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Inkjet Printed diF-TES-ADT Organic Thin Film Transistors

Yuanyuan V. Li[1,2], Devin A. Mourey[1,3], Marsha A. Loth[4], Dalong A. Zhao[1,2], John E. Anthony[4], and Thomas N. Jackson[1,2]

[1]Center for Thin Film Devices and Materials Research Institute,
[2]Department of Electrical Engineering, Penn State University
[3]Department of Material Science and Engineering, Penn State University
[4]Department of Chemistry, University of Kentucky

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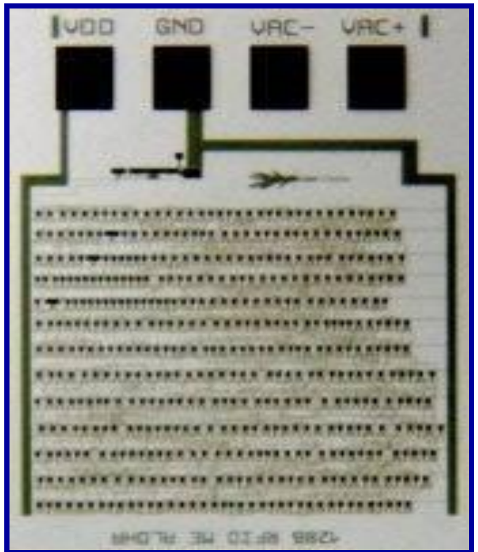
Organic Electronics

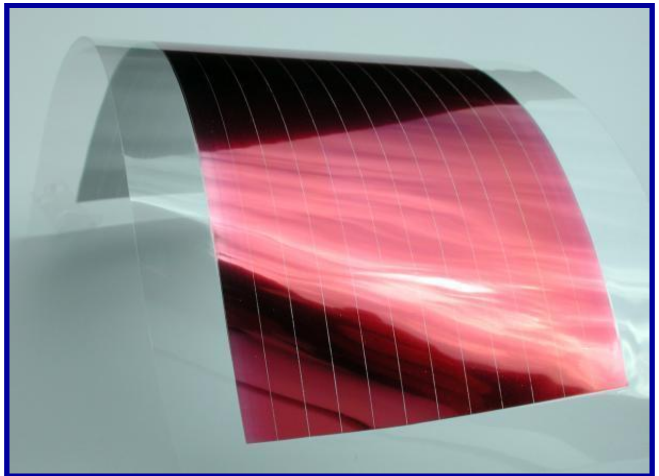
Wide range of potential low cost, large area, organic semiconductor applications

SONY OTFT AMOLED display

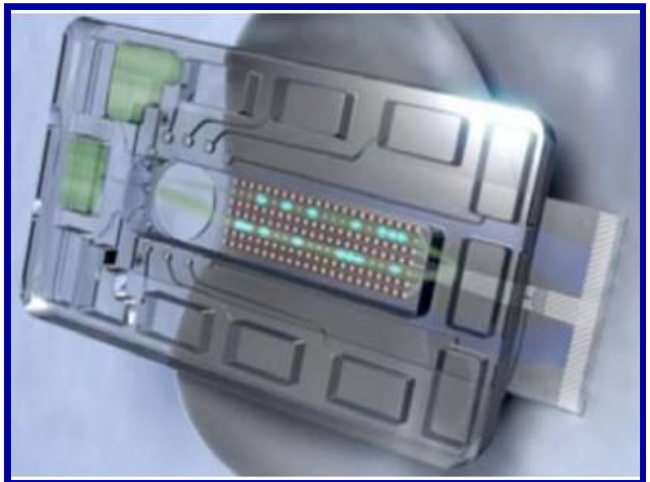
Plastic Logic e-paper



Holst Centre RFID



Fraunhofer ISE Solar cell



BIOIDENT Biosensors

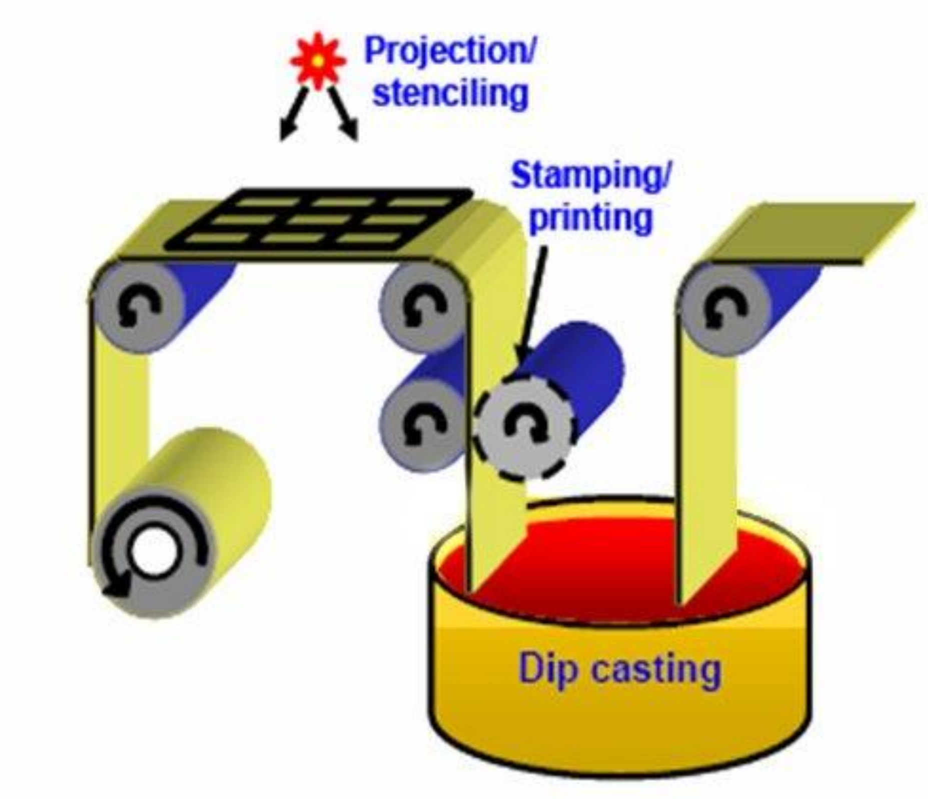
Solution-Processable Organic Semiconductors

Many large area electronic applications will be cost driven

Cost of vapor deposited organic semiconductor is likely to be similar to current inorganic

→ **Need solution processable organic semiconductors**

Polymers, pentacene precursor, soluble rubrene, et cetera



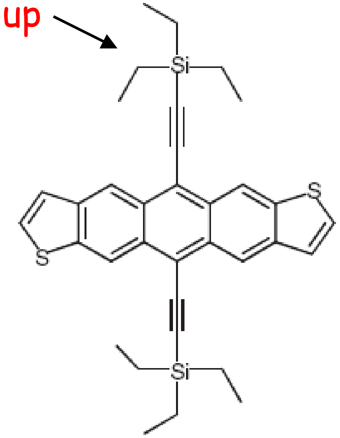
For low cost processing:

- **Additive processes**
- **Arbitrary substrates**
- **Possibly roll-to-roll**

Solution Processable Small Molecule Organic Semiconductors

Small molecule organic semiconductors use molecular design to drive device properties

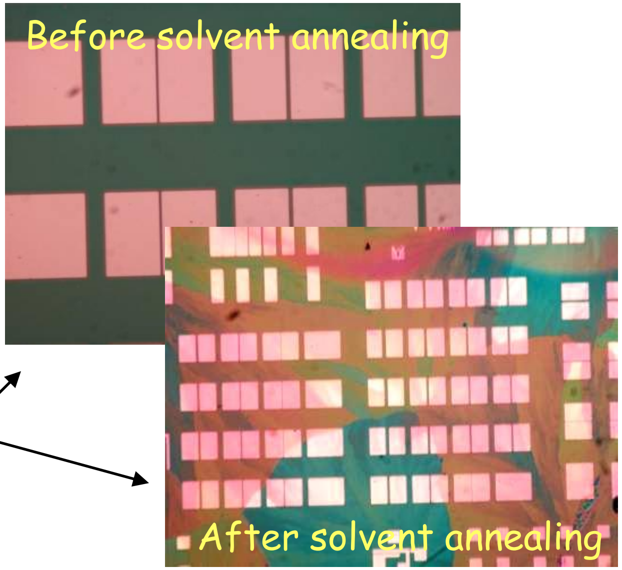
Bulky group



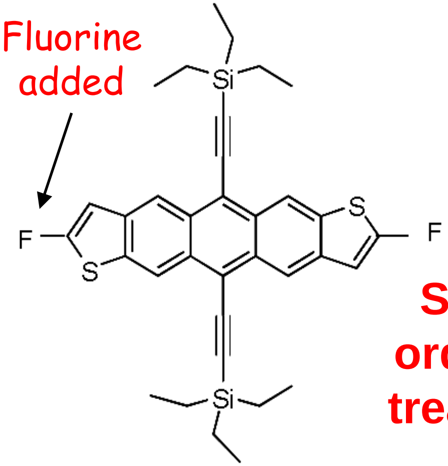
Triethylsilylethynyl anthadithiophene (TES-ADT)

TES-ADT uses bulky groups for solubility and backbone design (anthracene core, thiophene ends) for molecular ordering

Spin cast TES-ADT, amorphous as deposited, forms well-ordered thin films after solvent vapor annealing



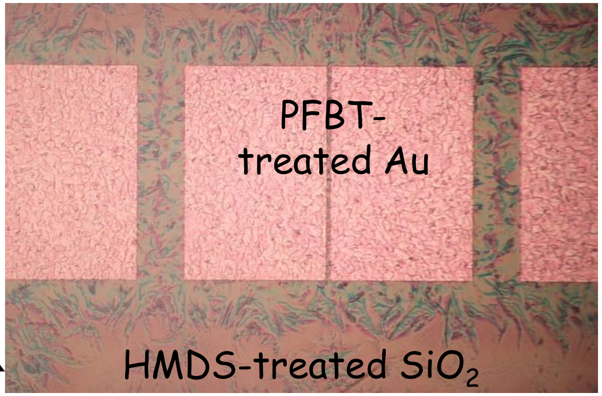
Fluorine added



5,11-Bis(triethylsilylethynyl) anthradithiophene (diF TES-ADT)

Flourine added to diF TES-ADT gives surface feature related differential microstructure

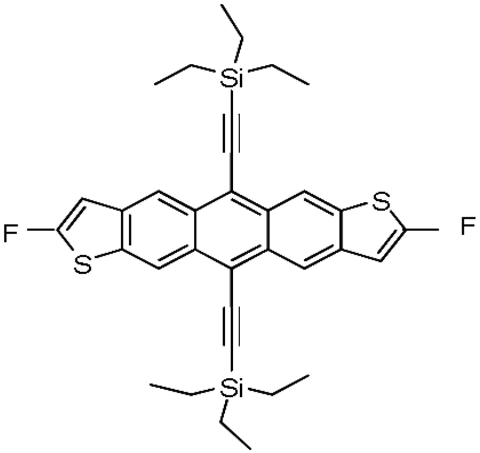
Spin cast diF TES-ADT forms well-ordered thin films on and near PFBT* treated Au electrodes, poorly ordered films on HMDS treated SiO_2



