FLEXIBLE ELECTRONICS

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Materials Science and Engineering Division
National Institute of Standards and Technology (NIST)

NIST
National Institute of
Standards and Technology

NIST's mission:

To promote U.S. innovation and industrial competitiveness by advancing measurement science, standards, and technology in ways that enhance economic security and improve our quality of life.

NIST campus in Maryland near Washington DC

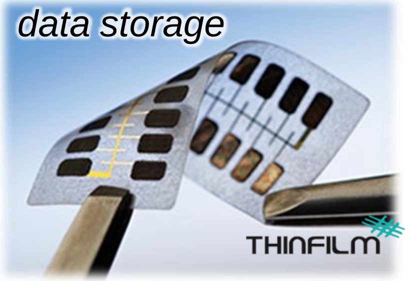
- A National Laboratory of the U.S. Department of Commerce
- 3,000 employees
- 3,500 associates and facilities users
- $864M budget (FY15)
- Two main campus: Gaithersburg, MD and Boulder, CO.
- Est. 1901
- National measurement standards
- Large-facility infrastructure:
  - NIST Center for Neutron Research
  - Center for Nanoscale Science and Technology
  - Synchrotron Measurement Science Group

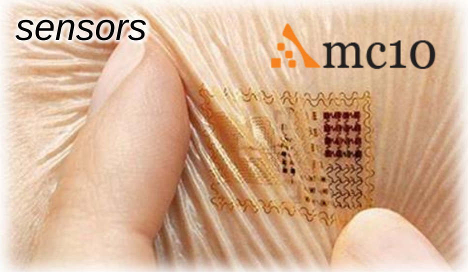
FLEXIBLE ELECTRONICS

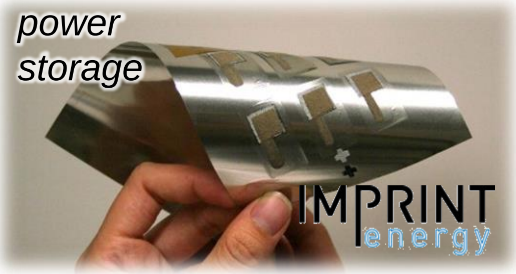
Flexible electronics is the production of electronic components on a flexible substrate, typically plastic.

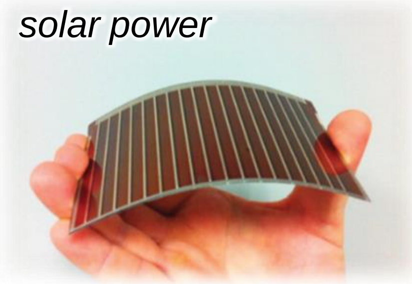
A very wide array of products are envisioned.

Flexible electronics technology is currently breaking through into the consumer marketplace.







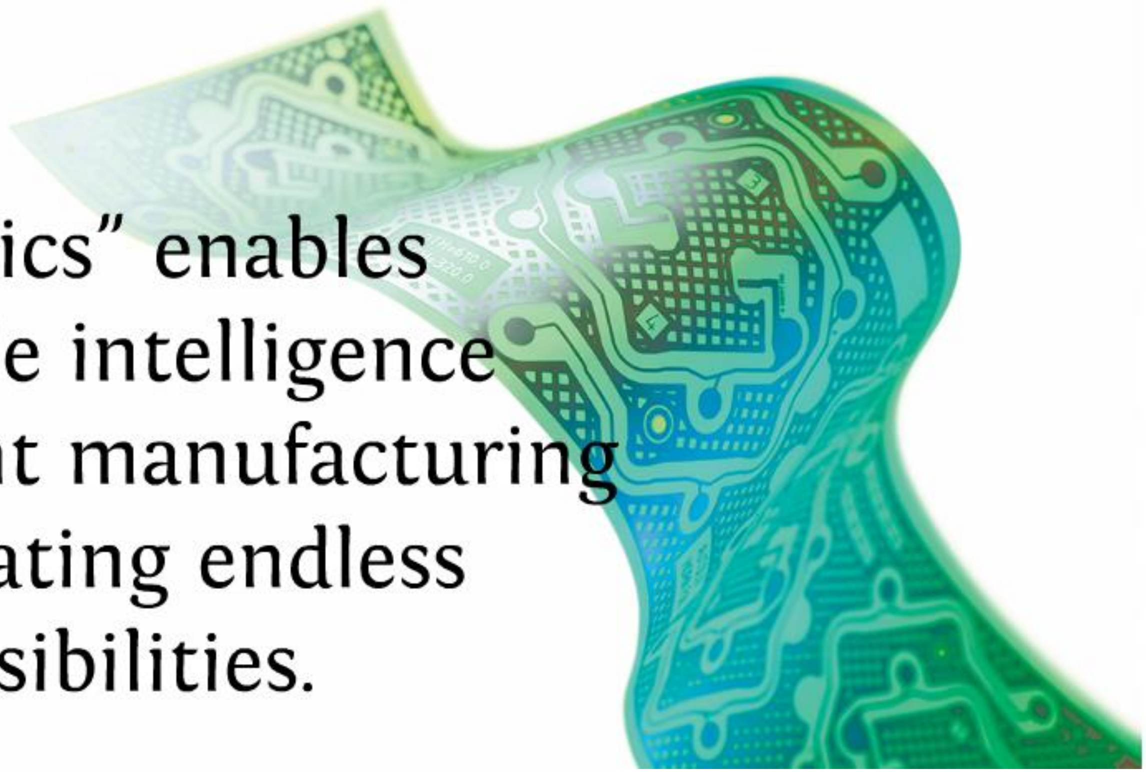


FLEXIBLE ELECTRONICS KEY ADVANTAGE: MANUFACTURING COST

Modern Intel Fab
Capital cost > $3 billion

Modest Flex Electronics Fab
Capital cost < $3 *million*

"Printed electronics" enables embedding simple intelligence with cost-efficient manufacturing techniques -- creating endless new product possibilities.

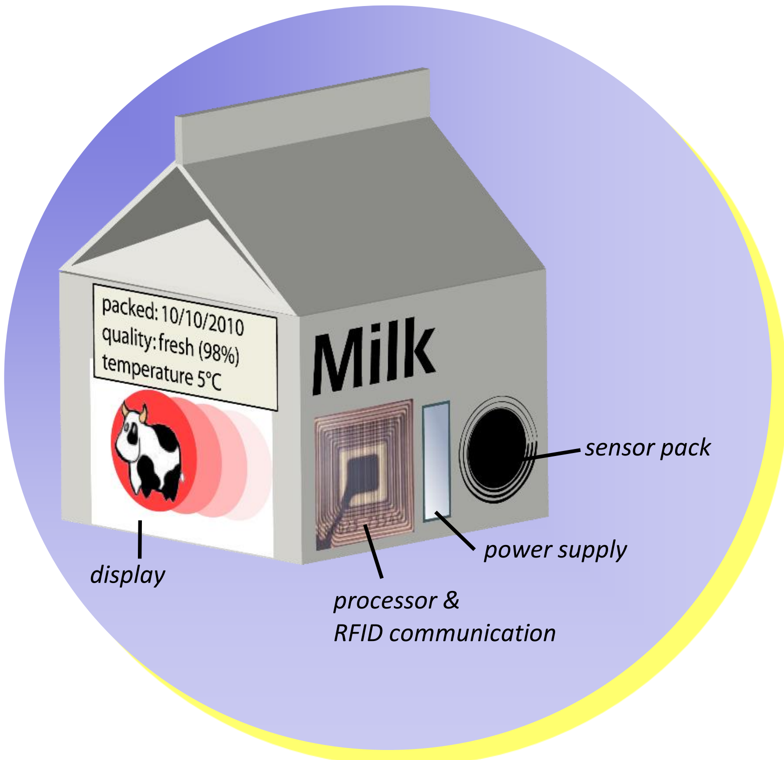


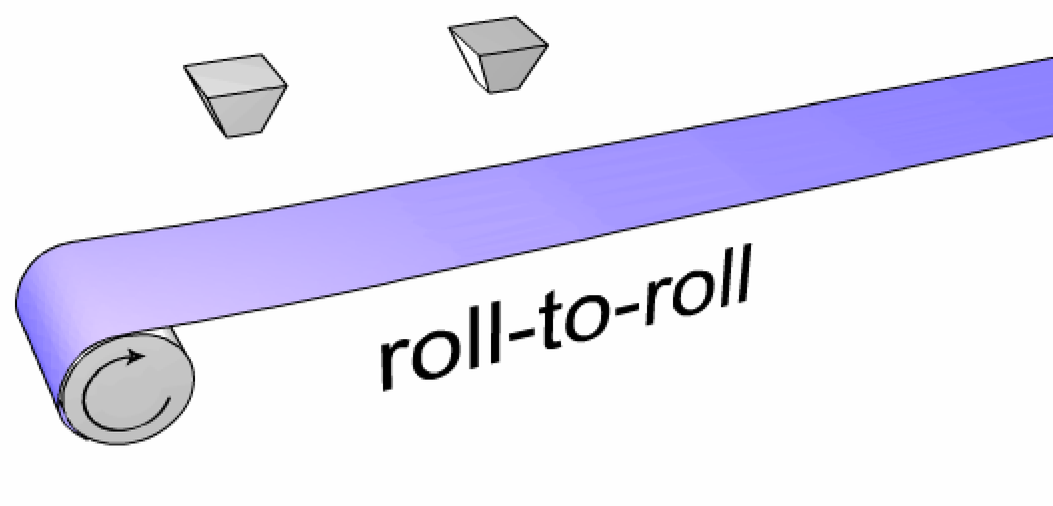
Today's Market Opportunity - $9.4 Billion

Inks, e-paper, OLEDS & other displays, batteries, logic, memory, photovoltaics

(source: Flex Tech Alliance)

LOW-COST, UBIQUITOUS ELECTRONICS

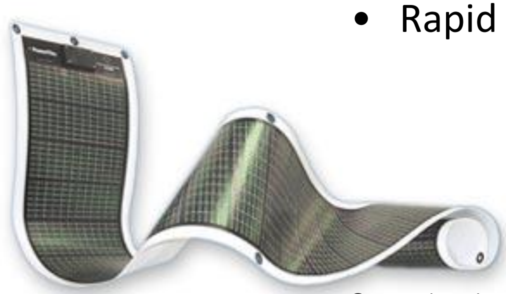




- Fabricate using graphic arts tools (printers)
- Large area / flexible form factor
- Bespoke functionality
- Rapid prototyping

self-destructs

orders refills



© Iowa Thin Film

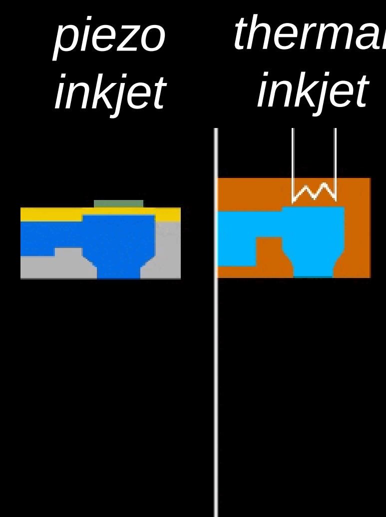
rollable photovoltaics

NOT a replacement for silicon:

new products from
new materials and
new methods of production

PRINTING METHODS FOR FLEXIBLE ELECTRONICS: INKJET

- To make patterned elements (electrodes, circuits)
- Preferred for rapid pattern changes
- Slow – one drop at a time per head
- Difficult to make *extremely* large

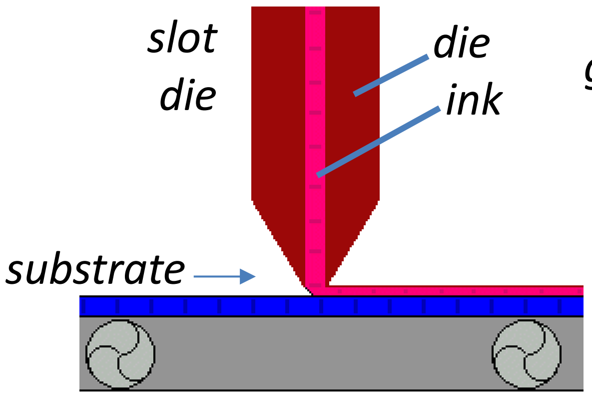


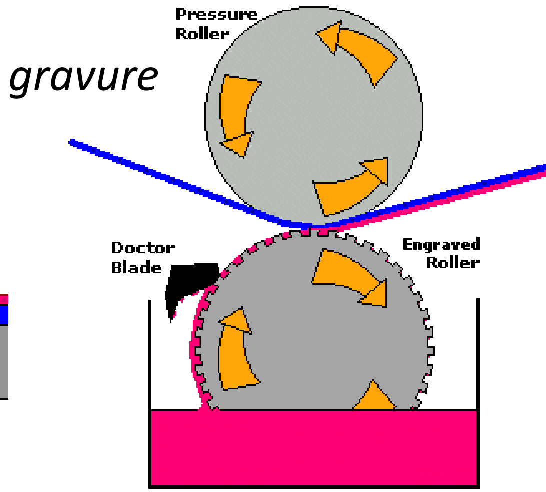
Source: Dimatix

Source: Litrex

PRINTING METHODS FOR FLEXIBLE ELECTRONICS: SLOT DIE

- To make continuous elements (solar, lighting)
- Can be patterned with a die (gravure, screen printing)
- Fast – high volume
- Essentially the cousin of the newspaper press





