuit level: Overlap capacitance, shunt resistances
 - **Material properties**
 - Viscosity, solvent, thermal properties
 - Conductivity, stability
 - **Economic / Ecological aspect**
 - Throughput, Costs
 - Resolution
 - CO₂ emissions/ other ecological impacts

4. Processing of Organic Electrochemical Devices

Introduction

- **Applications of organic electrochemical devices**
 - Biosensors → slow but high level of reliability (large structures)
 - Printed circuit for signal processing → fast and low-power (small structures)
 - RF-Communication → (large but fast structures)
 - Batteries/ super-caps → (large with high level of reliability)

4. Processing of Organic Electrochemical Devices

4.1 Photolithography

- **Advantages**
 - Very high level of reliability
 - Sub- μm resolution and fast
 - From sub- μm to cm structures
- **Disadvantages**
 - Very high cost / highest requirements on lab quality
 - High material consumption
 - Requires either sufficient chemical or

4. Processing of Organic Electrochemical Devices

4.1 Photolithography (<https://www.microchemicals.com/DOWNLOADS/Application-Notes/>)

- **Etching process or Lift-off/ Peel-off**
 - Etching process is used when underlying layer is not sensitive to resist, developer, etchant, remover, or process conditions (heat)
 - **Starting point:** Substrate with layer for patterning (thickness ideally < feature size)
 - Applying photoresist (resin) using e.g., spin- or spray coating
 - Spin coating layer thickness of resist $\sim (\text{rpm})^{-1/2}$ of coater.
 - Target thickness: Thick resist for good etching projecting, too thick resist gives poor feature accuracy



Substrate with layer for patterning



Spin-coating/ Spray coating of photoresist

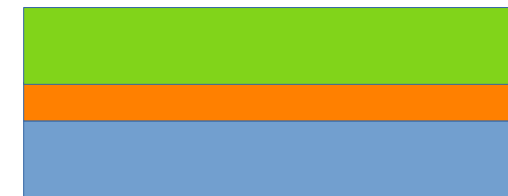
4. Processing of Organic Electrochemical Devices

4.1 Photolithography

- **Spincoating**
 - Typical layer thickness of resist for 200nm thick layer for etching = 1...3 μm
 - Often additional pretreatment steps before spincoating to improve adhesion of resist to surface (e.g., thermal annealing to remove H₂O)
 - **After spincoating every resist requires a pre-bake to remove solvent from resist! (temperature depends on resist, usually ~100°C but not too high to induce thermal crosslinking)**



Substrate with layer for patterning

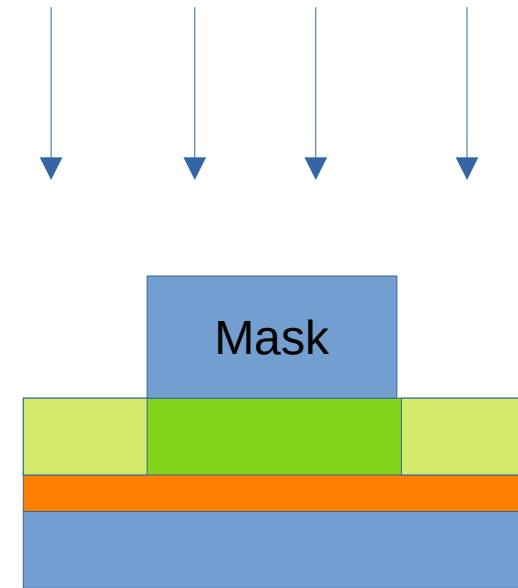


Spin-coating/ Spray coating of photoresist

4. Processing of Organic Electrochemical Devices

4.1 Photolithography

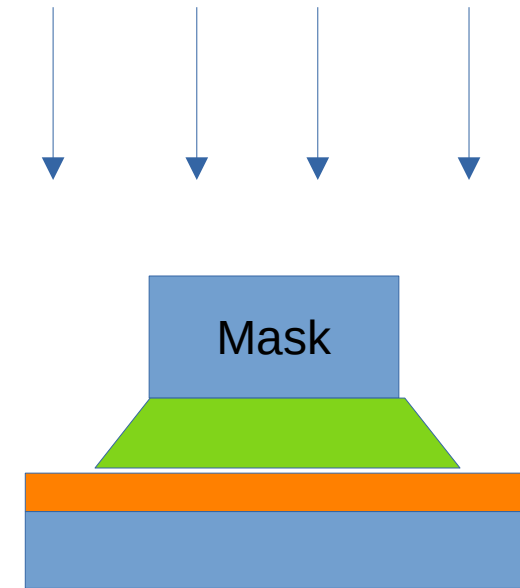
- **Exposure process**
 - Two types of resist: positive tone vs. negative tone
 - **Positive tone: gets removed by developer in exposed areas**
- Positive tone: (recipe for most common resist materials)
 - Resist of mixture of low (LD) and high molecular weight (HD) polymer
 - LD high solubility, HD low solubility
 - UV exposure activates Dinaphthoquinone (DNQ) (**UV broadband**)
 - Wolf rearrangement reaction (H₂O) needed
 - increase fraction of LD polymer increases solubility of exposed areas



4. Processing of Organic Electrochemical Devices

4.1 Photolithography

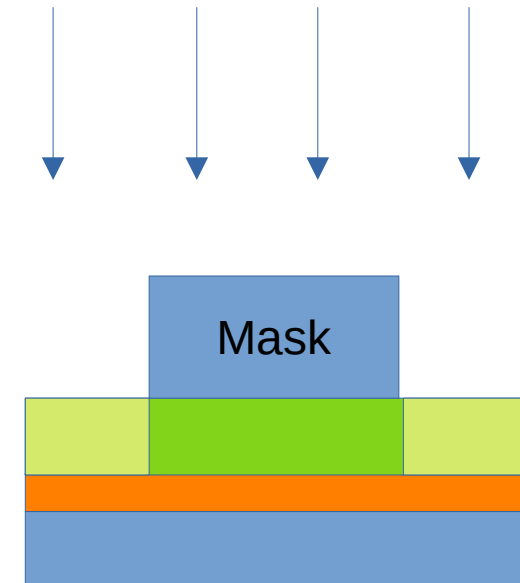
- **Development process**
 - Base developers are most common (e.g., NaOH or TMAH)
 - **LD polymer is washed away. Typically solubility contrast between exposed and unexposed areas only 1:10-1:100**
 - Limited solubility ratio leads to typical resist angle (positive edge)
 - High temperature or long development make angle more shallow



4. Processing of Organic Electrochemical Devices

4.1 Photolithography

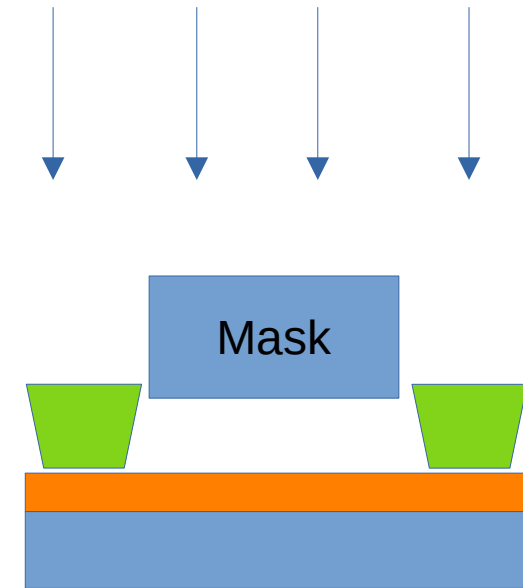
- **Exposure process**
 - Two types of resist: positive tone vs. negative tone
 - **Negative tone: removed by developer in unexposed areas**
 - **Negative tone: (recipe for most common resist materials)**
 - Resist of is composed of a crosslinkable polymer (e.g., epoxy)
 - UV exposure activates Photoacid generator (**usually just one wavelength, e.g., 365 i-line**)
 - PAG initiates oxidative polymerization → x-linking
 - Post-exposure bake needed at critical temperature to make x-linking happen
 - Reduced solubility in developer