*pentafluorobenzenethiol

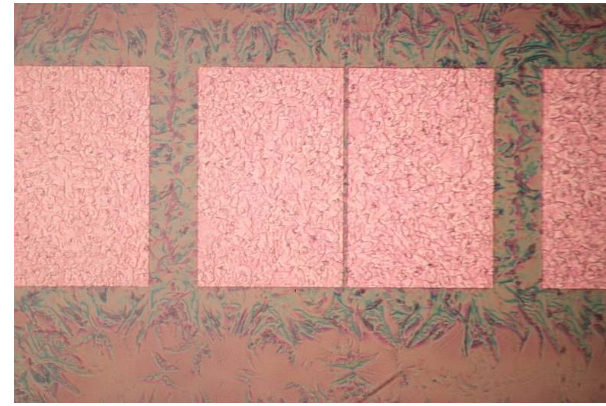
Small Molecular Organic Semiconductor Transistors

X-ray diffraction shows strong ordering for solution-deposited thin films

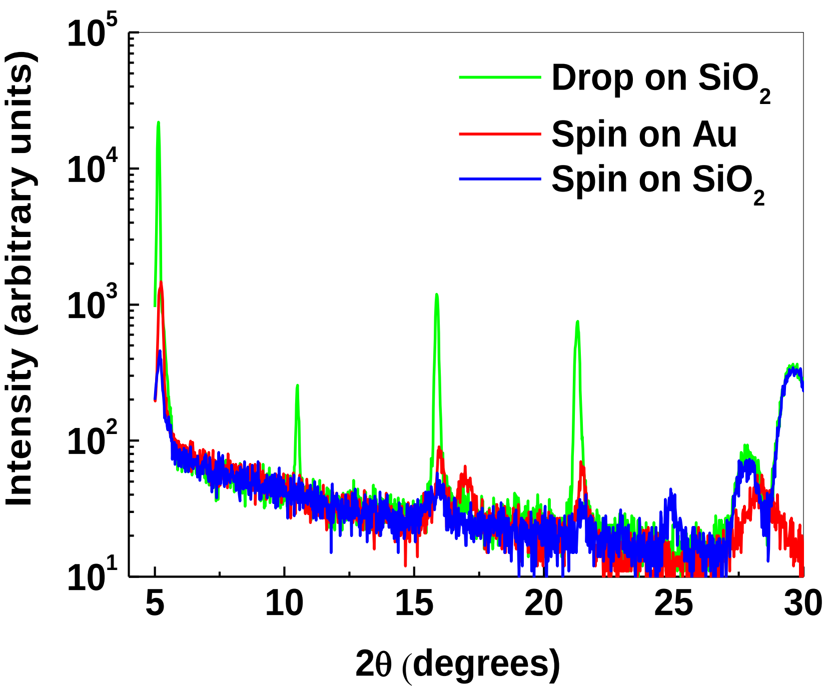


diF TES-ADT

Drop coated diF-TES-ADT



Spin coated diF-TES-ADT



High mobility OTFTs have been fabricated with both drop coated and spin coated diF TES-ADT

Drop coated TFTs ~ 2 $cm^2/V \cdot s$

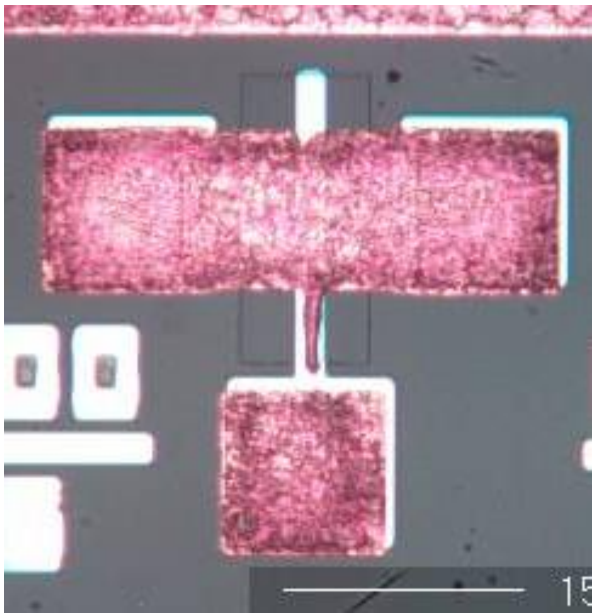
Spin coated TFTs ~ 1.5 $cm^2/V \cdot s$*

*S.K.Park et. al, *App. Phys. Lett.*, 93, 043301 (2008)

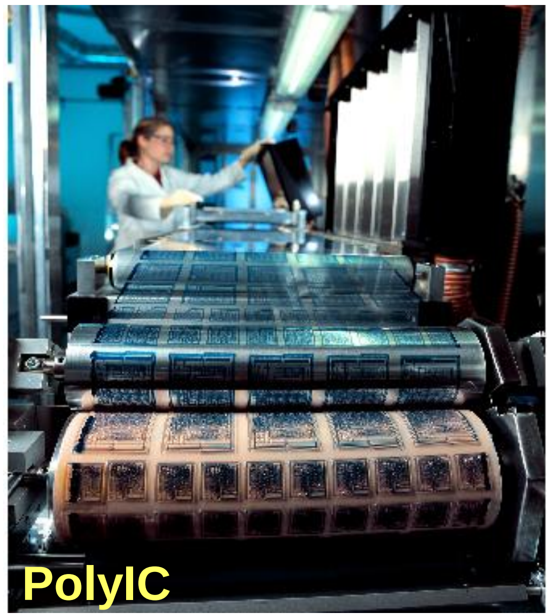
Organic Semiconductor Patterning

Need low-cost, simple, organic semiconductor patterning

Conventional lithography may be a barrier for low-cost mass-production of organic electronics



Non-relief pattern lithography*



Printing

Ink-jet printing

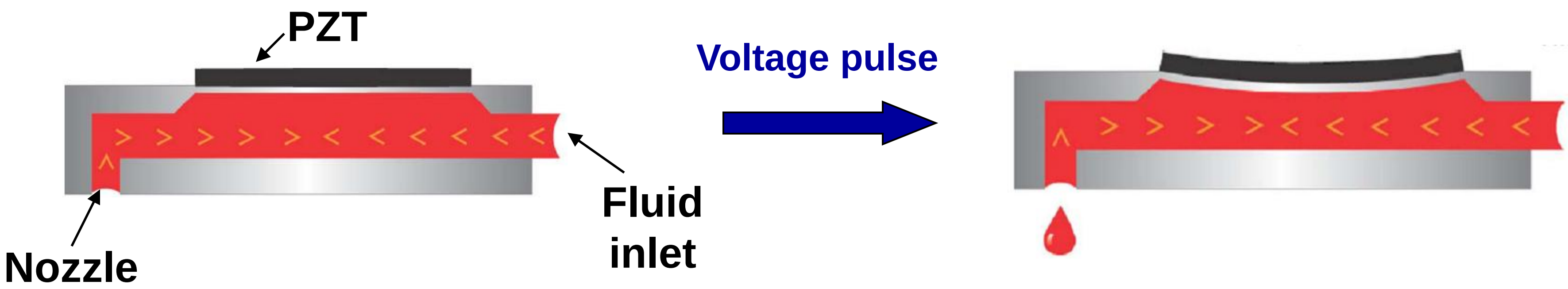
- Non-contact pattering
- Low material usage (additive process)
- Digital control pattering

Dimatix 2381 Inkjet Printer

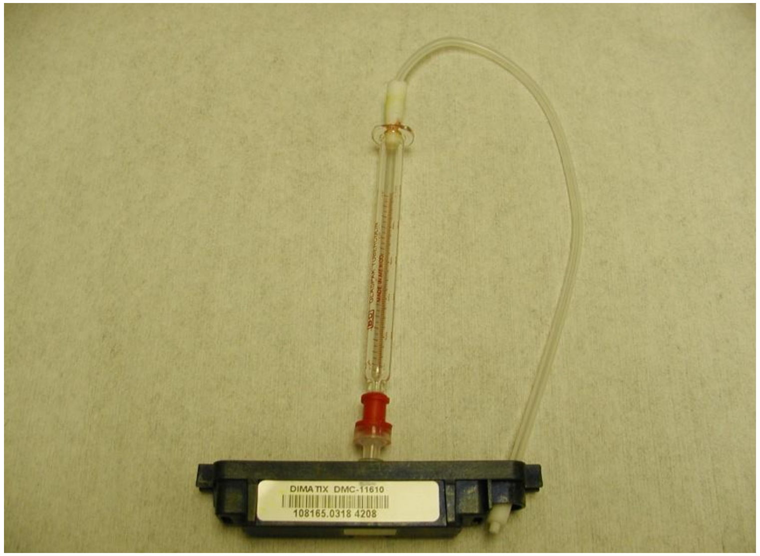
*S.K.Park et. al, *Adv. Mater.*, 2008, 20, 1–3

Inkjet Printing

Piezoelectric ink-jet printing



Slightly modified printhead cartridges allow small amounts of printing material to be conveniently used



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Solution Processed Organic Thin Film Transistors

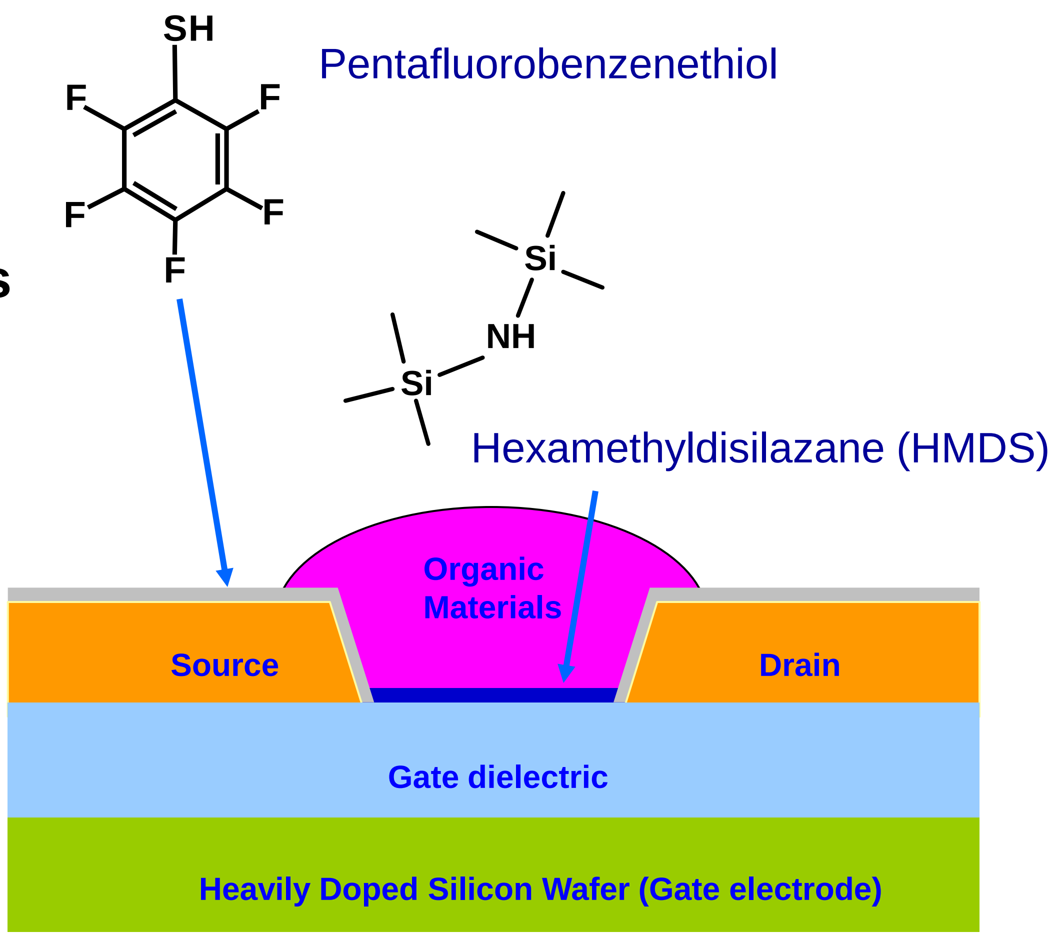
Simple OTFT test structure

Oxidized silicon wafer used as gate, gate dielectric, and substrate

Au source and drain electrodes

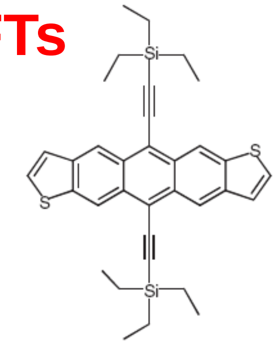
Self-assembled monolayers often used to modify electrodes and dielectric:

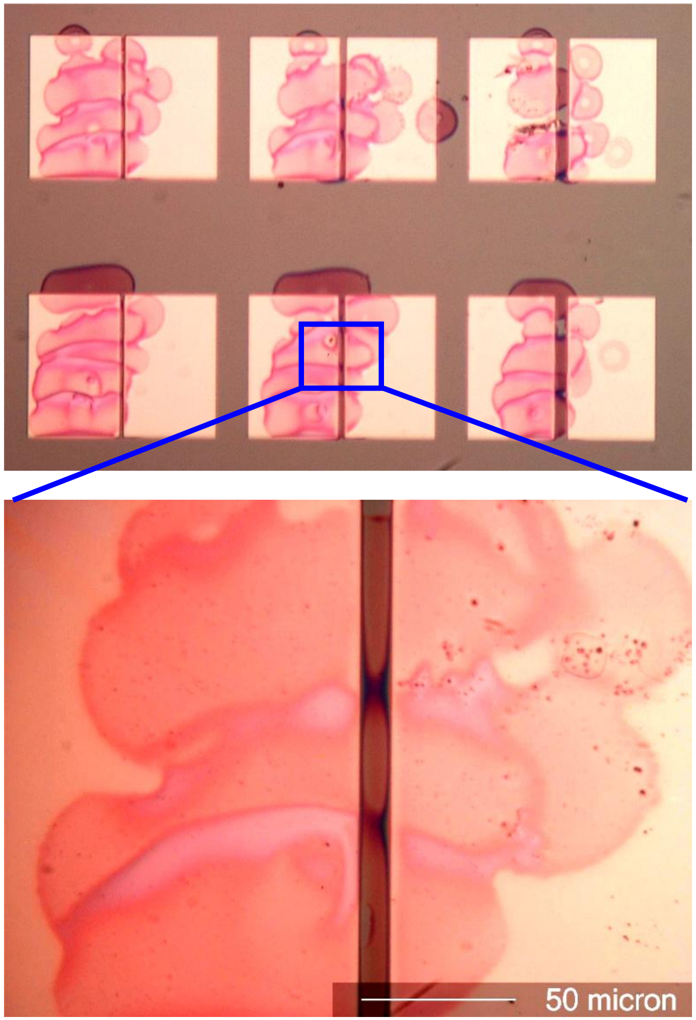
- **PFBT SAM on source and drain electrodes**
- **HMDS on SiO_2 gate dielectric**



Inkjet Printed TES-ADT OTFT

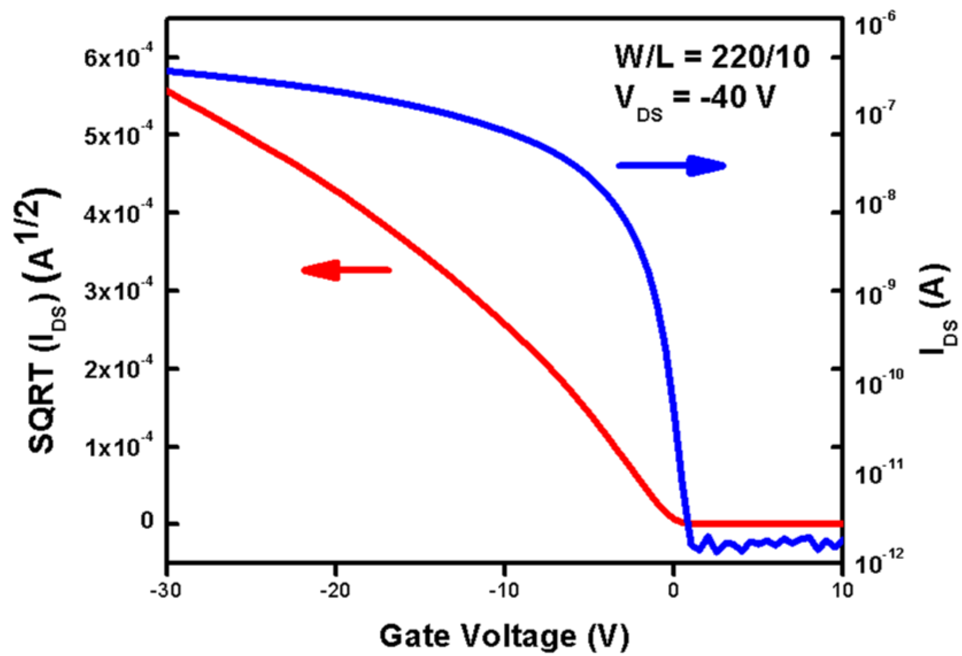
Solutions of TES-ADT are simple to inkjet print, but result in poorly ordered films and low mobility OTFTs





Printed from 2 wt% TES-ADT in toluene

Printed TES-ADT films appear amorphous with no crystal domains & no change after solvent annealing



- As printed field effect mobility ~ 2×10^{-2} $cm^2/V \cdot s$
- No change with solvent annealing

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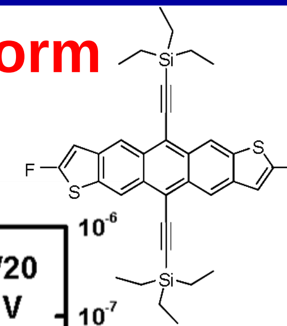
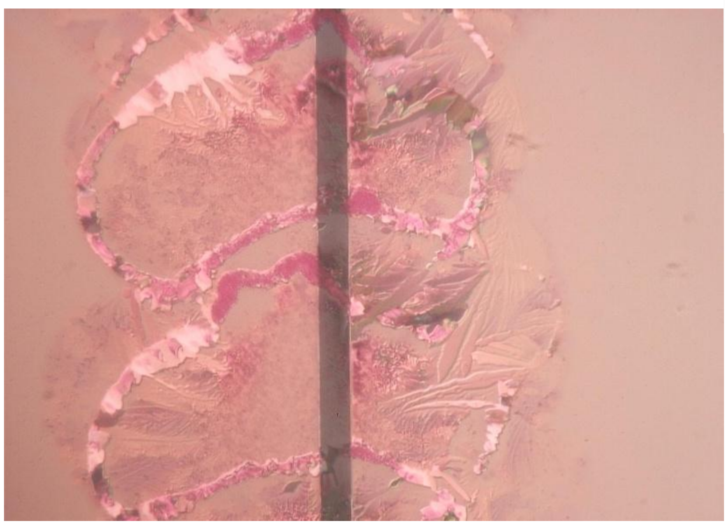
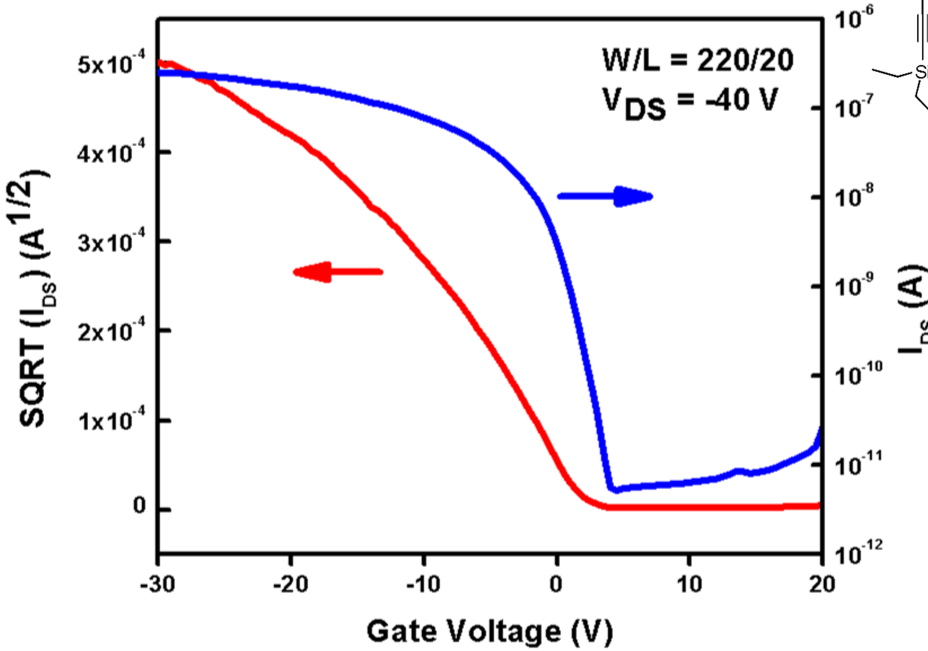
Inkjet Printed diF-TES-ADT OTFT

Inkjet printed diF TES-ADT films have small, non-uniform crystal domains, but only slightly higher mobility





Printed from 2 wt% diF TES-ADT in cholobenzene



Field effect mobility ~ 5 x 10^{-2} $cm^2/V{\cdot}s$

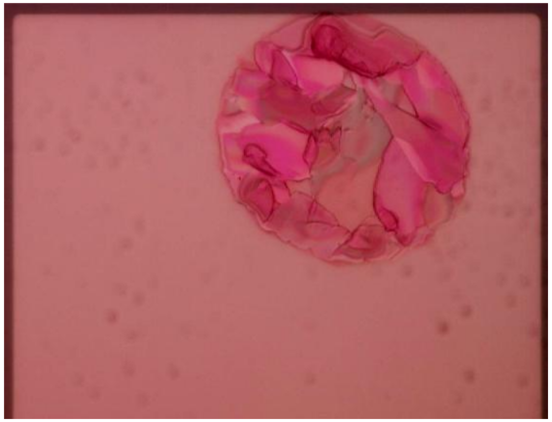
Guess: chlorobenzene (bp 132 °C) evaporates too fast & leads to incoherent crystal domains

⟶ Try higher boiling point solvent

Inkjet Printing with High Boiling Point Solvent

Trichlorobenzene (bp 214 °C), gives large domains, but does not readily wet treated surfaces