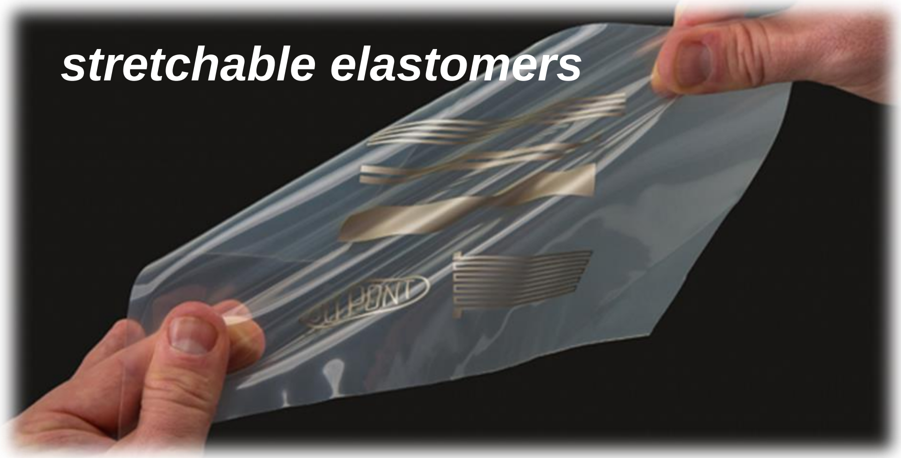
Source: Coatema

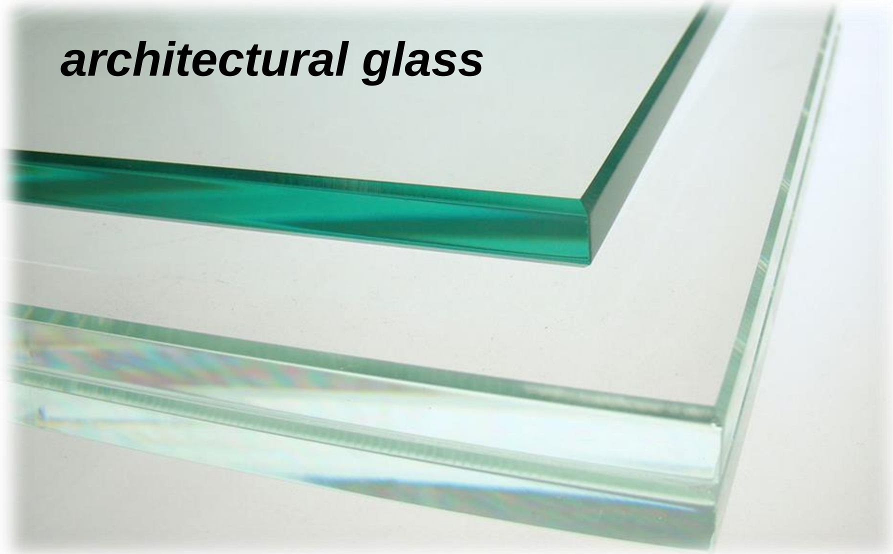
“MAKER” COMMUNITY EXPLORING PRINTED ELECTRONICS

- These images from startup Voxel8
- Conductive inks deposited using syringe-style 3D printer
- Logic, motors, batteries manually “pick & placed”
- Ink drying process somewhere between inkjet & slot die

VOXEL8

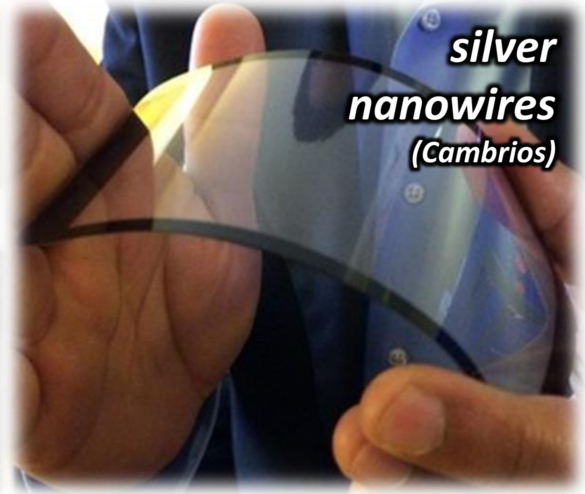
SUBSTRATES FOR FLEXIBLE ELECTRONICS





CONDUCTING INKS FOR FLEXIBLE ELECTRONICS

silver particles
(ANP)



silver nanowires
(Cambrios)

graphene
(Vorbeck)

carbon nanotubes
(NanoIntegris)

SEMICONDUCTORS FOR FLEXIBLE ELECTRONICS

Near-term:
Low-cost integrated circuits

"pick and place" robot
(Samsung)

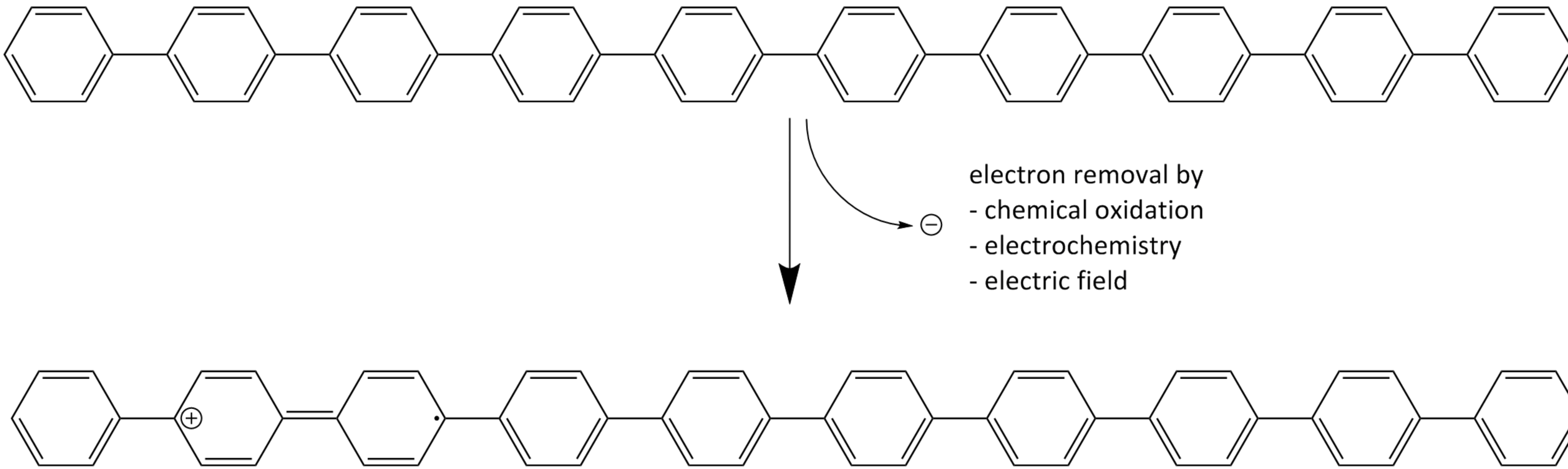
Far-term:
Printable semiconductors

***organic semiconductors** (CDT)*

"2D" materials

carbon nanotubes
(NanoIntegris)

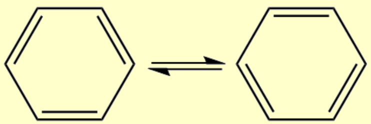
HOW CAN MOLECULES ACT LIKE SEMICONDUCTORS?



What really happens:

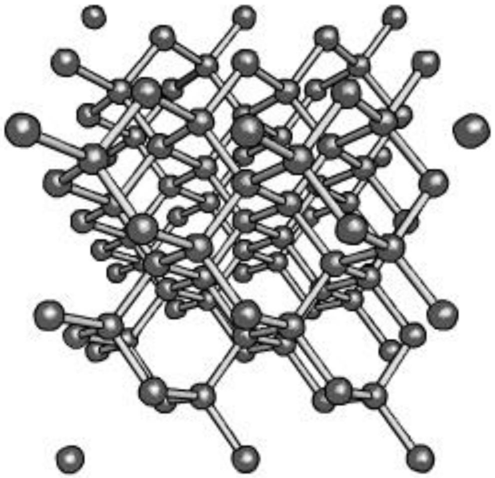
- Charge is delocalized over several (~4-10) rings
- Possibly delocalized over adjacent chains if pi-overlap
- Molecular distortion accompanies polaron, imposes fundamental upper limit on its mobility
- Molecule-molecule hopping imposes practical limit on mobility

(this is just a fancy version of the freshman chemistry concept of aromatic resonance)



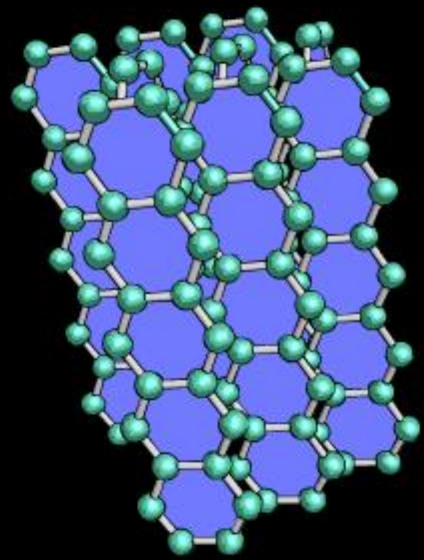
Inorganic	Organic

silicon



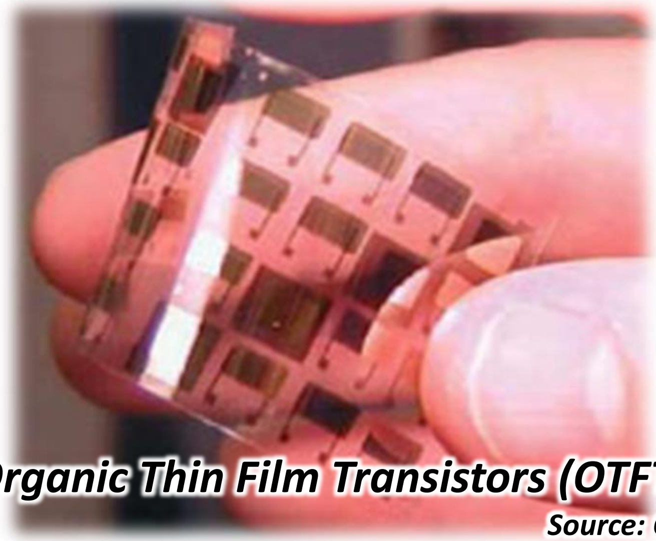
- Covalent crystal
- Mobility: 100 to 1000 $cm^2V^{-1}s^{-1}$
- Processing by lithography; cutting a formed single crystal
- Performance dominated by lattice defects *within crystals*

pentacene



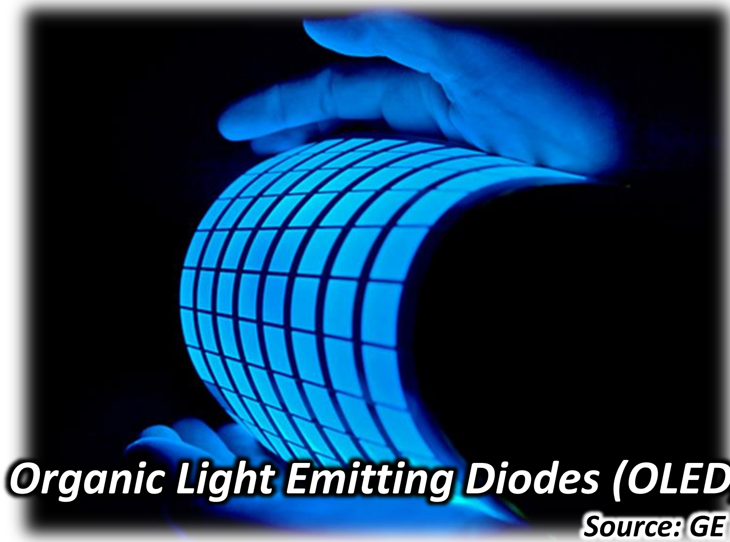
- Van der Waals crystals
- Mobility 0.0001 to 10 $cm^2s^{-1}V^{-1}$
- Processing from fluids; microstructure forms dynamically
- Performance dominated by complex microstructure, including amorphous domains, crystal orientation, grain boundaries, all at key interfaces.

THREE KEY ORGANIC ELECTRONIC DEVICES



Organic Thin Film Transistors (OTFT)

Source: Orgalight



Organic Light Emitting Diodes (OLED)

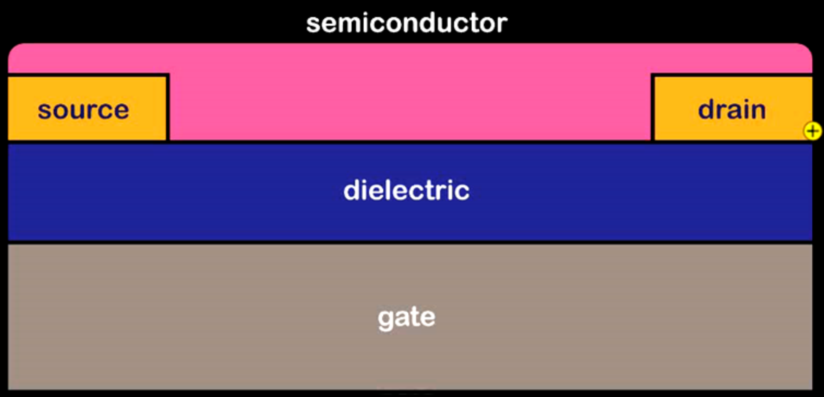
Source: GE OLED

Organic PhotoVoltaics (OPV)

Source: Galagan et al., Third Generation Photovoltaics, 2012.

