

MARKS GROUP RESEARCH STYLE



- ❖ Highly Interdisciplinary
- ❖ Integrated Synthesis, Spectroscopy, Mechanism
- ❖ Organometallics, Catalysis, New Reactions & Ligands
- ❖ Hard and Soft Matter, Interfaces, Solar Energy, Molecular Electronics
- ❖ Collaborations with Physicists, Engineers, Industrial & National Lab Scientists (Visits, Internships)
- ❖ Spirit of Teamwork

MARKS GROUP RESEARCH PROGRAM

t-marks@northwestern.edu

<http://www.chem.northwestern.edu/~marks/index.html>

Themes

✓ ***Unconventional Electronics***

Building Blocks for Hybrid Inorganic/Organic Circuitry

Molecular and Polymer Photovoltaics

Materials for Organic Photovoltaics and Displays

✓ ***Catalysis with Homogeneous and Surface Metal Electrophiles***

Catalytic Routes to New Materials

Organometallic Chemistry of f-Elements; Green Chemistry

Thermochemical Strategies for New Catalytic Transformations

GOAL: FLEXIBLE ELECTRONIC CIRCUITRY

RF ID tags, display backplanes, e-books, sensors, “smart” packaging,
“smart” displays, photovoltaics, “internet of things”

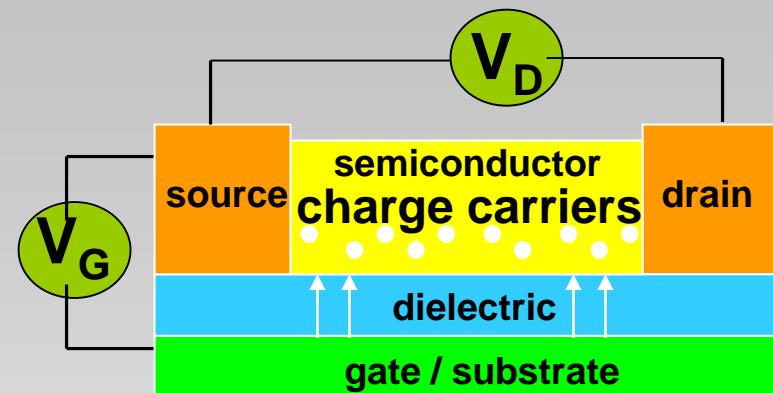


Science Needed for: *Versatile, Unconventional Materials*
n- and p-Type Semiconductors for CMOS
Compatible High-k Gate Dielectrics
Synergy of Soft Matter & Hard Matter Constituents

NRC/National Academies, “The Flexible Electronics Opportunity” National Academies Press, 2014

MRS Bulletin, articles and references therein, February 2017, 42

Transistor Structure & Function



OFF
 $V_G = 0$

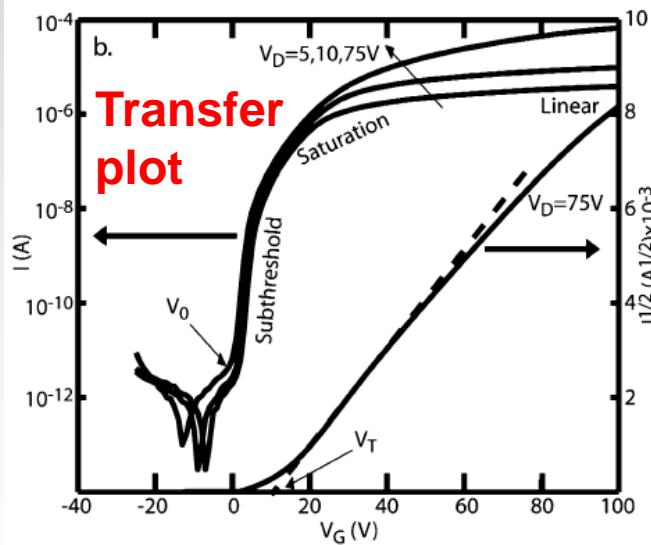
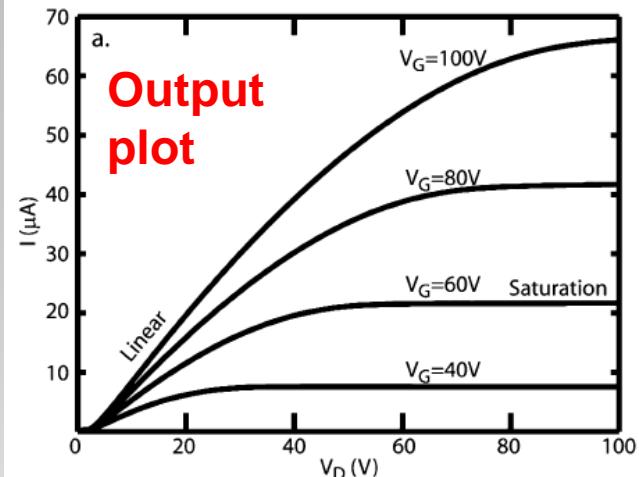
**NO CHARGE CARRIERS
BETWEEN s AND d => $I_D = 0$**

ON
 $V_G \neq 0$

**CREATES CHARGE CHANNEL IN
SEMICONDUCTOR LAYER
=> $I_D \neq 0$**

New Materials Must Optimize:

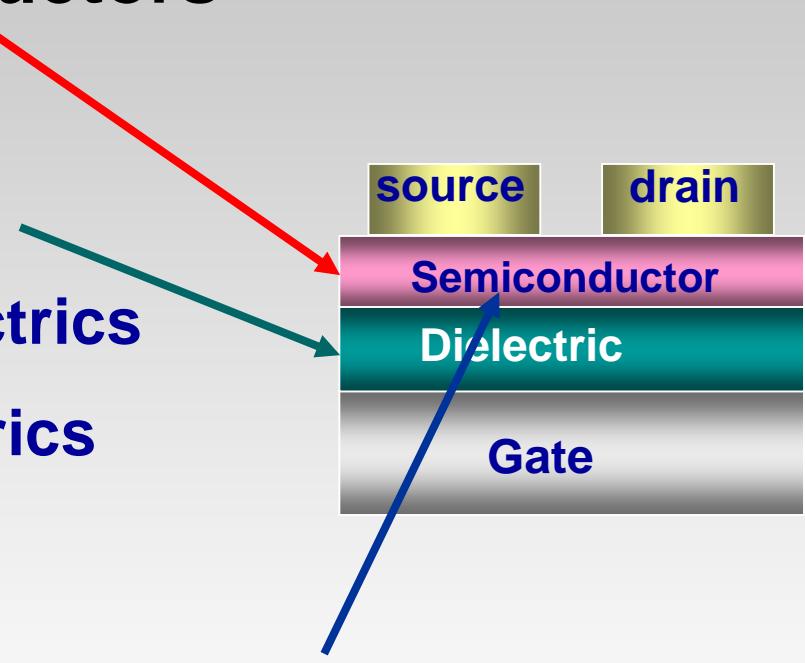
- Carrier mobility (μ) & Stability
- Current on/off ratio (I_{on}/I_{off})
- Threshold voltage (V_T)
- Subthreshold swing (SS)
- Dielectric capacitance (C_i)



LCD Display Backplanes use a-Si:H
 $\mu \sim 0.5 \text{ cm}^2/\text{V}\cdot\text{s}$ $I_{on}/I_{off} > 10^6$
 n-type only, poor current carrier

Lecture Outline

- I. Challenges, Opportunities
- II. New Organic Semiconductors
Properties Tuning, Devices
- III. Nanoscopic Dielectrics
Self-Assembled Nanodielectrics
(SANDs). Designer Dielectrics
- IV. Amorphous Oxides
Transistors, Hybrid Devices, Heterojunctions
- V. Conclusions, Acknowledgments



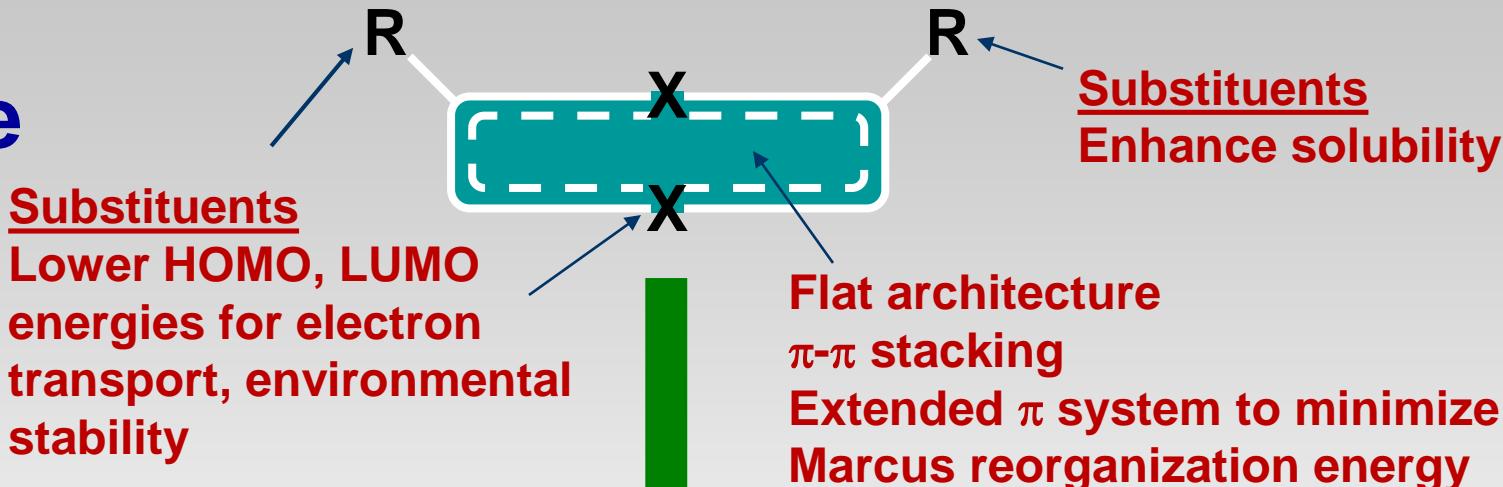
Materials Design for n-Type Semiconductors

Enablers of Organic CMOS

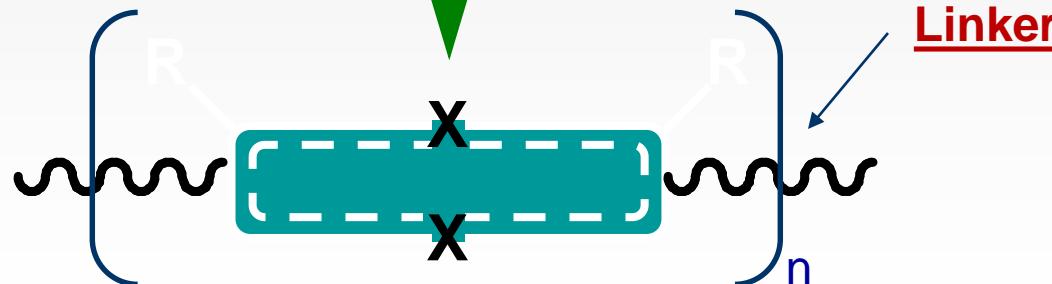
p-Type = Radical cation (h^+) conduction through highest occupied MOs (HOMOs)

n-Type = Radical anion (e^-) conduction through lowest unoccupied MOs (LUMOs)

Molecule

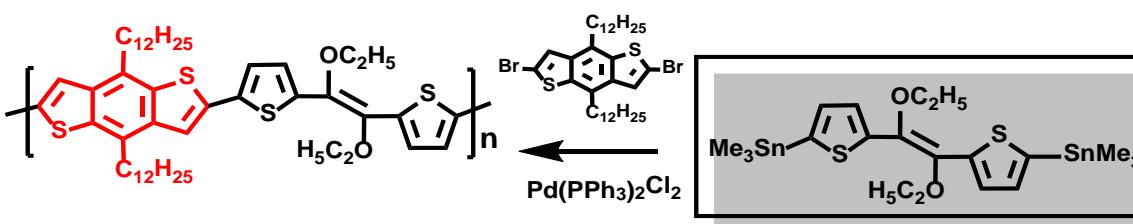


Polymer



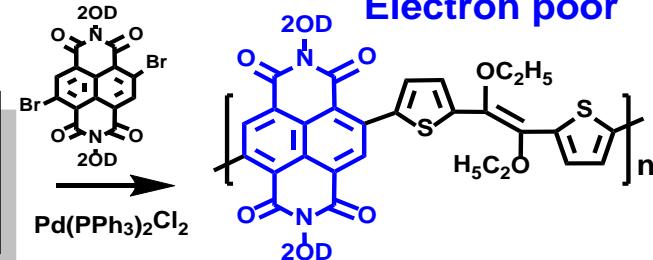
p- and n-Type Copolymers & Devices

Electron rich



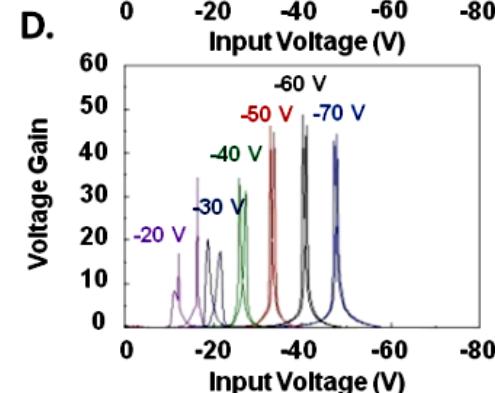
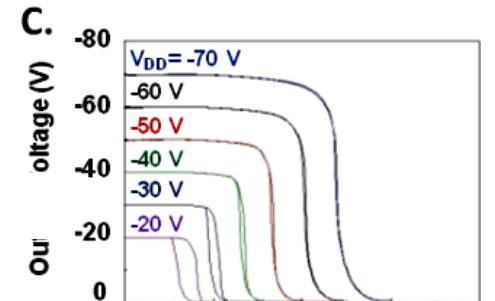
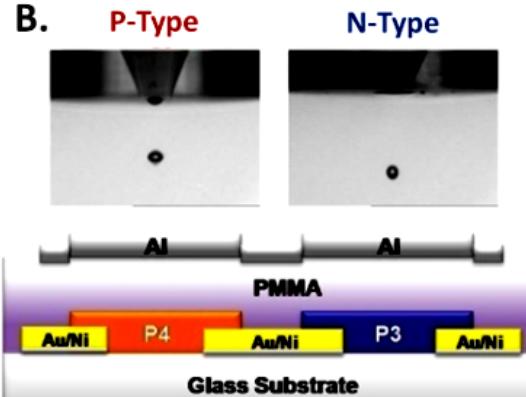
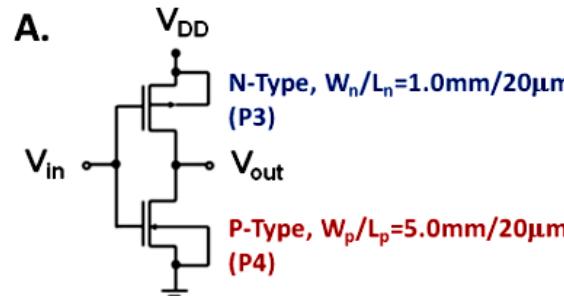
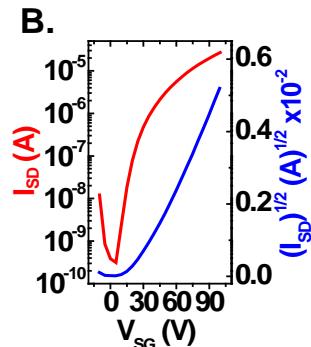
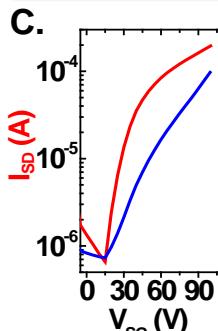
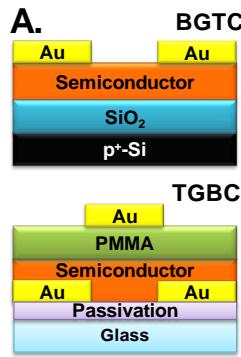
PBDT-TVOE (p-type)

Electron poor



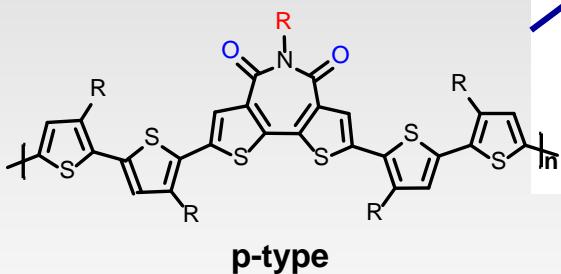
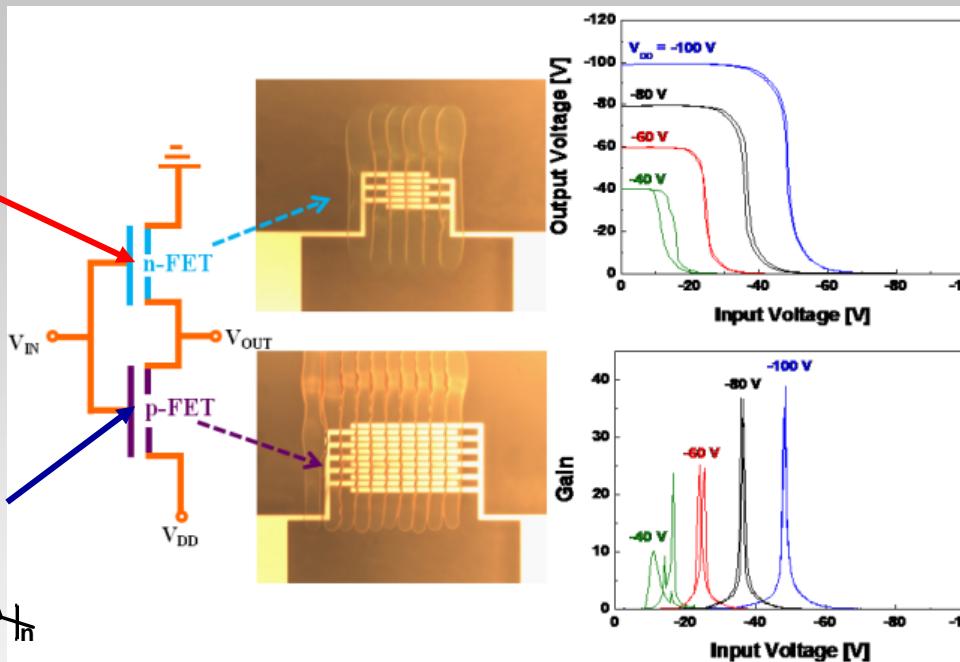
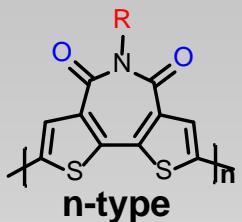
PNDI-TVOE (n-type)

Complementary inverters: inkjet printed p- and n-type copolymers



Inkjet-Printed Bithiophene-Imide-Based Air-Stable Complementary Polymer Inverters

Gain ~ 40 at VDD = - 100V

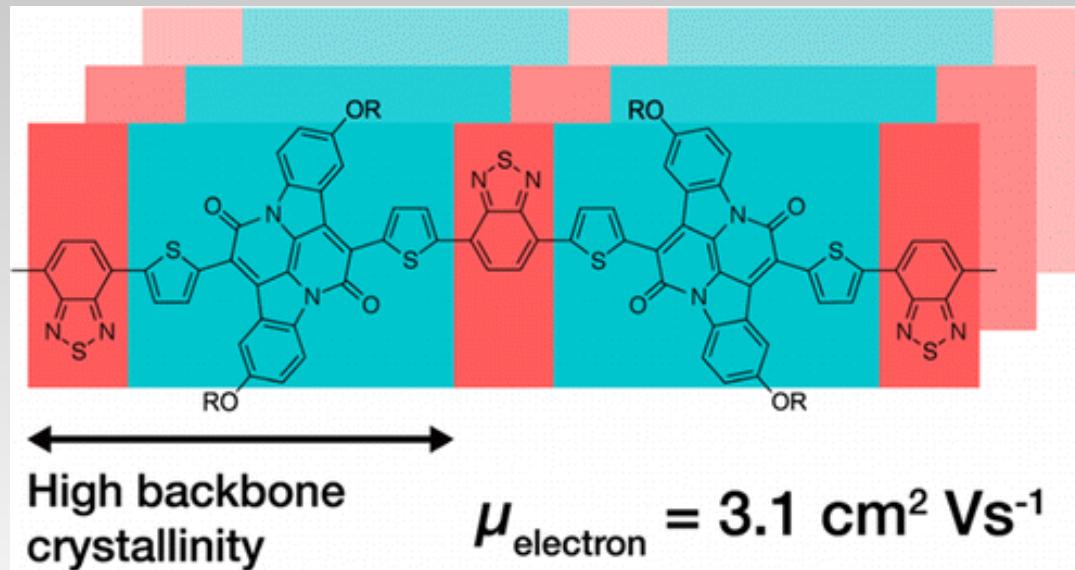


❖ Ceradrop X-Serie
Materials printer



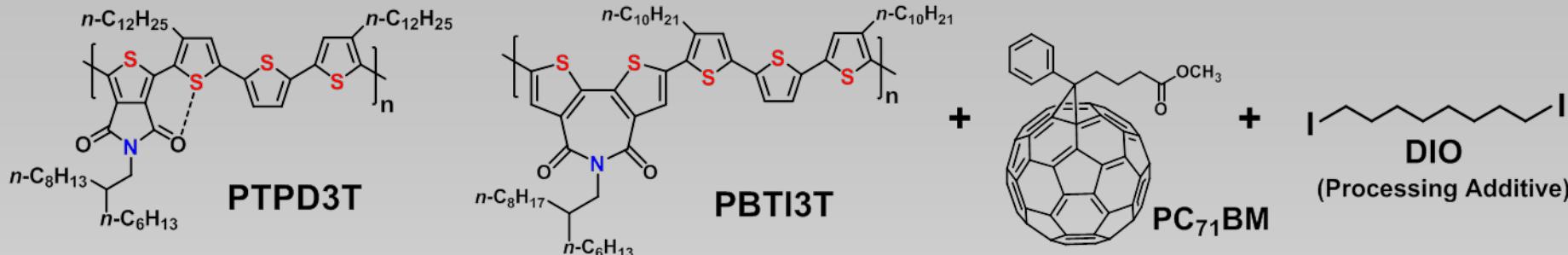
Remarkable n-Type Polymer Semiconductors