4. Processing of Organic Electrochemical Devices

4.1 Photolithography

- **Development Process**
 - Crosslinking is strongest close to the surface
 - **Non-crosslinked or weakly crosslinked areas are washed away quickly (high solubility contrast)**
 - Typical negative tone resist profile (undercut)
 - Negative tone resist far less sensitive to overdevelopment
 - Typical developers are also NaOH and TMAH
 - NaOH and TMAH damage PEDOT:PSS and many other OMIECS irreversibly!
 - Direct lithography only possible with different chemistry

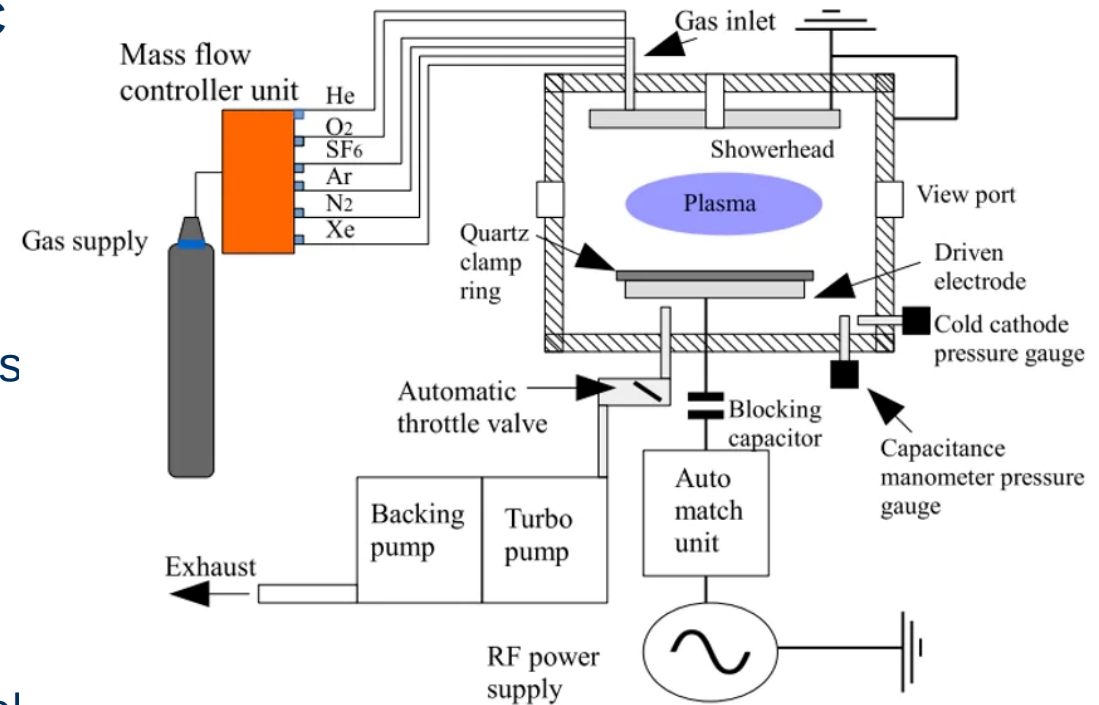


4. Processing of Organic Electrochemical Devices

4.1 Photolithography

- **Etching process**

- OMIEC cannot be etched using wet-chemical materials (except Piranha)
- **Reactive Ion Etching is used instead to etch OMIEC**
- Low power Plasma (usually pure O₂, possibly with Ar) with V_{bias} to accelerate O₃ radical towards the substrate
- Reactive O₃ forms CO₂, CH, CO, CN volatile fragments (pumped out)
- Ar used to mechanically sputter surface
- Etching rate mainly given by RF power and O₂ flow
- After etching resist needs to be removed (either in devel .



4. Processing of Organic Electrochemical Devices

4.1 Photolithography

- **Lift-off or Peel-off process**
 - Useful if material cannot withstand lithography process
 - Conventional litho process (usually negative tone resist) is used to form a relief on the surface
 - Sometimes are additional underlayer (e.g., parylene for mechanical peel-off)
 - Underlayer is etching using resist mask
 - Targeted material is coated onto the substrate
 - Resist relief leads to continuous film formation
 - Resist and underlayer can be peeled off or dissolved



4. Processing of Organic Electrochemical Devices

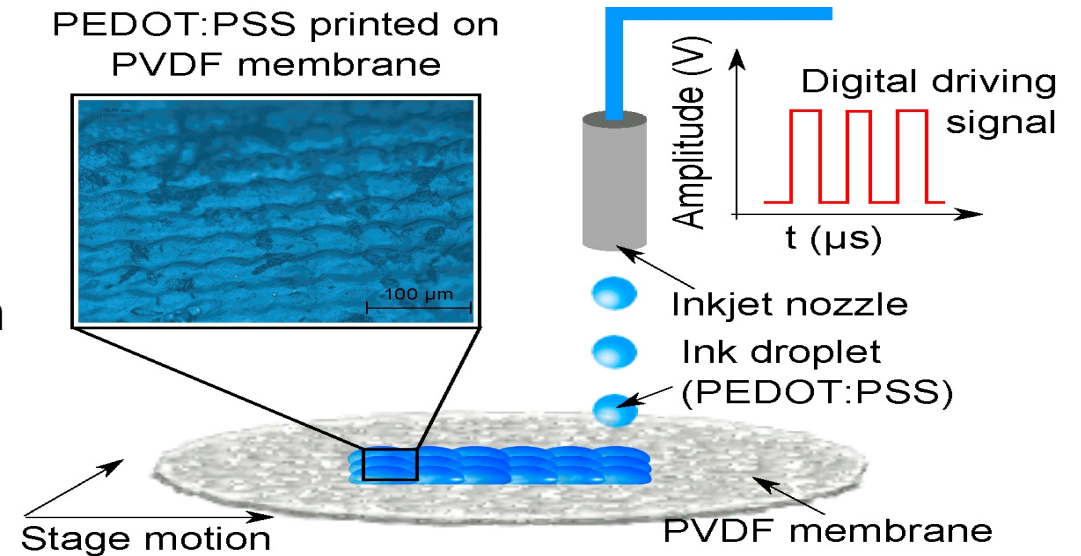
4.1 Photolithography

- **Lithography for OMIECs**
 - **Peel-off and lith-off process can give resolution down to 1 μ m or below**
 - Conventional lithography + etching usually not tolerated by OMIEC
 - Fluorinated resins can be used for OMIECs but Carbon footprint 20000x larger

4. Processing of Organic Electrochemical Devices

4.2 Printing

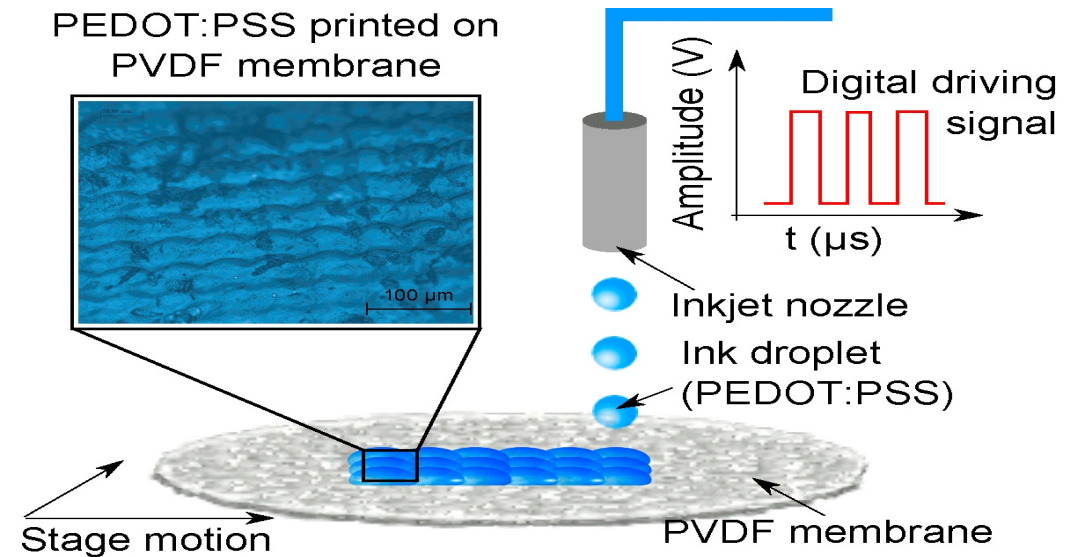
- **Inkjet Printing (Drop-on-Demand Printing)**
- PEDOT:PSS (but also many others) films can be deposited from dispersion
- Printing resolution 10s of microns
- Resolution depends on surface wetting of drops, drop formation and drop volume
- High throughput-cost effective
- Processing parameters such as viscosity, surface tension will affect the resolution and quality of the deposited films
- Film thickness from $<10\text{nm}$ to $>50\mu\text{m}$ possible but uniformity not good (droplet waviness)



