New Worlds for Polymers: Organic Transistors, Light Emitting Diodes, and Optical Waveguides

Ed Chandross

*Materials Chemistry, LLC*
Polymers in the Electronic Industry

Enabling Materials

Active Materials?
Polymers in the Electronics Industry

Enabling Materials

Photolithography

Photoresists: the classic case
Photolithographic Process

- **Coating**
  - Photoresist → Si Substrate → SiO₂

- **Exposure**
  - Mask → $hν$ → Negative → Positive

- **Development**
  - Aqueous Base

- **Transfer**
  - Transfer

- **Strip**
  - Strip
Submicron Photoresist History

~1975
Deep UV resist research begins

~1990
“193nm” resist research begins

Decreased Absorbance
Photoresist Images (real nanotechnology!)

Exposed

unexposed

T

0.20µ

0.17µ

0.15µ

0.13µ

0.11µ

0.08µ
Polymers in the Electronics Industry

Enabling Materials

New Techniques for Nanoimaging
Conventional Imprint Lithography

- Place template on thermoplastic
- Apply pressure at $T > T_g$ then cool to $T < T_g$
- Separate the template from the substrate.

- High temp and pressure requirements create distortion
- Precision alignment is difficult
- Pattern density sensitive

Grant Willson UT Austin

Steve Chou, Princeton
Molecular Imprinting: Grant Willson, Texas

Imprint:
- Etch barrier
- Template
- Release treatment
- Transfer layer
- Imprint
- SiO₂

Expose:
- UV Cure
- Residual layer

Separate:

Breakthrough Etch:

Transfer Etch:
Polymers in the Electronics Industry

Electrically Active Polymers

Charge Transport: ca. 1970

The Xerographic Photoconductor

![Chemical structures]
Organic Semiconductors

Pentacene has the best mobility **BUT** it must be deposited by evaporation

![Pentacene molecule]

Soluble polymers offer the possibility of printing

![Soluble polymer structure]
Pentacene Transistor

Diagram of a Pentacene Transistor with labels for Source, Drain, Gate, and p-Si layers.
High Mobility Requires Order
Motivation for Printing of Electronics

- Photolithography cost is high for large arrays.
- Sub-micron features are often not required.
- Roll-to-roll processing is desirable

Display industry reduces cost by increasing substrate size.

Printing is an attractive method for fabrication of large area electronics
Low Cost Printing Technology

<table>
<thead>
<tr>
<th>Cost of fabrication</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon ICs</td>
<td>$100,000 /m²</td>
</tr>
<tr>
<td>a-silicon (AMLCD)</td>
<td>$10,000 /m²</td>
</tr>
</tbody>
</table>

Compare:

- a-silicon solar cell: $400 /m², not materials
- Newsprint: $0.1 /m², Roll-to-roll

- Jet-printing
  - Multi-ejector
  - Printed mask or additive
- Micro-contact printing
- Solution processed materials compatible with jet printing
Organic Transistors (PARC)

Technical Requirements

- Well defined features
- Accurate layer-to-layer registration
- Materials in the form of solutions, dispersions or melts
- Processing on flexible substrates
- High printing speed; AMLCDs have kilometers of address lines

**PARC approach:**

- Jet-printing
  - Additive and subtractive
- Stamping and other printing techniques
Organic Transistors (PARC)

Hybrid Patterning Approach

**Digital Lithography (subtractive)**
- Simplify lithography

**Direct Write Etch Mask**

**Digital Deposition (additive)**
- Integrate materials

**Direct Write Active Material**

- Conventional deposition:
  - Metals - sputtering
  - Insulators - plasma

- Multi-ejector print-head – high printing speed
- Wax ink - feature size control, resists chemical etchants, simple to remove
- Digital imaging – maskless, software registration


- Polymeric semiconductors – printed in ambient conditions at room temperature
- Compatible with flexible substrates

未来的可能性: print also metals and insulators

Organic Transistors (PARC)

Polymeric Semiconductors: surface treatment enhances TFT mobility

F8T2: poly(fluorene-co-bithiophene)

PQT-12: regio-regular poly(thiophene)

A. Salleo et al., APL 81, 4383 (2001)

Organic Transistors (PARC)