Highly ordered microstructure → ultra-high electron mobility



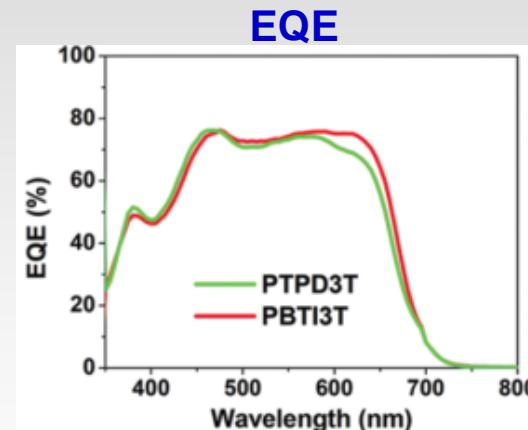
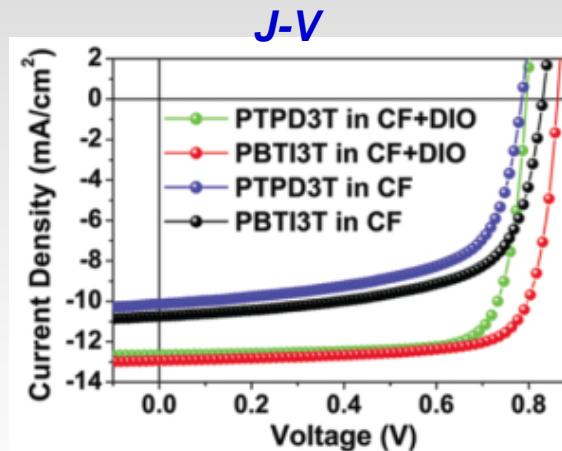
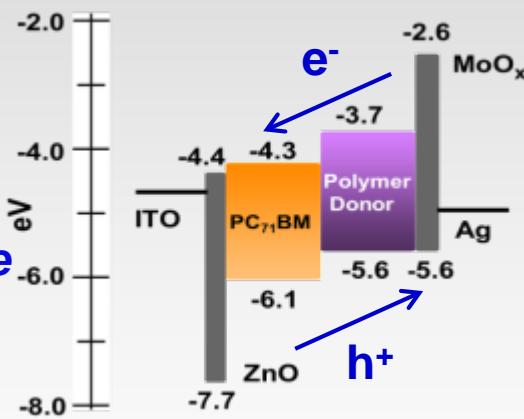
X-ray diffraction shows very high crystallinity, close packing of the chains
Very small bandgaps, absorption out to ~1000 nm
Preliminary OPV efficiency = 4.1% ; photocurrent out to 1000 nm

80% FF Moderate Bandgap D-A OPV Copolymers



Polymer	M _n (kDa)	PDI	$\lambda_{\text{max}}^{\text{abs}}$ film (nm)	$\lambda_{\text{onset}}^{\text{abs}}$ film (nm)	E _{HOMO} (eV)	E _{LUMO} (eV)	E _g ^{opt} (eV)
PTPD3T	40	2.5	582	681	-5.55	-3.73	1.82
PBTI3T	31	2.9	628	686	-5.58	-3.77	1.81

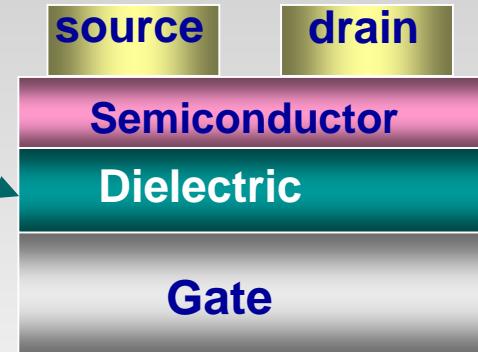
Inverted Cell Structure



Polymer	μ_h (TFT) (cm ² /Vs)	μ_h (SCLC) (cm ² /Vs)	V_{oc} (V)	J_{cs} (mA/cm ²)	FF (%)	PCE (%)
PTPD3T	5.87×10^{-2}	1.2×10^{-3}	0.786 (0.795)	12.3 (12.5)	78.7 (79.6)	7.72 (7.95)
PBTI3T	2.74×10^{-3}	1.5×10^{-3}	0.850 (0.859)	12.8 (12.9)	76.3 (77.8)	8.42 (8.76)

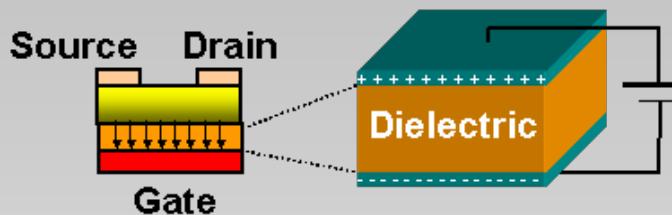
Lecture Outline

- I. Introduction, Challenges, Opportunities
- II. New n-Type Organics
Rylenedimides
- III. Nanoscopic Dielectrics
Self-Assembled Nanodielectrics
(SAND)
- IV. Amorphous Oxides
Transistors
- V. Conclusions, Acknowledgments



Need for Better Gate Dielectric: SANDs Enhance Organic & Inorganic Transistor Mobility; Reduce Voltage & Hysteresis

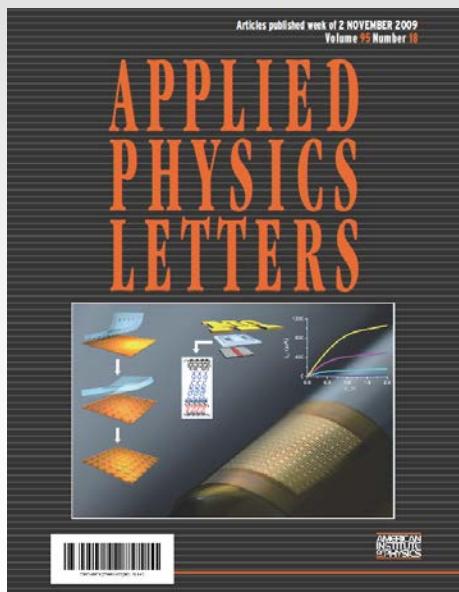
- ❖ n- and p-Type Organic Semiconductors
- ❖ Carbon Nanotubes, Graphene
- ❖ ZnO & In_2O_3 Nanowires
- ❖ GaAs, 2D MoS₂
- ❖ Oxide Thin Films
- ❖ Conventional & Nanomembrane Si



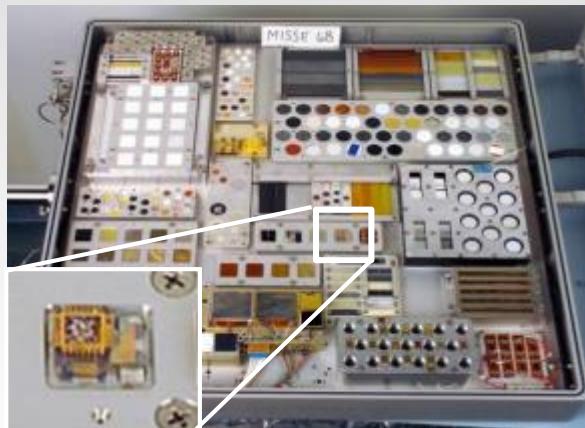
$$I_{SD} \sim \mu V_G C_i$$



Si Nanomembrane TFTs

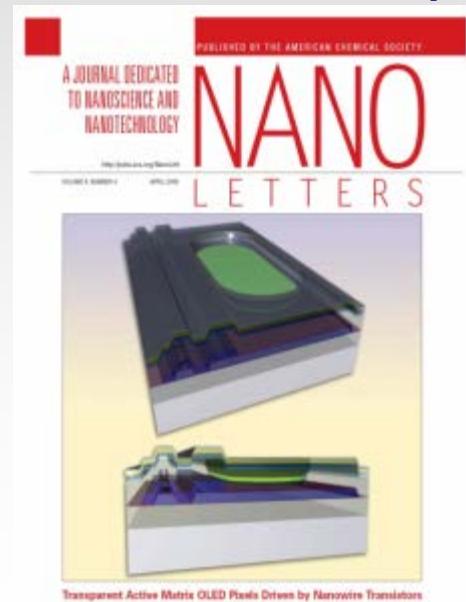


H⁺ Radiation-Hard SAND TFTs



Materials module deployed on the International Space Station. Inset: SAND-based transistors fabricated by Northwestern scientists

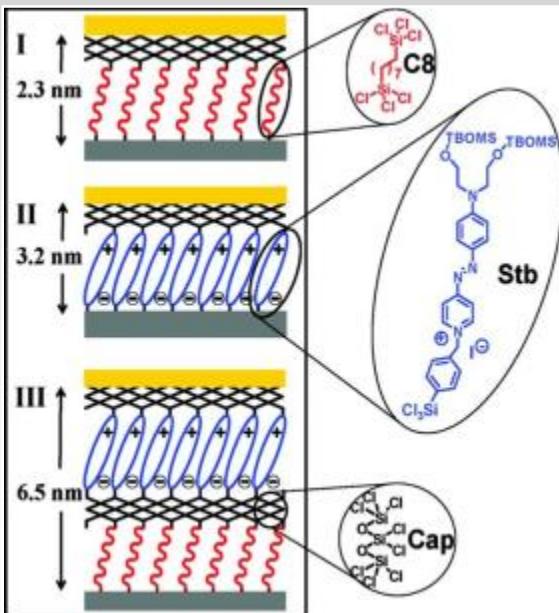
Active Matrix ZnO NW/SAND OLED Display



Next-Generation SANDs Customized for Specific Function

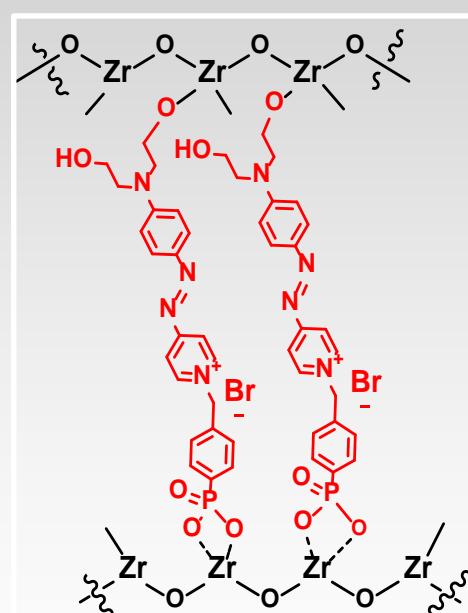
Type III SAND

Non-Ambient Growth
Hydrocarbon Solvents



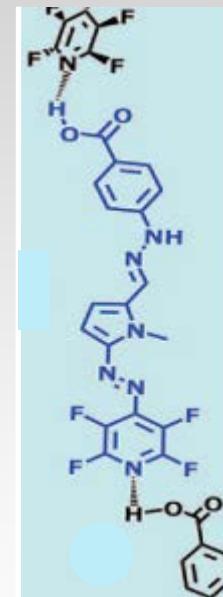
Zr-SAND & Hf-SAND

Ambient Growth
Alcohol Solvents



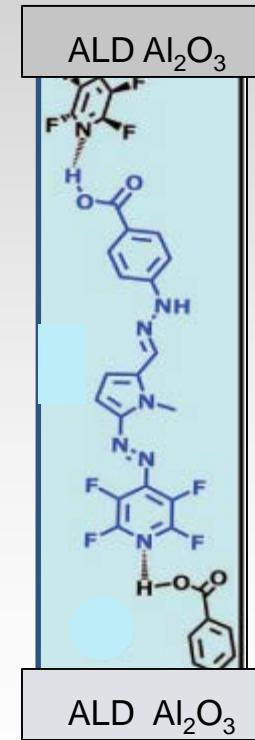
V-SAND

Vapor Growth
Avoid Solvents



VA-SAND

Vapor Growth
Avoid Solvents

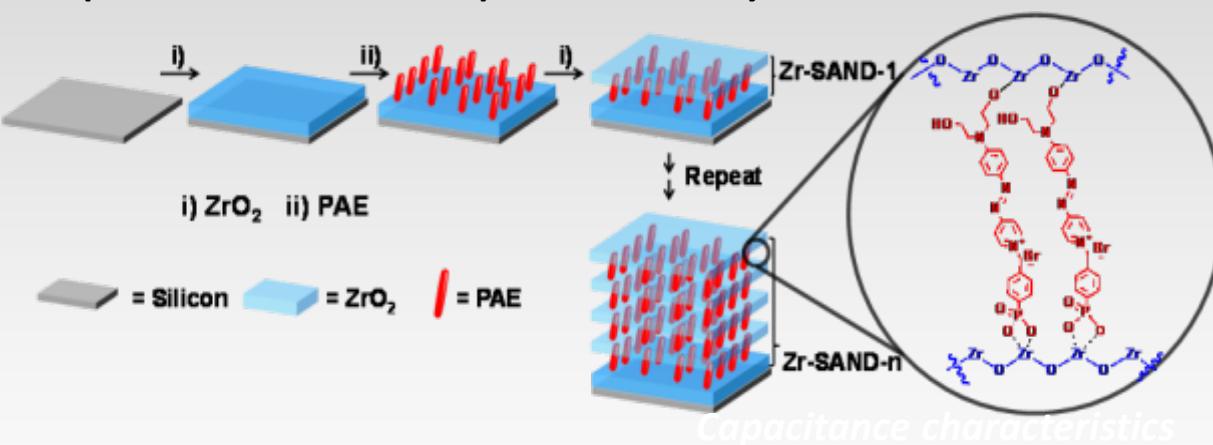


Zr, Hf-SAND Self-Assembled Nanodielectrics

- Organic/inorganic hybrid multilayer
- Solution processable under ambient
- Controllable thickness, large-area uniformity, well-defined structure
- High capacitance, superior insulating properties
- 350° C thermal stability

Fabrication

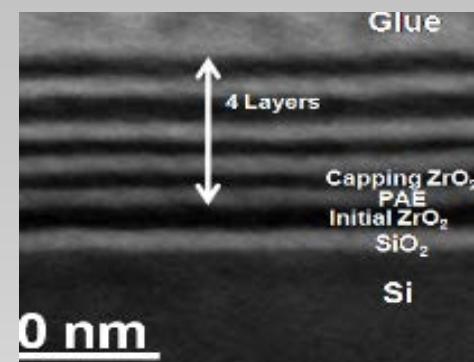
- Self-assemble phosphonic acid-based polarizable π-molecule
- Spin coat ultra-thin ZrO_x primer & interlayers



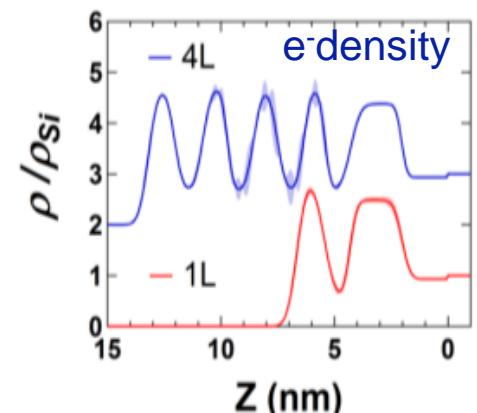
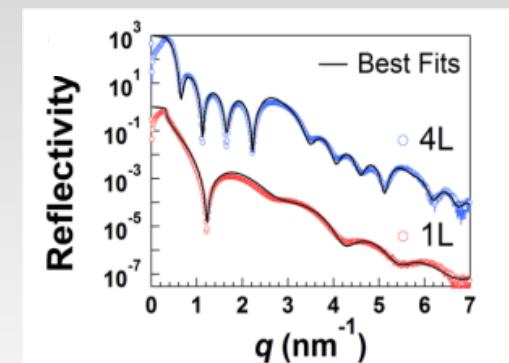
M-SAND-4 (4 layer)

- Leakage: 10^{-7} A/cm² @ 2 MV/cm
- C_i : 465 nF/cm² (Zr), 1 μ F/cm² (Hf)
- $k \approx 11$ (Zr), 20 (Hf)
- Roughness(RMS): <0.4 nm

TEM Cross-section



XRR

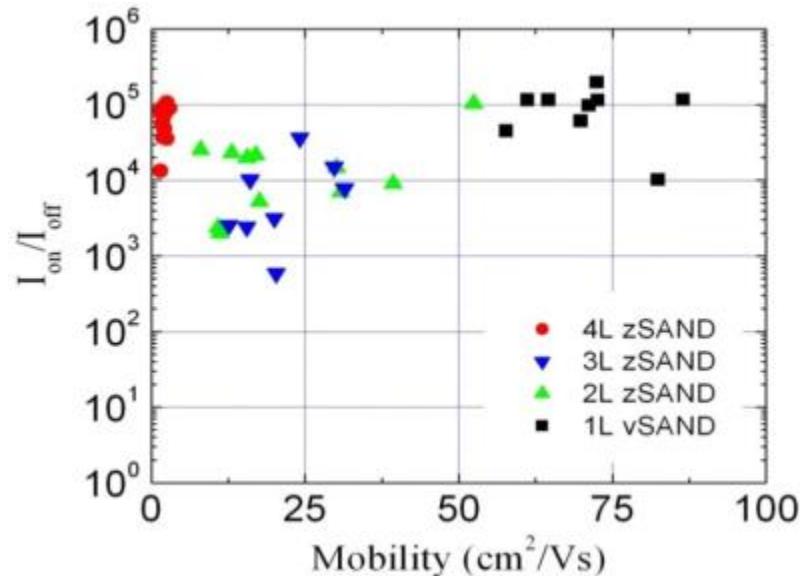
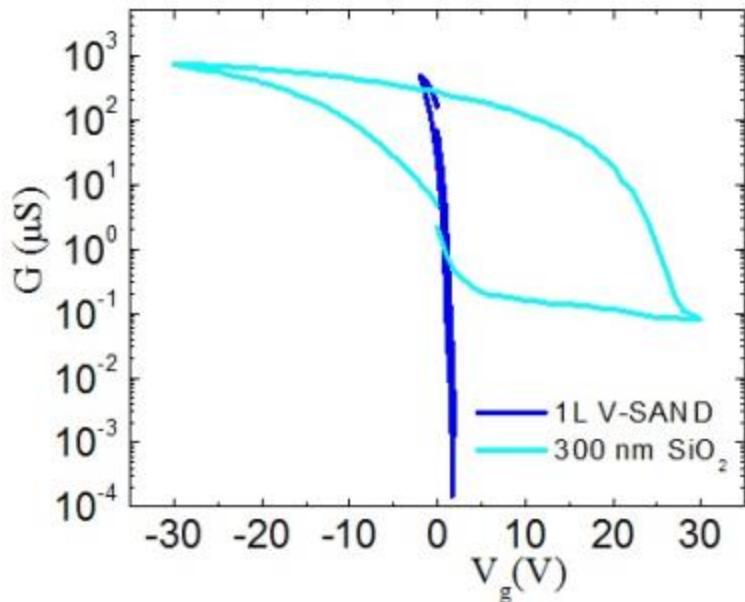


High Performance Sorted SWNT TFTs with SAND Dielectrics

Solution-Processed Z-SAND & Vapor-Deposited V-SAND

- Reduced operating voltage (2 V)
- Reduced hysteresis: reduced interfacial trapped charge; phonons?
- Higher field-effect mobility ($\sim 70 \text{ cm}^2/\text{Vs}$) versus SiO_2 dielectric ($\sim 15 \text{ cm}^2/\text{Vs}$)
- Higher on/off ratio for same on-state conductance