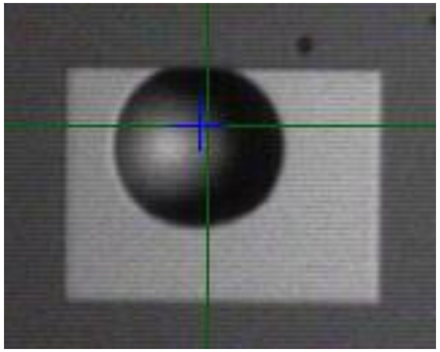
Ink-jet from 1 wt% in 1,2,4-trichlorobenzene (BP ~ 214 °C)



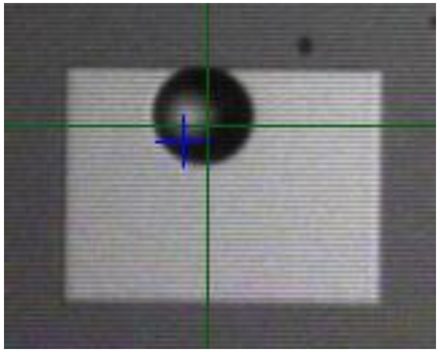
Large domains result when drop finally dries

Drying drop moves on treated surface

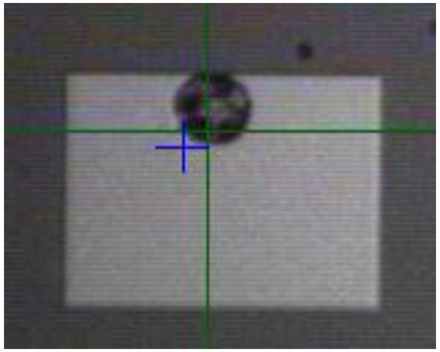
Inkjet printed diF-TES ADT droplet drying on PFBT treated Au



10 s



20 s

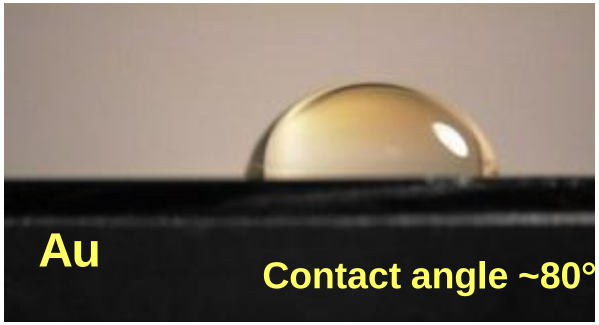


30 s

Surface Energy and Wetting

PFBT and HMDS treated surfaces have low surface energy and allow the contact line to recede during drying

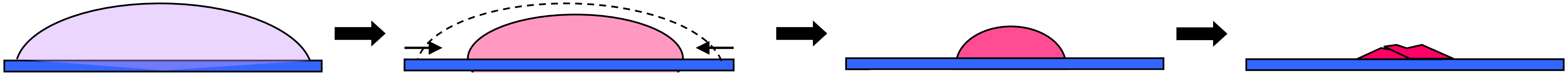
PFBT treated Au:



PFBT treated and HMDS treated SiO_2:

DI water was used as liquid for contact angle measurement

Evaporation of a droplet printed on a low energy surface:

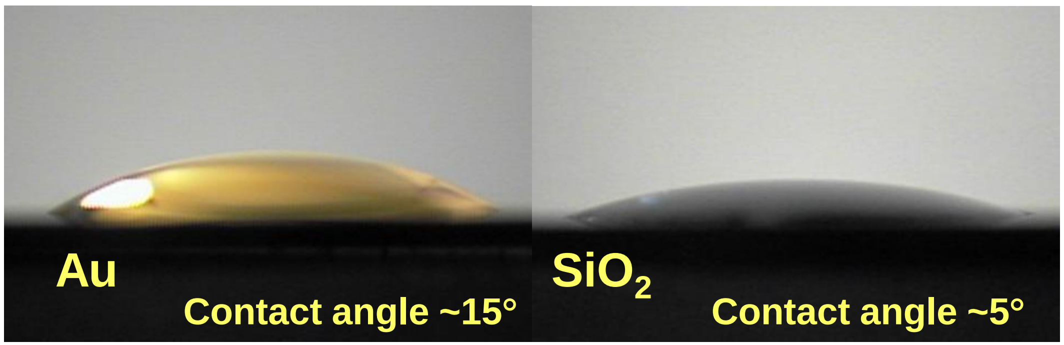


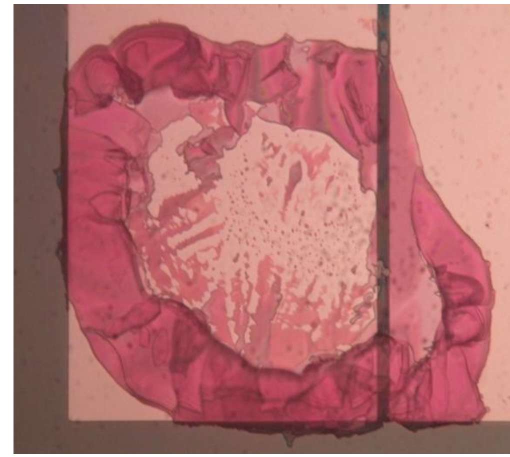
Droplet diameter decreases as drying proceeds, finally, solid material is deposited

High Surface Energy

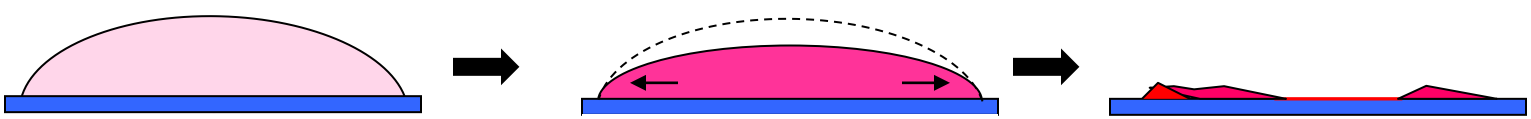
High energy surface improves wetting

UV-ozone treatment results in high surface energy





Evaporation of a droplet printed on a high energy surface:



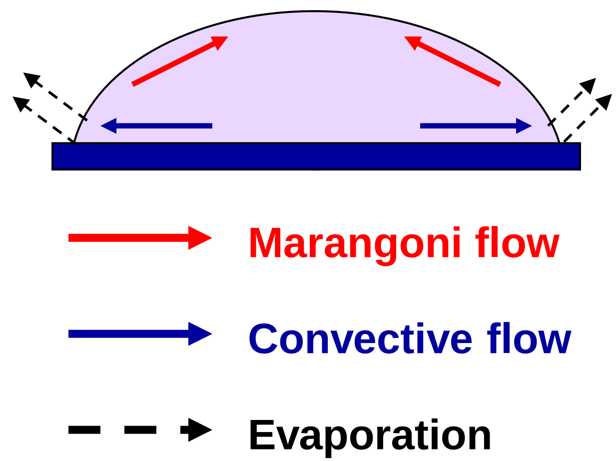
"Coffee-stain" effect* caused by pinned contact line and outward convective flow

*R.D.Deegan et. al, Nature 1997,389,827

Inkjet Printing from Mixed Solvents

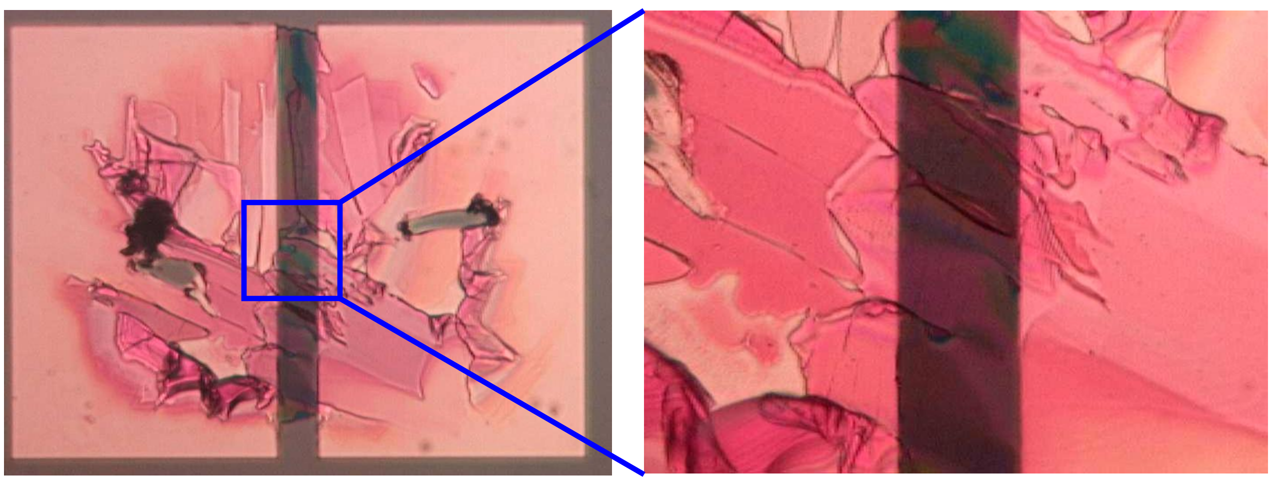
Mixed solvents can allow control of substrate wetting and hydrodynamic flow in drying droplets*

"Coffee stain" behavior of ink-jet-printed organic semiconductor films avoided by balancing Marangoni and convective flows*



Chlorobenzene, boiling point 132 ^{o}C, high surface tension

1,2,4-trichlorobenzene, boiling point 214 ^{o}C, low surface tension



No "Coffee Stain"

Large crystals across channel region

*J.A.Lim et. al, *Adv. Funct.*, Mat, 18, pp. 1-11 (2008)

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Inkjet Printed F-TES-ADT OTFT

Inkjet printed OTFT with mixed solvents has mobility higher than 0.4 $cm^2/V \cdot s$