4. Processing of Organic Electrochemical Devices

4.2 Printing

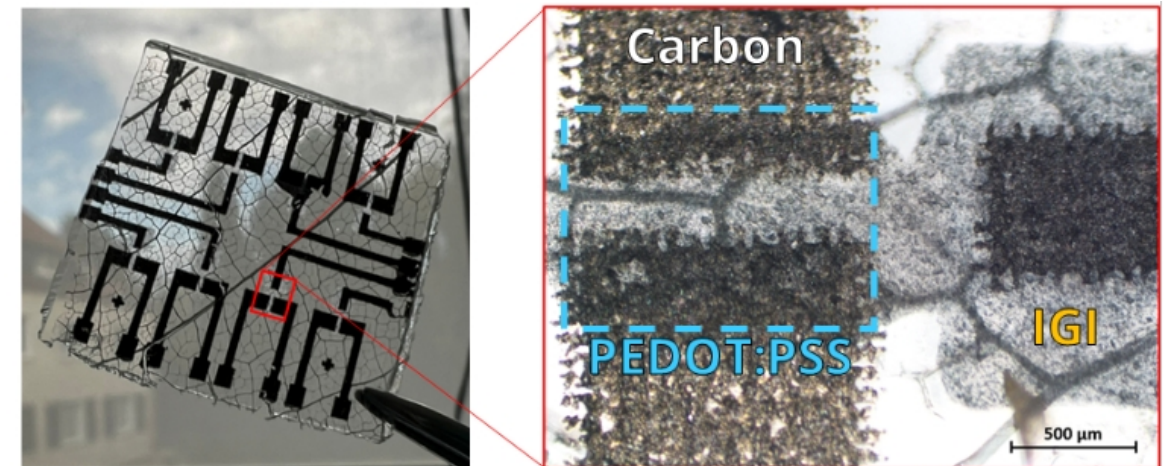
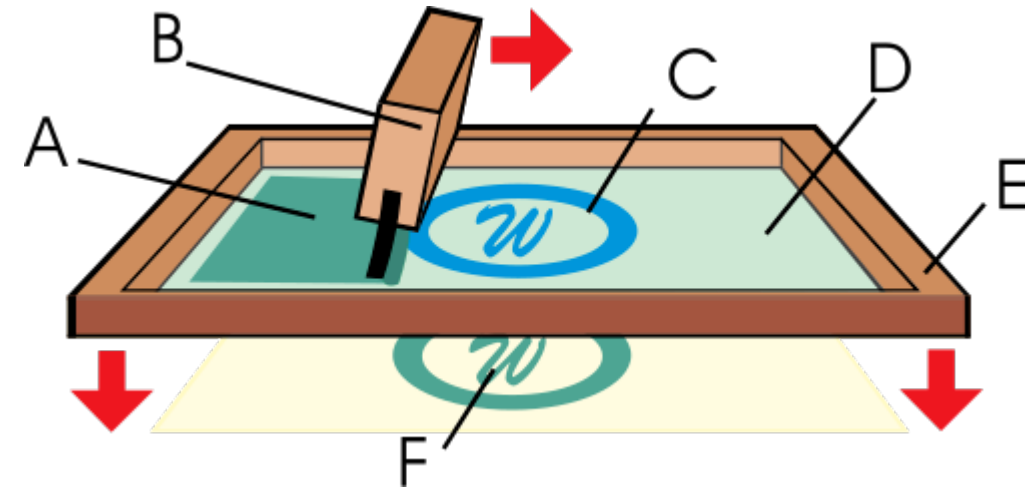
- **Inkjet Printing (Drop-on-Demand Printing)**
 - Has medium resolution (<math><5\mu\text{m}</math> possible) and is an additive method (effective use of materials)
 - However, very limited due to possible choice of solvents (no low boiling point solvents) and viscosity (droplet formation)
 - Inkjet well suited e.g., for electrolytes (thickness control not important)



4. Processing of Organic Electrochemical Devices

4.2 Printing

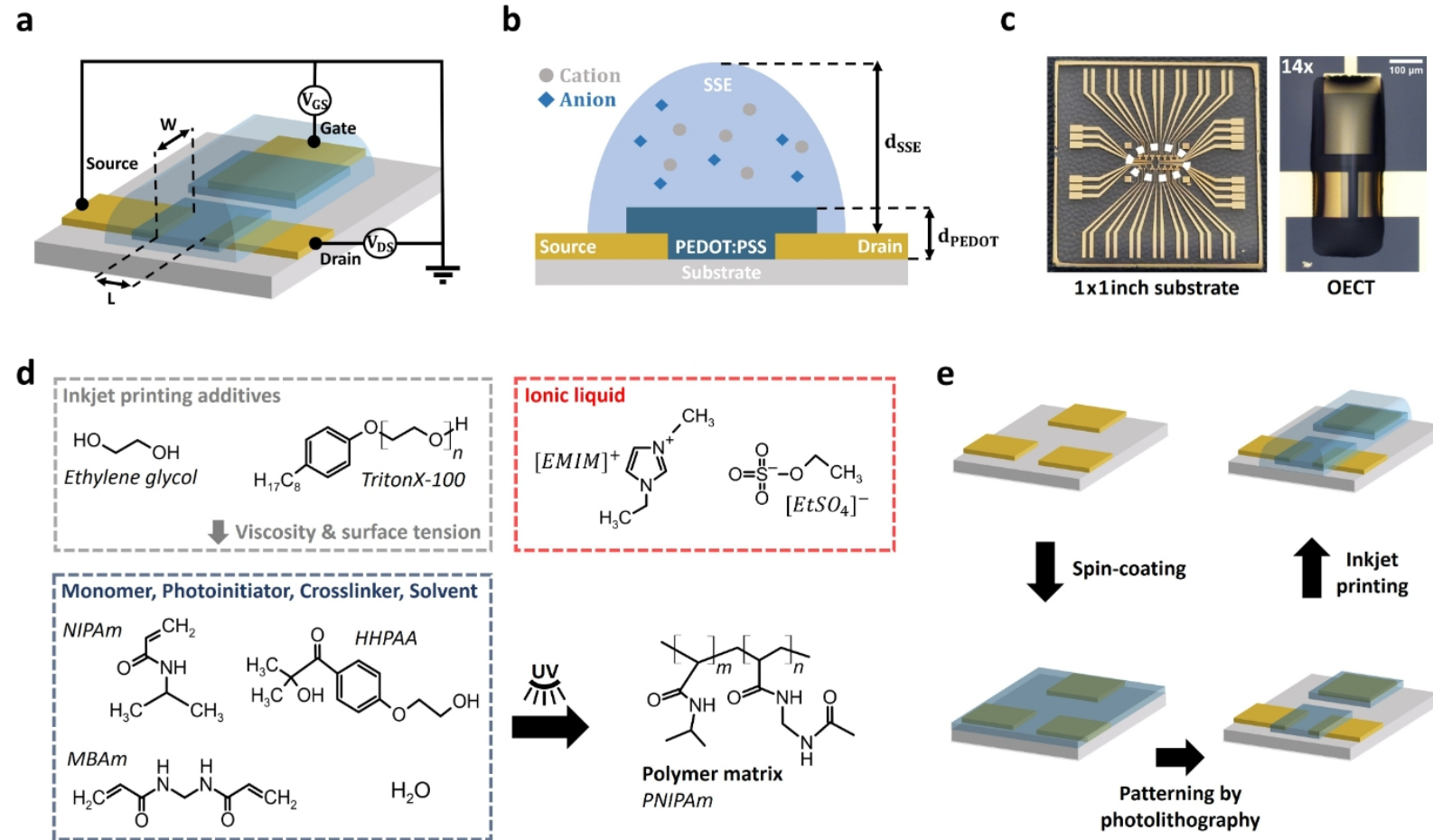
- **Screen-printing**
 - High throughput low resolution techniques
 - Squeegee is used to press ink / paste through screen
 - Resolution $>20\mu\text{m}$
 - Thickness of layers $> 100\text{nm}$
 - Thickness not very precise but for many applications not relevant (e.g., electrolyte, electrodes,...)
 - Can adopt wide range of viscosity