SWNT Film TFT Gate Dielectric Effects



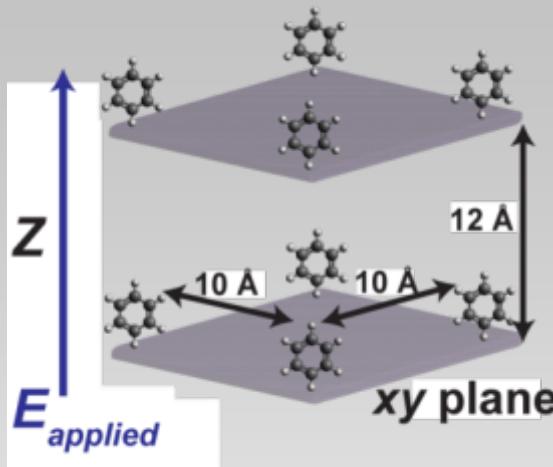
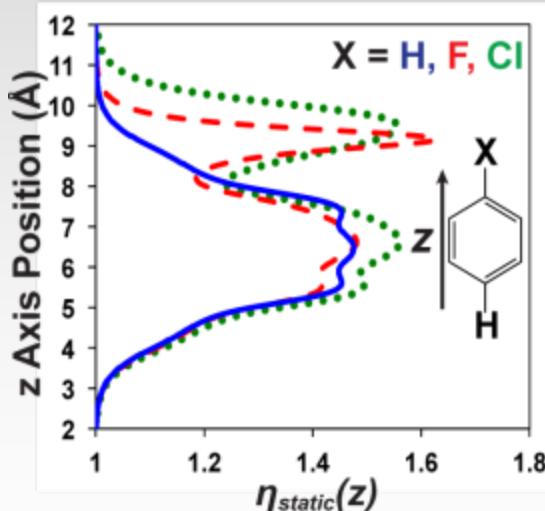
VA-SAND Dielectric: $\mu = 150 \text{ cm}^2/\text{Vs}$; on/off = 5×10^5 , transconductance = $6.5 \mu\text{S}/\mu\text{m}$
SS = 150 mV/decade

SAND Design. First-Principles Calculation of Dielectric Response in Molecule-Based Materials

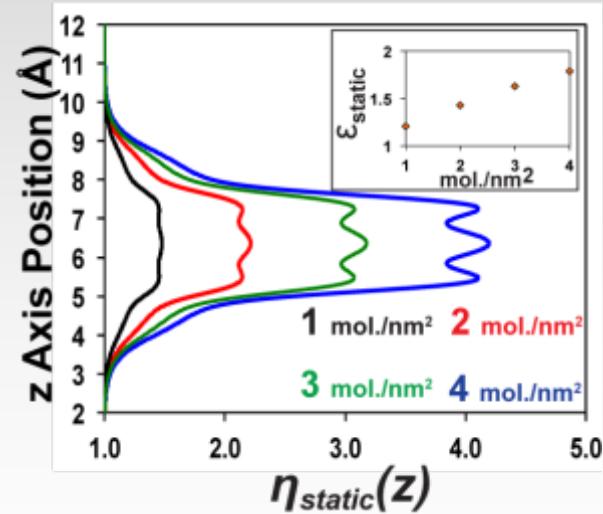
Scheme for plane-wave DFT computation of static dielectric response:

$$\eta_{\text{static}}(z)$$

$\eta_{\text{static}}(z)$ w/ substitution



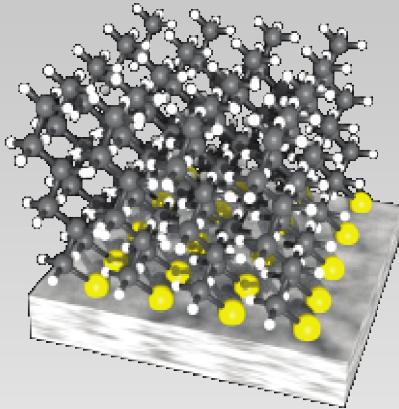
$\eta_{\text{static}}(z)$ versus coverage



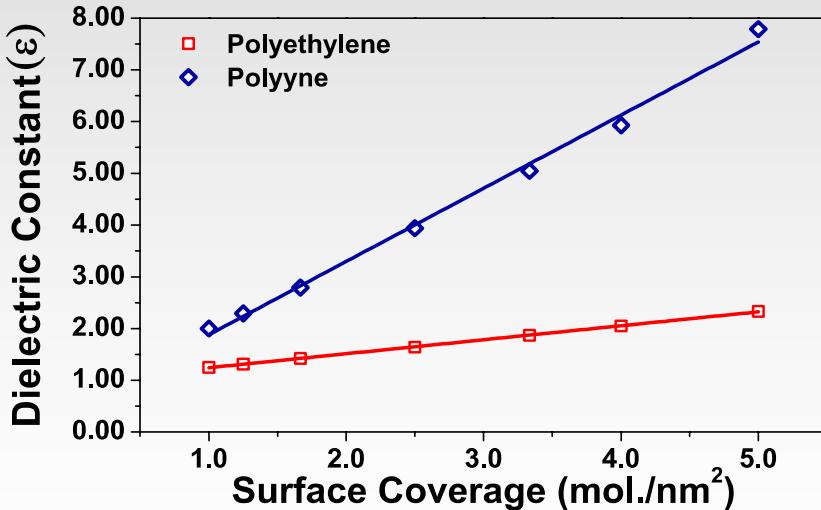
- Benzene Crystal: Computation: $\epsilon = 2.39$; Experiment: $\epsilon = 2.34$
- First powerful tool for the design of new hybrid dielectric materials

Materials Design. First-Principles Calculation of Dielectric Response in SAND-Type Materials

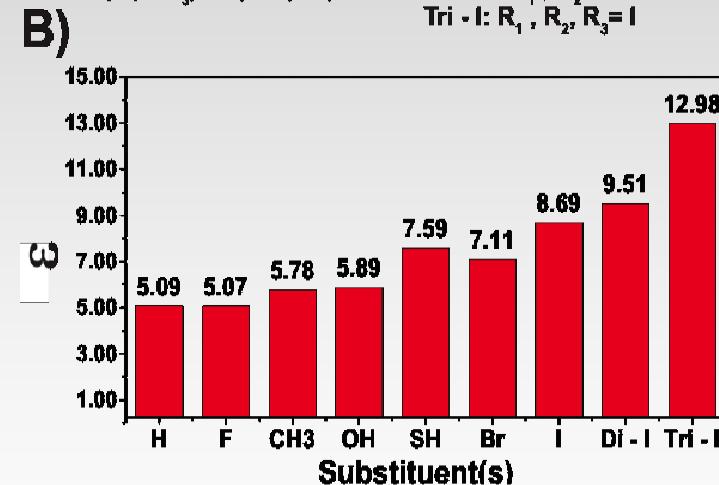
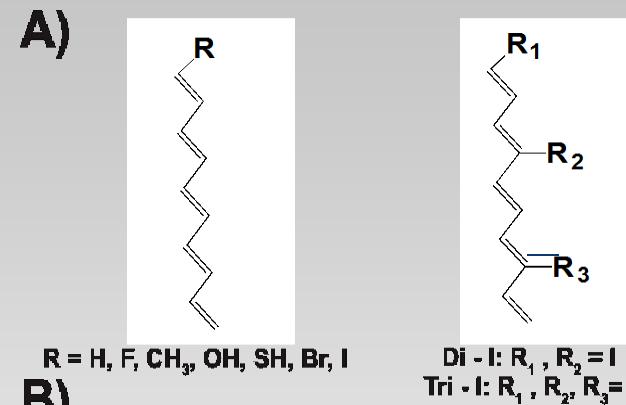
How to increase dielectric constant (ϵ) and capacitance (C) of molecular films?



Typical organic films have $\epsilon \approx 3.0$,
 $C < 1.0 \mu\text{F}/\text{cm}^2$

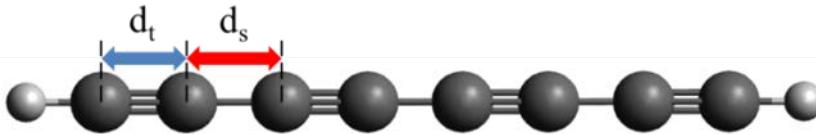


Computed dielectric constant of saturated & polyacetylenes at varying coverages. $\epsilon > 7.0$
($C > 3.0 \mu\text{F}/\text{cm}^2$)



Computed dielectric constant of polyenes with polarizable substituents achieve $\epsilon > 12$ at 4 molecules/nm² coverage

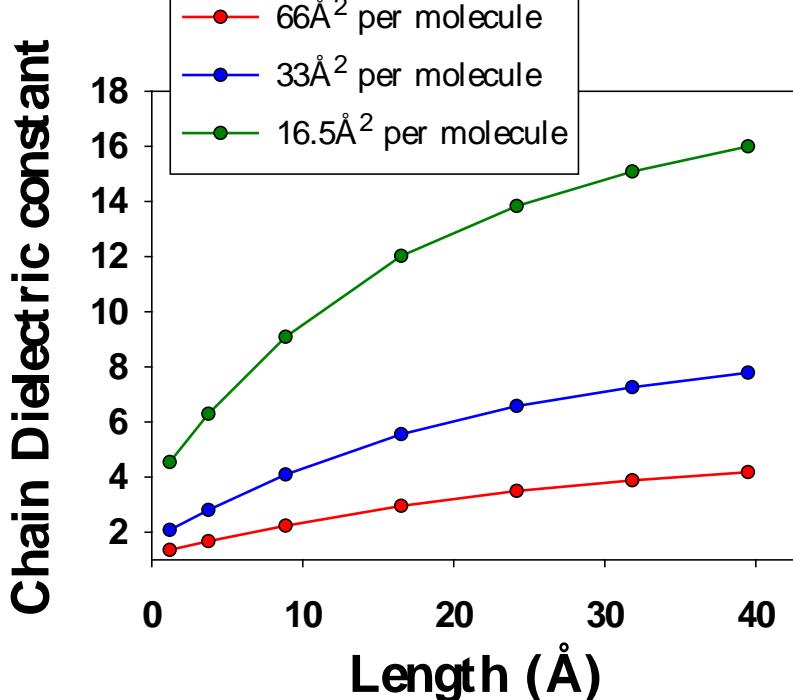
Synergistic Effects with Tight Packing



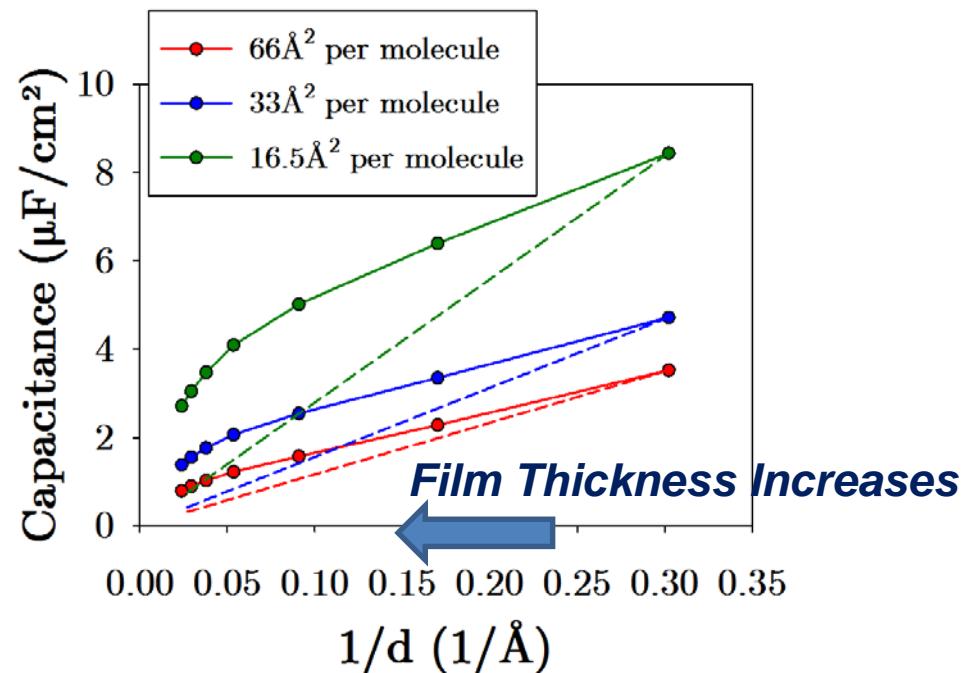
Dielectric constant increases with chain length

$$C = \frac{k(d)}{4\pi d}$$

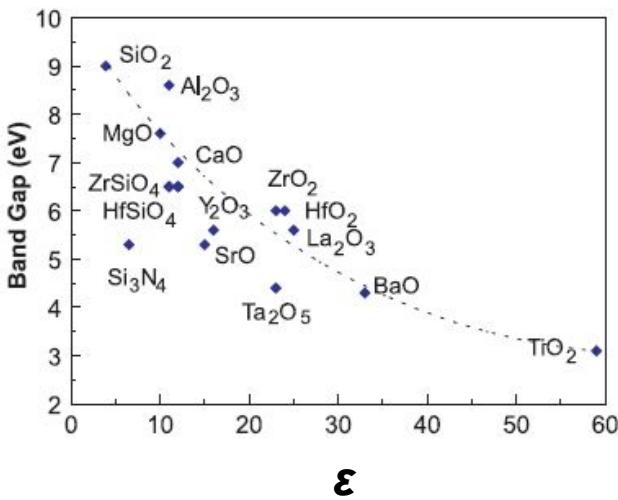
d = film thickness



Capacitance does not decline as $1/d$ for conjugated chains.
Capacitance reaches higher values than a linear extrapolation (-----)

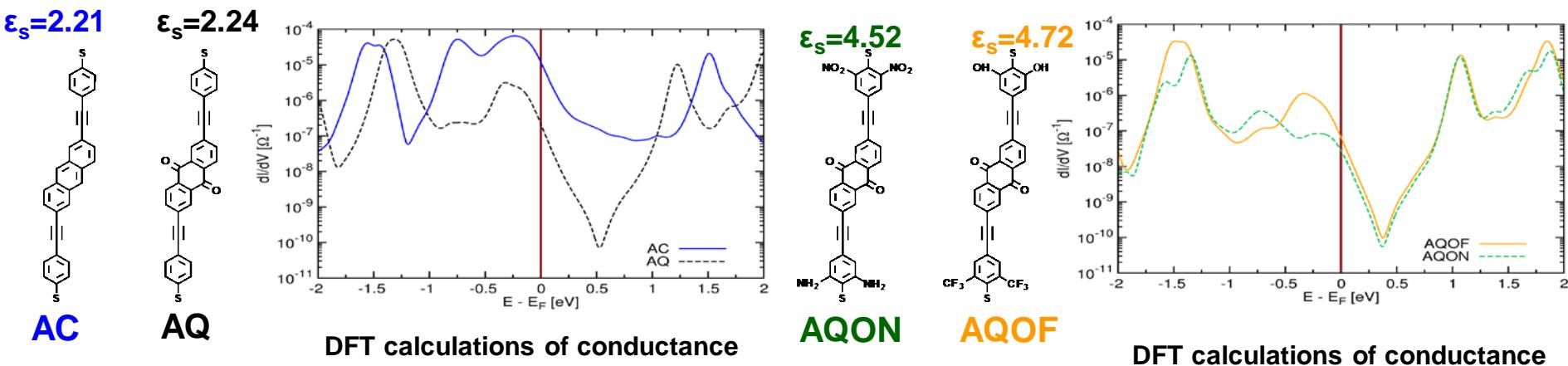


Design Challenge: High ϵ with Low Leakage



In oxides, smaller band gap leads to higher ϵ , but also larger leakage current

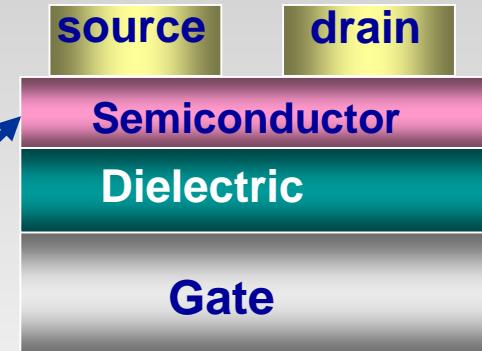
*Can dielectric constant be increased while leakage current is kept constant?
Quantum Interference*



Conductance in organic molecules reduced by orders of magnitude
without compromising dielectric performance.

Lecture Outline

- I. Introduction, Challenges, Opportunities
- II. New n- and p-Type Organics
 - Rylenedimides
- III. Nanoscopic Dielectrics
 - Self-Assembled Nanodielectrics
(SAND)
 - Unconventional Semiconductors
- IV. Amorphous Oxides
 - Transistors, new tools, heterojunctions
- V. Conclusions, Acknowledgments



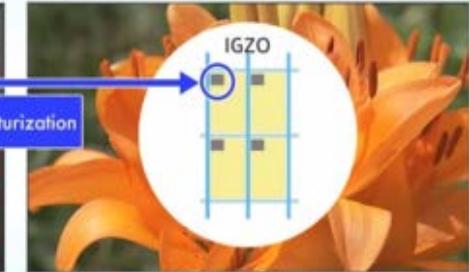
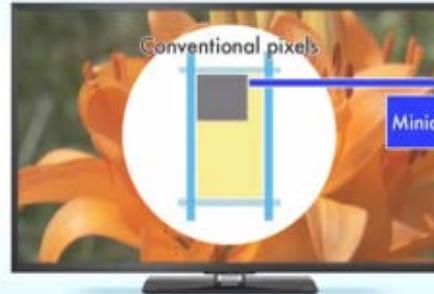
Transparent Electronics Could Use Oxide TFTs + Organics

Flexible Transparent Displays



Samsung Transparent OLED TV

Comparison with TFT



a-Si(Amorphous silicon)

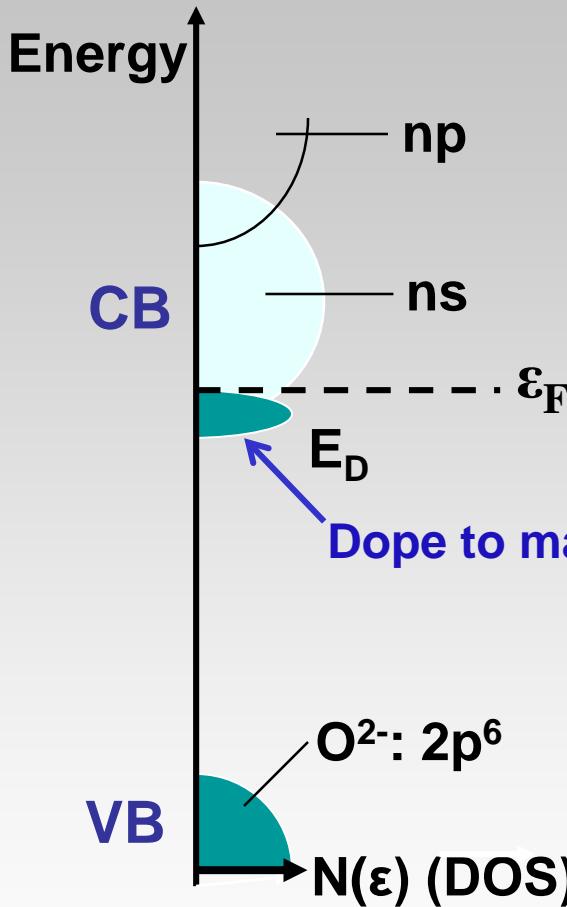
Sharp IGZO Displays

IGZO

***Amorphous Oxide Driving Electronics: In-Ga-Zn-O?
Can We Hybridize with Organic Materials?***

TRANSPARENT CONDUCTING OXIDE (TCO) ELECTRONIC STRUCTURE MODEL

J. Goodenough



Metal Cation Conduction Band

- Lies above top of O-2p π VB by $\Delta E_{gap} \geq 3.1\text{eV}$
 - Low enough in energy to accept electrons
 - Itinerant electrons cannot be excited into higher band by light absorption
- Dope to make conductive (e.g., Sn in In_2O_3)

Cation Requirements Usually Met by

- 5s CB of Cd^{2+} , In^{3+} , Sn^{4+}
- Burstein-Moss increase in ΔE_{gap} with doping

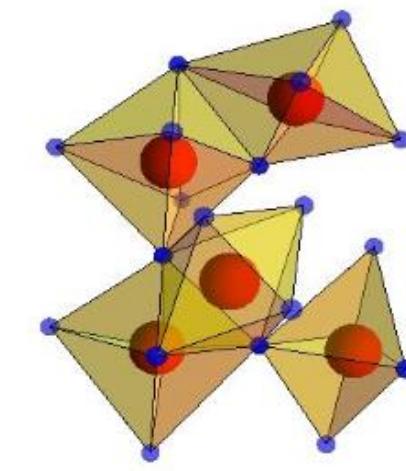
What are the Limitations and Implications of this Picture?

Can We Use These for TFTs?