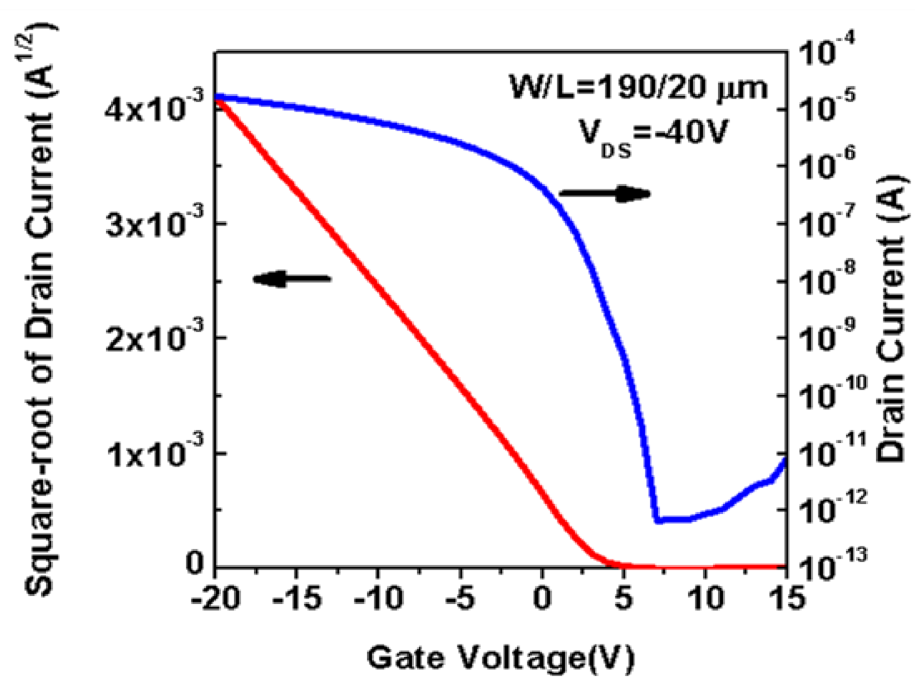
1 wt% in mixed solvents

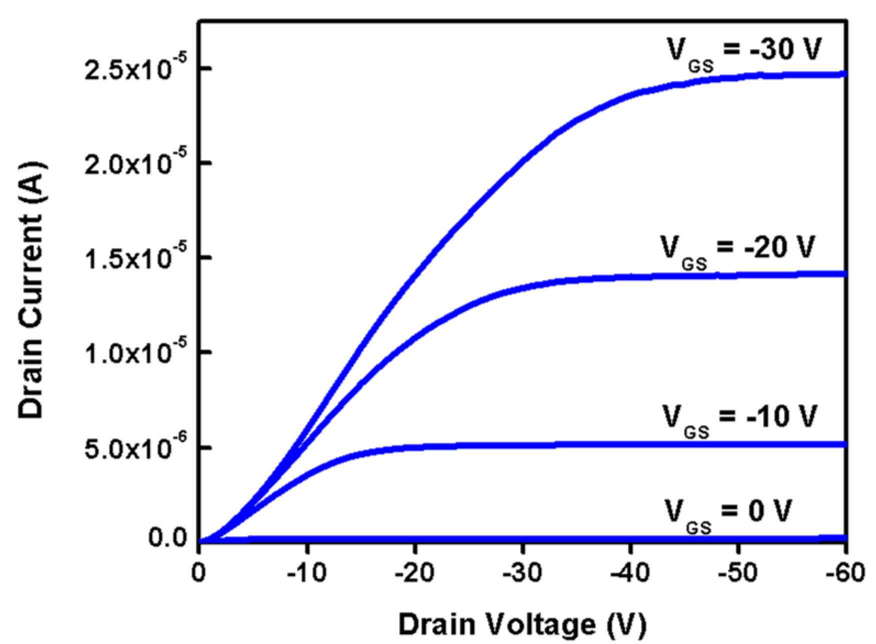
(chlorobenzene:1,2,4-trichlorobenzene=1:1)

UV-ozone treated surface

Closely spaced drops merge to form large drop

$\mu = 0.42\ cm^2/V \cdot s$, $V_{th} \sim 3$ V,
$I_{on}/I_{off} > 10^7$, S < 1 V/dec

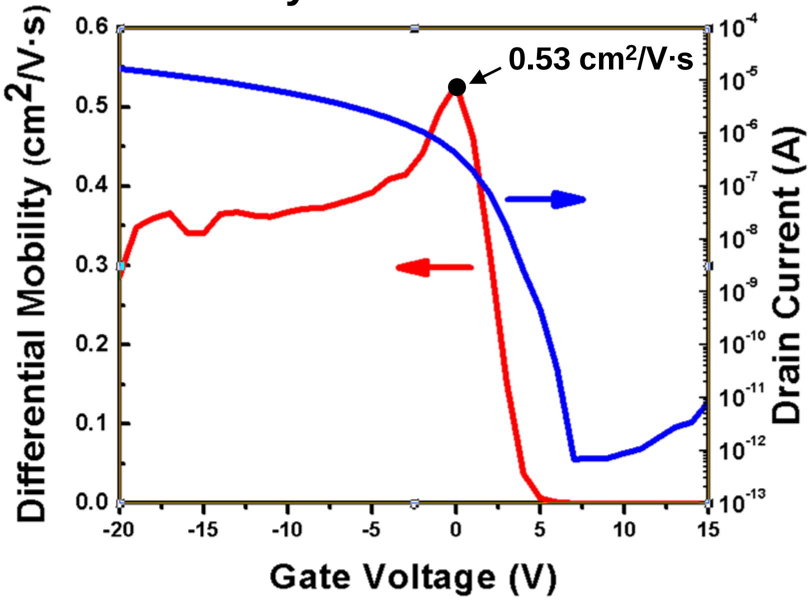




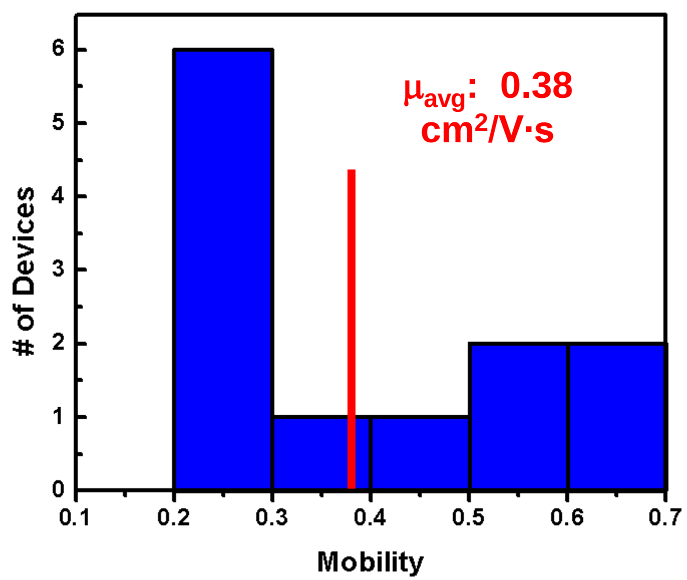
Uniformity

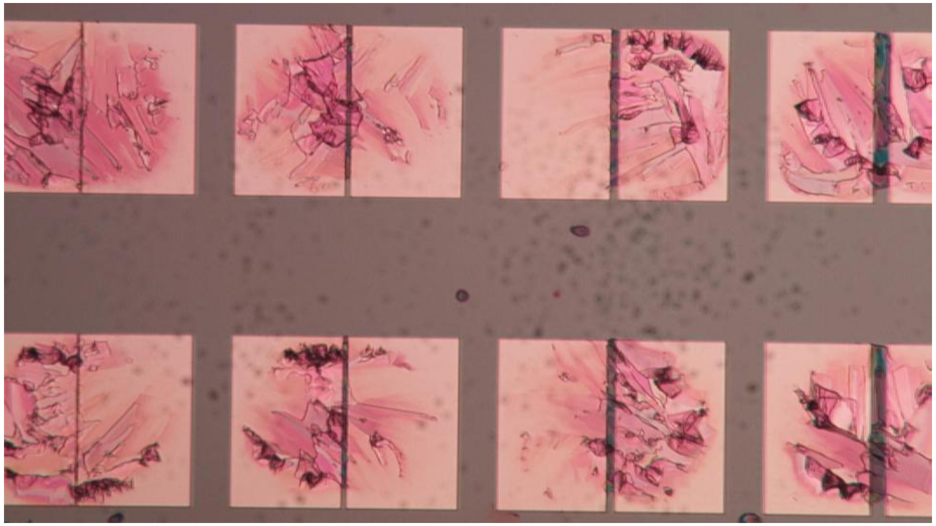
Significant device-to-device variation

Mobility and ID versus VG



Peak mobility statistics





Need to improve film growth

- Bring PFBT and HMDS treatment back or other surface treatments
- Other solvents

Improvement likely, but there is another problem to consider

Organic Semiconductor Competition

Pentacene OTFT backplane

Sony - 2007 **Polyester substrate**

Indium gallium zinc oxide (IGZO) TFT backplane

LG - 2007 **Stainless steel substrate**

IGZO TFT backplane

Samsung - 2009 **Polyimide substrate**

Oxide semiconductors:

- **Low temperature process (~200 °C)**
- **High mobility (>10 $cm^2/V{\cdot}s$)**
- **Good uniformity**
- **Good stability**
- **Strong competitor for organic electronics**

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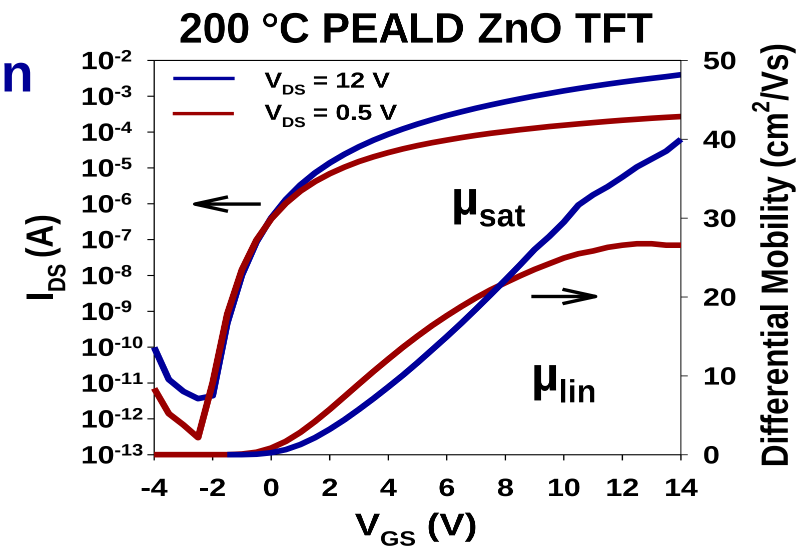
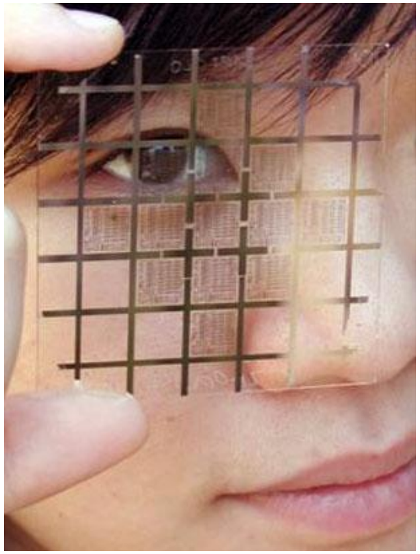
PSU PEALD ZnO TFTs and Circuits

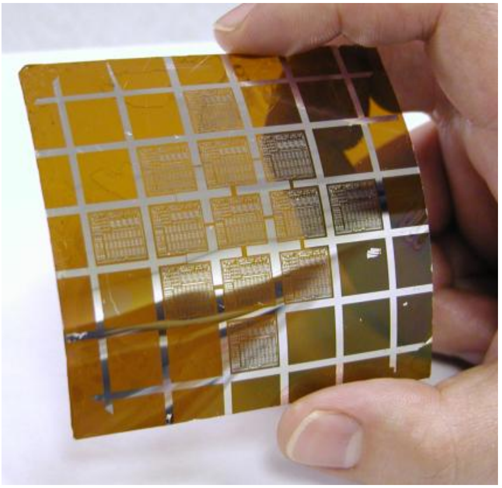
Simple, low cost, low temperature process, high mobility, and fast circuits

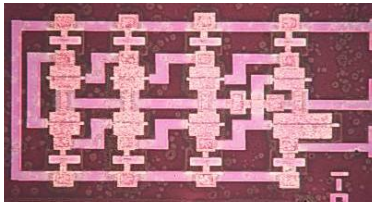
Plasma enhanced atomic layer deposition

- **Simple, non-critical process**
- **Low temperature and large area**
- **Excellent uniformity**
- **High mobility, stable ZnO TFTs**

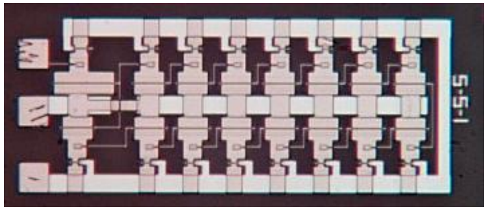








Organic TFT ring oscillator



ZnO TFT ring oscillator

Circuit propagation delay

Organic TFTs few µs/stage

ZnO TFTs few tens of ns/stage

What role for organics?