4. Processing of Organic Electrochemical Devices

4.2 Printing

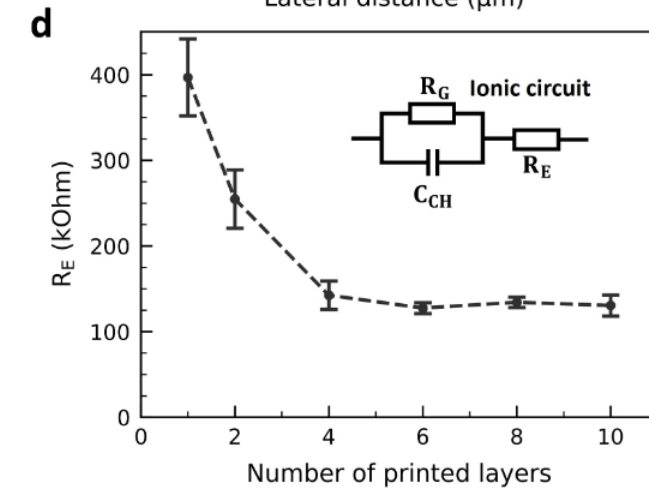
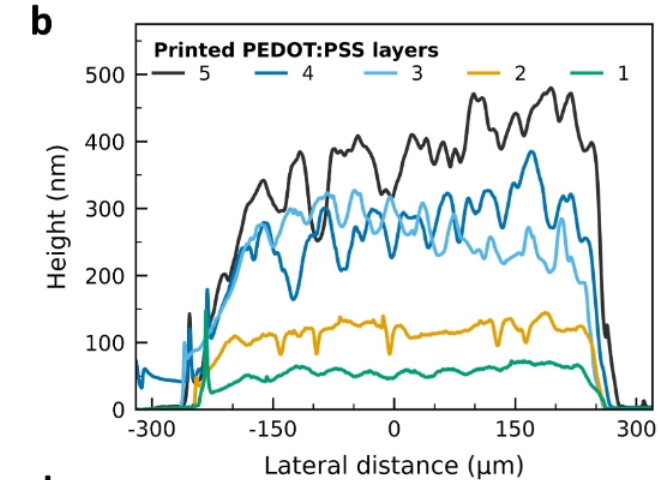
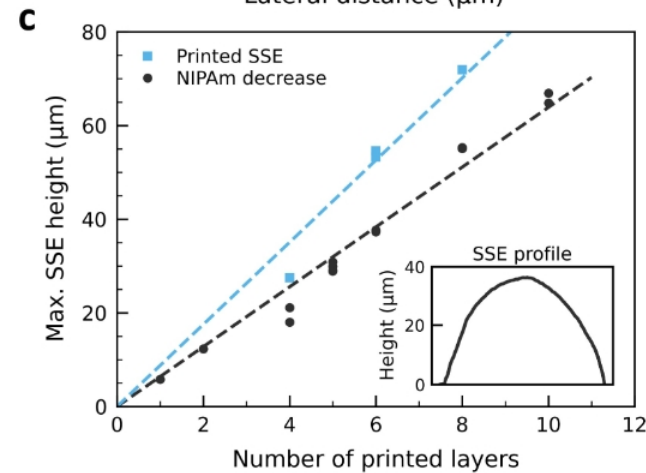
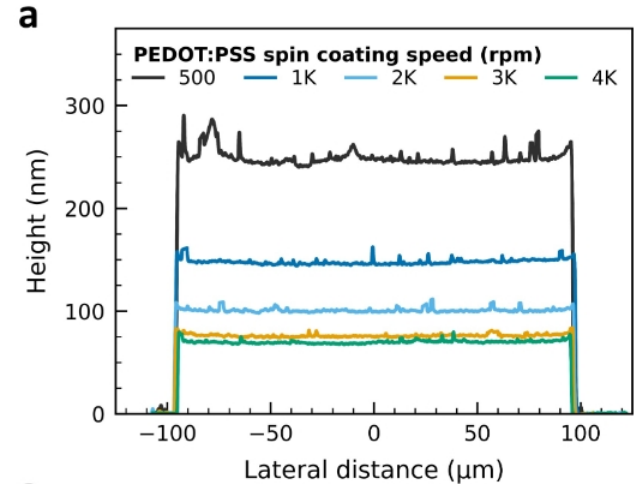
- **Hybrid process**
- Combining best properties from printing and lithography
- Litho is used to define electrode and OMIEC layer
- Ink-jet printing is used to print solid-state electrolyte due to high thickness



4. Processing of Organic Electrochemical Devices

4.2 Printing

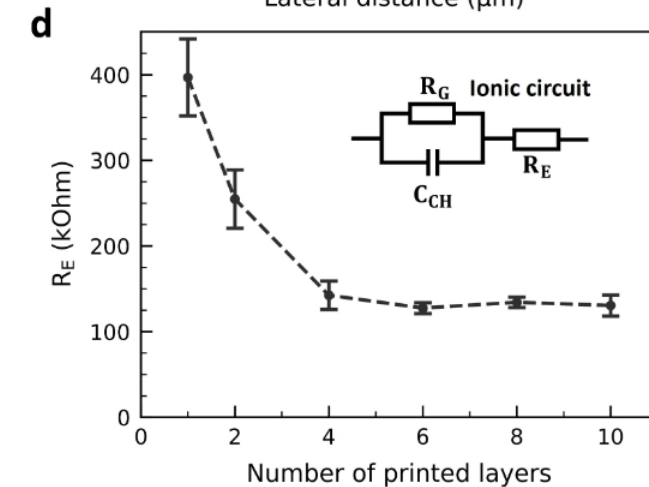
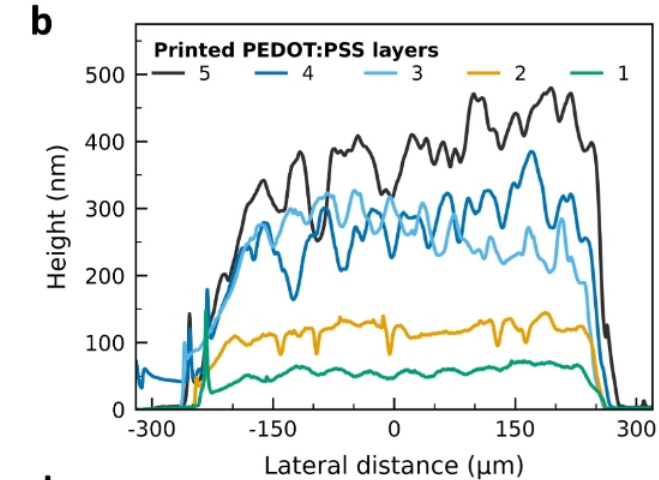
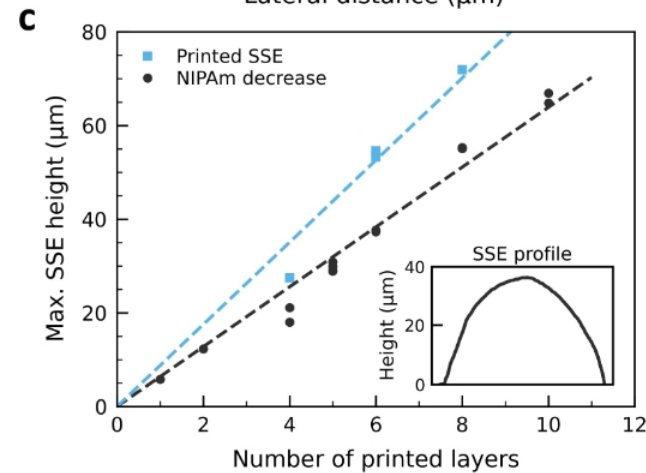
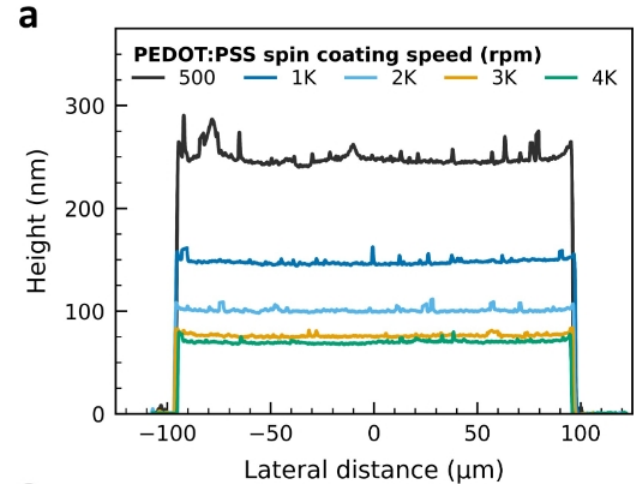
- **Hybrid process**
 - Lithography gives much higher quality and thickness control over inkjet for OMIEC
 - Conductivity of electrolyte independent of thickness for thickness $> 50\mu\text{m}$ (4 layers)
 - easy to print
 - Electrolyte can be UV x-linked after printing