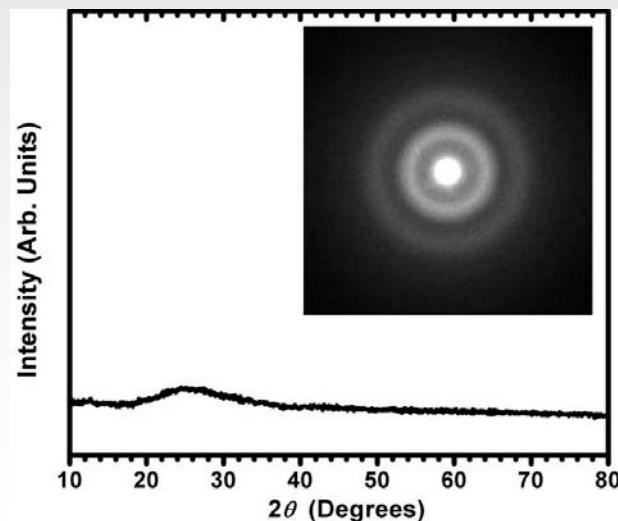
Attractions of Amorphous Oxide Semiconductors (AOSs) for High-Performance TFTs

Disordered Crystal Structures

- ❖ High Mobility, s-State Conduction Band
- ❖ Low Deposition, Processing Temperatures
- ❖ Very Smooth Surfaces, No Grain Boundaries
- ❖ Mechanical Flexibility
- ❖ Optical Transparency
- ❖ Properties Tunable between Insulating, Semiconducting, Highly Conducting by Doping



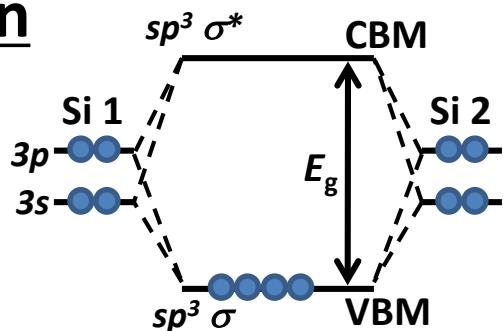
Film XRD and Electron Diffraction



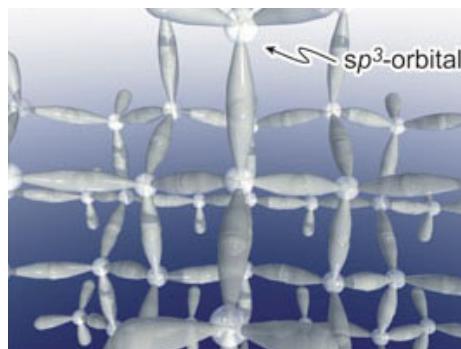
Bellingham, Hosono, Mason, Wager

Amorphous Semiconductor Electronic Structure

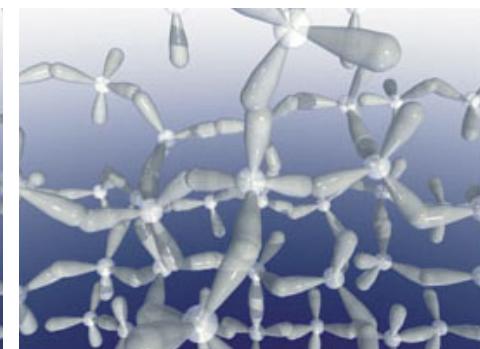
Silicon



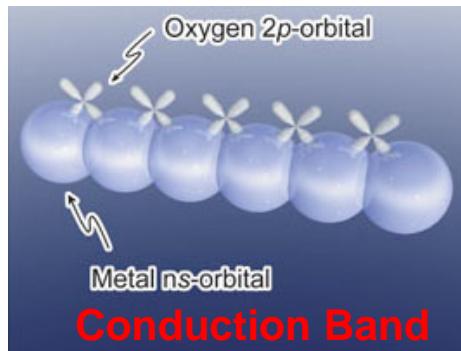
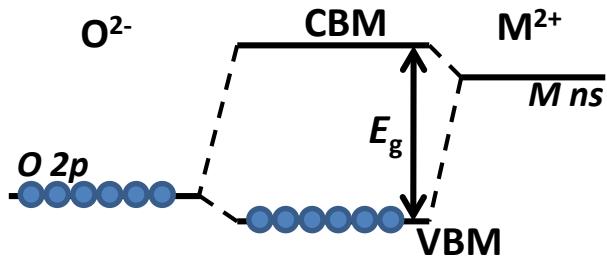
Crystalline



Amorphous



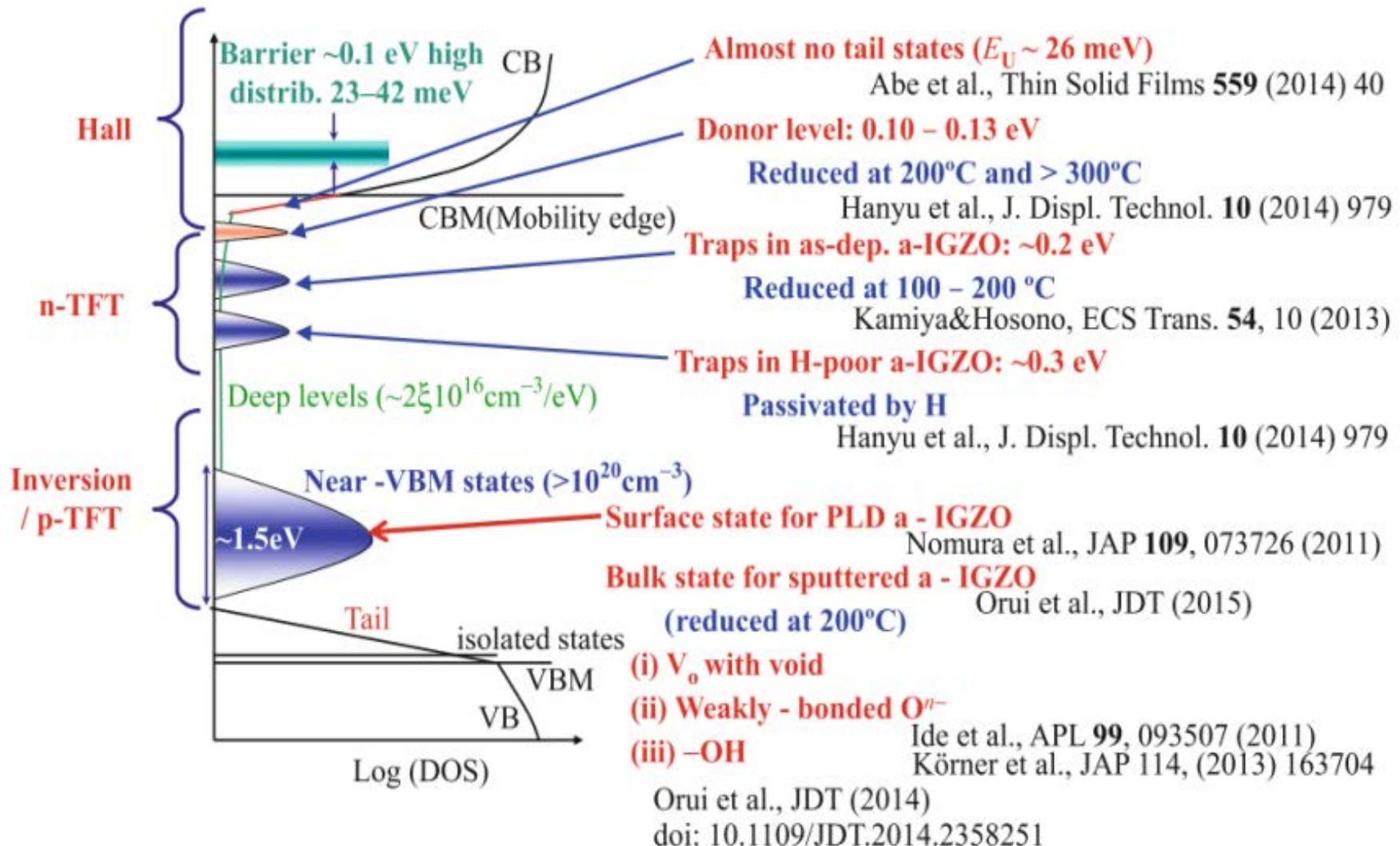
Transparent Oxide



Attractions of a-Transparent Oxide Semiconductors:

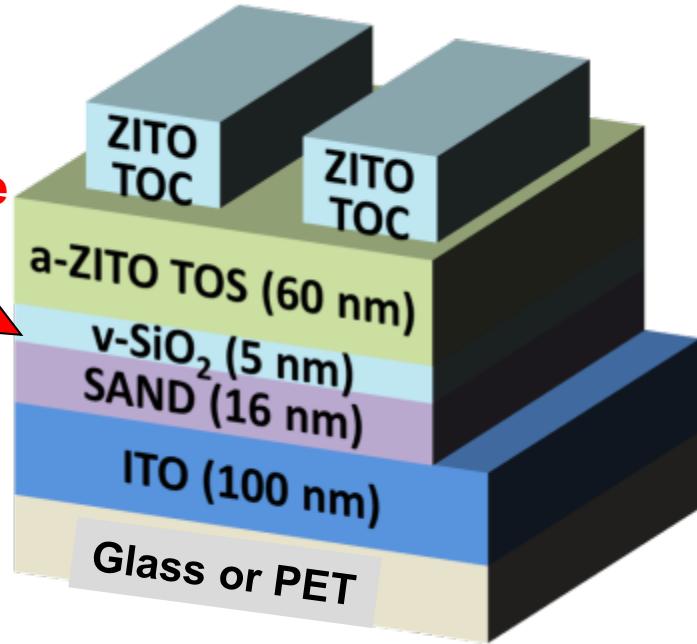
- Comparable carrier mobility
- Low processing temperature
- Uniformity, smoothness
- Mechanical flexibility

Schematic Electronic Structure Around the IGZO Band Gap

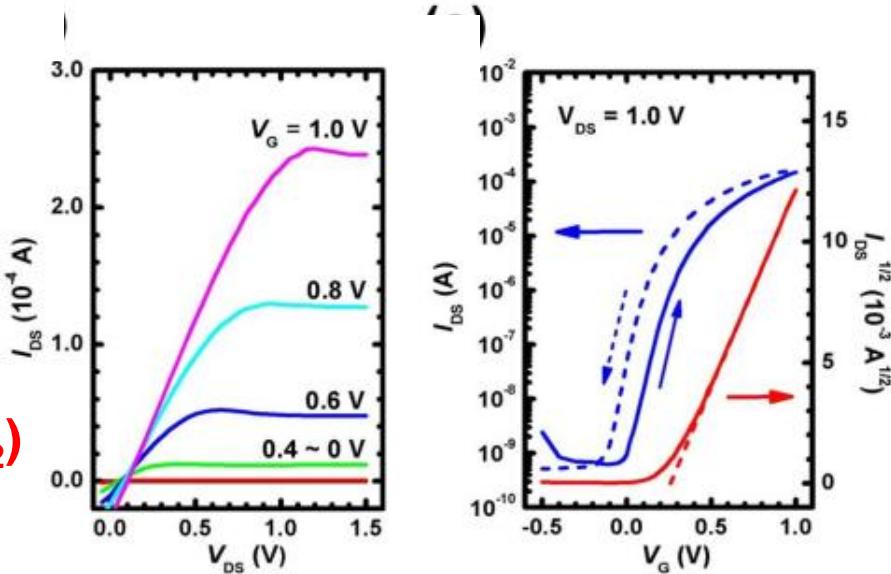
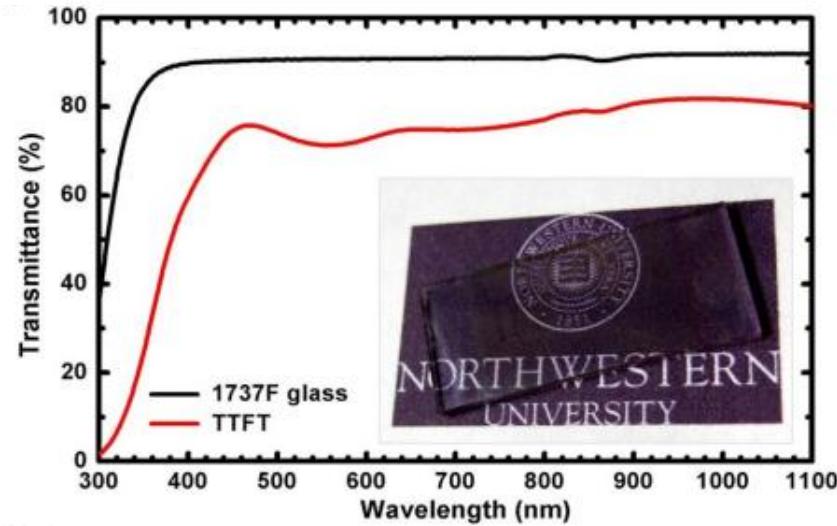


Transparent α -Zn-In-Sn-O TFTs Grown by Pulsed Laser Deposition

Protective Layer



Transmittance ~75% (glass ~90%)

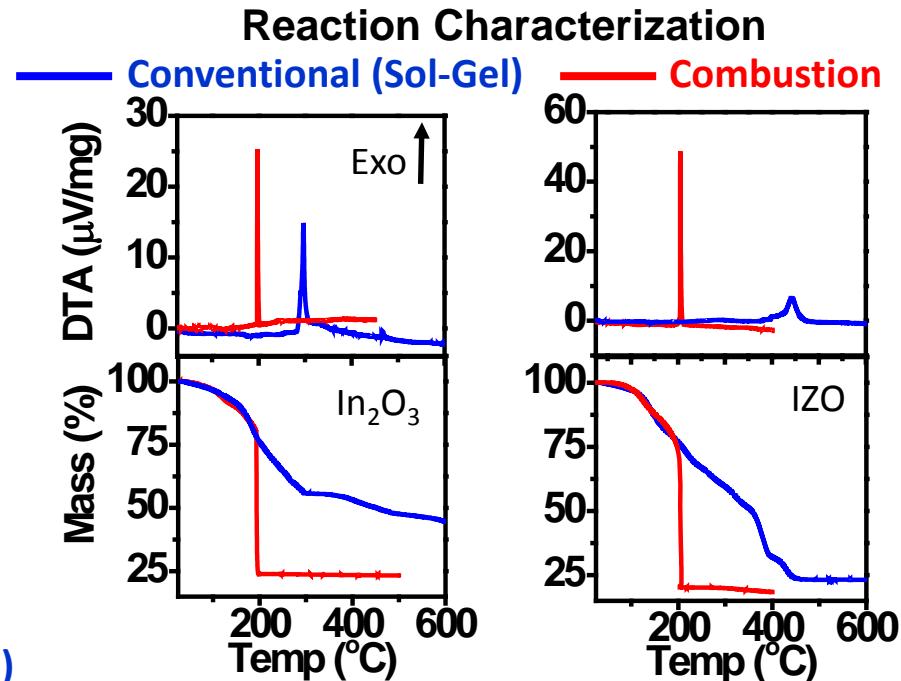
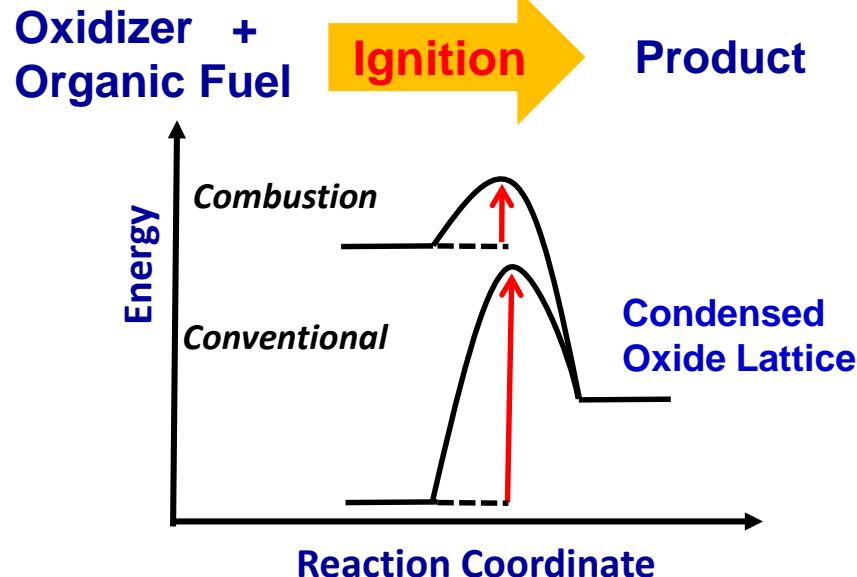


This Isn't Solution Processing!

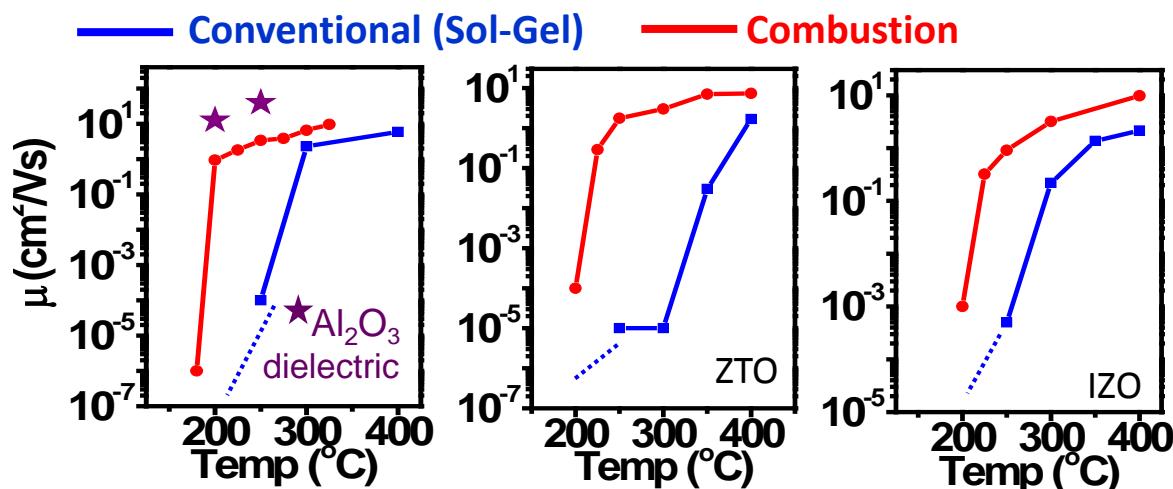
SS ~0.13 V/decade

Low Temperature Combustion Synthesis of α -Oxide Films

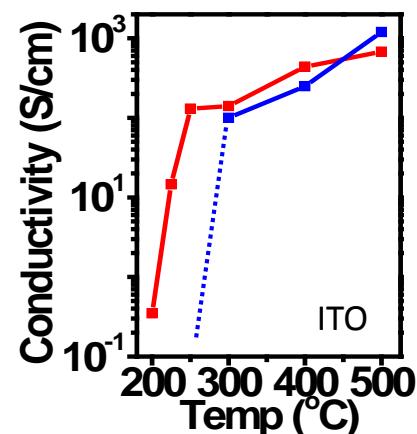
Solution Precursors



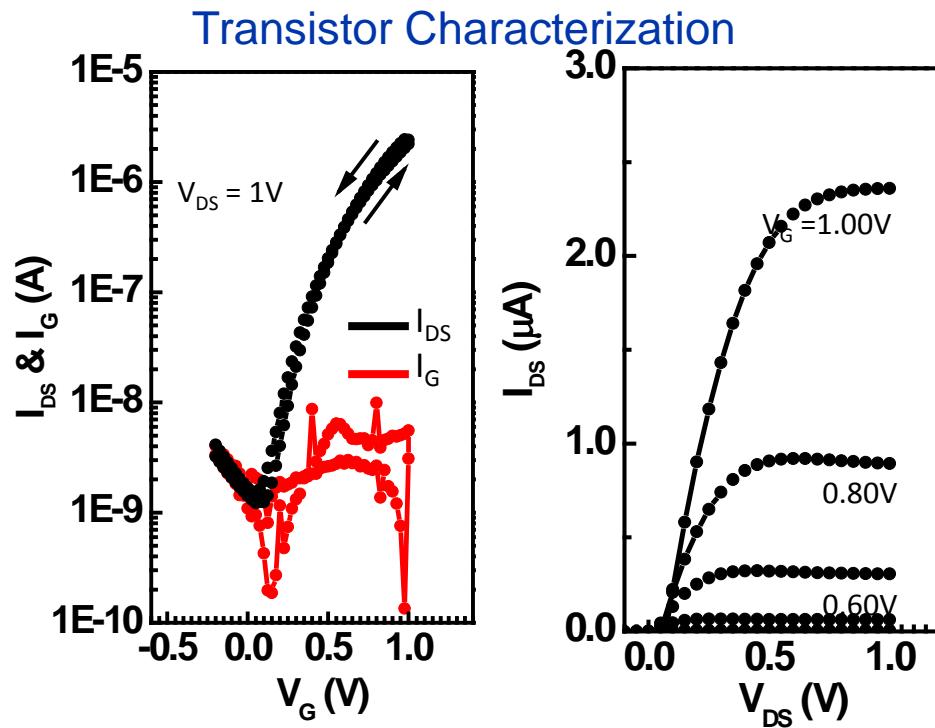
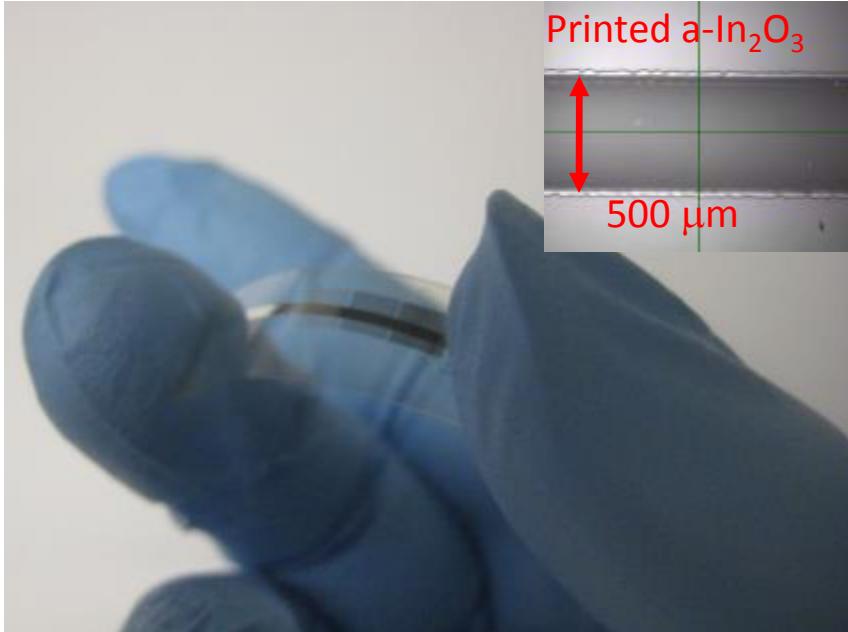
TFT Performance (Si/SiO₂ Substrates)