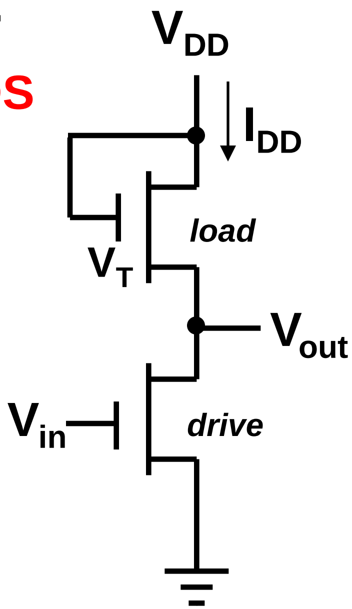
One role: CMOS!

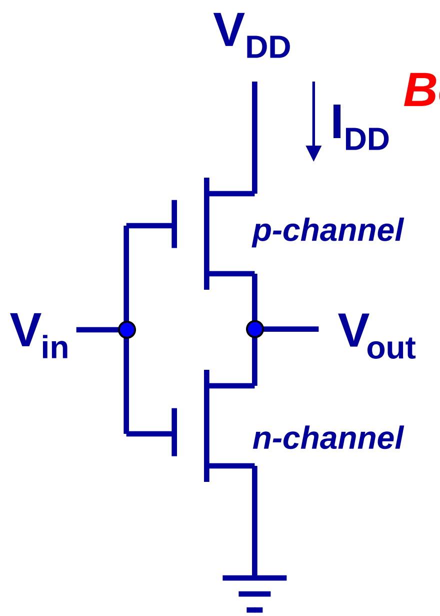
CMOS provides critical advantages for digital and analog circuits

Unipolar inverter

Either NMOS or PMOS

- $I_{DD} \neq 0$ for low output
- $V_{HIGH} \sim V_{DD} - V_T$
- V_{LOW} circuit dependent





CMOS inverter

Both NMOS and PMOS

- $I_{DD} \sim 0$ for both low & high output
- $V_{HIGH} \sim V_{DD}$
- $V_{LOW} \sim 0$

CMOS advantages:

- Logic level conservation
- Low power for digital circuits
- Simple circuit design
- High gain analog circuits

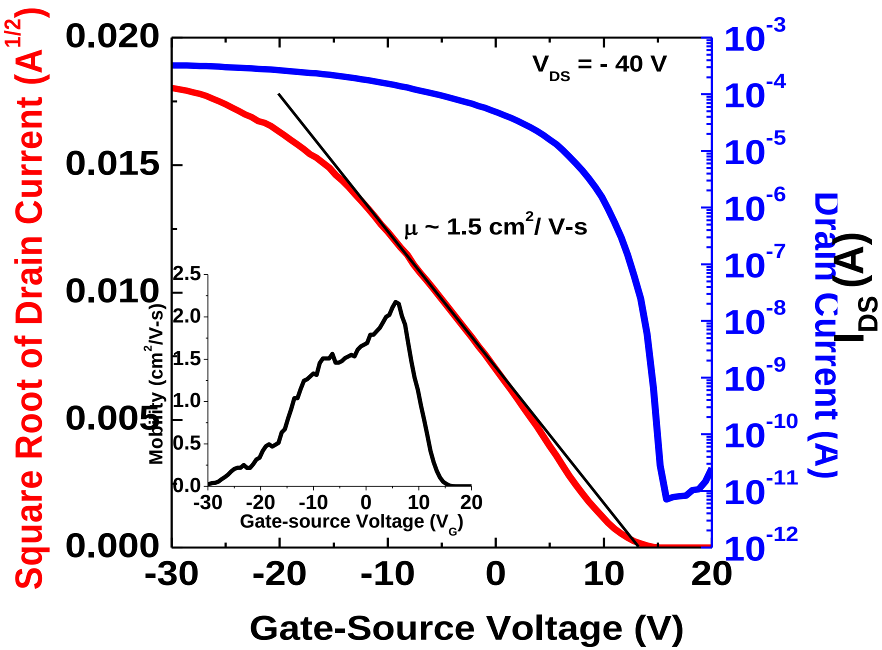
Hybrid Organic – Inorganic CMOS

Low cost, low temperature CMOS needed

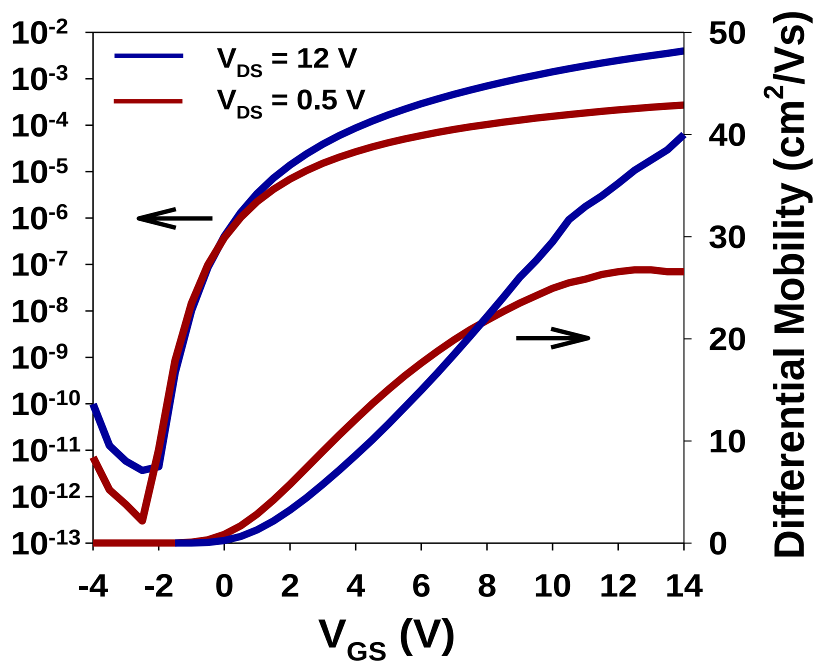
No all-oxide semiconductor CMOS demonstrated

All-organic CMOS has low performance

High mobility p-channel diF TES-ADT



High mobility n-channel PEALD ZnO



Simple idea: combine p-channel diF TES-ADT TFTs and n-channel ZnO TFTs

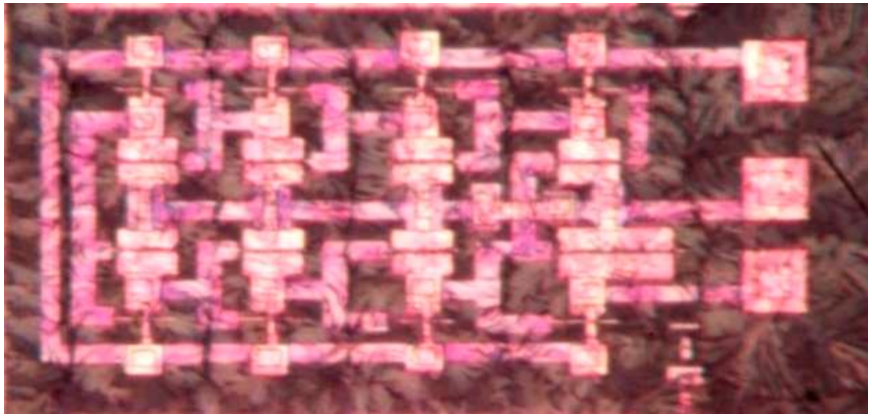
ZnO and Spin Coated diF TES-ADT Hybrid CMOS

First attempt: use diF-TES-ADT differential μ-structure with spatial ALD ZnO foundation

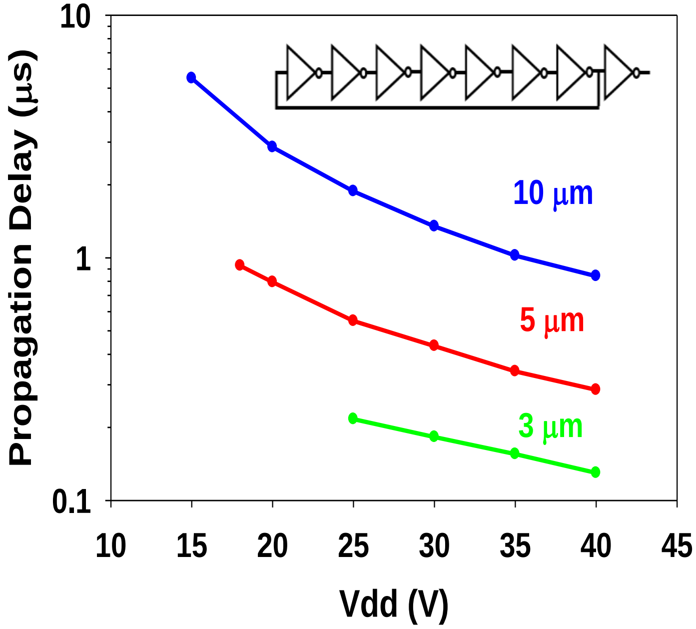
Hybrid ZnO and spin coated diF TES-ADT CMOS circuits work well and have high speed

n-channel ZnO TFT
mobility ~ 10 - 15 $cm^2/V\cdot s$

p-channel diF TES-ADT TFT
mobility ~ 0.1 - 0.2 $cm^2/V\cdot s$



7-stage ring oscillator



Minimum propagation delay ~150 ns/stage even with p-channel mobility ~0.2 $cm^2/V\cdot s$

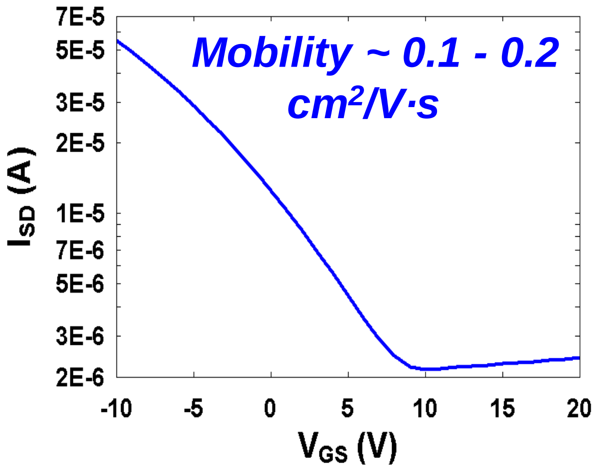
Kodak

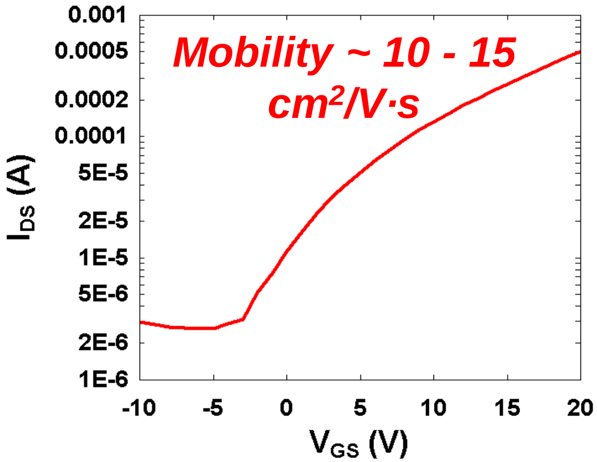
D. A. Mourey et. al. "High-Speed, Low-Temperature Integrated ZnO/Organic CMOS Circuits." *2008 Device Research Conference Digest*, 147, *2008.* submitted to *Organic Electronics*