4. Processing of Organic Electrochemical Devices

4.2 Printing

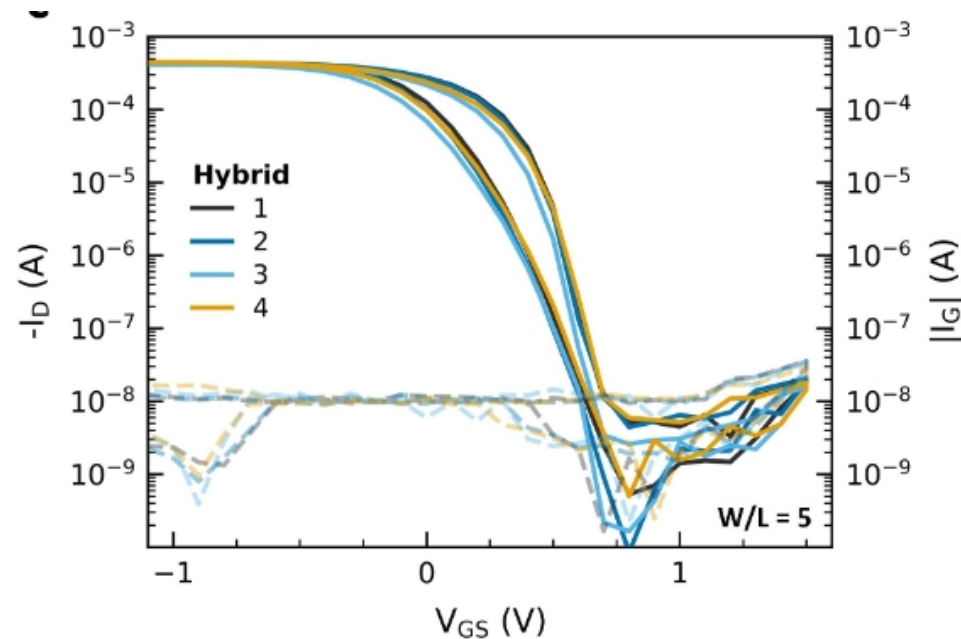
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4. Processing of Organic Electrochemical Devices

4.2 Printing

- **Hybrid process**
 - Combination of printing and lithography gives highest uniformity and stability
 - Litho → high density of integration → low power consumption and high speed
 - Inkjet printing: Convenient low cost process for electrolyte

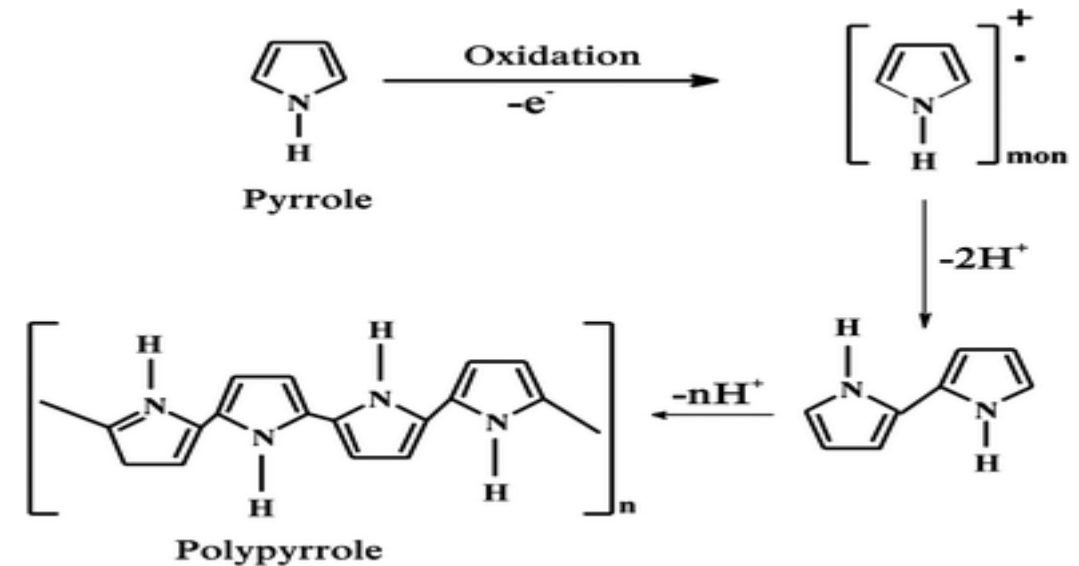


	Lithography	Printing	Hybrid
V_T (V)	0.68 ± 0.17	0.88 ± 0.11	0.4 ± 0.04
g_{max} (mS)	0.45 ± 0.07	0.5 ± 0.1	0.59 ± 0.06
Ψ (V)	5.2 ± 2.4	5.1 ± 0.7	2.7 ± 0.4
On/Off	3877 ± 1308	23476 ± 16183	30430 ± 3038
SS (mV/dec)	150 ± 12	70 ± 12	82 ± 6

4. Processing of Organic Electrochemical Devices

4.2 Printing

- **Electropolymerization**
 - Many OMIEC can be deposited directly from solution by polymerization (electropolymerization)
 - Oxidative polymerization due to radical formation is used to form polymers
 - Example: Pyrrole



4. Processing of Organic Electrochemical Devices

4.2 Printing

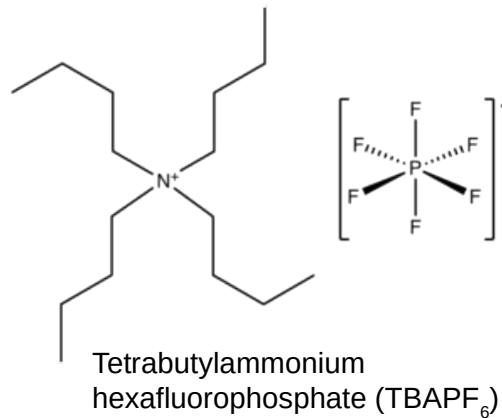
- **Electropolymerization**

- Positive potential → high concentration of PF_6^- → causing EDOT radical formation
- Radicals for dimers,.....