TCO Conductivity



Result: Inkjet Printed, Combustion-Processed Flexible Amorphous In_2O_3 Transistors on Plastic



Research Agenda

- Materials Scope
- Microstructure Evolution
- Performance Limits, SAND

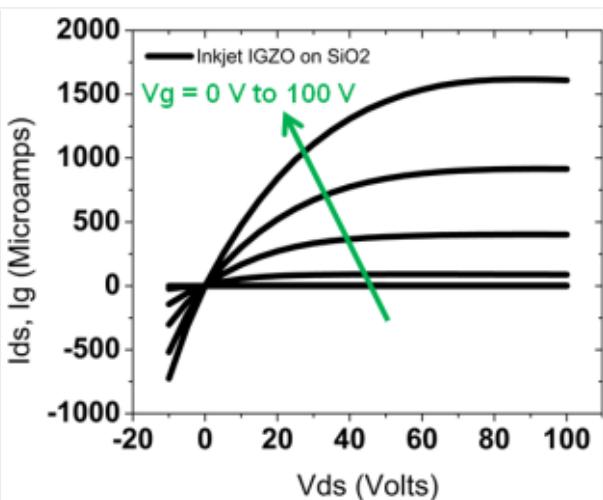
Plastic: $\mu = 8 \text{ cm}^2/\text{V}\cdot\text{s}$ $I_{on}:I_{off} \sim 10^4$

Glass: $\mu = 40 \text{ cm}^2/\text{V}\cdot\text{s}$ $I_{on}:I_{off} \sim 10^5$

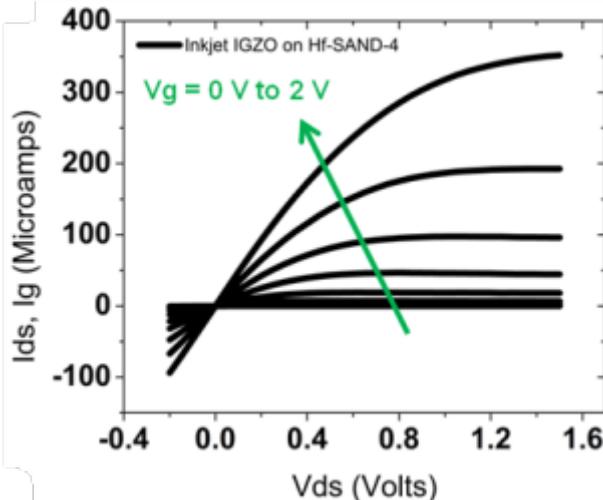
a- Al_2O_3 Gate Dielectric

SAND Also Works

Inkjet-Printed Combustion α -IGZO on Hf-SAND



SiO_2 Dielectric
 $\mu \approx 5 \text{ cm}^2/\text{Vs}$
High operating voltage

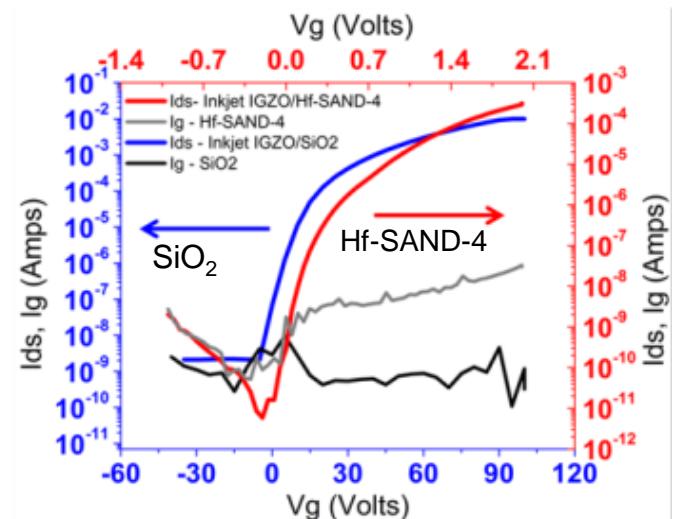
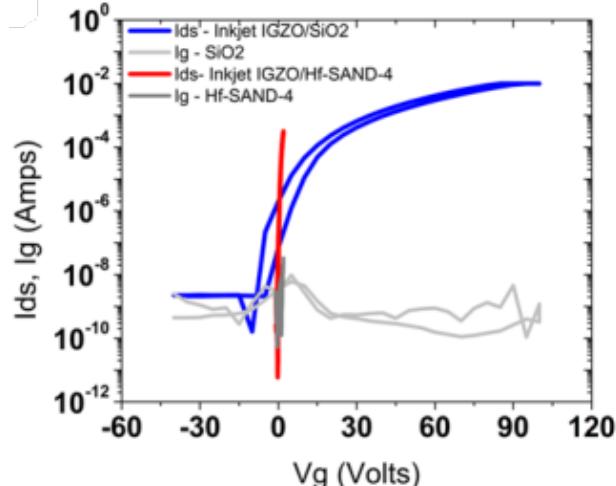


Hf-SAND Dielectric
 $\mu_{\text{MAX}} > 40 \text{ cm}^2/\text{Vs}$
All-solution processed
<3V TFT operation



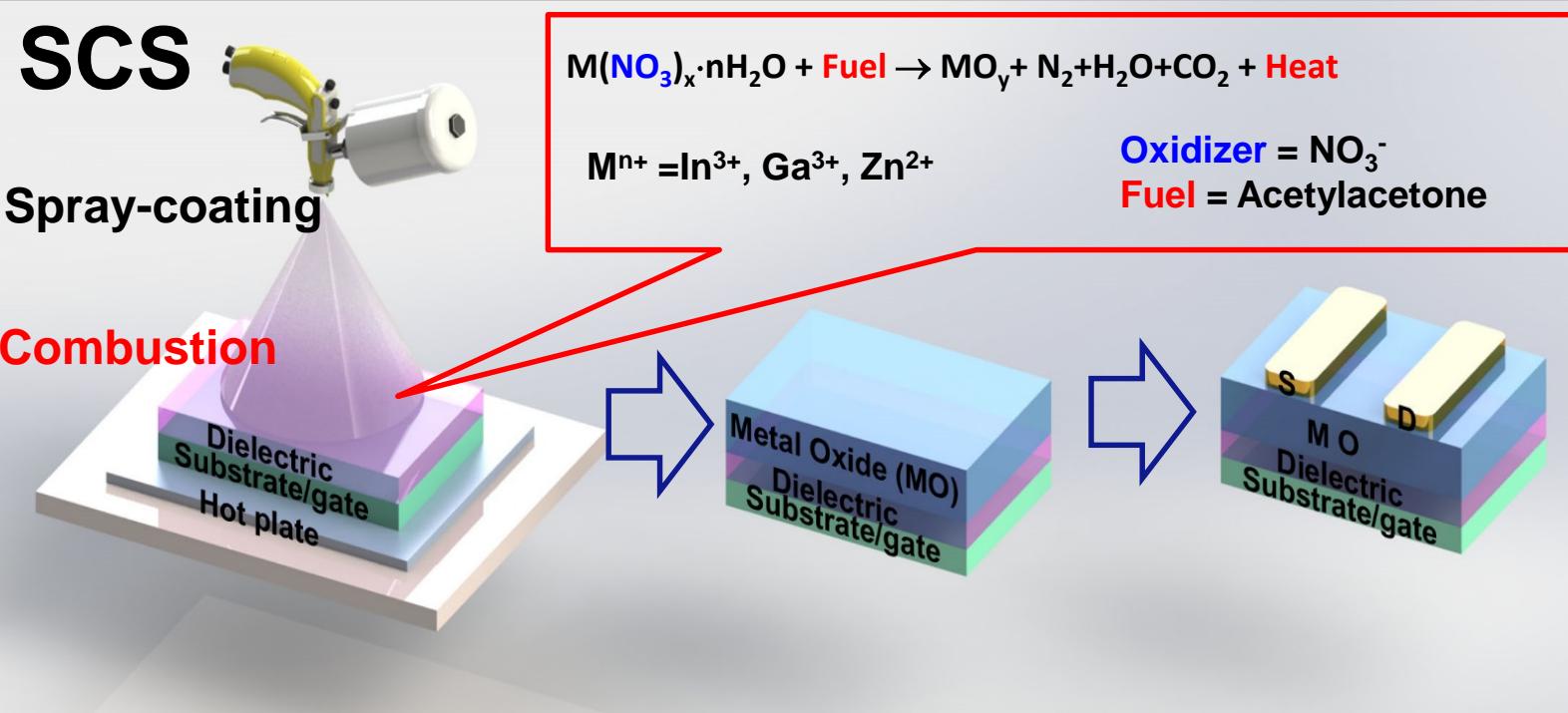
Sputtered IGZO:
iPad Mini Retinal Display

Dramatic operating voltage reduction



High mobility, no reduction in $I_{\text{ON}}:I_{\text{OFF}}$

Enhanced α -TCO Performance & Low-Temp Processing Continuous Processing: Spray Combustion Synthesis (SCS)



**IGZO Films: Defect Density, Mobility,
Porosity \approx Magnetron Sputtered IGZO!**

Microsoft Surface 4
has sputtered IGZO
TFTs driving display



Spray Combustion Synthesis (SCS) Films Rival Sputtered IGZO Films in Properties

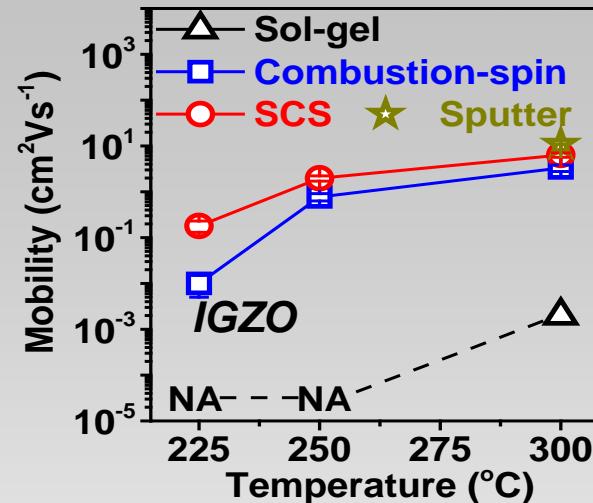
IGZO/SiO_x dielectric

SCS TFTs have >2× mobility vs. spin-coated combustion >> sol-gel.

IGZO TFT performance **approaches sputtered ones**.

IGZO/ZrO_x dielectric

Mobility >20 cm²/Vs at 2V operation

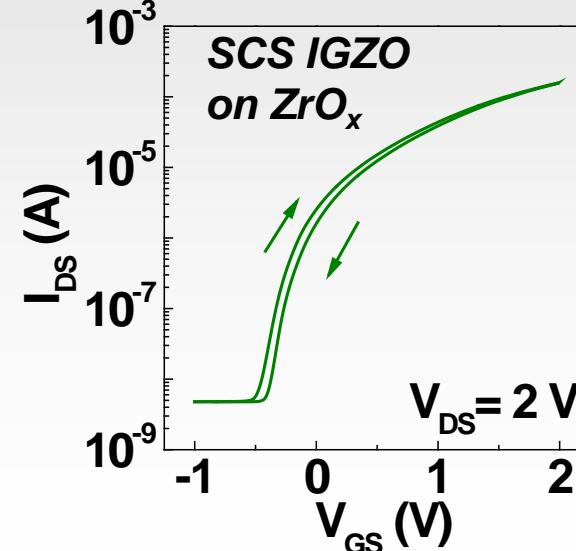


IGZO Density by Positron Annihilation Spectroscopy & X-ray Reflectivity:

Sputtered ≈ SCS >> Sol-gel

IGZO Defect Density by C-V; Sputtered ≈ SCS >> Sol-gel

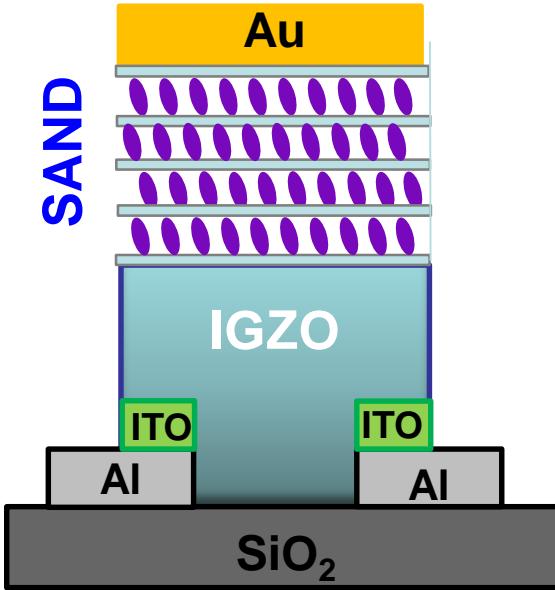
Microsoft Surface 4 has sputtered IGZO TFTs driving display



Top Gated SAND/Oxide Transistors

Combine **SAND** Dielectric + **Combustion Processed** IGZO

SAND



Fundamental Questions:

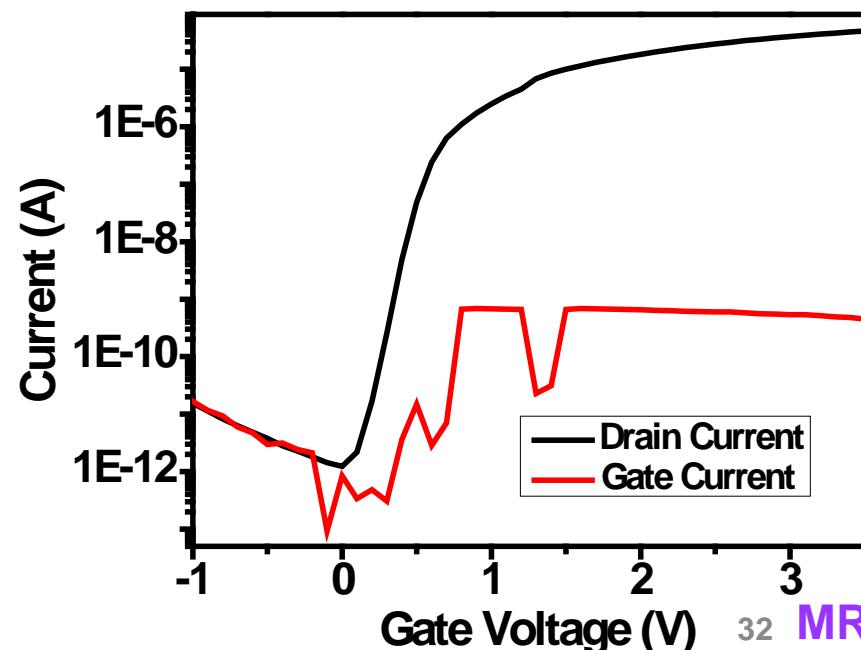
- Is **SAND** adaptable to **top gate TFTs**?
- Can **SAND** be grown on **combustion processed oxide**?
- What are characteristics of this novel **interface**?

Future:

- Characterize microstructure, interfacial defect densities as a function of oxide and oxide surface preparation
- Computation of interface characteristics

Initial results are:

- $\mu_{\text{sat}} \sim 20 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$
- $V_{\text{th}} = 0.79 \text{ V}$
- $\text{Log}(\text{On}/\text{Off}) = 7.16$



'Invisible' Flexible TFTs Enabled by Amorphous Metal Oxide/Polymer Channel Layer Blends

In combustion precursor

$\text{In}(\text{NO}_3)_3 + \text{AcAc}$ in
2-Methoxyethanol -- 0.5 M

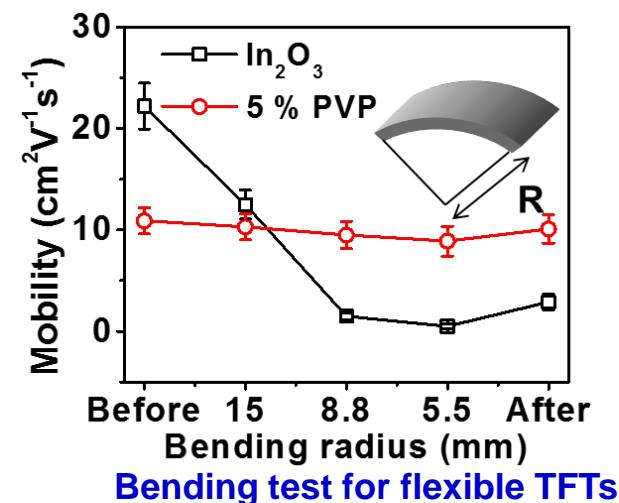
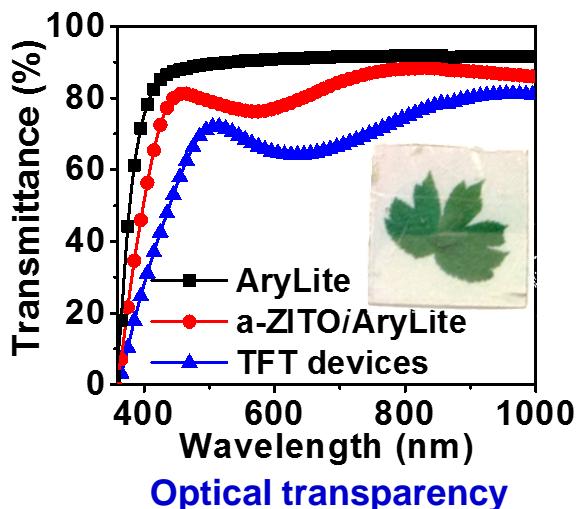
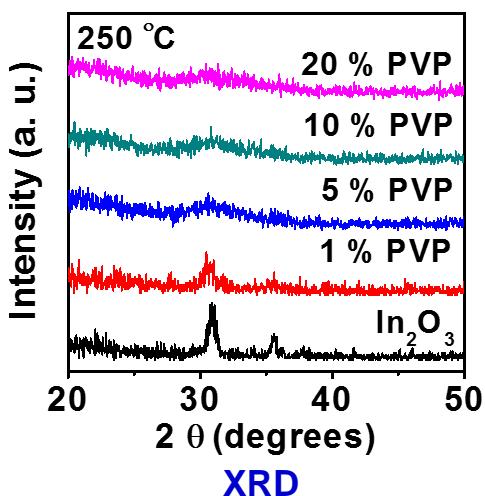
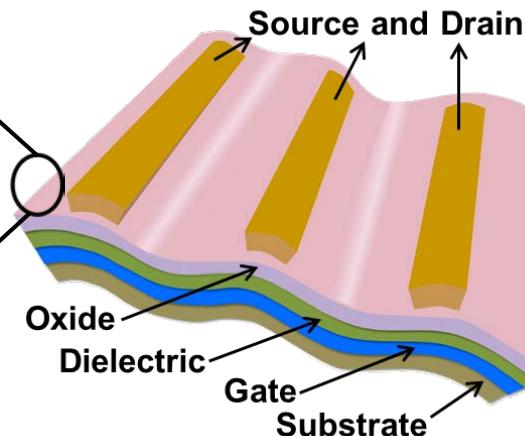
PVP