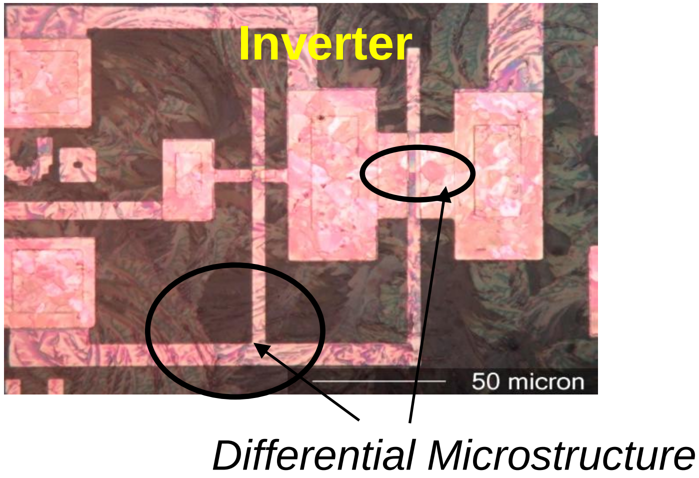
Spin Coated Organic Hybrid CMOS Problem

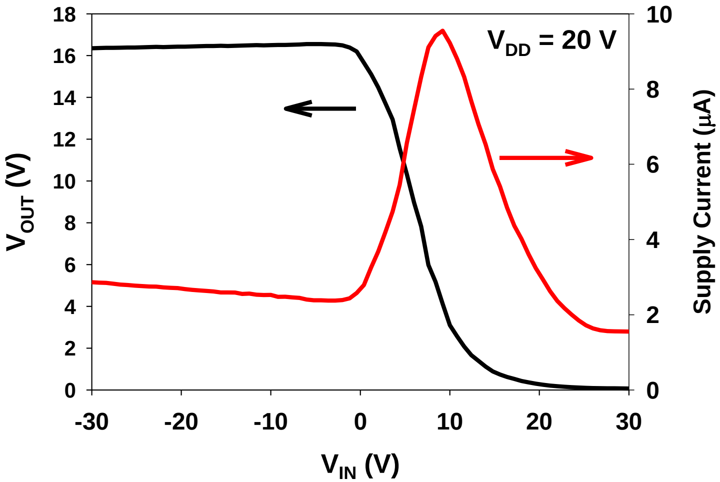
diF-TES ADT differential μ-structure provides insufficient isolation

→ On and off state leakage, reduced inverter gain







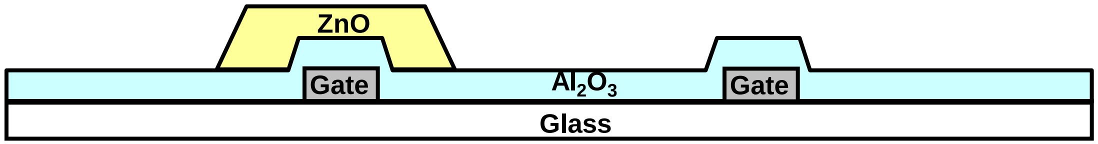


Solution: printed organic

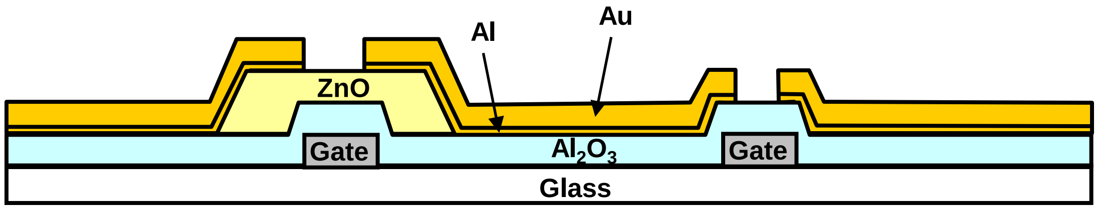
ZnO/Organic Hybrid CMOS Process

Simple hybrid CMOS process

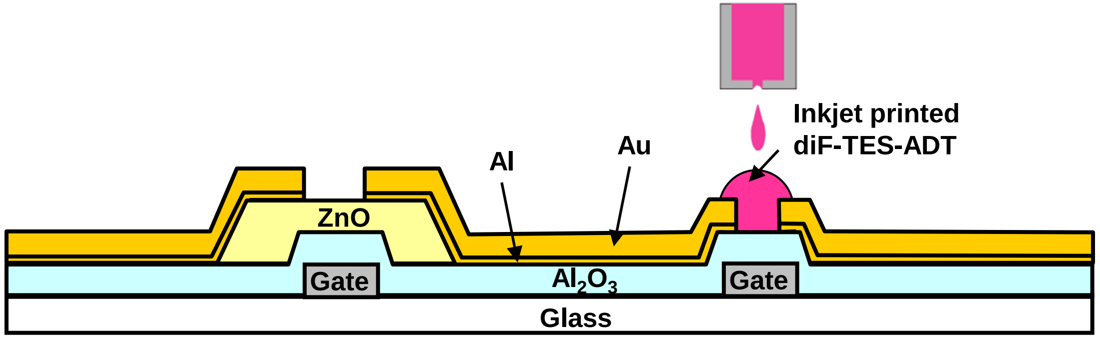
Sputtered nickel gate



PEALD Al_2O_3 and ZnO



Bi-functional Al/Au contact



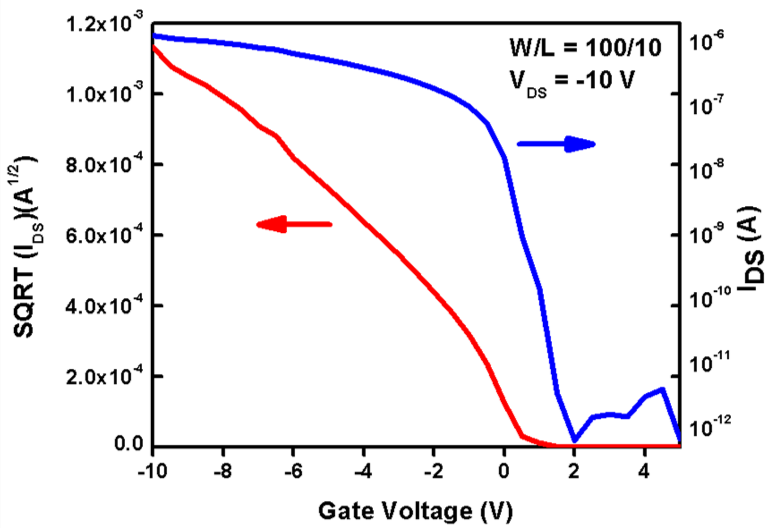
Ink-jet printed diF TES-ADT

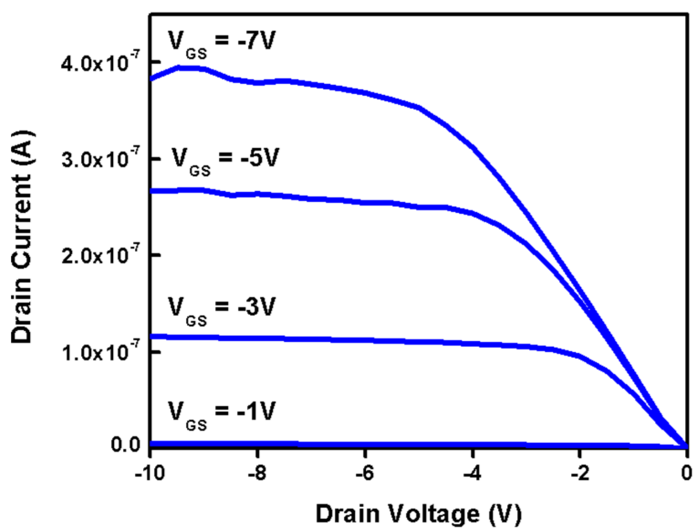
PEALD ZnO and Ink-Jet Printed TFTs

Organic performance worse on ZnO circuit structure

diF TES-ADT (p-channel)

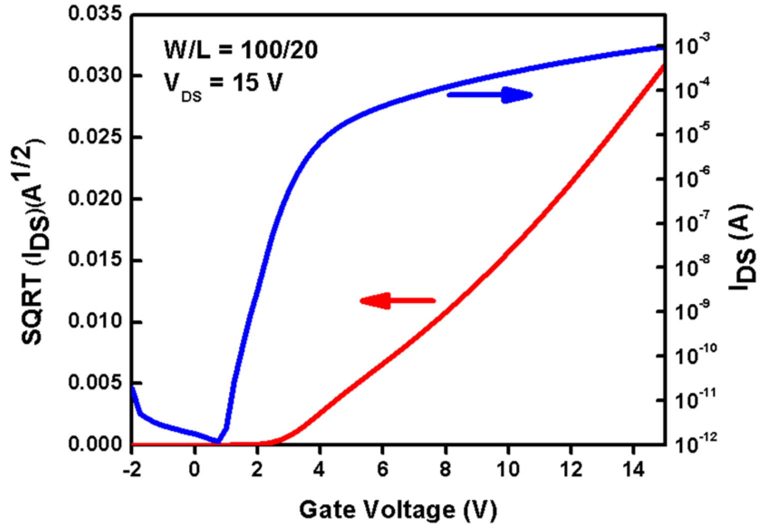
Mobility ~ 0.06 $cm^2/V{\cdot}s$, V_T ~ 3 V

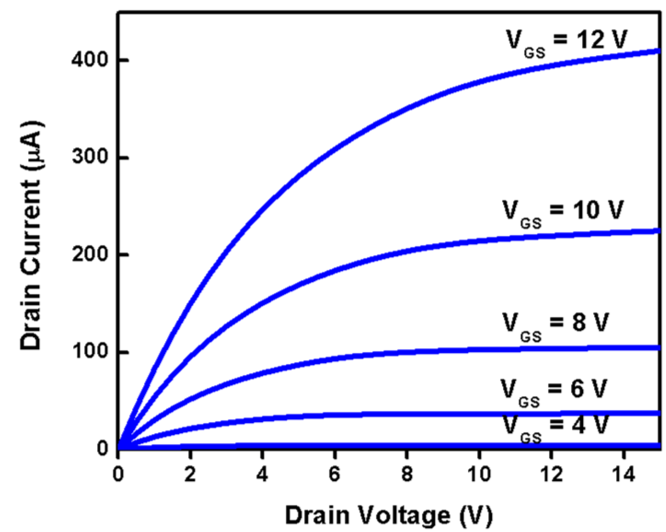




ZnO (n-channel)