ORGANIC THIN FILM TRANSISTORS

- The active layer “channel” extends from source to drain electrode, adjacent to a non-conducting dielectric
- Voltage on the gate creates charges in the channel
- Charges carry current between source and drain
- The transistor acts as a switch. Different amounts of voltage on the gate (which itself accepts negligible current) change the amount of current through the source-drain



typical OTFT solution

Source: Rieke Metals

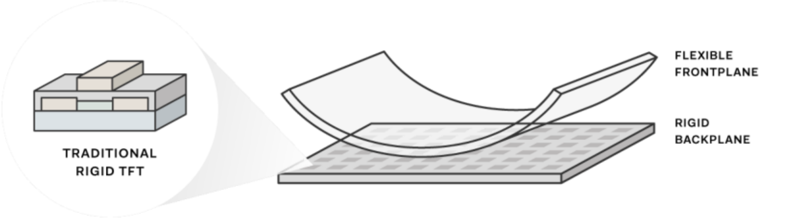
NEW DEVELOPMENTS IN OTFT: POLYERA'S WOVE BAND

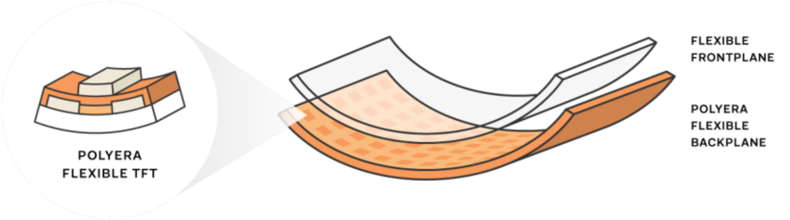
Polyera's Wove Band:

- Announced ***10/2/2015***
- OTFT (organic-TFT) flexible backplane
- Touch E Ink display
- 30 mm x 156 mm
- 1040x200 resolution

Polyera was started in 2005 based on technology developed at Northwestern University (Tobin Marks, Antonio Facchetti).

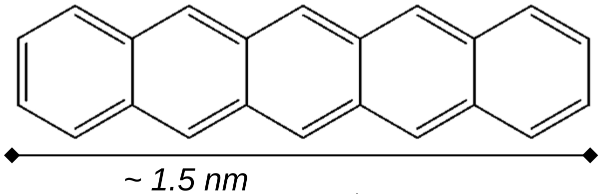
Polyera





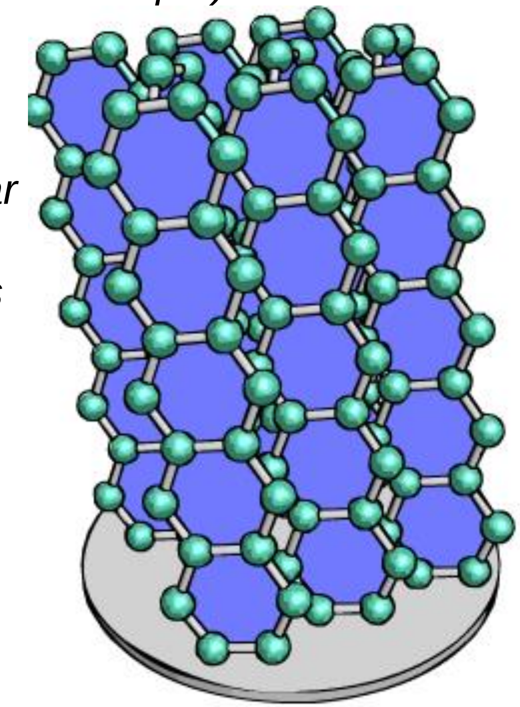
STRUCTURE IN OTFT MATTERS AT MANY LENGTH SCALES

Primary chemical structure:
extended conjugation

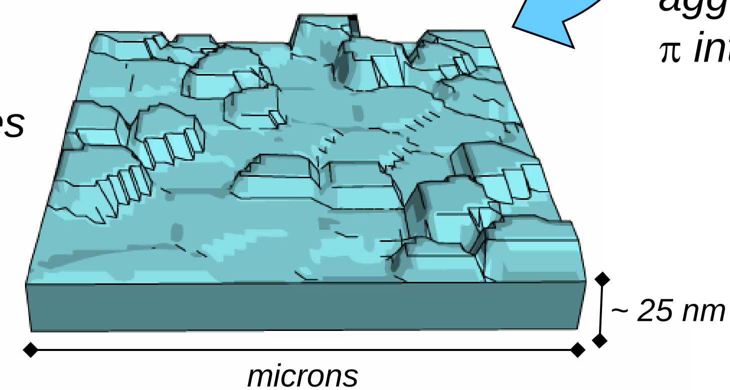


pentacene
(for example)

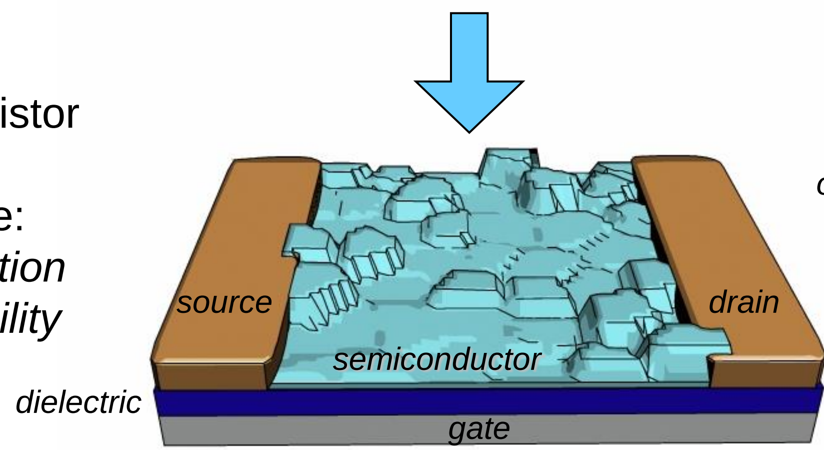
via
intermolecular
aggregation
π interactions

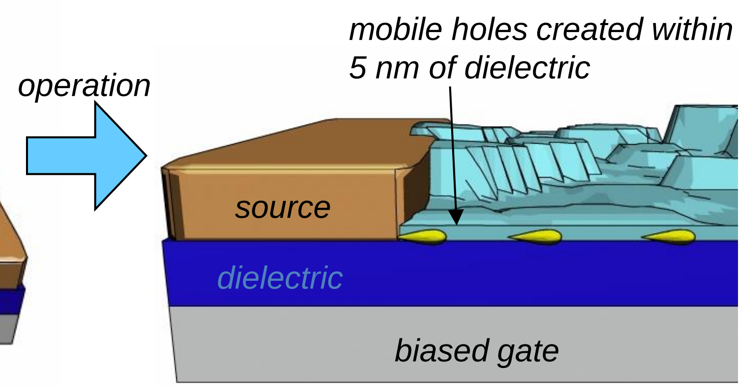


Thin Film
few grain boundaries
wide crystals



Thin Film Transistor
OTFT / OFET
Device structure:
carrier instantiation
and lateral mobility





EXAMPLE OF NIST WORK IN OTFT

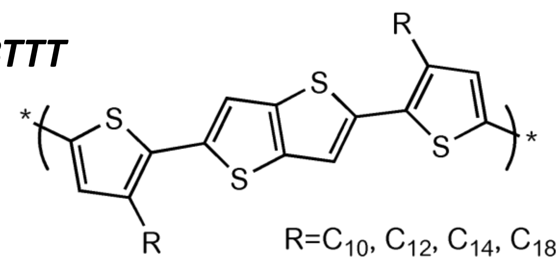
Measurement Challenge

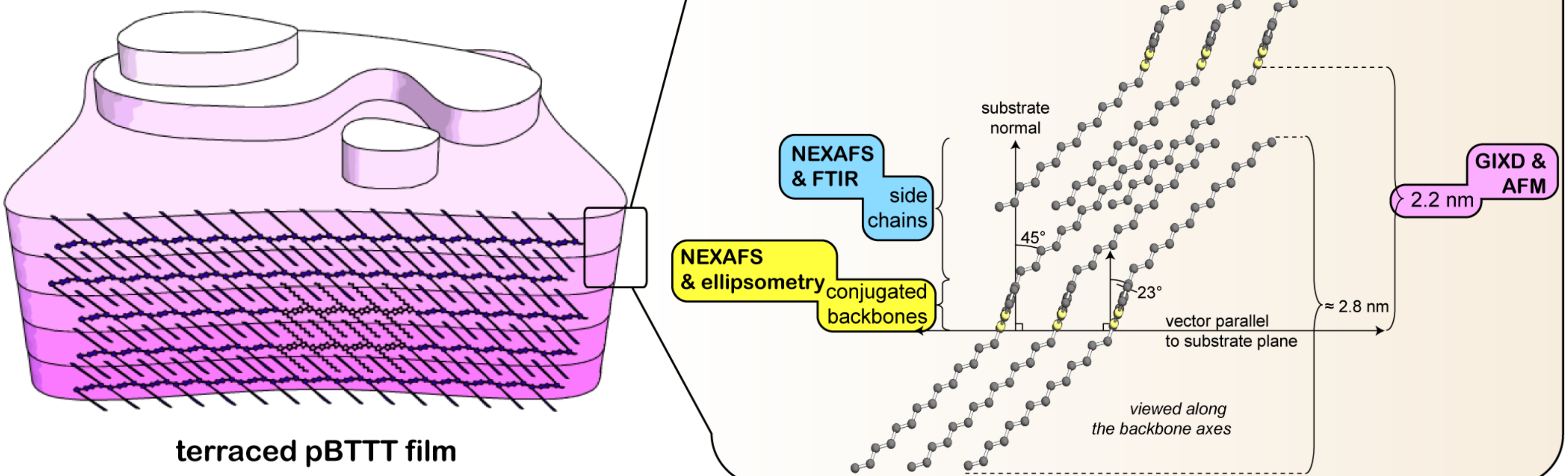
- Merck Chemicals serendipitously discovered a world-champion polymer semiconductor, but needed to determine the structural origins of its performance.
- Conventional methods could not resolve the details of its molecular packing.

Approach

- Developed an integrated suite of measurement capabilities including X-ray diffraction (specular, grazing) and spectroscopies (X-ray, vis, IR)
- Integrate the information from the suite of techniques to determine the importance of the **conjugated plane tilt** and **side chain interdigitation**.

pBTTT





terraced pBTTT film

MECHANICAL PROPERTIES OF ORGANIC SEMICONDUCTORS

Measurement Challenge

- Elastic moduli and crack-onset strains unknown for most organic semiconductors.
- These mechanical properties are critical for manufacturing and flexible product design.

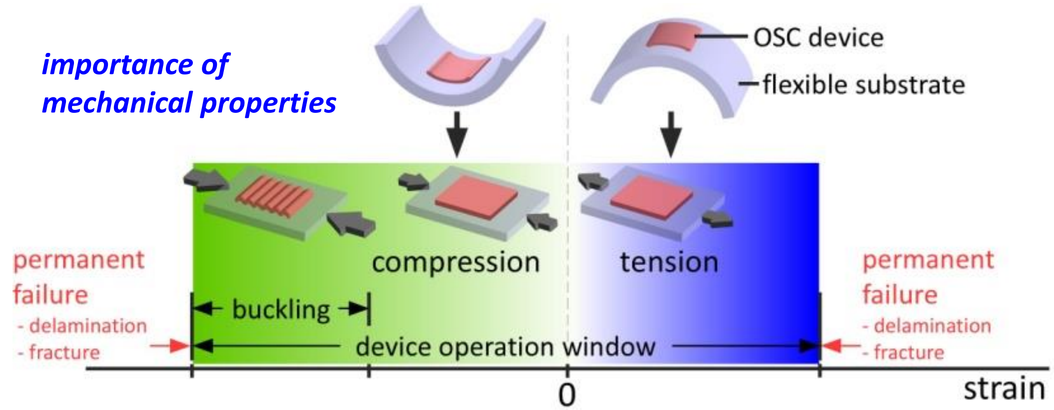
Approach

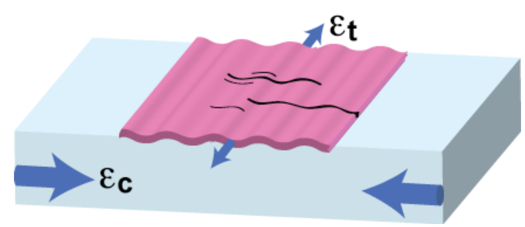
- Buckling-based strategy for mechanical property measurement.
- Analysis of strain- induced orientation and reorganization.

Impact

- Results showed that a common approach to performance enhancement in organic semiconductors (increased crystallinity) ***stiffens*** and ***embrittles*** the semiconductor.
- Less-crystalline organic semiconductors can exhibit large strain-induced orientation.
- Our highly oriented films revealed critical mechanisms for charge transport via microwave conductivity experiments in collaboration with the DOE's National Renewable Energy Laboratory.