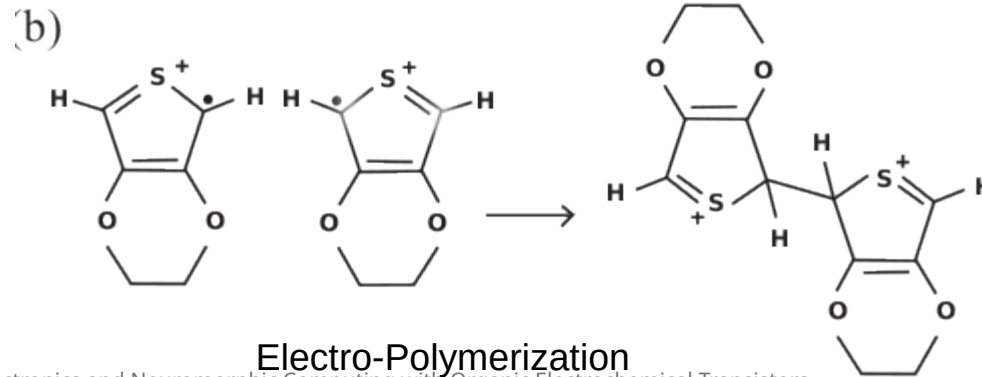


EDOT

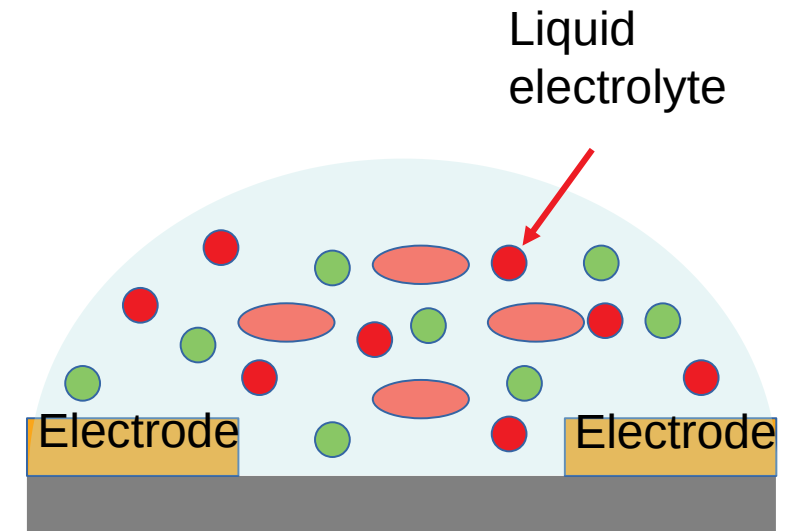
3,4-ethylenedioxythiophene
EDOT Monomer



Tetrabutylammonium
hexafluorophosphate (TBAPF_6)



Electro-Polymerization



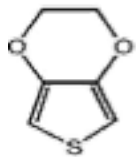
Oxidative
Polymerization

4. Processing of Organic Electrochemical Devices

4.2 Printing

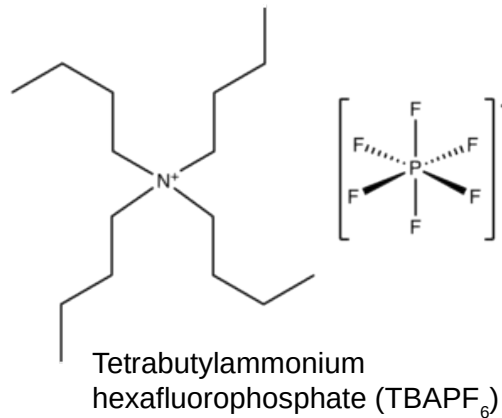
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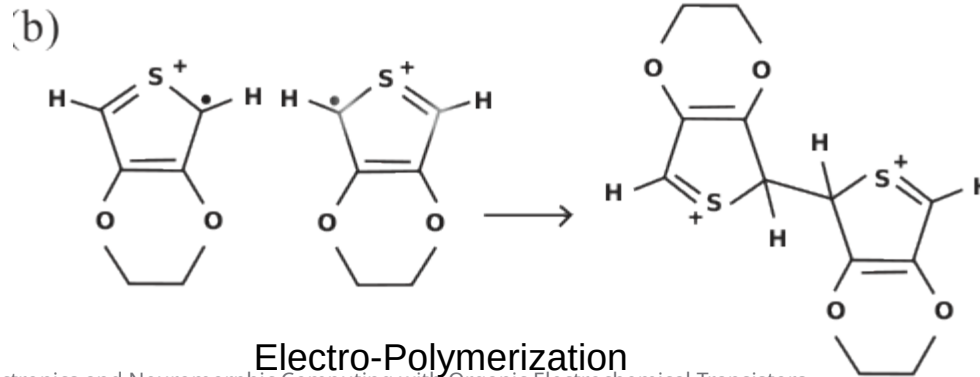


EDOT

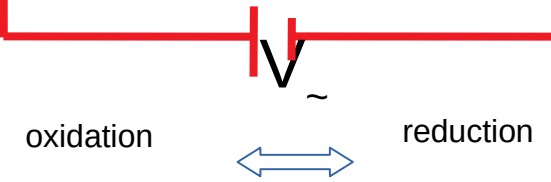
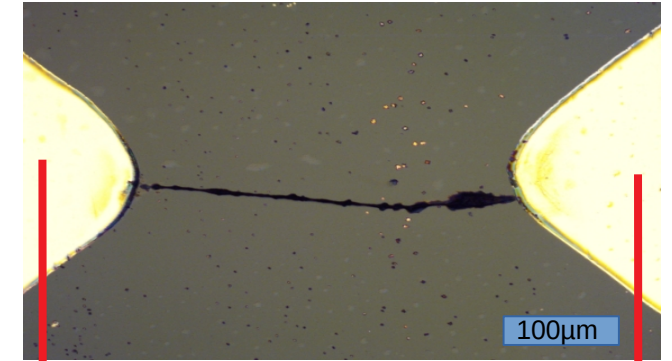
3,4-ethylenedioxythiophene
EDOT Monomer



Tetrabutylammonium
hexafluorophosphate (TBAPF_6)



Electro-Polymerization



Oxidation starts at 1.4V (IP of EDOT monomer) but often higher voltage needed

4. Processing of Organic Electrochemical Devices

4.2 Printing

- **Electropolymerization**
- Voltage and frequency govern film properties
- DC voltage = growth of film (current and time determine the thickness and speed of growth towards the counterelectrode). Often μm -thick films
- AC voltage: fiber growth – diffusion limited aggregation. High frequency \rightarrow thinner fibers
fibers follow the electric field

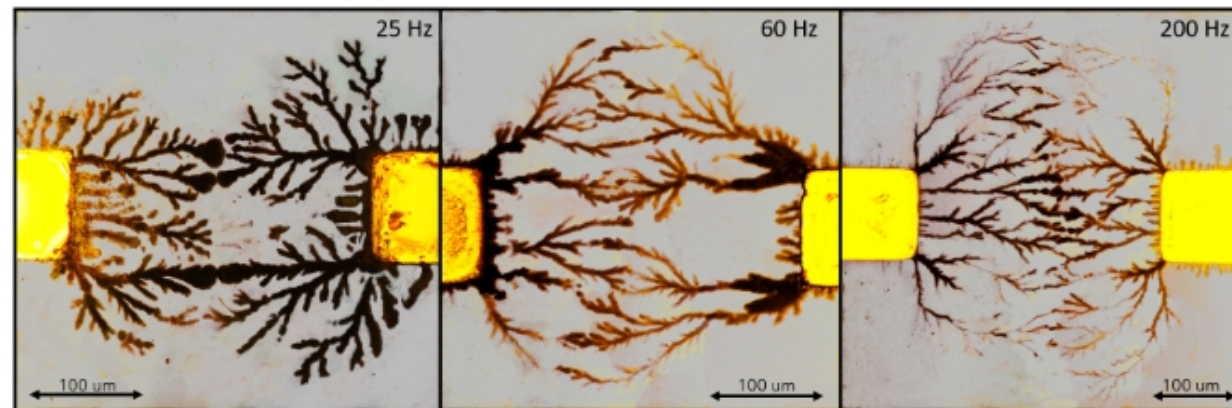


Figure 6.1: FDP-grown devices polymerized at 25 Hz, 60 Hz, and 200 Hz

Oxidative
Polymerization

4. Processing of Organic Electrochemical Devices

4.2 Printing

- **Electropolymerization**

- Deposition rate depends on monomer load (M) and charge (Q)