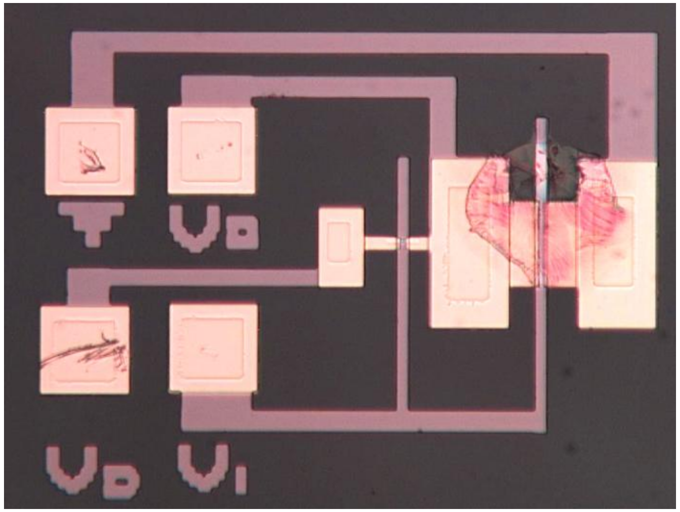
Mobility ~ 17 $cm^2/V{\cdot}s$, V_T ~ 5 V

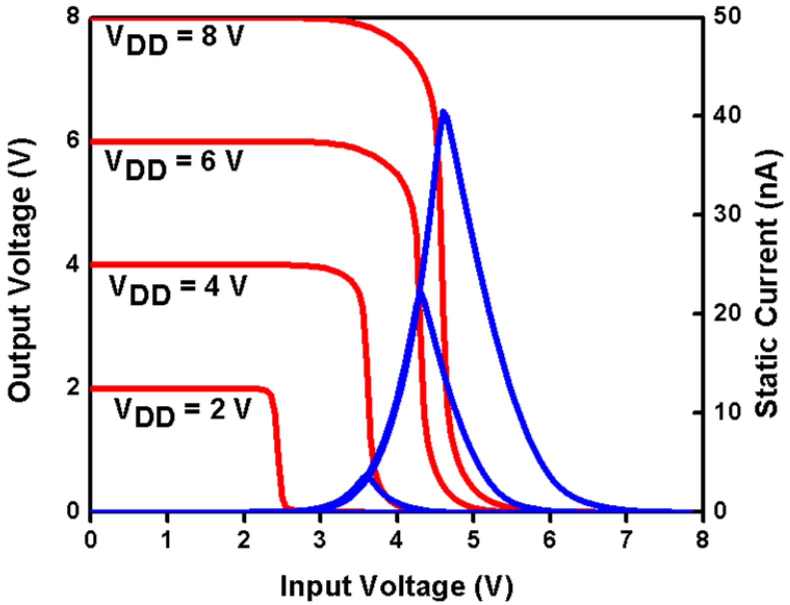


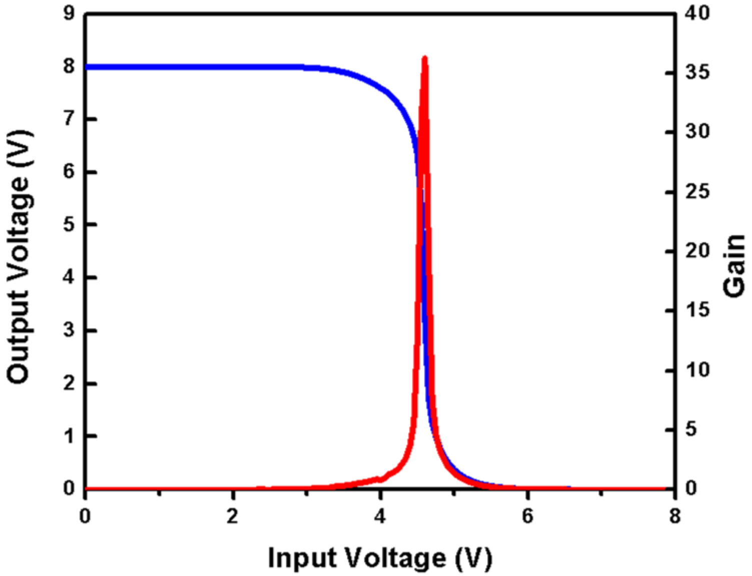


Printed hybrid CMOS inverter

Inverters have high gain and low static leakage

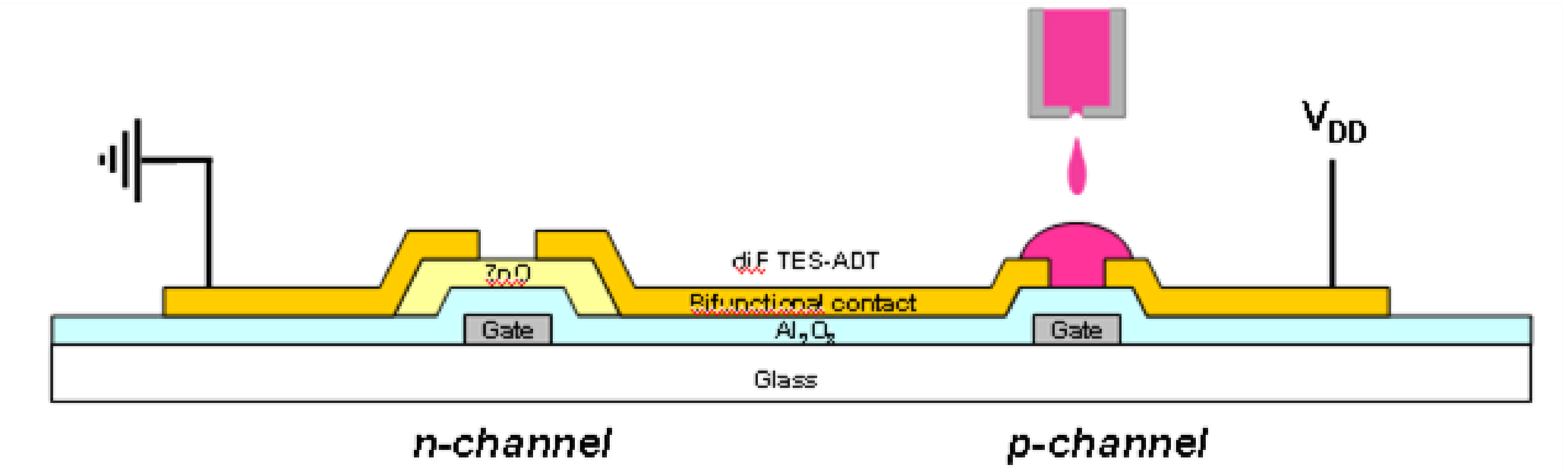


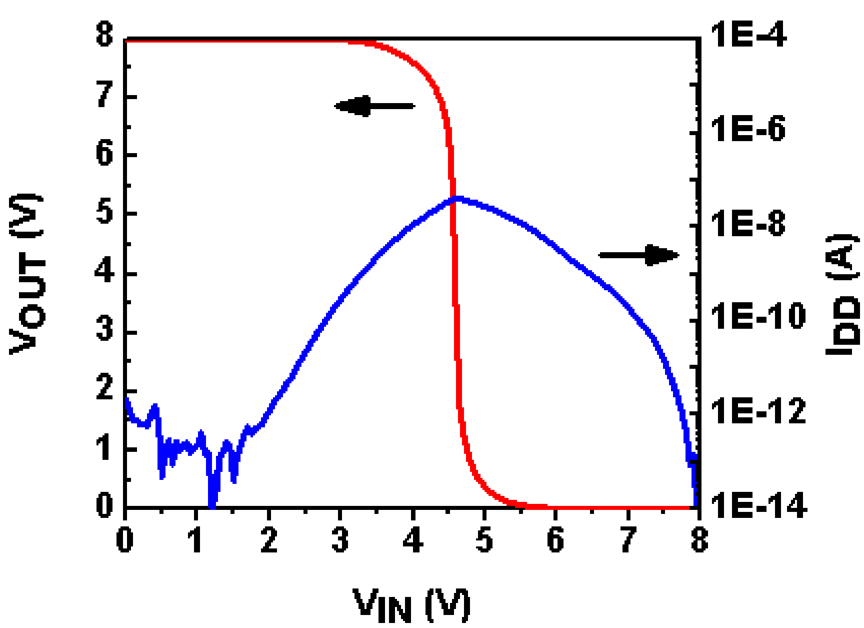




- **Logic level conservation**
- **Static leakage is sub-pA for both low and high input levels**
  (>1000x lower than spin cast)
- **Maximum gain is about 35**

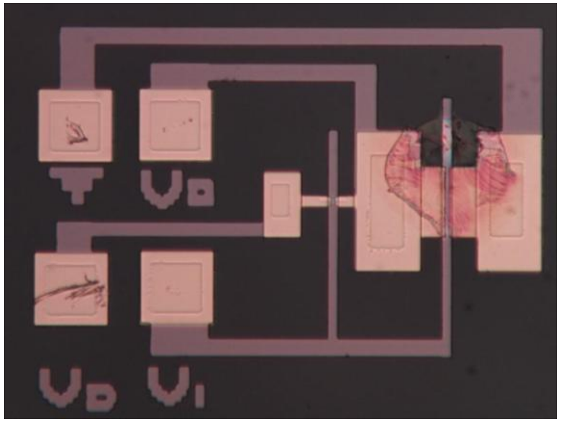
Ink-Jet Printed Hybrid Organic-Inorganic CMOS

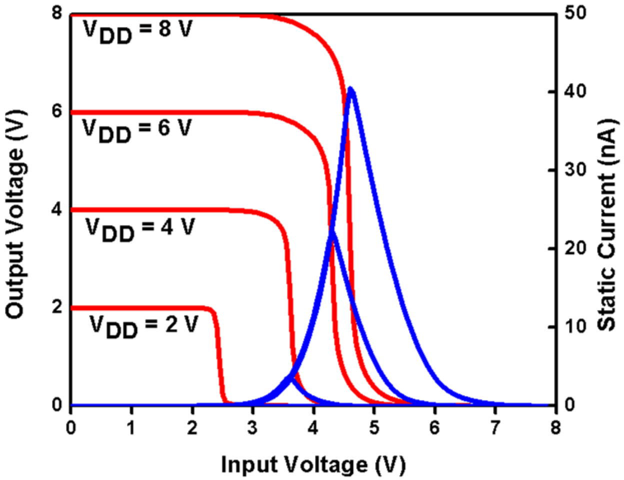




- Both ZnO and organic deposited at low-temperature
- Bifunctional contact for both ZnO and diF TES-ADT
- Organic layer can be selectively (digitally) patterned
- Only 4 lithography steps are used
- Very low leakage current and relatively high gain

Summary





- Small molecule materials are interesting for printed organic semiconductor devices
- Control of substrate surface energy and solvent characteristics gives small molecule films with useful morphology
- Inkjet printed small molecule organic semiconductor thin film transistors with mobility > 0.4 $cm^2/V \cdot s$
- PEALD ZnO – inkjet diF TES-ADT hybrid CMOS inverters with high gain and sub-pA leakage

UNIVERSITY OF KENTUCKY

CORNING

Kodak

NIST