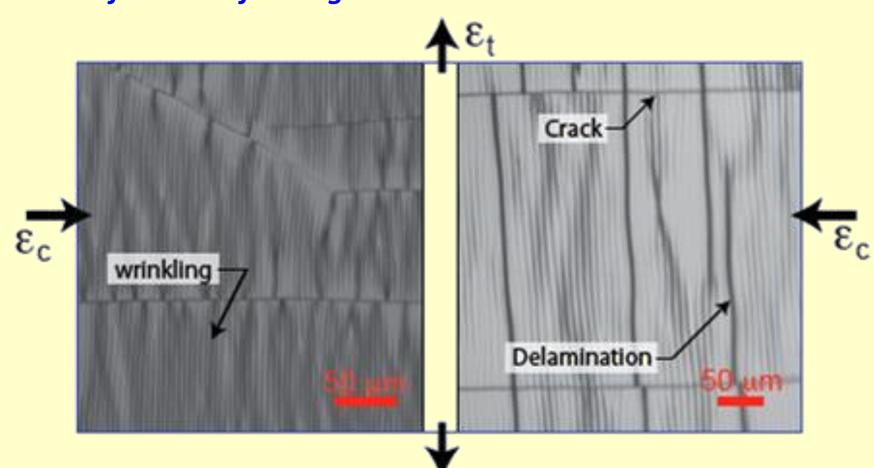
importance of mechanical properties



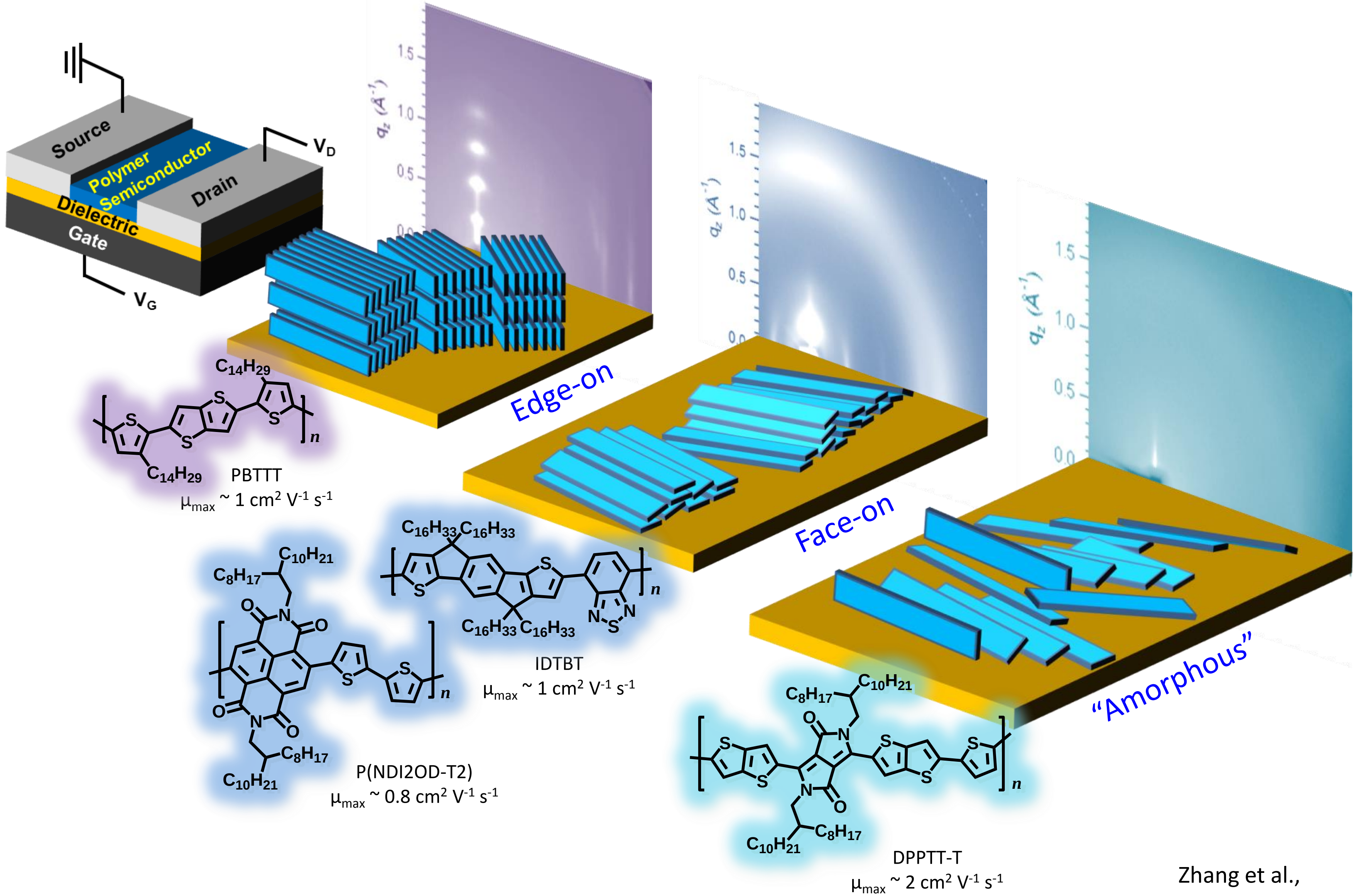


buckling-based measurement strategy

brittle fracture of an organic semiconductor



STRUCTURAL ORIGINS OF HIGH PERFORMANCE



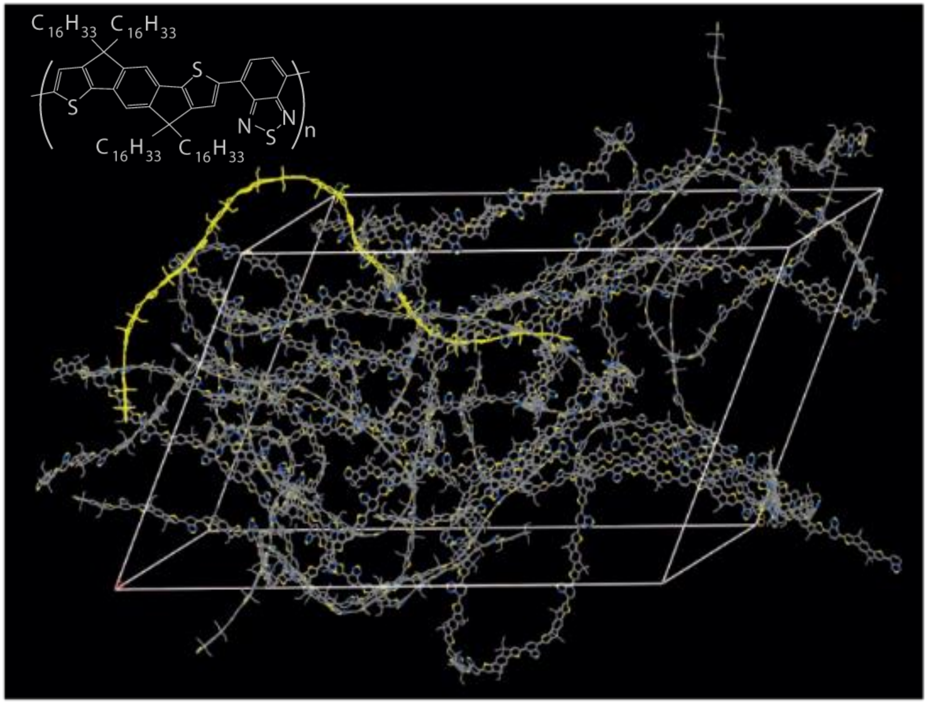
Zhang et al., *JACS* 2011

In collaboration with McCulloch, Heeney, Anthopoulos at Imperial College

EMERGENCE OF AMORPHOUS HIGH-PERFORMANCE POLYMER SEMICONDUCTORS

New polymers discovered:

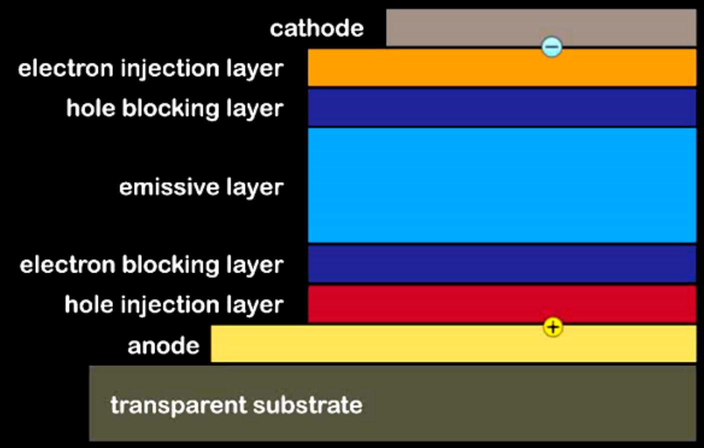
- Essentially amorphous (no features in XRD)
- Very high mobility of 2 to 4 $cm^2V^{-1}s^{-1}$
- Simulation of amorphous phase shows a torsion-free backbone
- Clearly illustrates that molecular, not long range order is responsible for high performance



Venkateshvaran et al., "Approaching disorder-free transport in high-mobility conjugated polymers." *Nature* **2014**, *515*, 384.

ORGANIC LIGHT EMITTING DIODES

- A voltage is put across the device stack
- Holes and electrons are injected on opposite sides
- When the hole and electron meet in the emitter, they create an excited state that decays by emitting a photon (light)
- Real OLED device stacks are significantly more complex than this one. They can have more than 20 layers!



OLED emitters
Source: Merck

IS OLED THE DISPLAY TECHNOLOGY OF THE FUTURE?

OLED is an organic electronics technology where the electronic properties of the organic exceed their inorganic counterpart.

Higher brightness & efficiency!

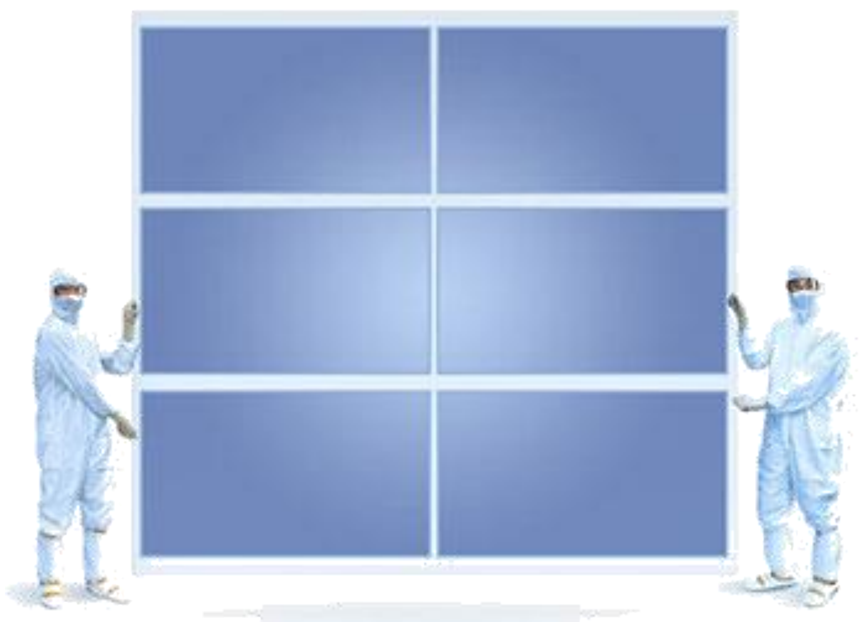
The active layers are 1/1000 the thickness of a human hair.

Most of the 1-2 mm thickness of this TV is just there to protect the screen from damage.

WHY ARE OLED DISPLAYS STILL SO EXPENSIVE?

OLED is made using vacuum deposition because thickness and uniformity are easy to control.

Vacuum chamber cost scales *exponentially* with chamber size.



Trend in the display industry is scaling to ever-increasing size.

This is a single sheet of “Gen10” display glass, which can be cut into six 65” panels.

SOLUTION PROCESSED OLED?

…is right around the corner.

But several serious challenges must be solved.

- Thickness control
- Defect / uniformity resolution
- Layer interactions

Solving these issues could cause OLED display production costs to plummet.

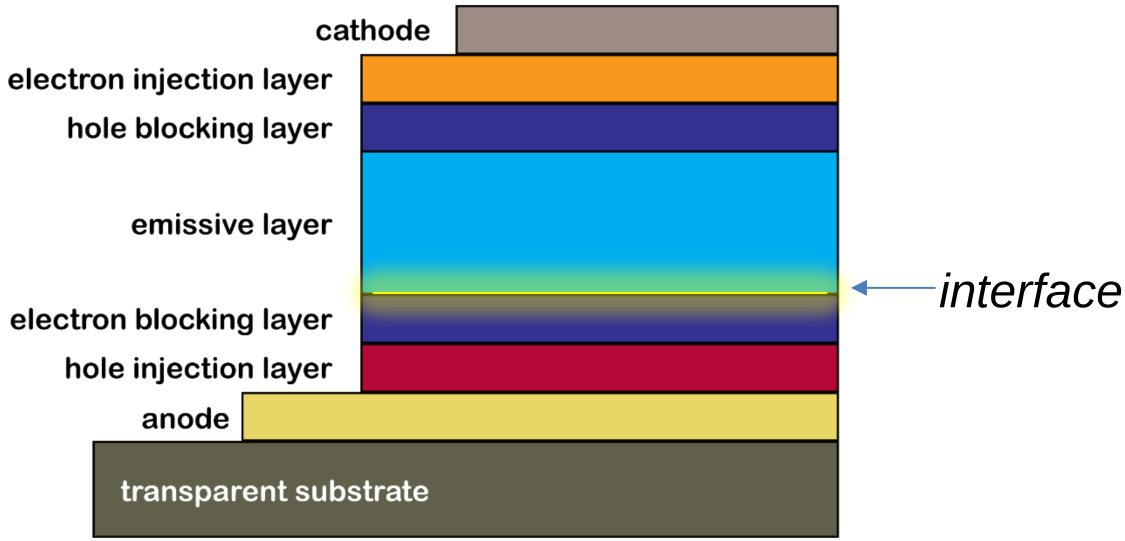
Early OLED Printer (2013, Kateeva)
(probably Gen 9 glass)

EXAMPLE OF NIST WORK IN OLED

NIST's partner Solvay OLED (Pittsburgh PA) is developing a printable electron blocking layer.