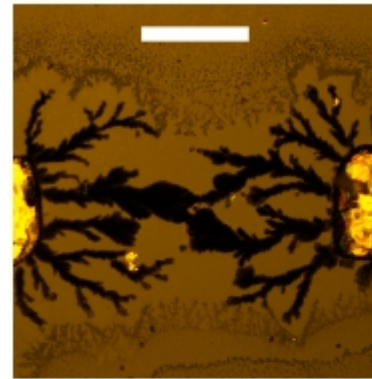
$$\frac{dP}{dt} \propto [M]^2 Q^2$$

- Total amount of material deposited

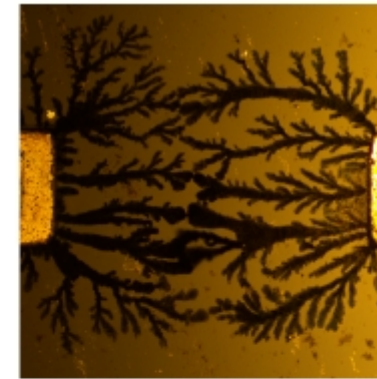
$$P = \int_0^{T/2} \frac{dP}{dt} dt \propto \frac{T}{2} ([M]CV)^2$$

- Growth voltage depends on electrode capacitance (voltage drop should

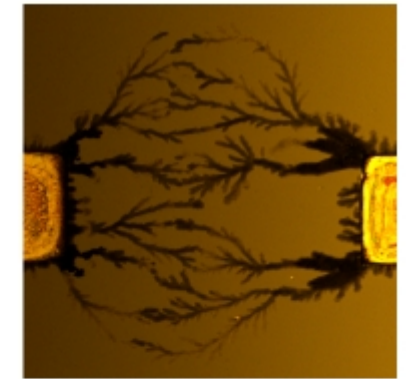
happen of electrode/ electrolyte double layer)



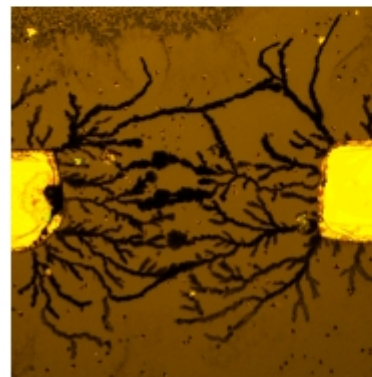
(a) $f = 20$ Hz



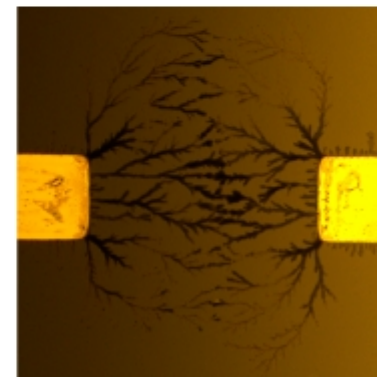
(b) $f = 40$ Hz



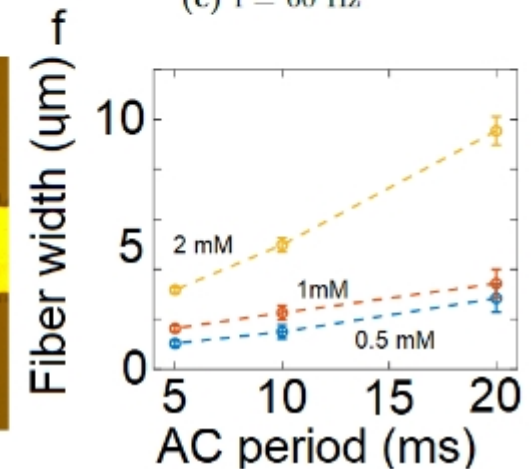
(c) $f = 60$ Hz



(d) $f = 80$ Hz



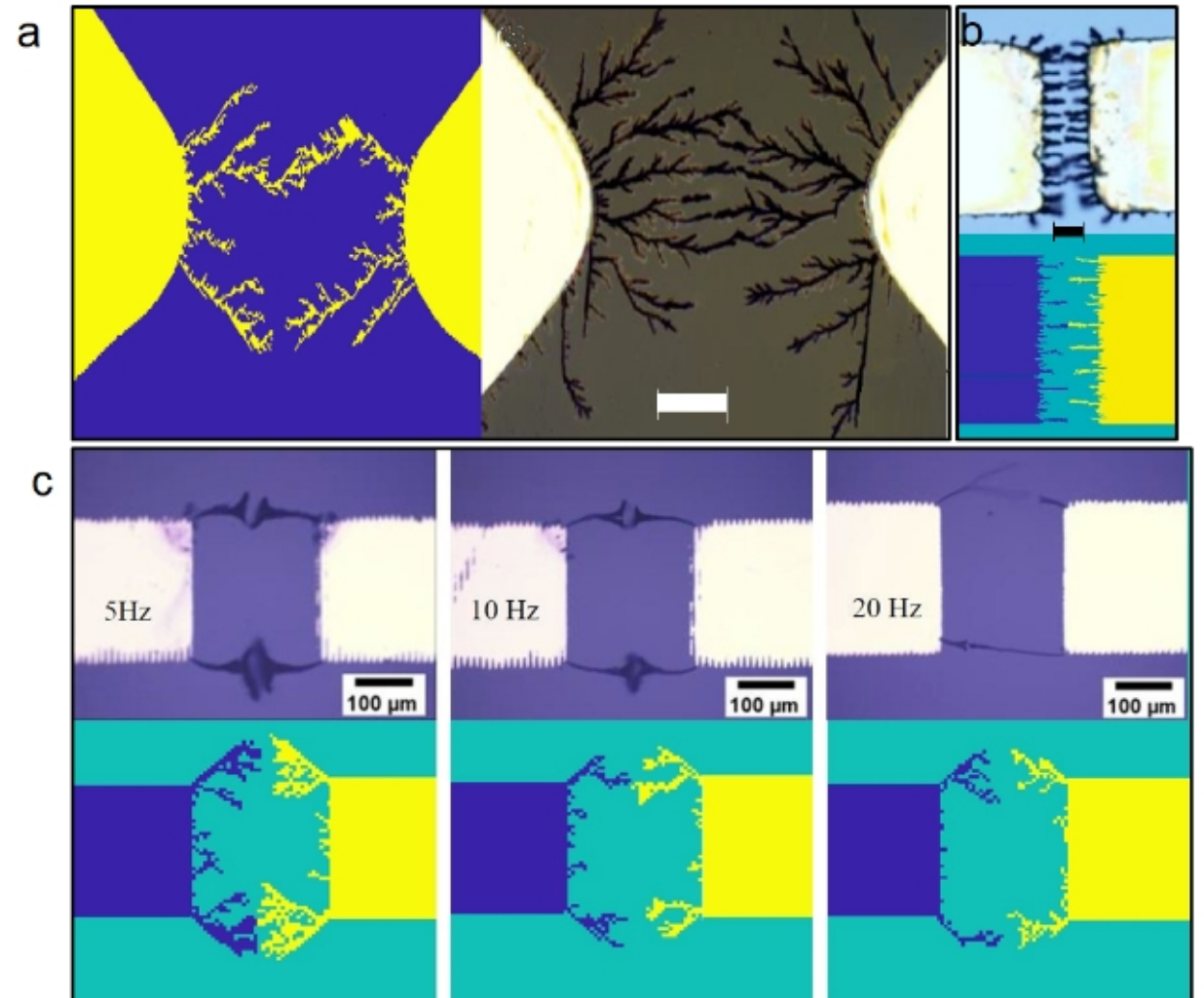
(e) $f = 100$ Hz



4. Processing of Organic Electrochemical Devices

4.2 Printing

- **Electropolymerization**
 - Modeling of fiber growth using drift-diffusion reaction equation
 - Growth is clearly governed by the field distribution
 - Branching is a random effect that gets strong for high field gradients
 - Fibers can be as thin as $1\mu\text{m}$