Poly(4-vinylphenol) in
2-Methoxyethanol – 10 mg/mL

PVP concentration

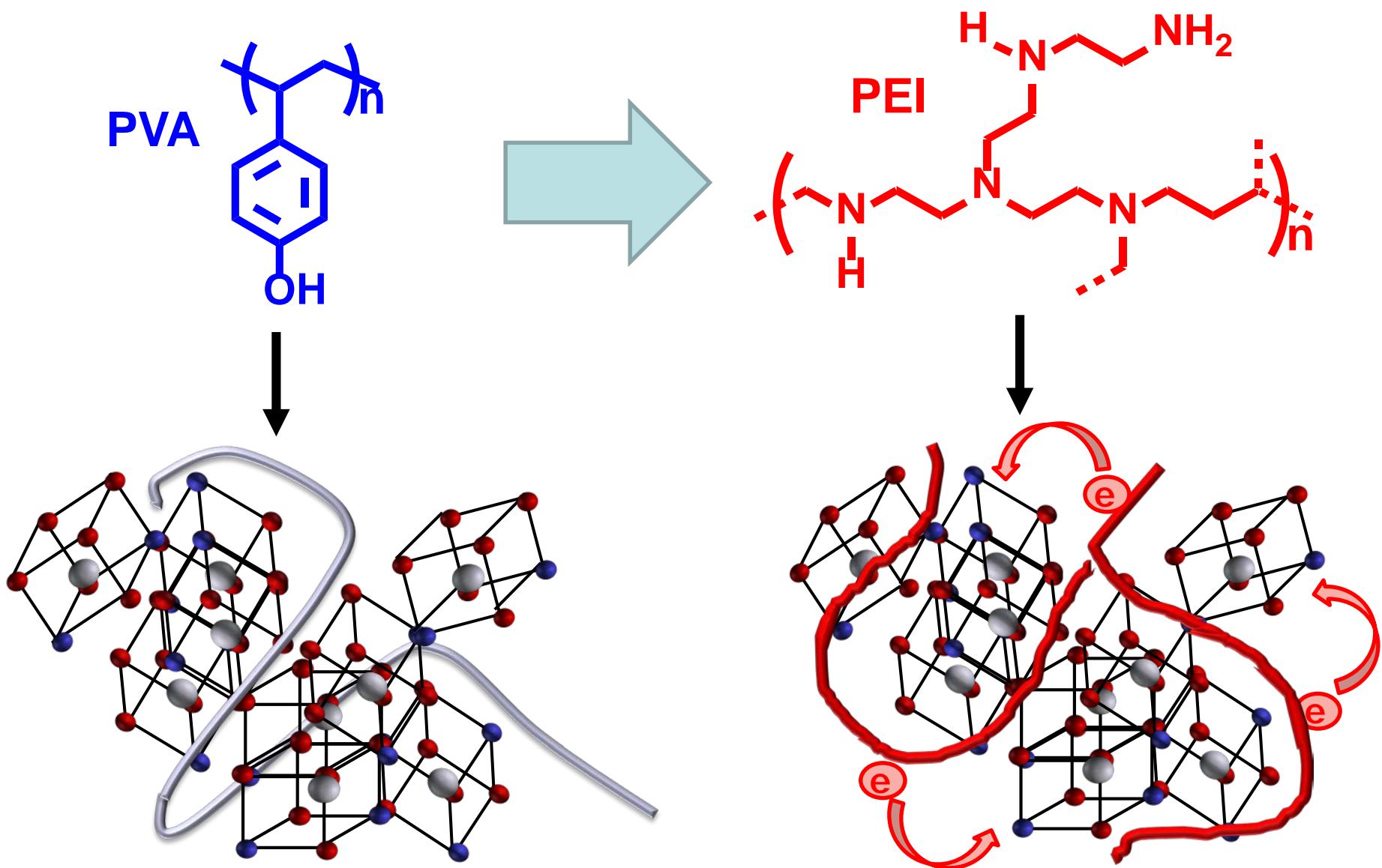
0 - 20 wt%

$\text{In}_2\text{O}_3 + \text{PVP}$



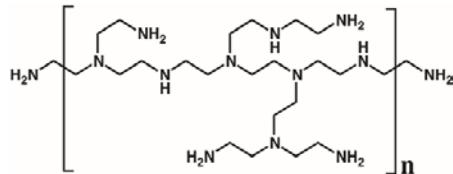
- Polymer blend + metal oxide: new route to amorphous oxide thin films
- MO:polymer blend films realize ultra-flexible electronic devices
- High performance flexible transparent transistors in solution process

What About an Electron-Rich Polymer?

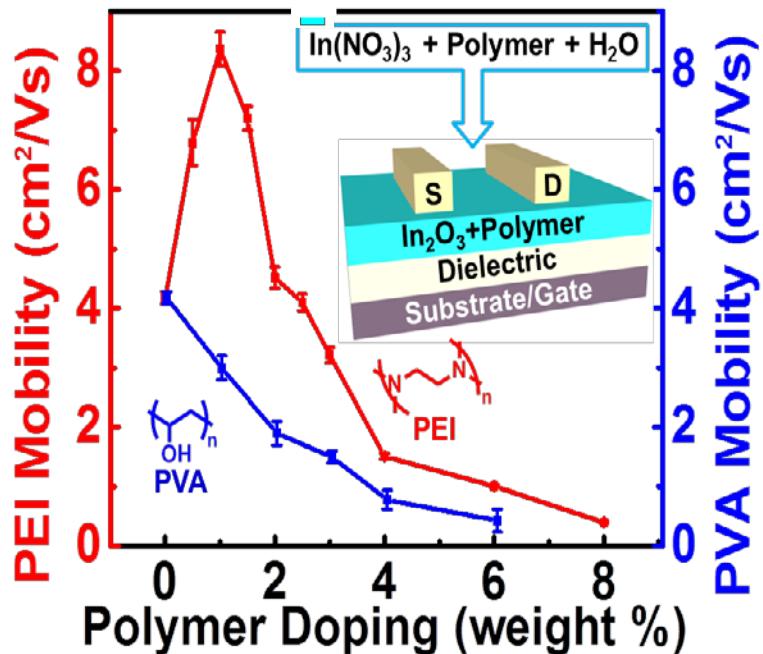


Doped Hybrid Combustion Materials. Electron-Rich PEI As Organic Oxide Dopant

PEI



Mobilities on Si/SiO₂ Dielectric



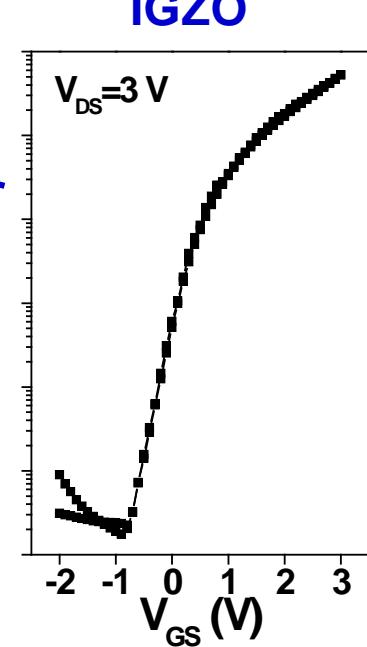
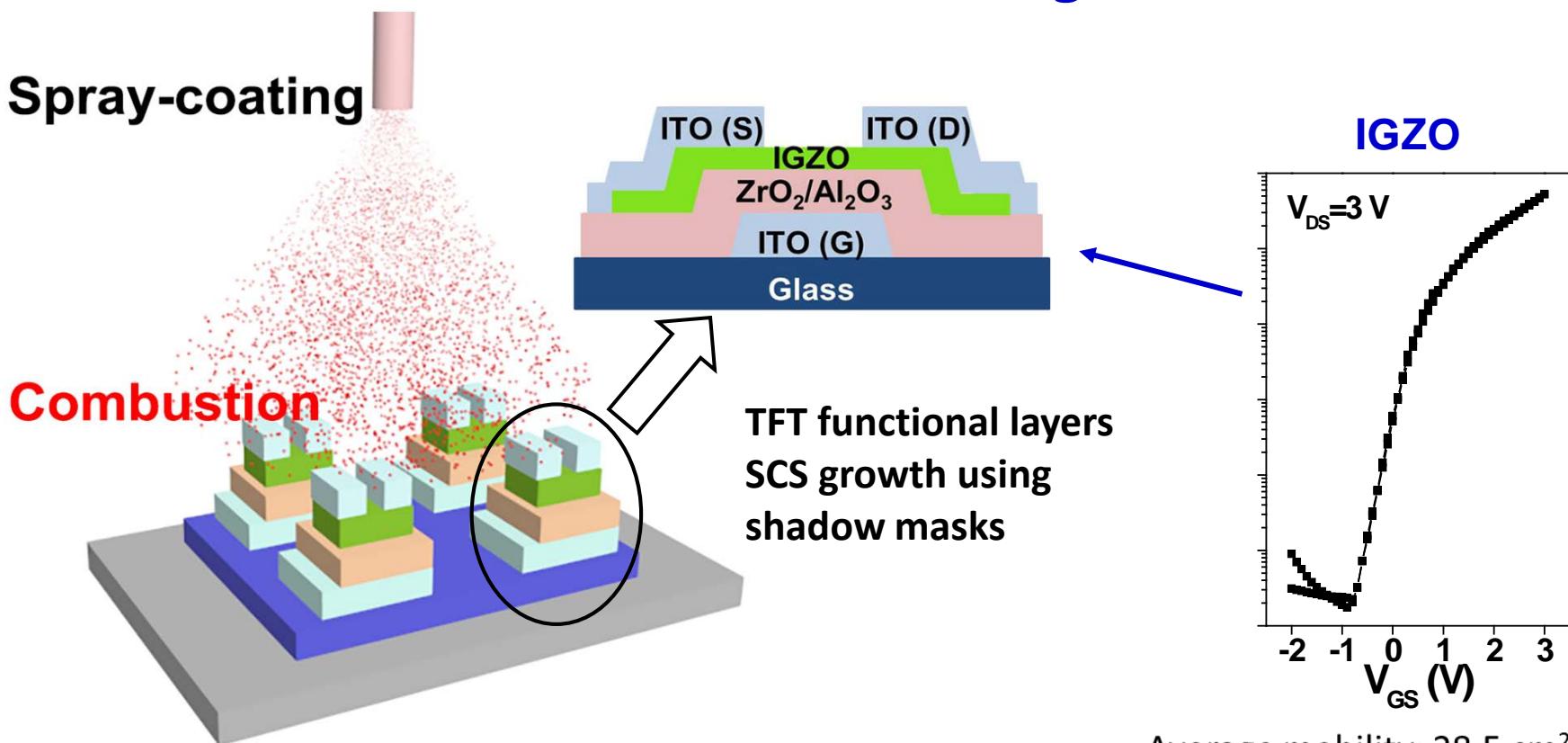
Film characterized by XRD, DSC, TGA, FT-IR, TGA, FET, AFM, XPS, XAS, PDF

Higher Mobilities, Lower I_{on}/I_{off}

Microstructure-Electronic Properties Relationships

No PEI	< 1%	1% - 1.5%	> 1.5%
<ul style="list-style-type: none"> Good crystallinity ~70% Extensive Oxygen vacancies 	<ul style="list-style-type: none"> Decreased crystallinity PEI electrons fill traps 	<ul style="list-style-type: none"> Mostly amorphous Deep traps filled Some shallow traps filled 	<ul style="list-style-type: none"> Mainly amorphous Deep traps cannot be filled
<ul style="list-style-type: none"> High I_{off} Negative V_T 	<ul style="list-style-type: none"> Reduced I_{off} Positively shifted V_T Minor increased mobility 	<ul style="list-style-type: none"> Low I_{off} Optimal V_T ~ 0 V Enhanced mobility 	<ul style="list-style-type: none"> Low I_{off} Positive V_T Decreased mobility
■ crystalline In ₂ O ₃	■ amorphous In ₂ O ₃	~ PEI	

Combustion Synthesis of All-Oxide IGZO Transistors Conformal Coating



$M^{n+} = Al^{3+}, Zr^{4+}, In^{3+}, Zn^{2+}, Ga^{3+}, Sn^{4+}$ Oxidizer = NO_3^-
Fuel = Acetylacetone

Average mobility: $28.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$

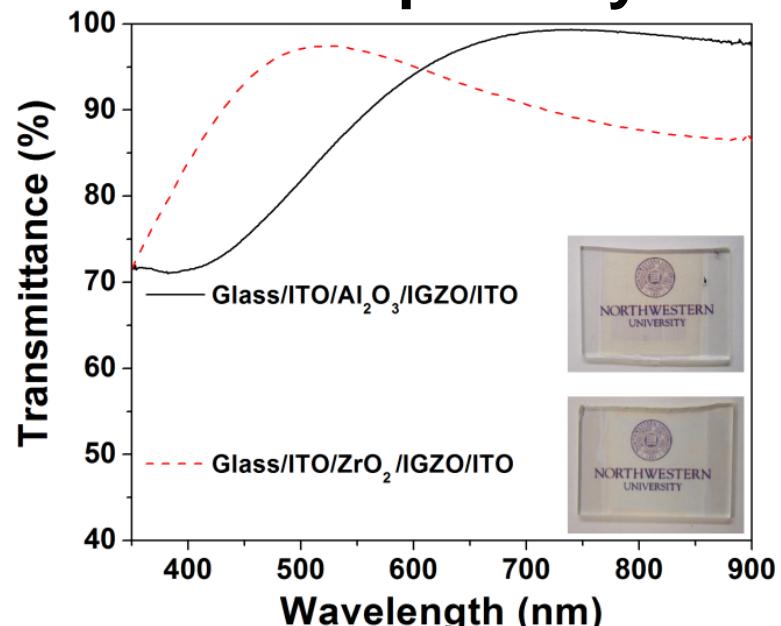
V_T : 0.7 V

$I_{on/off}$: 10^5

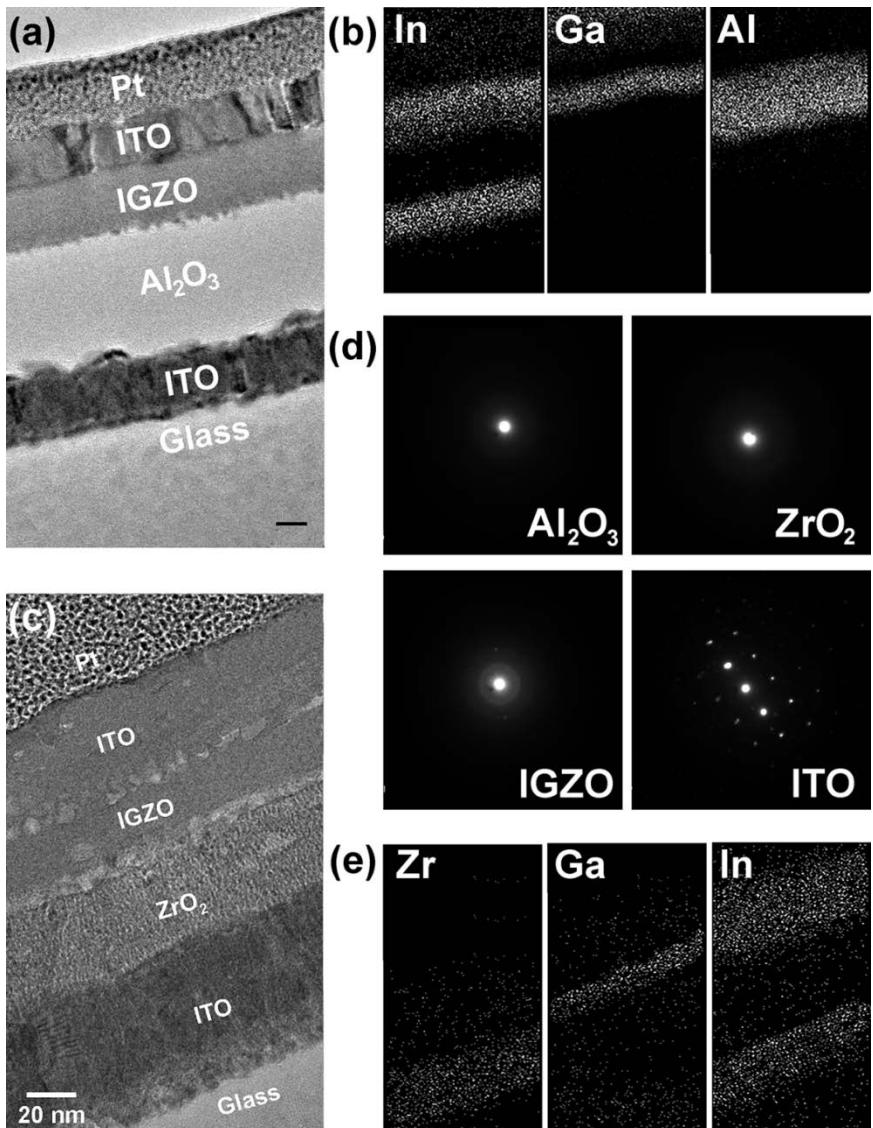
All SCS TFTs

TEM/EDX

Transparency



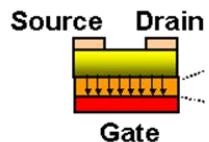
W/L=1000/150 μ m



PEI-In₂O₃ Hybrid Films

Bending Test for transparent electronics

TFT Stack



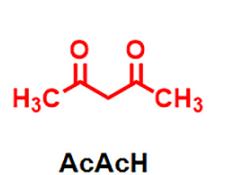
150 nm ZITO/40 nm Al₂O₃/20 nm (In₂O₃ + 1.5 wt% PEI)/100 nm ZITO

All Grown on Arylite Plastic by Combustion

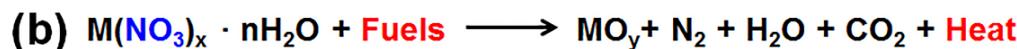
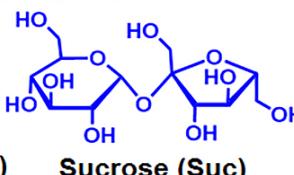
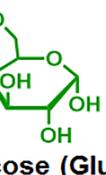
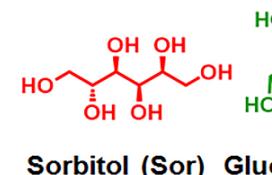
TFTs Maintain ≥ 90% μ after 100x Flexes

Sustainable “Sweet” Combustion Synthesis of IGZO

(a) Coordinating Fuel

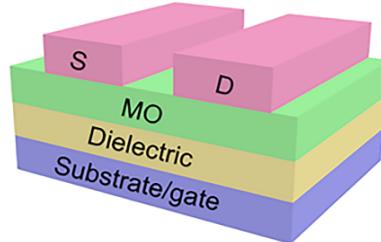


Assisting Fuels (Sugars)



$M^{x+} = In^{3+}, Ga^{3+}, Zn^{2+}$ Oxidizer = NO_3^-

(c)



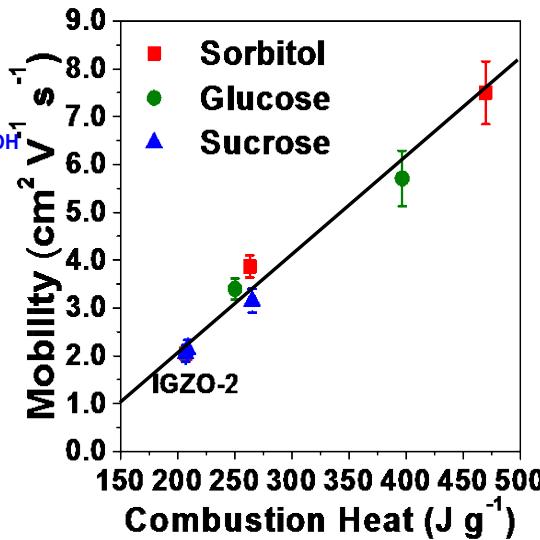
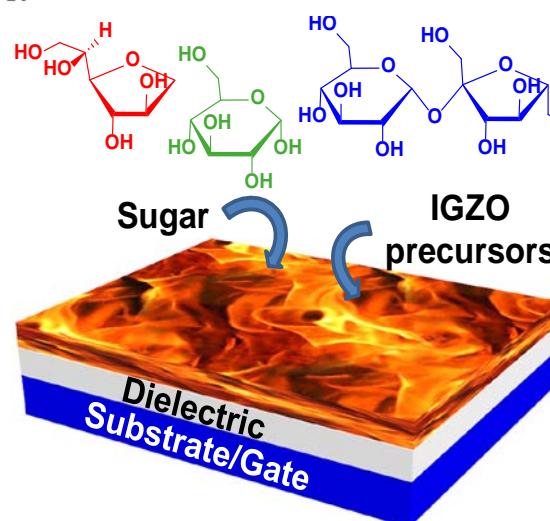
S, D = Al (~40 nm)

MO = IGZO (~10-11 nm)

Dielectric = SiO_2 (300 nm)

Gate = $n^{++}-Si$

Mobilities with Si/SiO_2 Dielectric
Much Higher than with AcAcH!