Device lifetime and efficiency can be greatly increased depending on the chemical structure of the electron blocking layer.

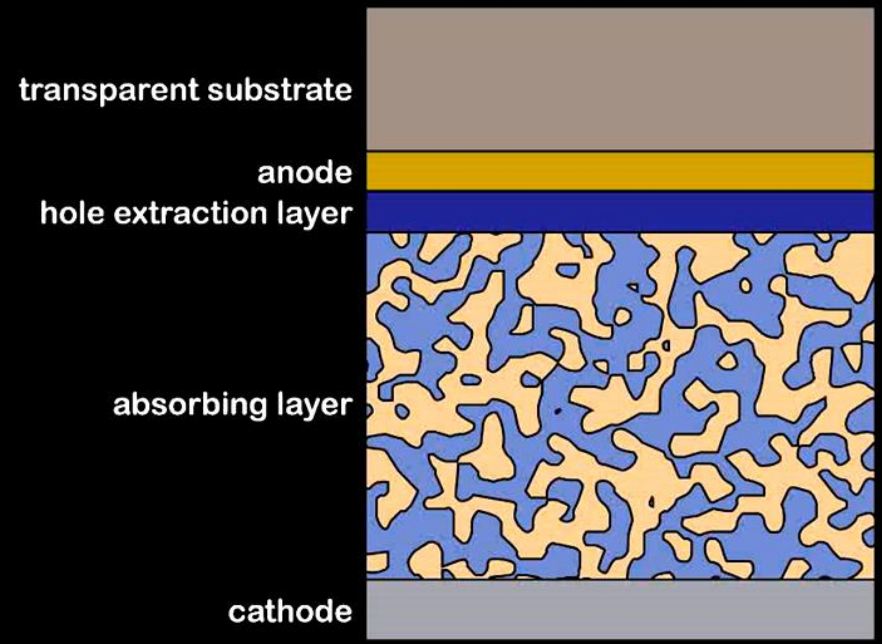
NIST used advanced spectroscopic and depth profiling techniques to identify subtle differences in the interface chemistry and structure

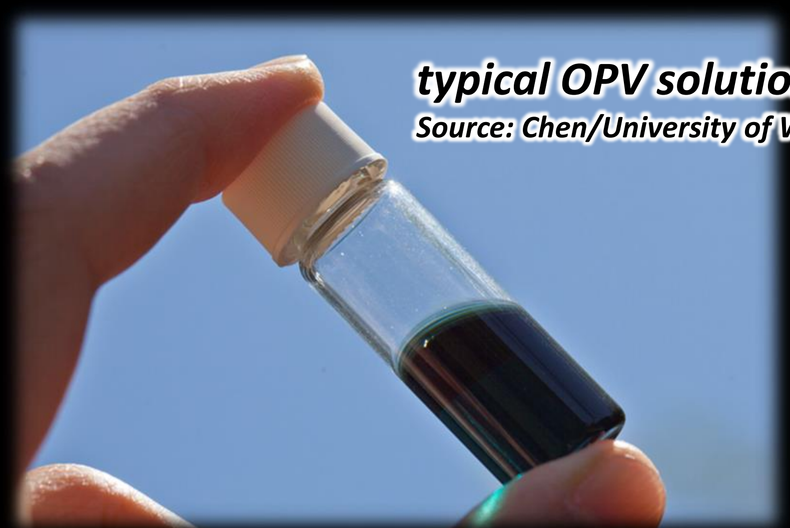


SOLVAY

ORGANIC PHOTOVOLTAICS

- The active layer is a blend of two materials
- Photons (light) are absorbed by one or both of the active layer materials, creating an excited state that splits
- The excited state migrates to an interface and splits into hole and electron
- Hole and electron migrate to respective electrodes, creating current





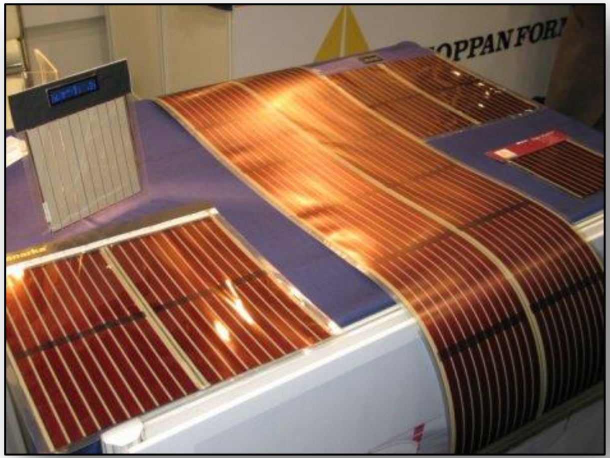
typical OPV solution

Source: Chen/University of Washington

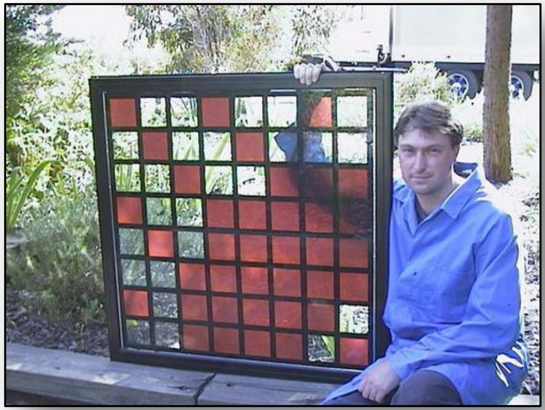
NEW PRODUCTS FROM ORGANIC PHOTOVOLTAICS

AIST

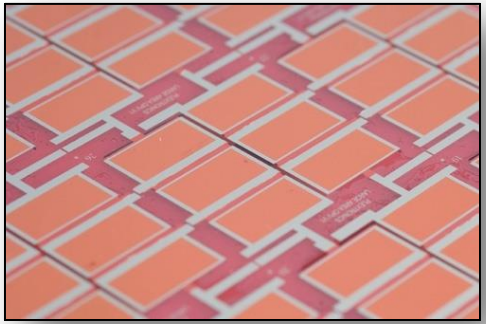
Fraunhofer



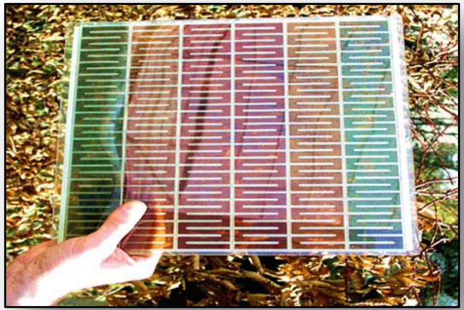
Konarka



EPFL



Plextronics



Massey University

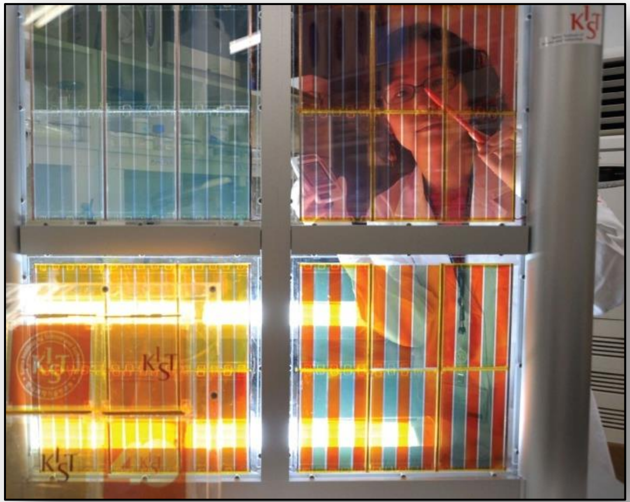
NEW PRODUCTS FROM ORGANIC PHOTOVOLTAICS

Riso

Sony

Konarka

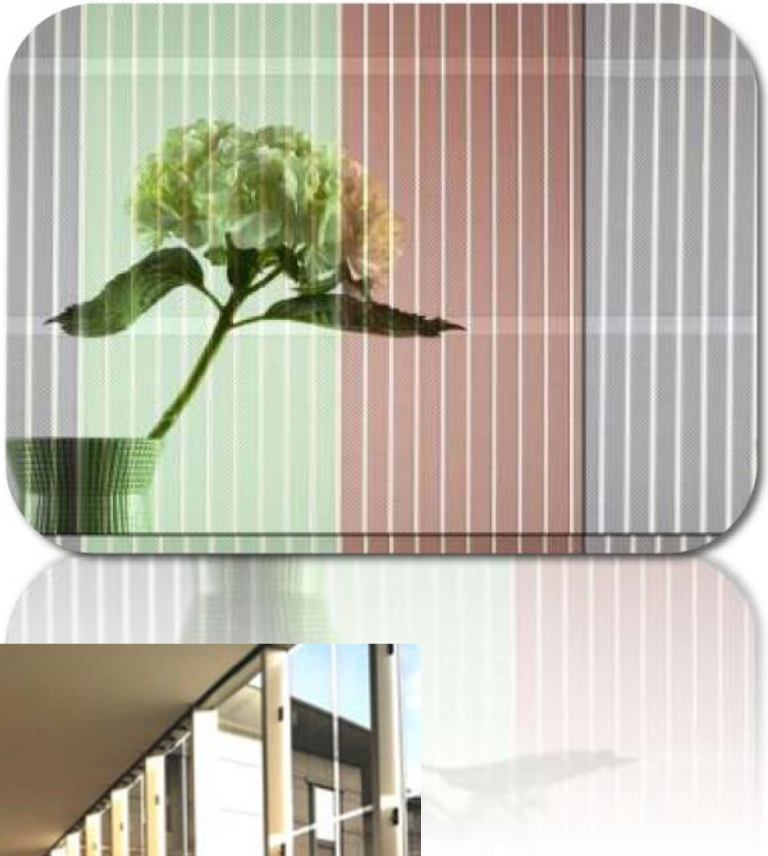
CSIRO



KIST

SEMITRANSPARENT BUILDING-INTEGRATED – AN EARLY OPV NICHE

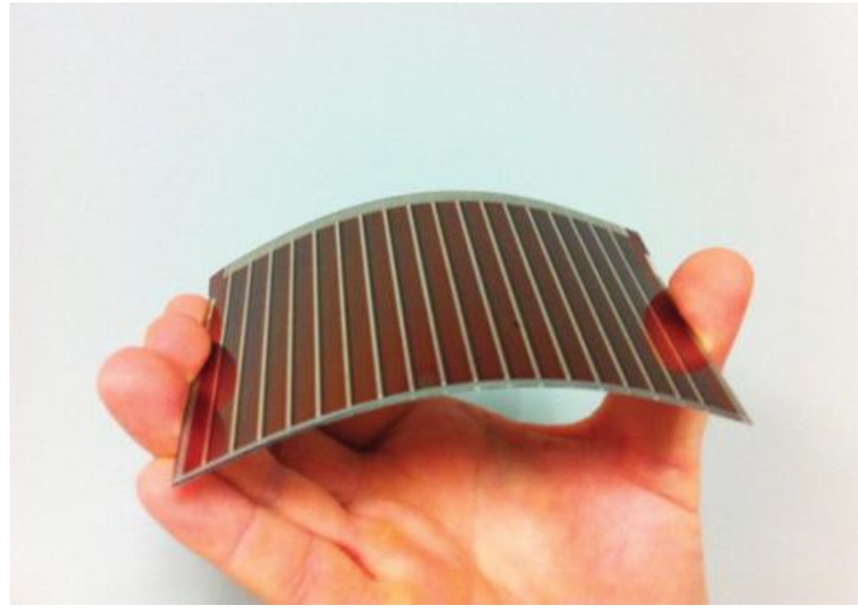
- Color variation is straightforward with OPV
- Functional and aesthetic design choices expand architectural options



Mitsubishi Chemical OPV test facility 2015

LOW-LIGHT (INDOOR) APPLICATIONS – ANOTHER EARLY NICHE

- Unlike inorganic PV systems, OPV performs well in low-light conditions
- Insensitivity to incident angle
- Lower index of organic absorber



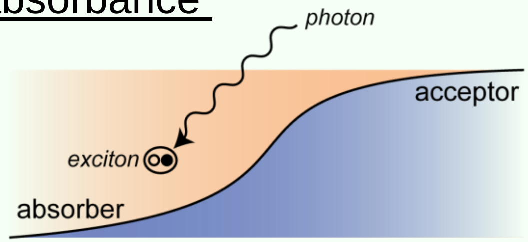
Scalable OPV module made by IMEC
Using Solvay OLED inks

SOLVAY

ORGANIC HETEROJUNCTION OPERATION

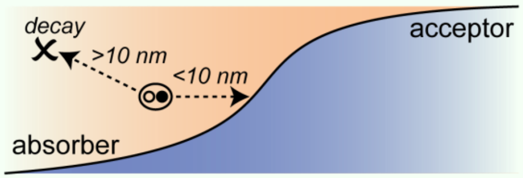
Physical process	***Structure and chemistry requirements***

absorbance



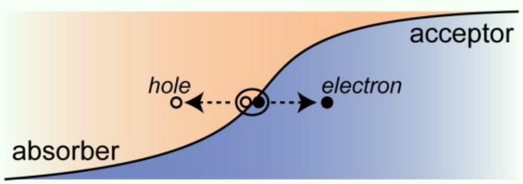
- broad absorption across solar spectrum (e.g. bandgap)
- high extinction coefficient
- light path through absorber > 100 nm
- transition dipole moment alignment

exciton diffusion



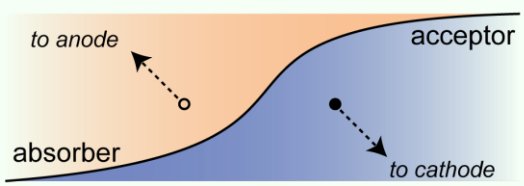
- absorber / acceptor interface within 3-10 nm
- structural order in absorber increases diffusion length

exciton splitting



- > 0.3 eV potential drop at interface (LUMO to LUMO)
- prevent geminate recombination
  - fast transport rate relative to recombination rate
  - relatively sharp interface (?)

