FLEXIBLE ELECTRONICS

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

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

![Diagram of slot die printing process]

Source: Coatema

MATERIAL MEASUREMENT LABORATORY
“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
SUBSTRATES FOR FLEXIBLE ELECTRONICS

- **PET** (water bottle plastic)
- Stretchable elastomers
- Thin, strong glass
- Architectural glass
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

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

- Covalent crystal
- Mobility: 100 to 1000 cm²V⁻¹s⁻¹
- Processing by lithography; cutting a formed single crystal
- Performance dominated by lattice defects *within crystals*

Organic

- Van der Waals crystals
- Mobility 0.0001 to 10 cm²s⁻¹V⁻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.

*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).
STRUCTURE IN OTFT MATTERS AT MANY LENGTH SCALES

Primary chemical structure: extended conjugation

Thin Film
few grain boundaries
wide crystals

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

via intermolecular aggregation π interactions

pentacene (for example)

mobile holes created within 5 nm of dielectric

microns

~ 1.5 nm

~ 25 nm
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.
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.
In collaboration with McCulloch, Heeney, Anthopoulos at Imperial College

Zhang et al., JACS 2011

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

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!
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 \textit{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)*
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.
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
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
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
## ORGANIC HETEROJUNCTION OPERATION

<table>
<thead>
<tr>
<th>Physical process</th>
<th>Structure and chemistry requirements</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>absorbance</strong></td>
<td>• broad absorption across solar spectrum (e.g. bandgap)</td>
</tr>
<tr>
<td></td>
<td>• high extinction coefficient</td>
</tr>
<tr>
<td></td>
<td>• light path through absorber &gt; 100 nm</td>
</tr>
<tr>
<td></td>
<td>• transition dipole moment alignment</td>
</tr>
<tr>
<td><strong>exciton diffusion</strong></td>
<td>• absorber / acceptor interface within 3-10 nm</td>
</tr>
<tr>
<td></td>
<td>• structural order in absorber increases diffusion length</td>
</tr>
<tr>
<td><strong>exciton splitting</strong></td>
<td>• &gt; 0.3 eV potential drop at interface (LUMO to LUMO)</td>
</tr>
<tr>
<td></td>
<td>• prevent geminate recombination</td>
</tr>
<tr>
<td></td>
<td>- fast transport rate relative to recombination rate</td>
</tr>
<tr>
<td></td>
<td>- relatively sharp interface (?)</td>
</tr>
<tr>
<td><strong>charge harvesting</strong></td>
<td>• interconnected morphology of both phases</td>
</tr>
<tr>
<td></td>
<td>• well-aligned electrode φ and contact w/ correct phase</td>
</tr>
<tr>
<td></td>
<td>• high / balanced mobilities prevent space charge buildup</td>
</tr>
</tbody>
</table>
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
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.
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.

Custom-built NIST blade coater

Erichsen Coatmaster 510

Konarka used this for prototyping R2R slot-die

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

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

Hanamanthu (Eastman Kodak), AIChE J., 1999, 45, (12), 2487
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.
A molecular-level picture of the number and nature of phases, and the dynamic transitions between them while drying.
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.