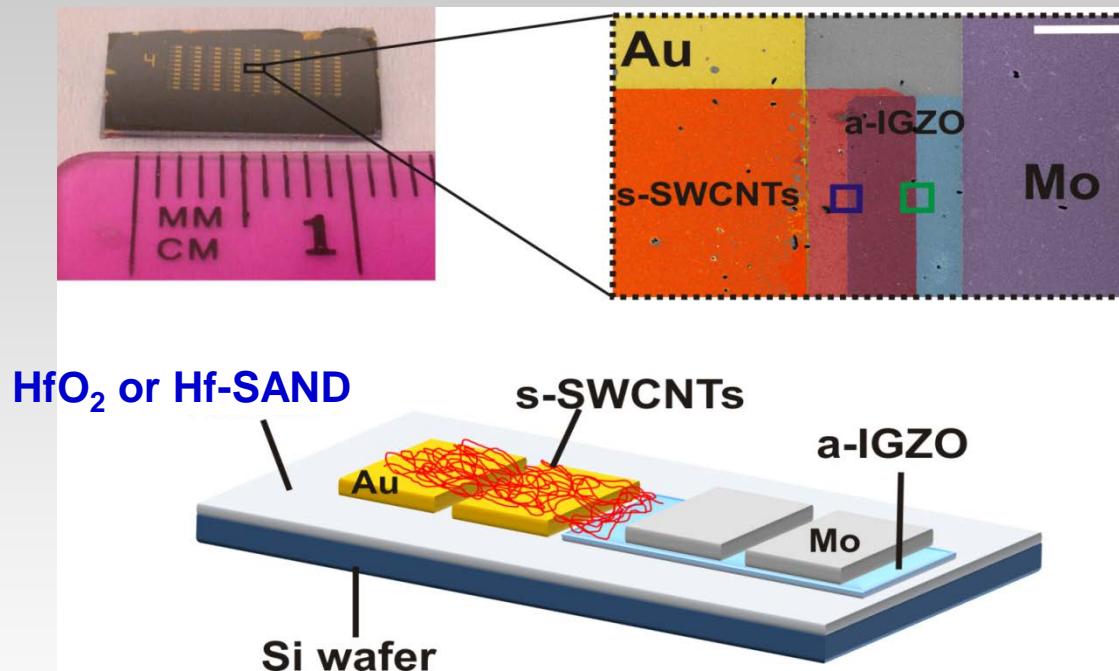


Combustion Synthesis

Film characterized by XRD,
DSC, TGA, FT-IR, TGA, FET,
AFM, XPS, XAS, PDF

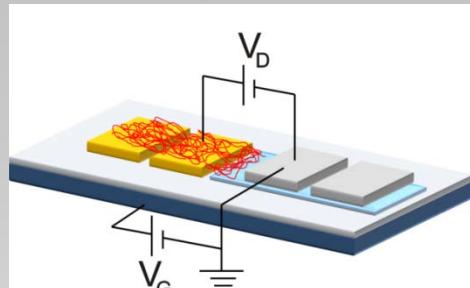
α -IGZO/p-SWCNT Heterojunctions

Goal Fabricate heterojunctions from solution processed p- (SWCNTs) and n- (α -IGZO) type semiconductors over large areas

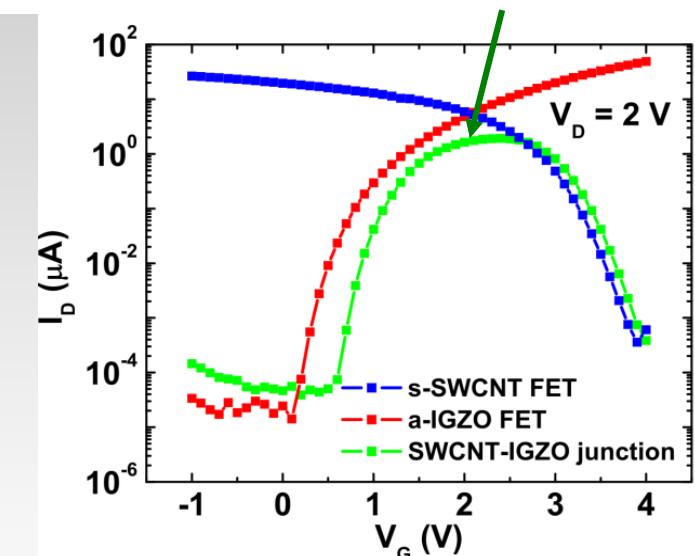
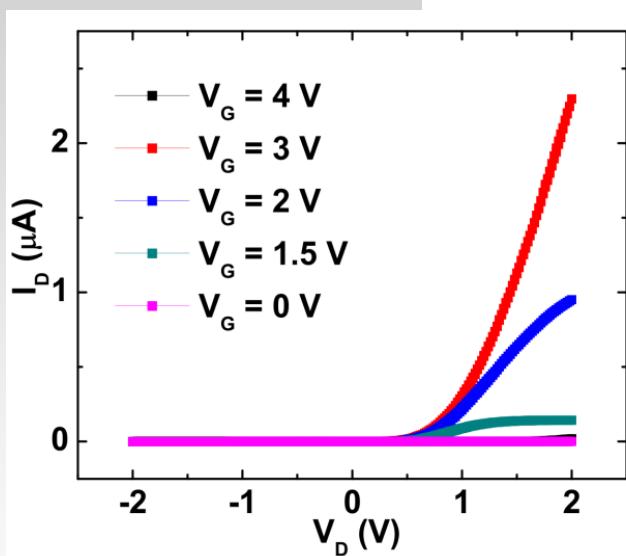


- ❖ Standard photolith & etching fabricate p-SWCNT/a-IGZO p-n heterojunctions over large areas
- ❖ Geometry allows fabrication of adjacent (control) p- and n- type MOSFETs next to heterojunction

α -IGZO/p-SWCNT Heterojunction Electrical Properties



Anti-Ambipolar !



- ❖ Rectifying diode-like output tunable with gate voltage
- ❖ Anti-ambipolar transfer with two off-states and one on-state
- ❖ Implications for communications keying circuitry

Truly Flexible, Manufacturable Printed Displays

Prototype: Polyera/Flexterra “Wove”

Electrophoretic Display(EPD) + Organic Transistors



CONCLUSIONS



**Goal: Low Temperature Fabrication of Printed, Flexible,
Transparent, Unconventional Electronic Circuitry**

Printable Materials for Air-Stable Organic CMOS

Design Rules for Stable n-Type Molecules, Polymers

High Performance Gate Dielectrics

Molecularly Engineered High- k SANDs for OFETs, IFETs
Low Voltage, Low Hysteresis

Hybrid Organic-Inorganic Circuitry

Organics + Inorganics: The Winner?

Theory & Modeling Essential to Materials Design

Understand known materials, design new ones

Applicable to Soft Matter Photovoltaics

Acknowledgments

Northwestern University

Antonio Facchetti

Mark Ratner

Michael Wasielewski

Mercouri Kanatzidis

Mark Hersam

Vinayak Dravid

Mike Bedzyk

Lincoln Lauhon

Bob Chang

Sara Dibenedetto

Zhiming Wang

Hakan Usta

Deep Jariwala

Choongik Kim

Xinge Yu

Jeremy Smith

Rocio Ortiz

Young-Guen Ha

Lian Wang

Jun Liu

Myung-Han Yoon

Brooks Jones

Henry Heitzer

Myung-Gil Kim

Vinod Sangwan

Li Zeng

Johns Hopkins U.

Howard Katz

U. Texas Austin

Ananth Dodabalapur

Northwestern U.

John Rogers

U. Missouri.

Julia Medvedeva

TAMU-Q

Mo Al-Hashimi

Cambridge University

Hugo Bronstein

AFRL

Mike Durstock, Ben Leever

U. Malago

Rocio Ortiz

Purdue U.

David Janes, Peter Ye

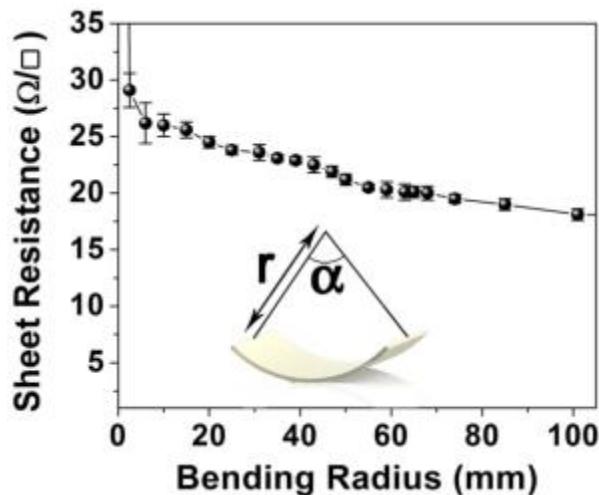
Numerous Colleagues in Europe and Asia!



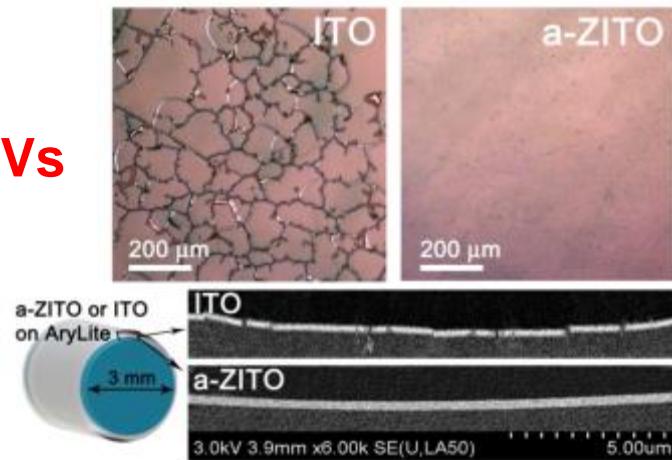
Many Thanks!

a- ZITO/Arylite Anode OPV Bending Tests

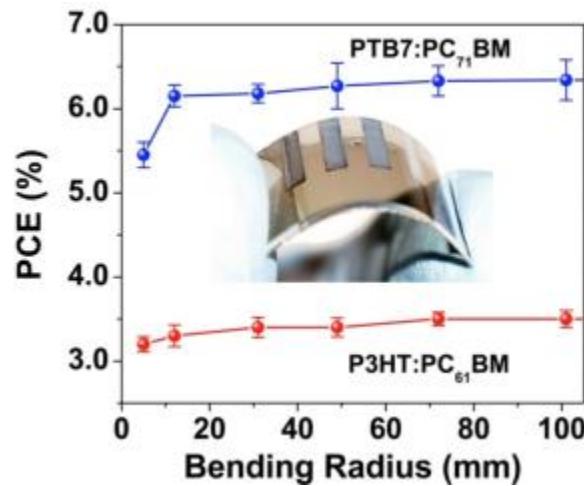
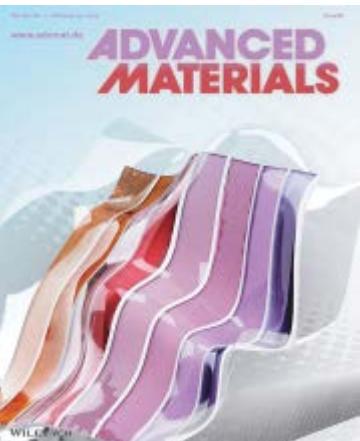
Sheet Resistance



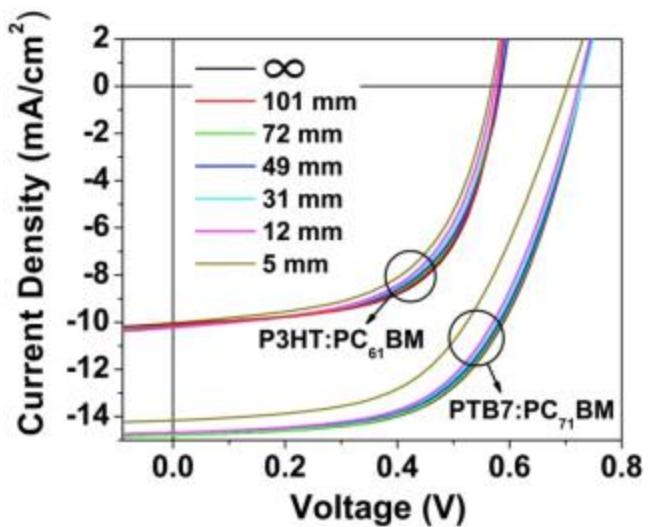
OPVs



OPV PCE

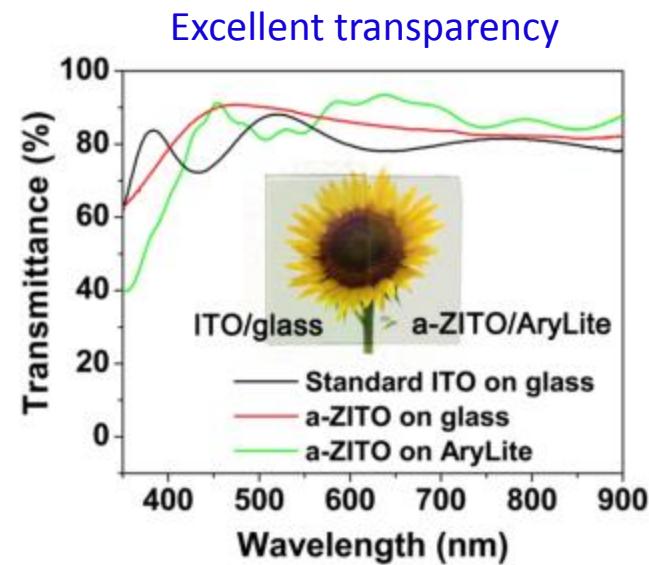
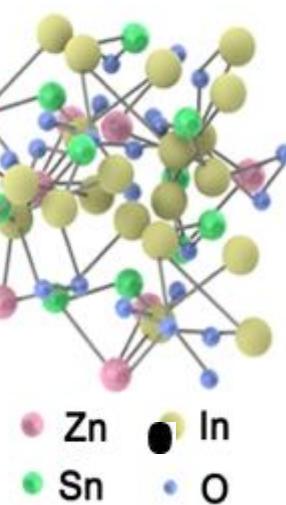
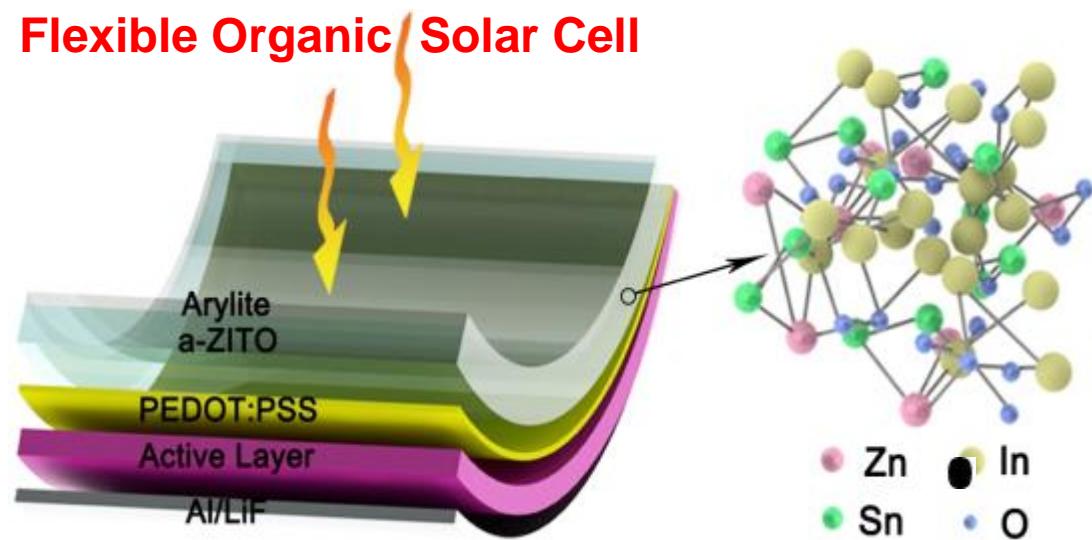


OPV J-V

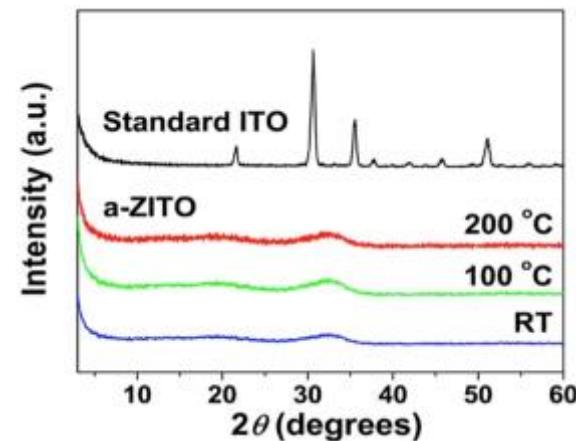


ITO Replacement: *Flexible Amorphous-ZITO Electrodes on AryLite Polyester (< 15 Ω/□)*

Flexible Organic Solar Cell



Film XRD



Amorphous character to 200° C
Important for device fabrication

OPV Performance

Active Layer	Substrate	V _{oc} [V]	J _{sc} [mA/cm ²]	FF(%)	PCE (%)*
P3HT:PC ₆₁ BM	Standard ITO/glass	0.585	9.79	66.0	3.77
P3HT:PC ₆₁ BM	a-ZITO/glass	0.585	9.90	66.2	3.83
P3HT:PC ₆₁ BM	a-ZITO/AryLite	0.582	10.0	62.0	3.63
PTB7:PC ₇₁ BM	Standard ITO/glass	0.745	14.4	68.0	7.29
PTB7:PC ₇₁ BM	a-ZITO/glass	0.738	14.7	67.5	7.41
PTB7:PC ₇₁ BM	a-ZITO/AryLite	0.729	14.7	59.4	6.42