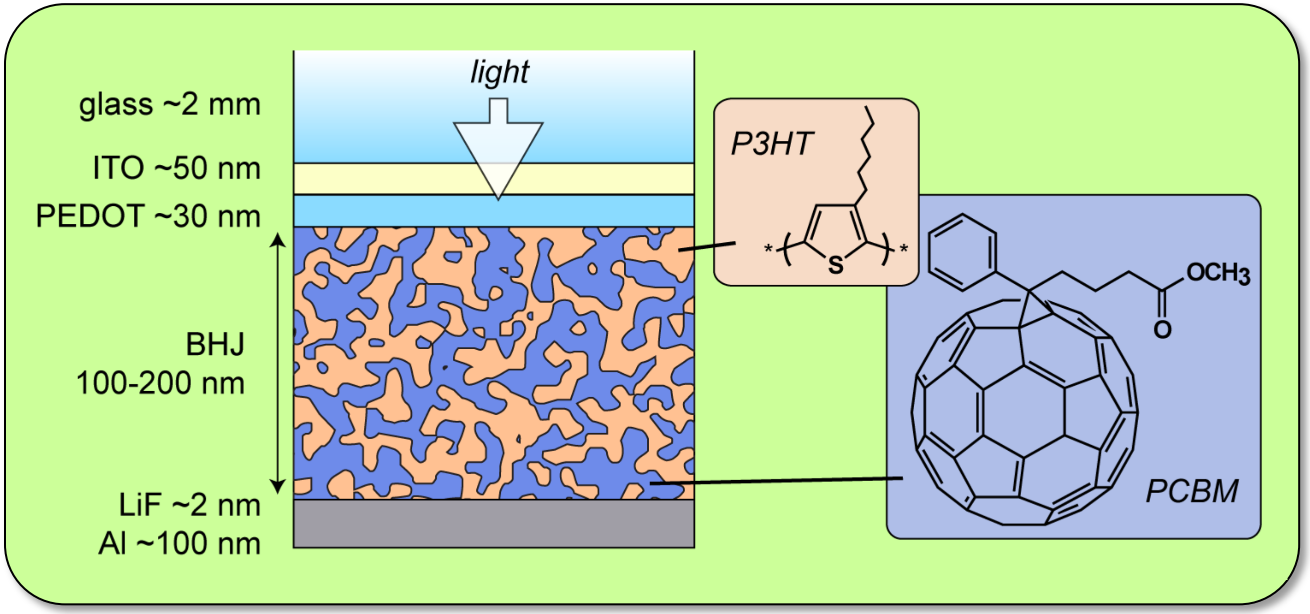
charge harvesting



- interconnected morphology of both phases
- well-aligned electrode ϕ and contact w/ correct phase
- high / balanced mobilities prevent space charge buildup

THE ORGANIC BULK HETEROJUNCTION

Design rationale: Finely intermixed phases reconcile the need for > 100 nm optical path with the < 10 nm exciton diffusion length.



Typical fabrication: Co-dissolve absorber and acceptor and cast. Variables include solvent, casting method, heat treatment, interface materials.

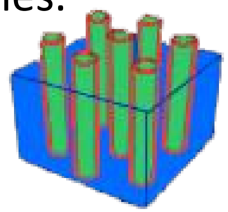
Technology Development Barrier:

- Synthetic changes to absorber-acceptor pair result in unpredictable morphology
- Minor changes in processing can change morphology
- Development is slow and expensive because synthetic / processing space is vast

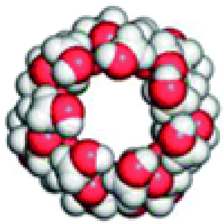
"TAILORED" BHJ MORPHOLOGY HAS BECOME AN OBJECT OF FASCINATION

The complexity of the BHJ morphology has attracted interest from a variety of more mature technical communities.

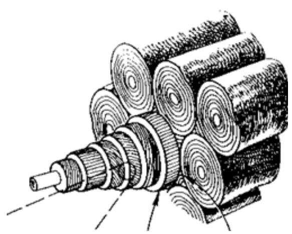
Block copolymers



Supramolecular chemistry

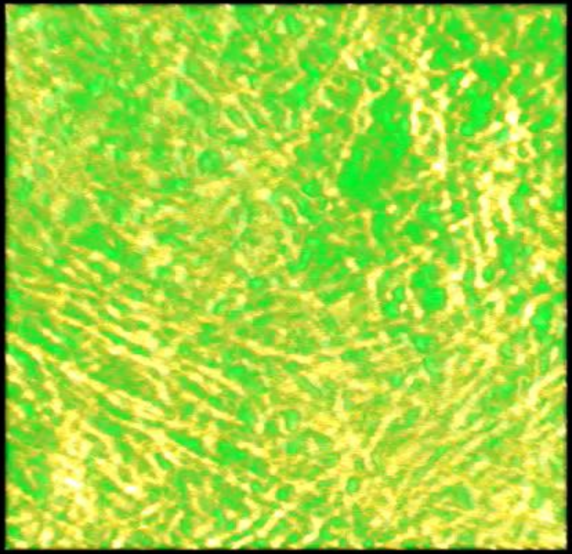


Hierarchical materials



So far none of these approaches has produced significantly efficiencies significantly greater than simple blending....

EXAMPLE OF NIST WORK IN OPV

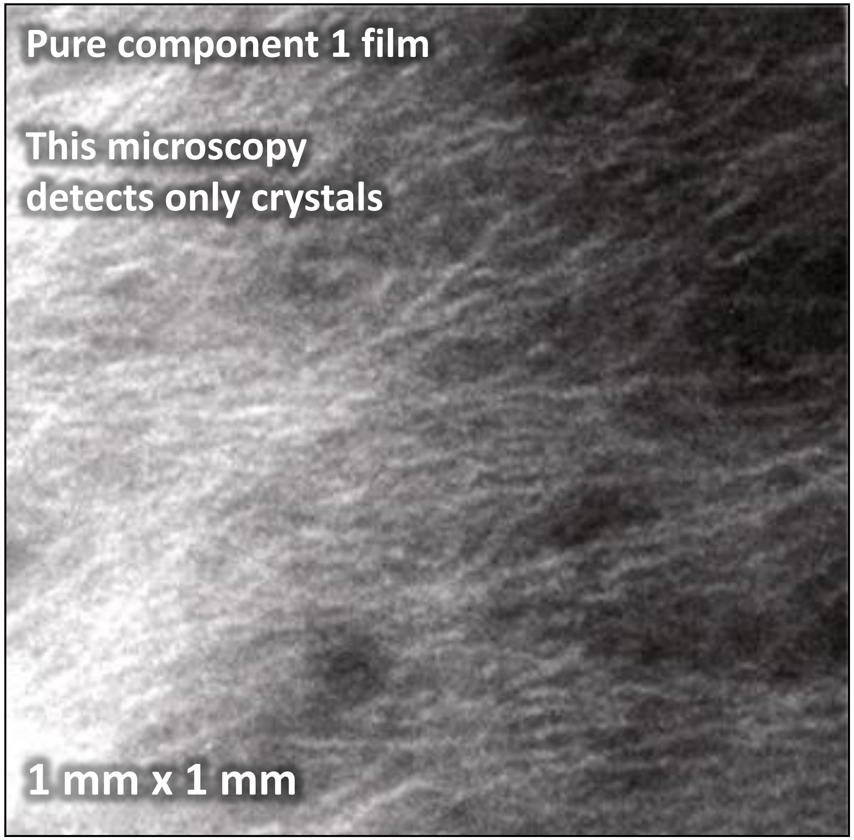


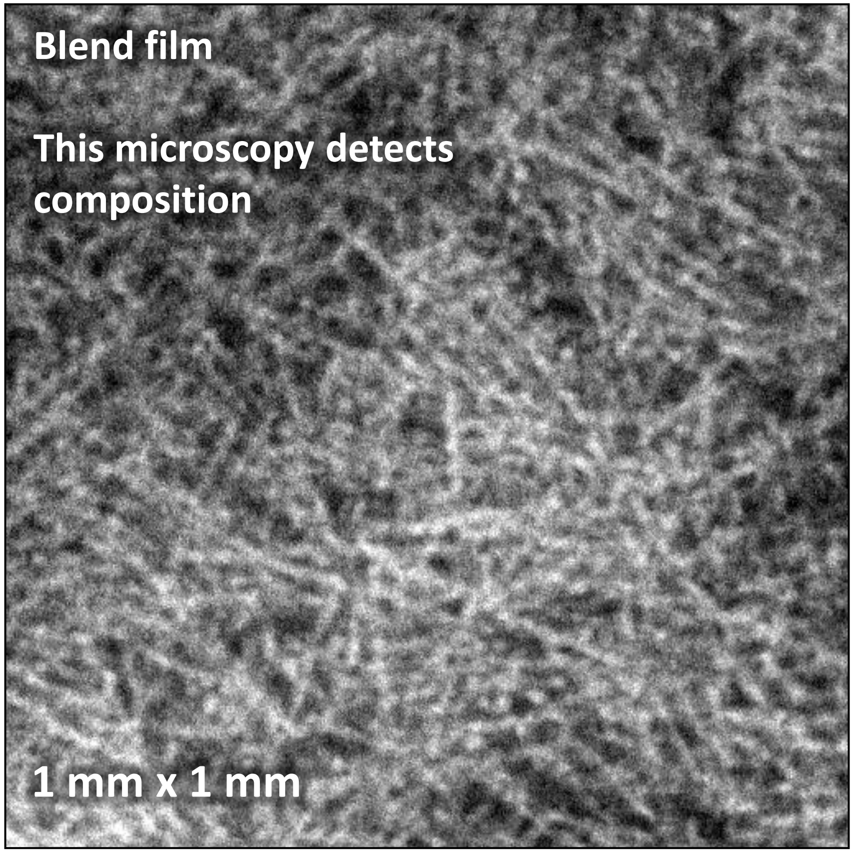
Advanced electron microscopy distinguishes structure in active layer

This entire image only 1 micron wide

by Andy Herzing, NIST Surface and Microanalysis

EXAMPLE OF NIST WORK IN OPV



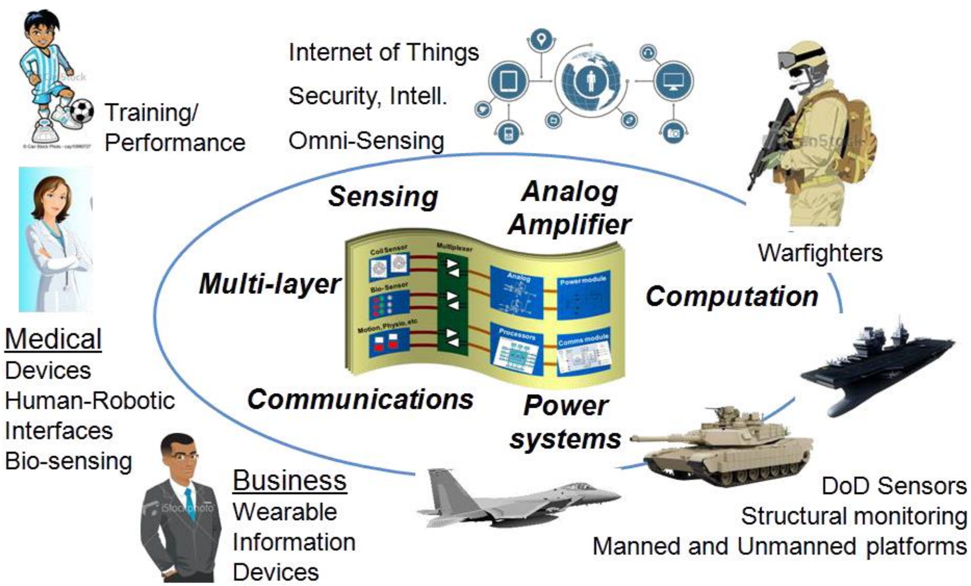


Similar structure in crystals of component 1 and the overall blend composition.

Therefore, the crystallization of component 1 drives structure formation!