4. Processing of Organic Electrochemical Devices

4.3 Vertical Devices

- **Motivation**
 - Lithography and printing cannot provide very short channel length (or would be very expensive)
 - However, short channel length needed for high amplification and fast devices
 - vertical integration

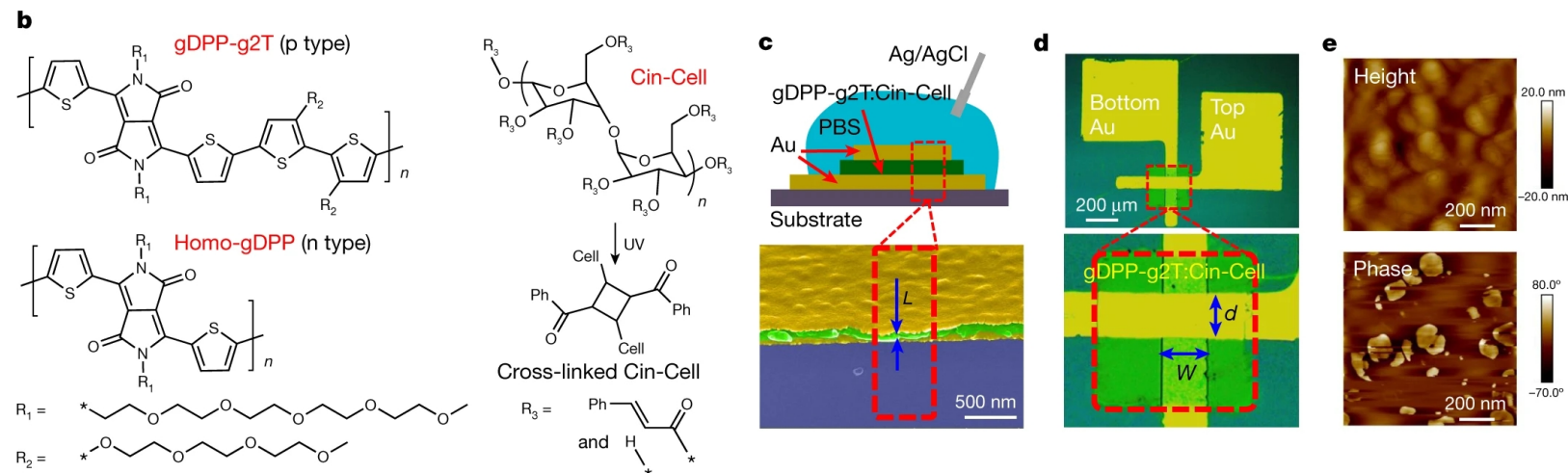
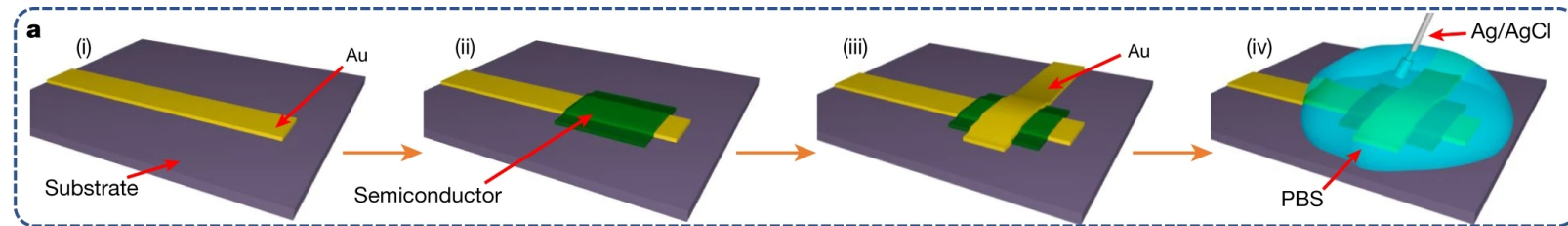
4. Processing of Organic Electrochemical Devices

4.3 Vertical Devices

- Simple stacked vertical OECTs

- Channel length defined by layer thickness (<200nm)

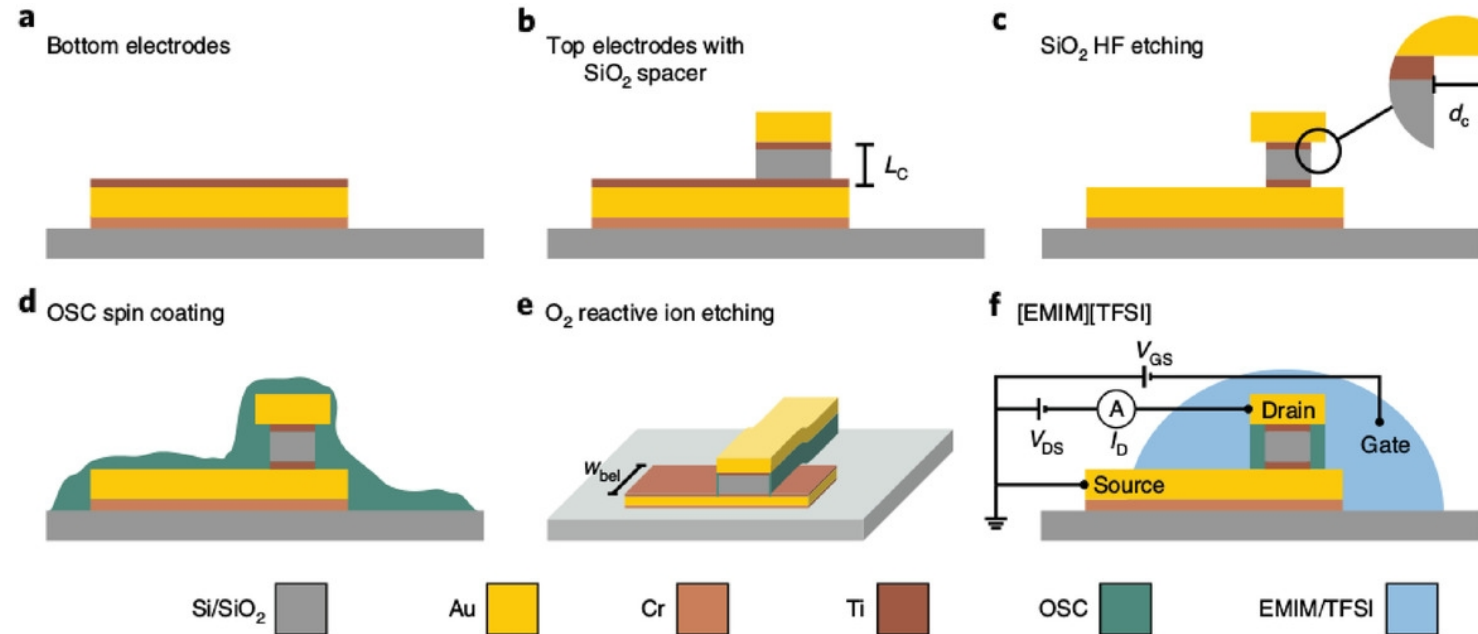
- Very high on-current but ions need time to penetrate from the side



4. Processing of Organic Electrochemical Devices

4.3 Vertical Devices

- **Vertical edge OECTs**
 - Microfabricate edge with height of $100\text{-}200\text{nm} = L$
 - OMIEC is coated at the side
 - easy ion penetration
 - Very high on/off ratio
 - Very high gain
 - Current density up to $1\text{MA}/\text{cm}^2$



4. Processing of Organic Electrochemical Devices

4.3 Vertical Devices

- **Vertical gate OECTs**
 - Vertical channel devices have high gain but speed is limited by gate resistance
 - Best option for high speed is a top-gate (vertical)
 - Requires solid-state electrolyte
 - Gate is printed onto solid-state electrolyte