Combustion Processing of 60 nm In_2O_3 Film



Video1_60nm direct heating.avi

Substrate: Si Wafer

Hot Plate Temp: 200°C

Spray Combustion Synthesis

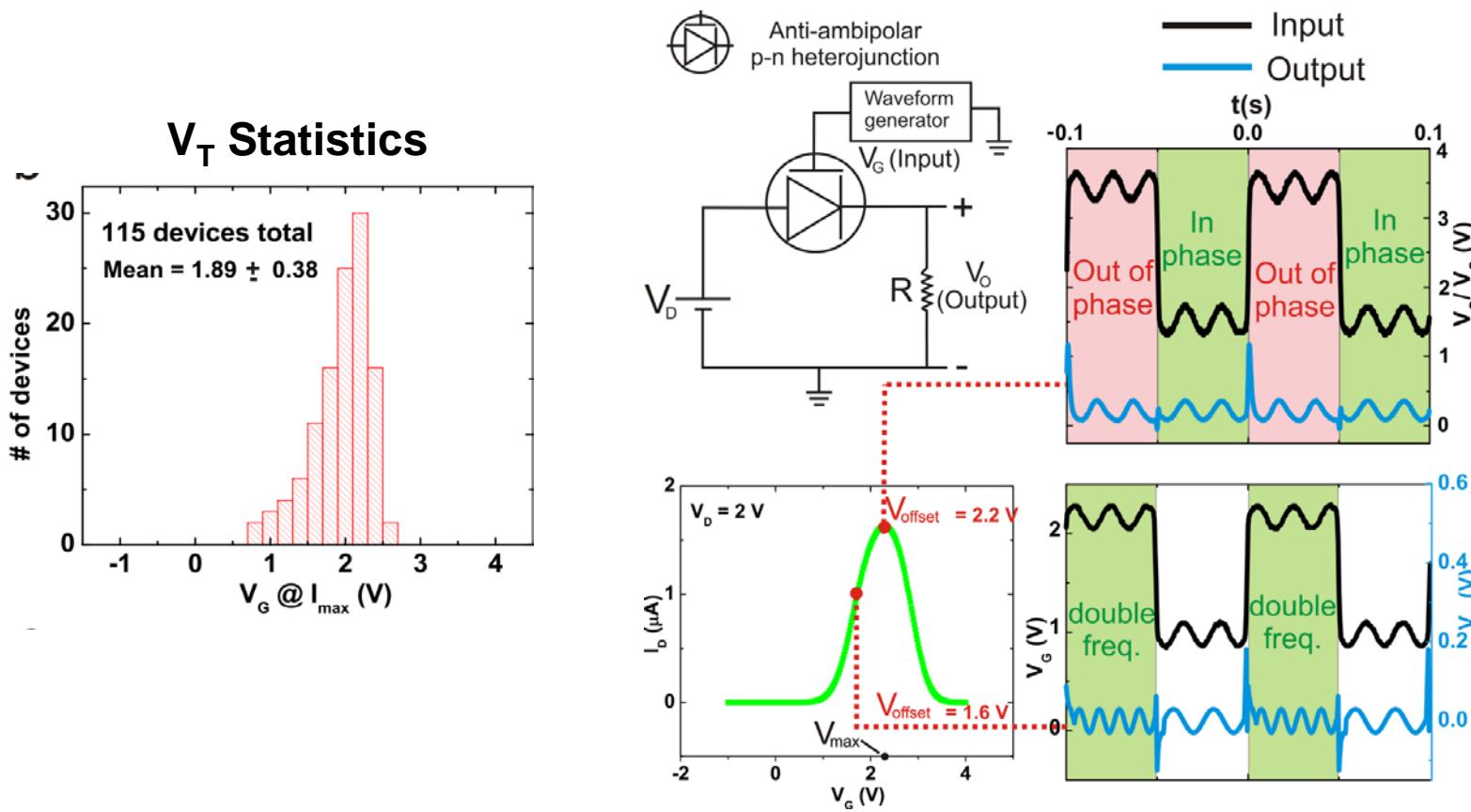


New Low Temperature Growth Process for Oxide Semiconductor Films

Bedzyk, Chang, Facchetti, Ferragut, Marks *Nature Nanotech.*, under revision

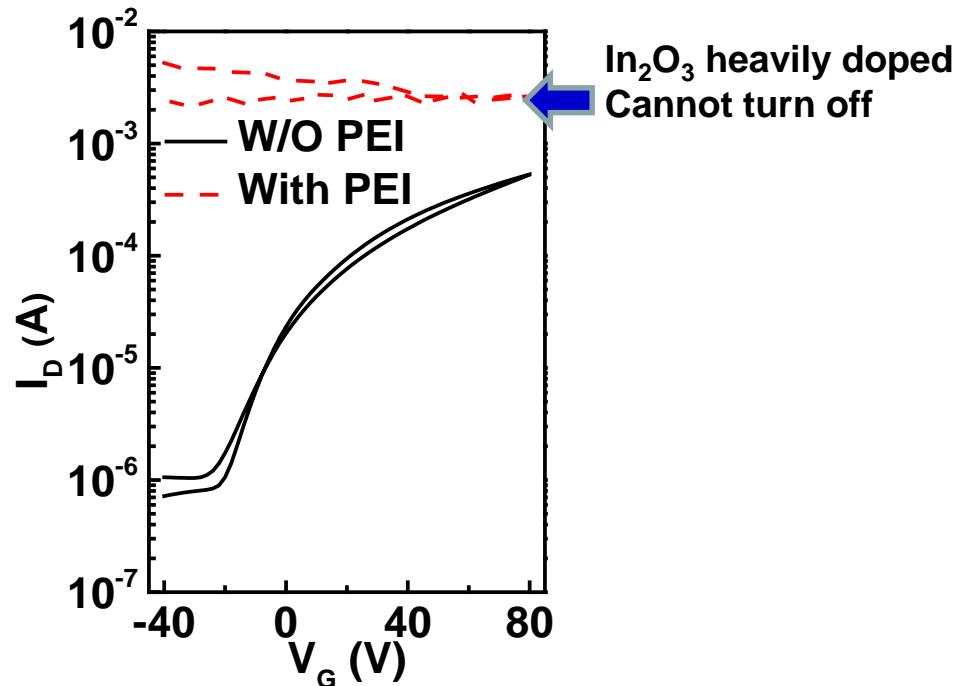
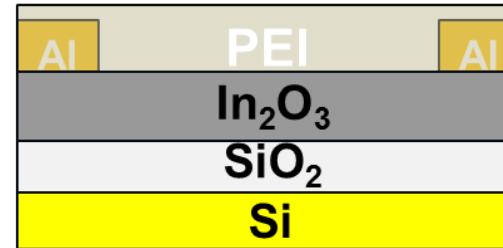
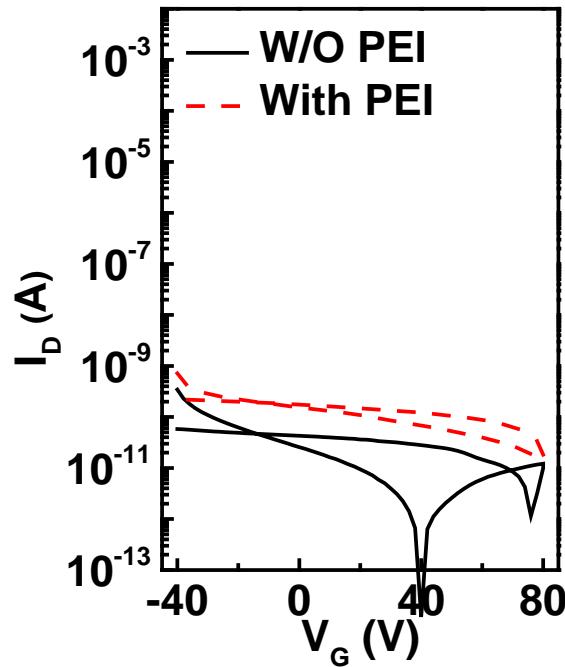
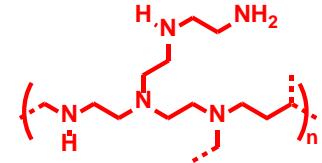
Analog Circuits from Anti-Ambipolar Heterojunctions

a-IGZO/p-SWCNT



- Keying circuits demonstrated using anti-ambipolar heterojunctions
- Depending on the input offset voltage, Binary Phase Shift Keying (top right) or Binary Frequency Shift Keying (bottom right) can be realized

Control Transport Experiments



PEI is an electrical insulator

PEI transfers electrons to MO

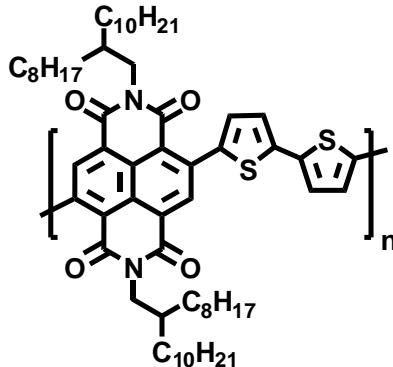
Bilayer structure cannot offer any advantage

First Demonstration of All-Printed N-Channel Polymer Transistors

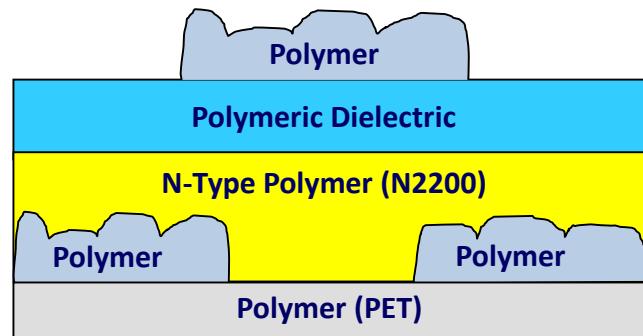
PET Substrate

Inkjet-Printed S, D, G Electrodes

N-Channel Polymer

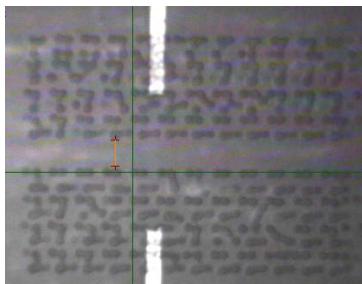


Collaboration: A. Facchetti, Polyera Corporation

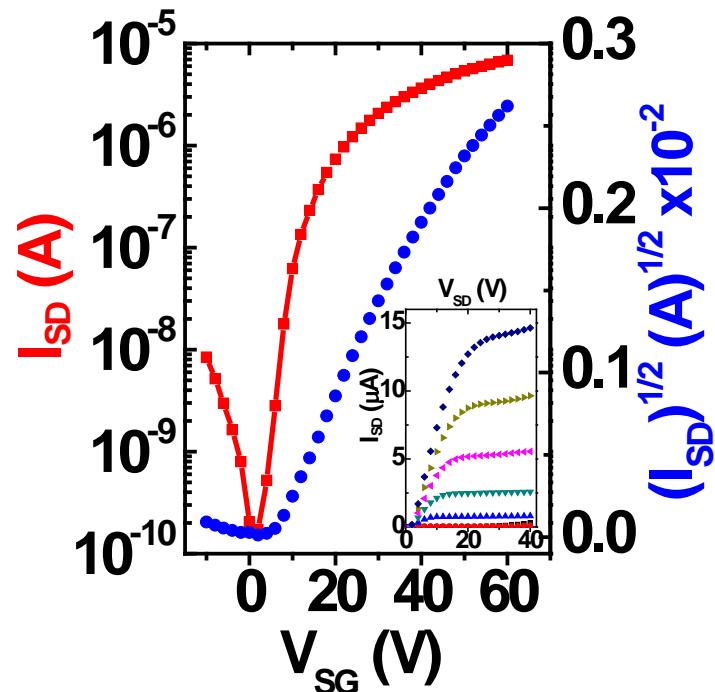
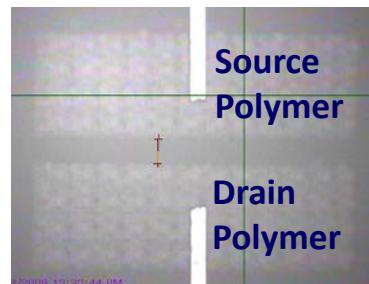


Conducting Polymer and Dielectric from Polyera

Un-optimized Printing

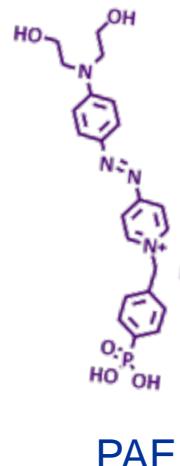
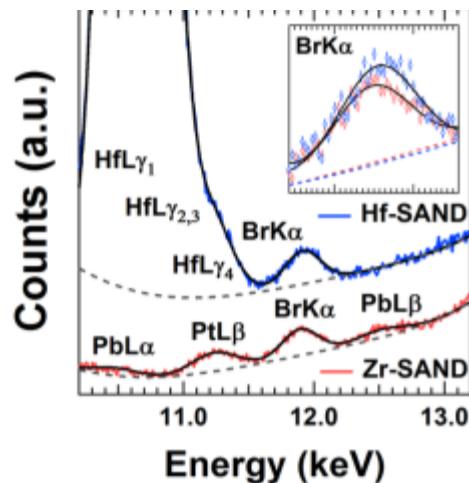
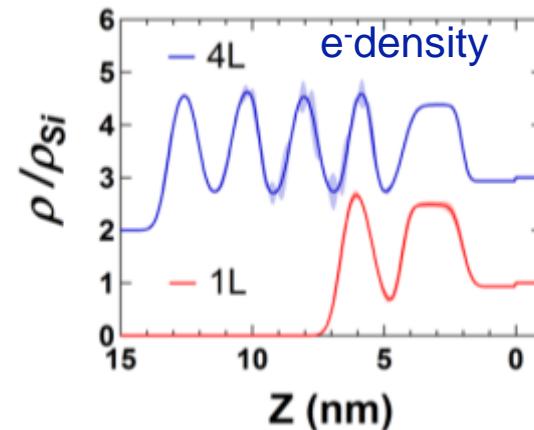
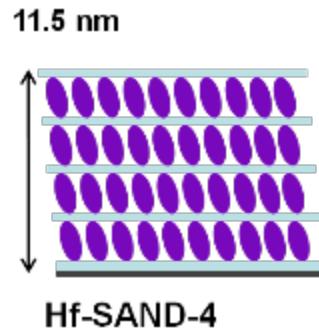
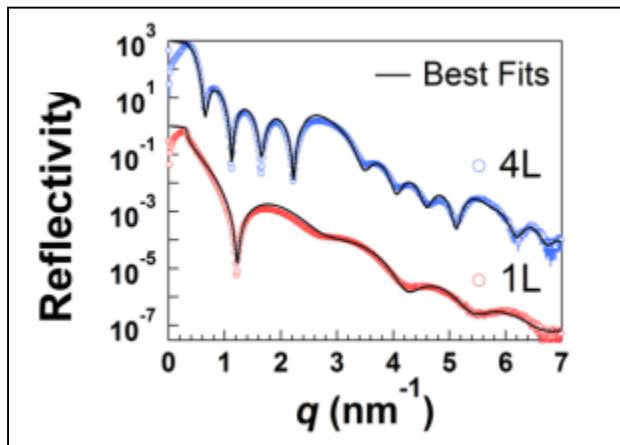


Optimized Printing



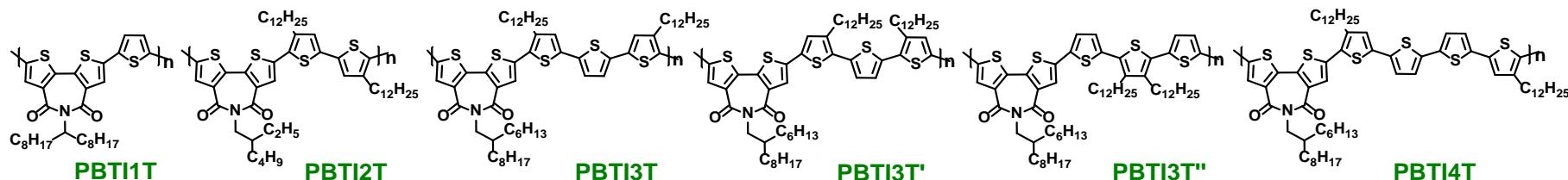
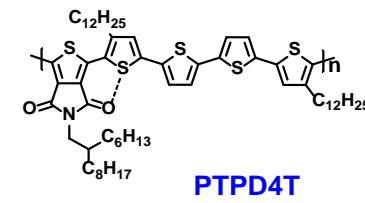
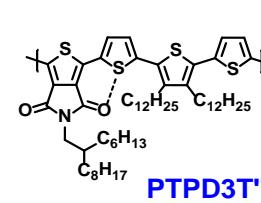
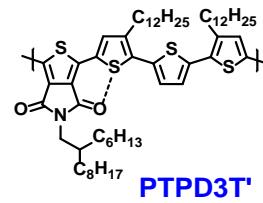
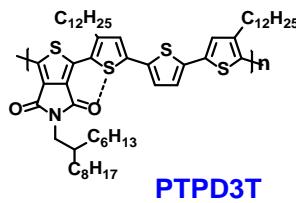
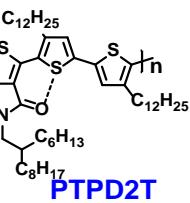
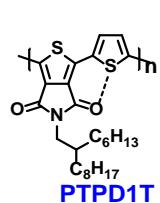
Why is Hf-SAND Capacitance >> Zr-SAND?

X-ray reflectivity reveals well-ordered nanostructures



- X-ray fluorescence assay of Hf-SAND composition & coverage.
- Denser PAE surface coverage on HfO_2 enhances capacitance ($1.1 \mu\text{F}/\text{cm}^2$)

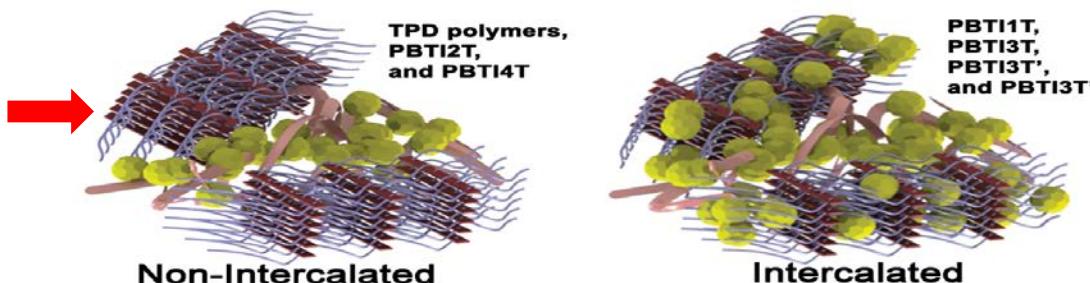
Consequences of 1T \rightarrow 4T Catenation in TPD and BTI Photovoltaic Copolymers



1T \rightarrow 4T OPV Trends for TPD & BTI Series

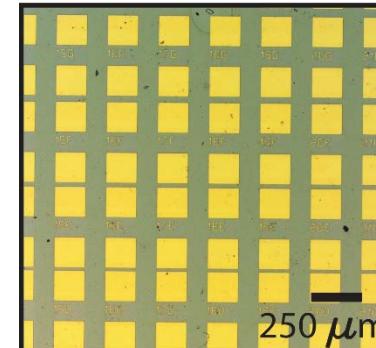
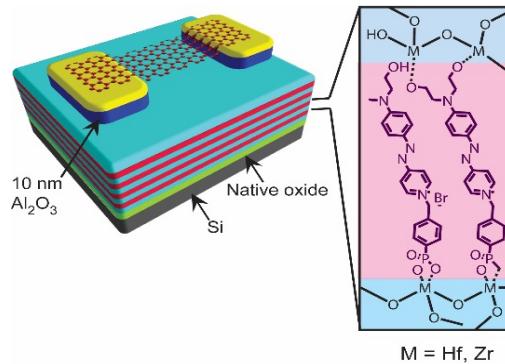
- Conjugation length saturates at ~ 3T; HOMOs continue to rise
- TPDs: computed most planar; XRD/TEM: more crystalline, domain-pure PC₇₁BM blends
- TPDs: higher mobilities & J_{sc}; FF, J_{sc}, PCE maximize at 3T
- PCE sensitive to alkyl substituent positioning. PTPD3T', PTPD3T'', PBTI3T' & PBTI3T'' have lower PCEs than PTPD3T & PBTI3T

Higher OPV Performance

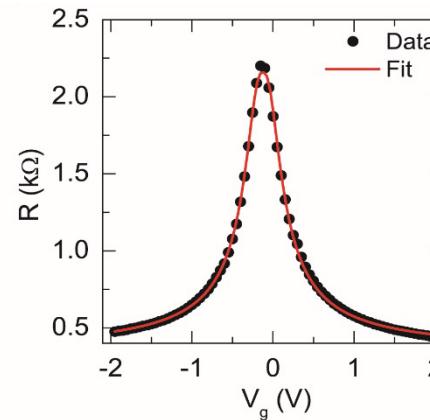
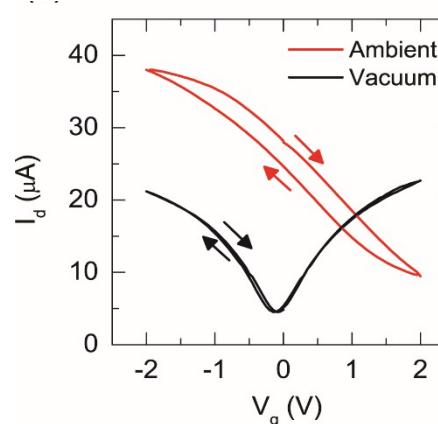


Wafer-Scale SAND for Graphene Electronics

- Bottom contact graphene field-effect transistors (G-FETs) on 4 layers of Hf-SAND on 3" wafers
- Graphene grown by chemical vapor deposition, transferred on SAND



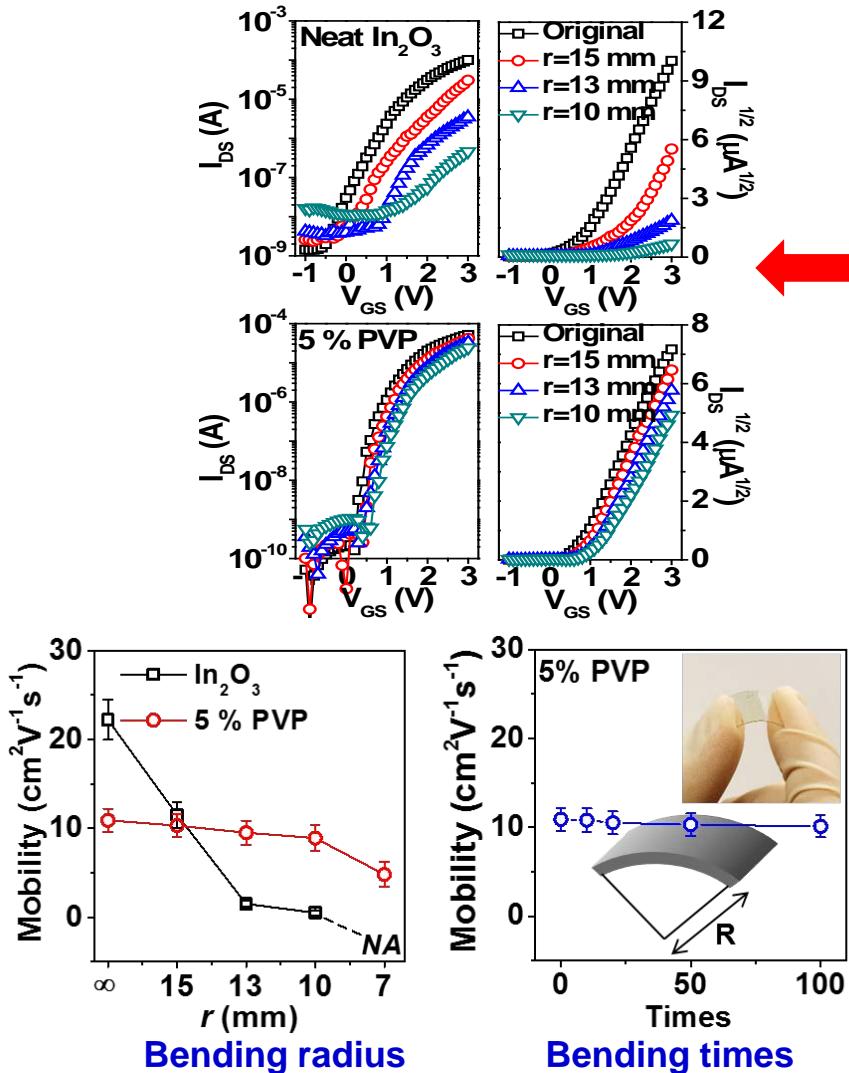
Optical micrographs of G-FETs on Hf-SAND-4L



- Low operating voltage (± 2 V) and negligible hysteresis on Hf-SAND in vacuum
- FET = $4,500 \text{ cm}^2/\text{Vs}$ (2x higher than on Si/SiO₂)
(limited by quality of CVD graphene, not dielectric)
- Current saturation with intrinsic gain > 1

'Invisible' Flexible Transistors Enabled by Amorphous Metal Oxide/Polymer Channel Layer Blends

TFT: AryLite/a-ZITO/ Al_2O_3 / In_2O_3 :PVP/ a-ZITO



Bending radius measurements:

Compare to neat In_2O_3 TFTs
fabricated & measured under same
conditions

SEM: neat In_2O_3 & In_2O_3 :5%PVP films after
bending at $r = 10$ mm

- Neat In_2O_3 films show cracks
- In_2O_3 :5%PVP films don't show cracks