GOVERNMENT AND INDUSTRY TURNING TO MANUFACTURING: THE NEXTFLEX MANUFACTURING INNOVATION INSTITUTE

Established: 28 August 2015
Funded by U.S. Department of Defense
Lead: FlexTech Alliance (Consortium)
Hub location and fab: San Jose, California
Proposed Members: 145+ in 27 states
Federal Funding: $75M
Gov't agency engaged: 17 DOD and OGAs



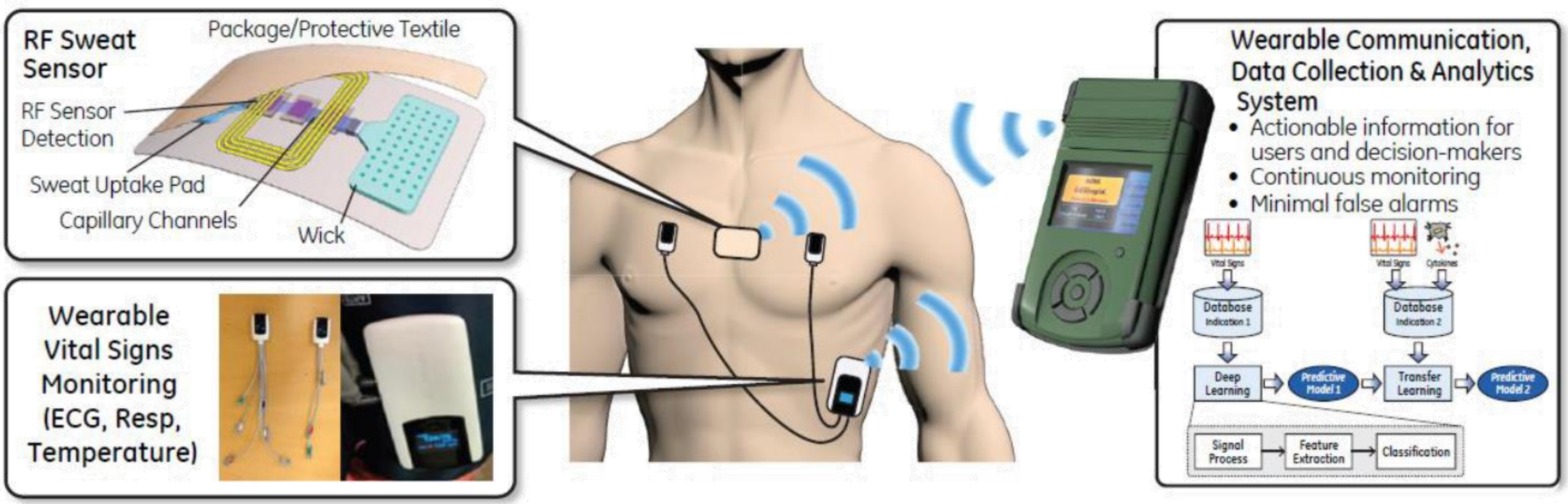
Focus: Combining the entrepreneurial & innovative culture of Silicon Valley with a national network of regional & technology nodes to commercialize FHE technology through manufacturing advancements in integrated printing & packaging, system design tools, materials scale-up, thinned device processing, and reliability testing & modeling.

... thanks to Eric Forsythe (ARL) for this slide

NEXTFLEX DEMO PROJECT #1

Wearable Medical and Human Performance Monitoring Systems

- Demonstrator vehicle for roll-to-roll (R2R) and pick and place (PnP) manufacturing process development
- Small area but low cost, high volume capable
- Modular flow defined by new design tools



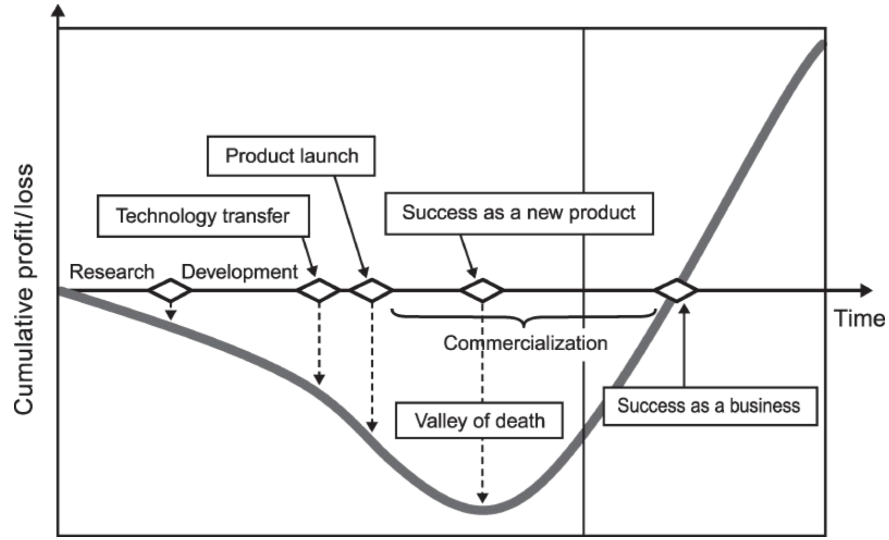
… thanks to John Batey (FlexTech Alliance) for this slide

WHY FOCUS ON MANUFACTURING?

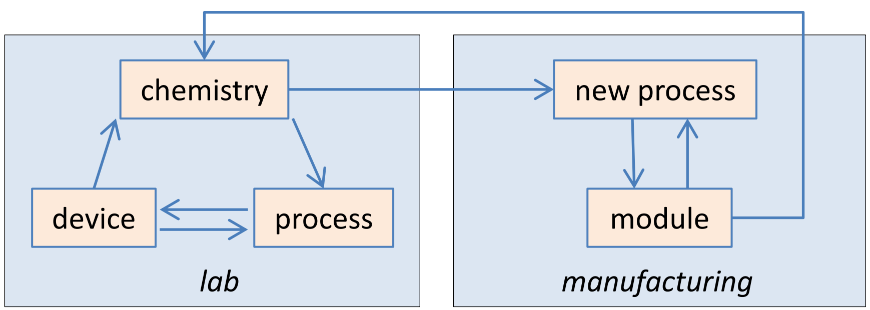
Flexible electronics has yet to become a mature industry.

Too many variables in high-speed commercial production.
- Formulation
- Complicated drying conditions
- Multiple material interactions

In-situ process measurements may accelerate a too-slow process development cycle.



forbes.com

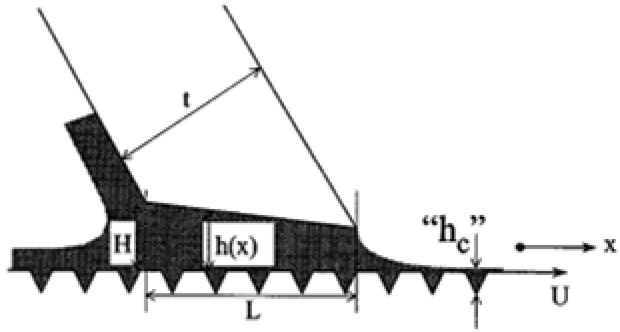


BLADE COATING FOR PROTOTYPING SLOT DIE

- This type of coating has many names:
  - Blade / Doctor blade
  - Flow coating
  - Knife-over-edge

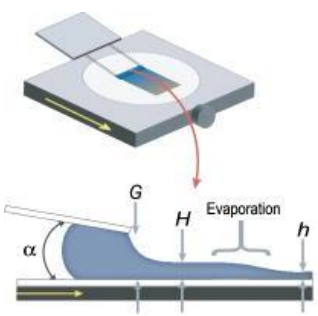
- Physics of ink application same as slot-die on moving web
  - Same speed
  - Same fly heights
  - Similar leading / following meniscus characteristics

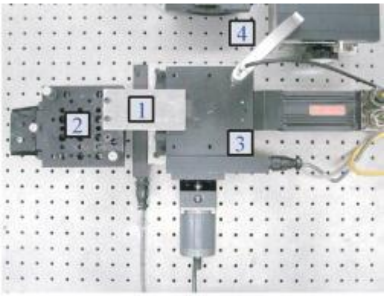
- Other benefits:
  - Substrates and ink under fine temperature control!
  - One 3 cm x 3 cm film requires only ≈ 20 μL of solution.



*Hanamanthu (Eastman Kodak), AIChE J., **1999**, 45, (12), 2487*

Custom-built NIST blade coater





*Stafford et al., RSI, **2006**, 77, (2), 023908*

Erichsen Coatmaster 510

Konarka used this for prototyping R2R slot-die

*Scharber et al., Advanced Materials, **2006, 18, (6), 789***

ABOUT INK

We take pen ink for granted. It is actually a sophisticated formulation with dozens of ingredients developed over centuries.

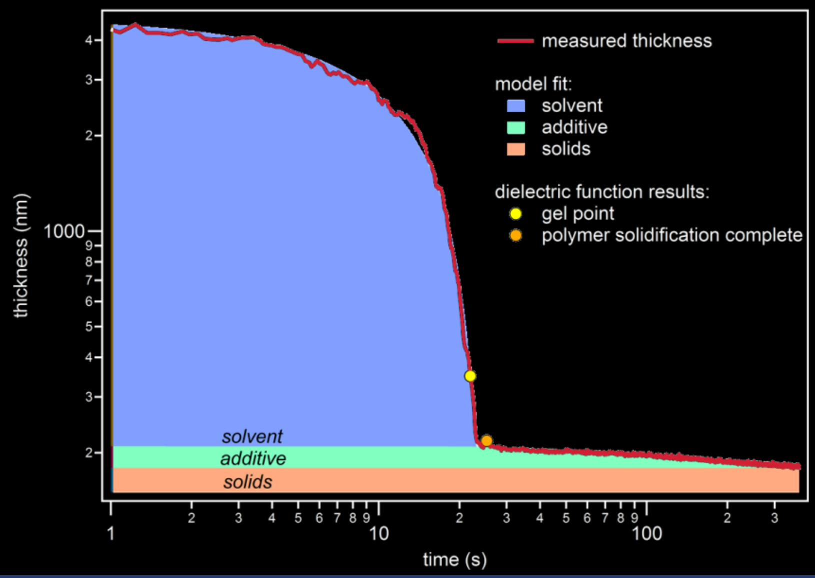
- Pigments (organic and inorganic)
- Dispersants (surfactants and polymers)
- Resins or polymers improve binding, rheology and mechanical properties
- Humectants retard premature drying
- Defoamers and antifoaming agents
- Leveling agents make it smoother
- Wetting agents enhance contact with the substrate
- pH modifiers (usually amine derivatives)
- Biocides and bacteriostats

Flexible electronics is currently in the stage of evaluating single additives in dispersions and solutions.

REAL-TIME STRUCTURE: WATCHING PAINT DRY

- Develop prototype coating technique (scaled down from industry coaters) with real-time optical monitoring at ≈100 ms resolution.
- Model optical results to follow film drying and conversion from liquid to solid.

- Focus on role of formulation
- Evaluate effects of coating temperature and coating speed.



with Lee Richter and Sebastian Engmann, NIST

REAL-TIME STRUCTURE: SYNCHROTRON MEASUREMENT

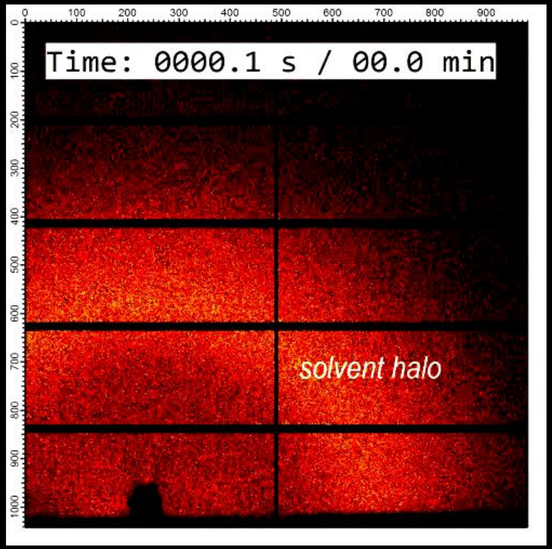
Measurement Challenge

- Ordering sequence of photovoltaic active layers not known.
- Optical techniques are not sufficient to probe long-range order.

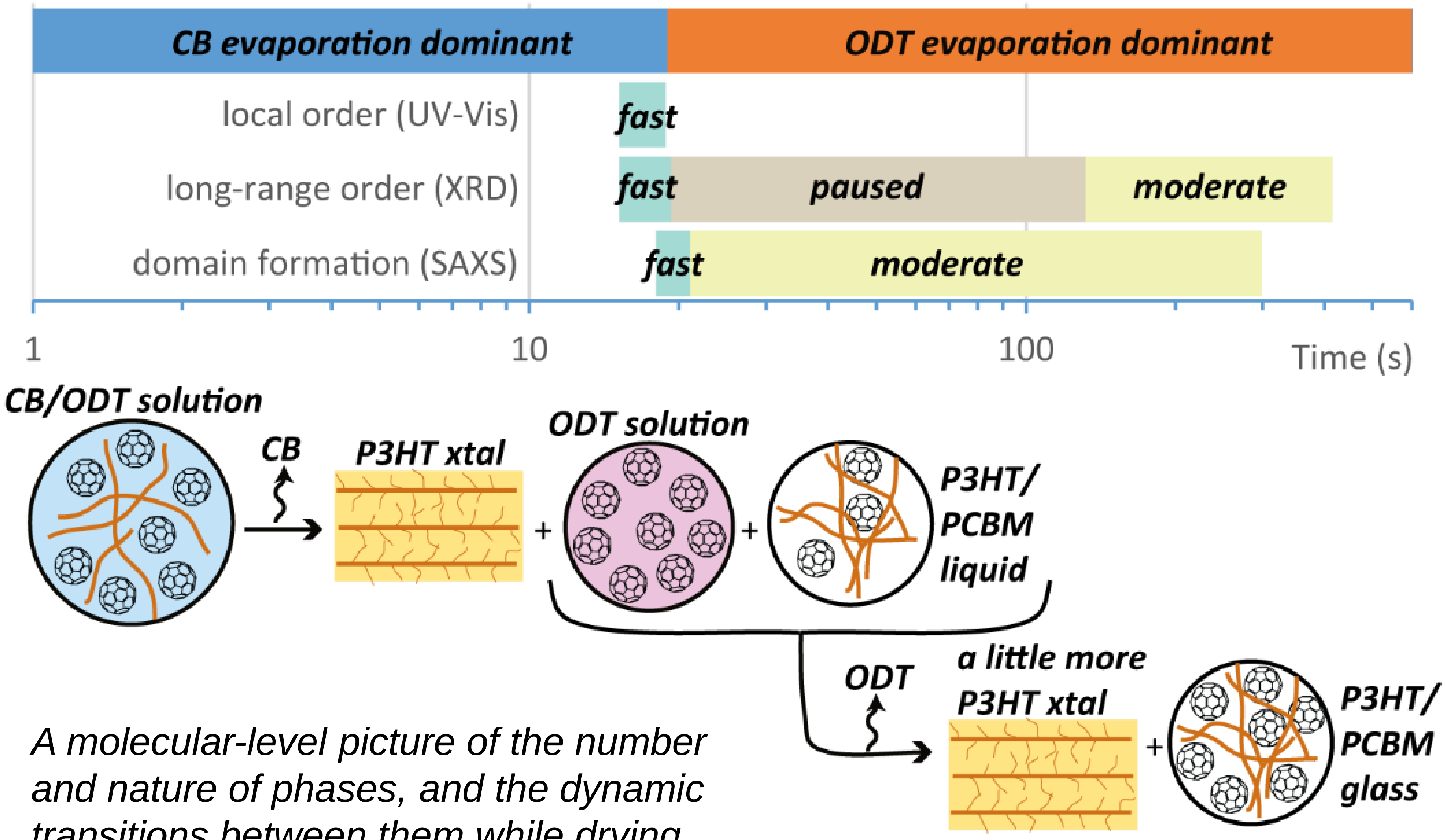
Approach

- Insert prototype coating technique (scaled down from industry coaters) into synchrotron diffraction line with ≈100 ms resolution.
- Beamline 7.3.3 at the ALS (Berekeley Labs)

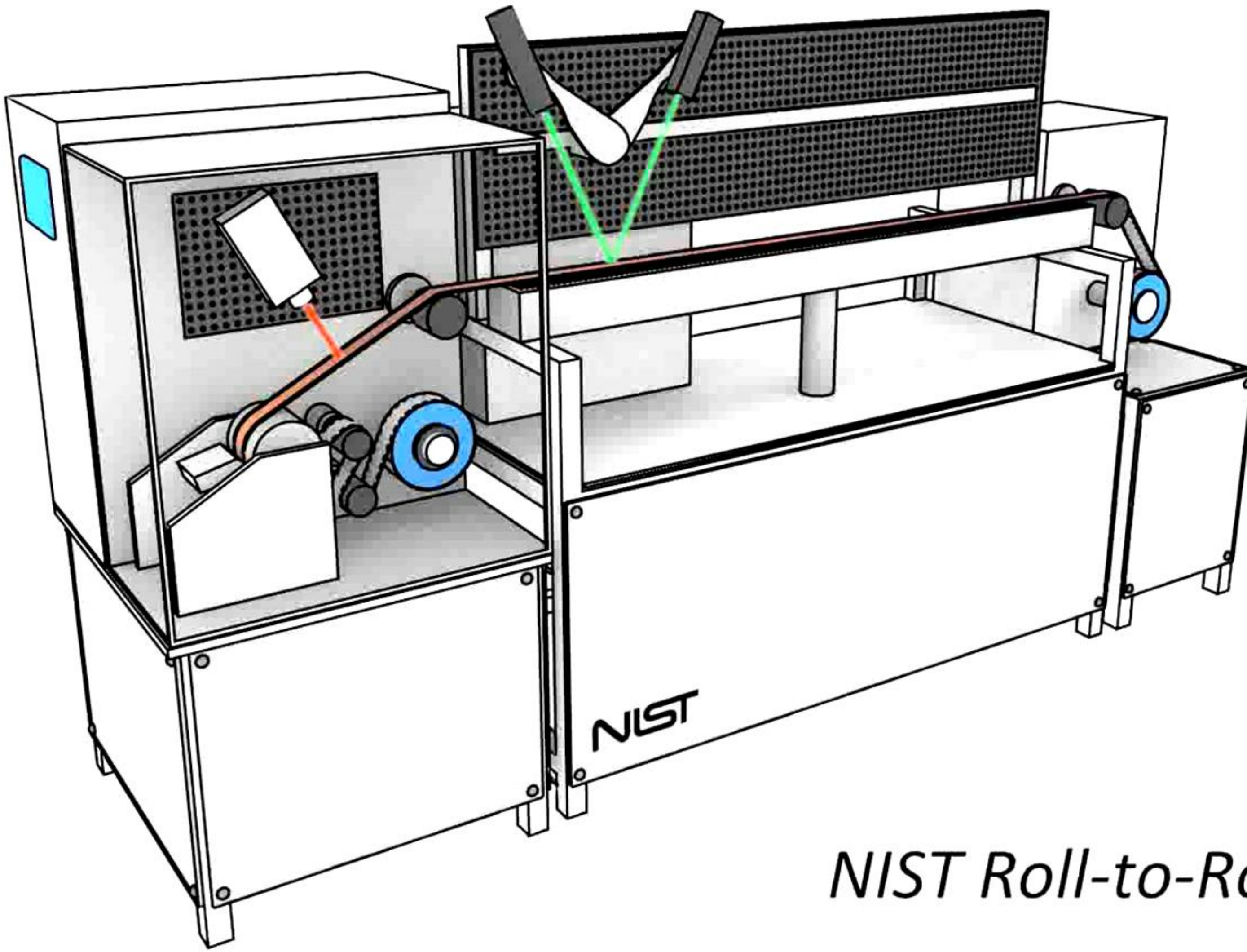
- Focus on role of formulation
- Evaluate effects of coating temperature and coating speed.



UNRAVELING THE EVOLUTION OF FILM STRUCTURE

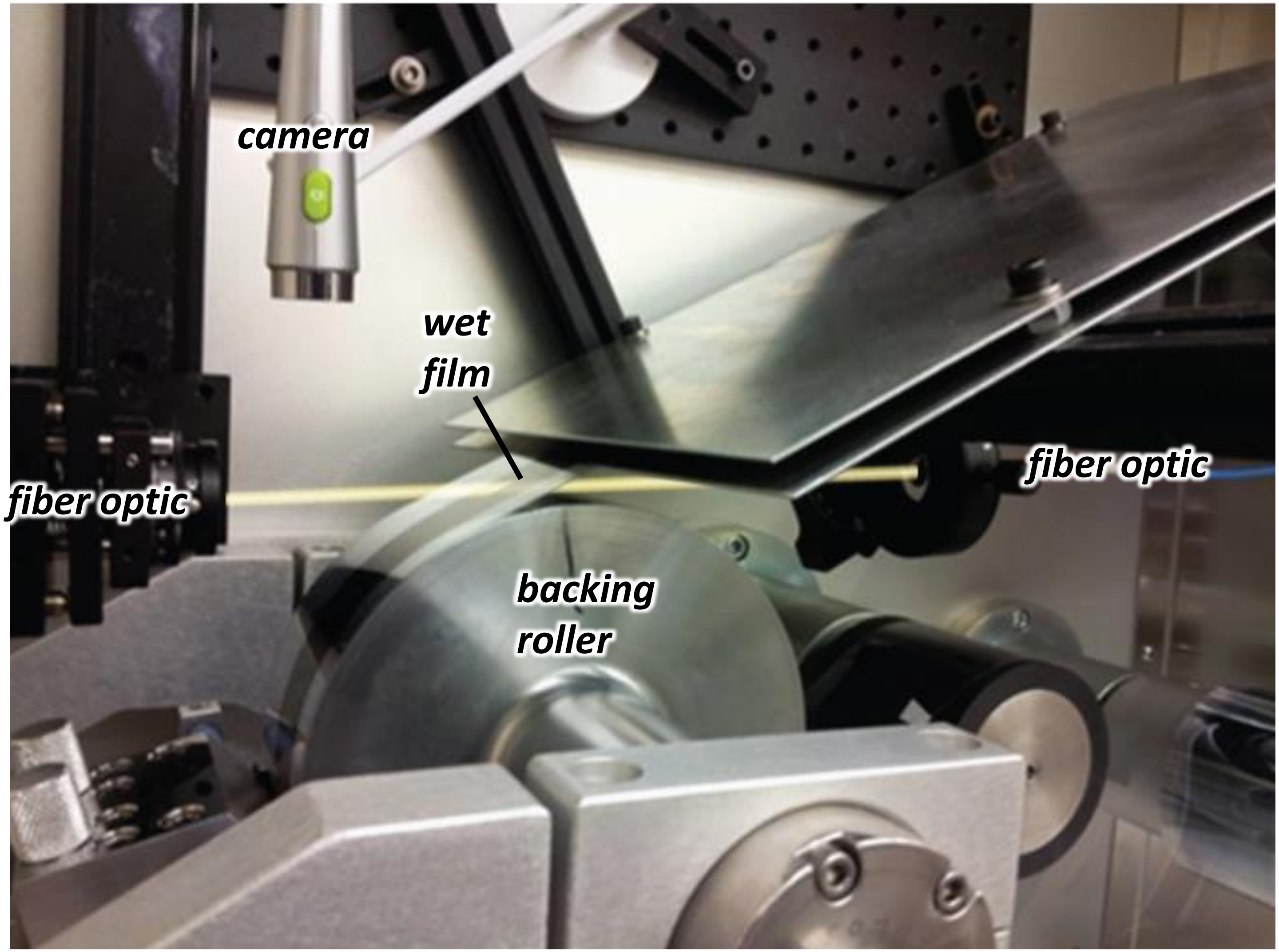


A molecular-level picture of the number and nature of phases, and the dynamic transitions between them while drying.



NIST Roll-to-Roll Unit

OUR R2R TOOL IN ACTION



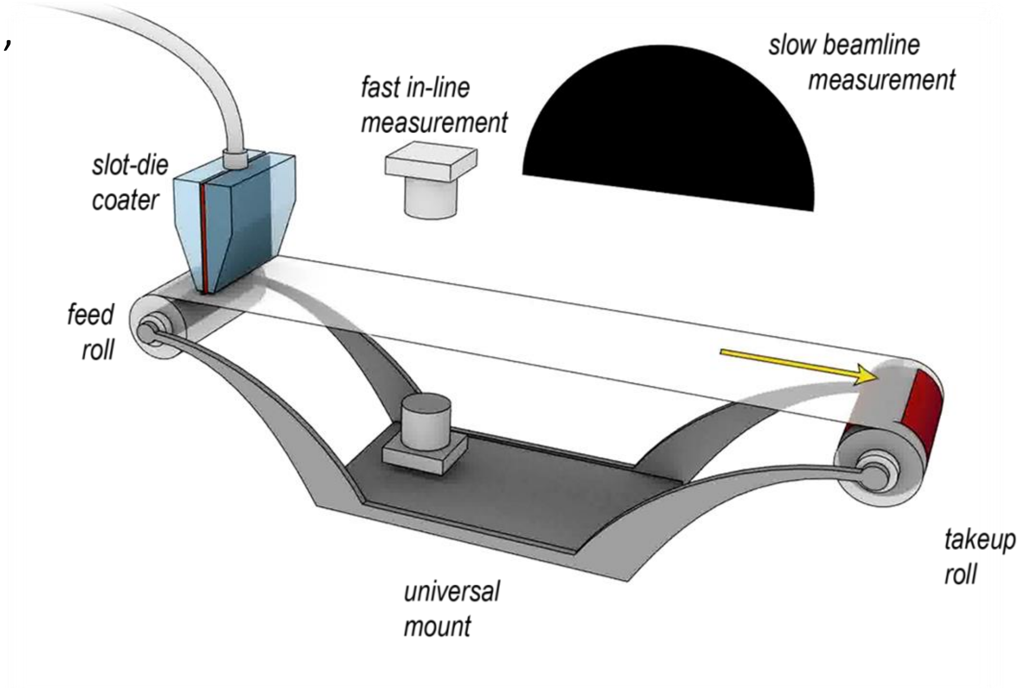
FUTURE PLANS: R2R FLEXIBLE ELECTRONICS MANUFACTURING

Measurement Challenge

- Solidification on a web results in non-equilibrium structure
- Measurements needed for process design, process control, and quality assurance.

Approach

- Develop prototype R2R coater with a stable-continuous process that can be run at a beamline.
- Measurement a constant distance away from coating head will provide time resolution even for slow measurements



Payoffs:

- Structure evolution information from diffraction, scattering, neutrons, etc.
- Correlation to fast in-line techniques to make recommendations, provide algorithms, etc.