Materials for Polymer-Based TFT Arrays

- Metal lines – Cr and Au
- Silicon Nitride and Silicon Oxide as dielectric layer
- Semiconductor PQT-12
  ![Chemical structure of PQT-12]
- Printed in air
- Single nozzle print head
- Mobility $\sim 0.05-0.10 \text{ cm}^2/\text{Vs}$
- On-Off ratio $> 10^6$
Flexible Display Backplanes

128x128 all Jet-Printed Patterned Backplanes

- Active matrix display backplane
- 16,000 pixels (128×128)
- 75 dpi
- Different platforms: glass and flexible

Display Technologies

- Transmissive
- Reflective
- Emissive
Electronic Paper and Electronic Signs

- High-resolution amorphous silicon backplane
  - ABCD 12345ab
  - 5 cm
  - ~250 dpi, 512x512 pixels

- ‘Printed amorphous silicon’ backplane
  - ABCD 12345ab
  - 4 cm
  - ~75 dpi, 128x128 pixels

- Printed organic electronics (POE) backplane
  - Gyronic signs
  - ~75 dpi, 128x128 pixels

- Margarita
  - 1 1/2 oz Tequila
  - 3/4 oz Triple Sec
  - Splash of Sour Mix & Dash of Lime Juice
  - Shake with ice & serve in a salt rimmed glass
Electronic Ink: E-ink’s system

E-INK

TOP ELECTRODE (TRANSPARENT)
WHITE PIGMENT CHIPS
CLEAR FLUID
BLACK PIGMENT CHIPS
BOTTOM ELECTRODE

LIGHT STATE  DARK STATE
Electronic Ink: Gyricon Technology

- Viewing Direction

- Top Transparent Electrode

- Bottom Electrode

- +

- -
Roll Up Displays (Philips)
Organic Light Emitting Diodes (OLED)

Ching Tang  Kodak 1985
First OLED Active Emitter

\[ \text{AlQ}_3 \]
Evaporation Through Shadow Mask

Fabrication of OLEDs

Note: the cathode is usually Ca or Mg/Ag
Printing Polymer OLEDs

Fabrication of PLEDs

Indium-Tin oxide (ITO) 0.1 μm

Glass, PET

Formulation of solution

Filtration of solution

Successive deposition of organic layers

Spin-coating: Cost-efficient deposition technique

Thermal evaporator

Encapsulation

mask
Ink Jet Printing a PLED Display
Hermetic Sealing for OLEDs

Cathode is sensitive to water and oxygen

Vitex Systems San Jose
Vision for OLED Displays
Fiber Optics 101: Gross Anatomy

Side View
- Multimode Fiber
- Core

Cross Section
- Single Mode Fiber

Spectral Response
- 0.02
- 0.006
Polymers in the Photonics Industry

Need low cost components for moderate bandwidth applications

Can we make them out of plastic?
Polymers in the Photonics Industry

Refractive Index Imaging

Optical waveguides

Diffraction gratings

Holography

Fig. 17 - Schematic cross sections of a photopolymer material in which a grating pattern is being written.  
a) The image exposure forms polymer and depletes the monomer concentration.  
b) Additional monomer diffuses into the exposed areas.  
c) An overall development exposure completes the polymerization to give a polymer with a modulated density.
Multicomponent Monomer Patterning

hv

hv

hv

“Methacrylate”
Fast

Slow
Polymer Waveguides

Negative resist (solvent developed)

Buried waveguides
Optical Waveguide Circuits

Polymer Planar Lightwave Circuits

Traditional FAB Approach to Polymer Waveguides

Waveguide Formation with Metal Etch Mask

Unexposed Waveguide system on 1000' rolls

Chrome on fused silica photomask

Buffer Layers added to top & bottom, creating symmetric package with waveguide centered vertically.

UV Exposure Lamp

Finished Waveguides are diced ready for fiber coupling or installation into electrooptic device.

Source: Lightwave Microsystems and Merrill Lynch

D.F. Eaton DuPont

DuPont Proprietary Acrylate Photopolymer Waveguide System
Holographic information storage

Advantages claimed:

Parallel readout; very high speed

The competition: magnetic storage steadily gets denser and cheaper
Holographic recording

Holographic storage using acrylate photopolymers

www.inphase-technologies.com
Holographic recording
Fiber Optics 101: Manufacturing

1. **Tube Setup**
   - Empty glass tube
   - Heat source

2. **Deposition**
   - Deposit
   - Reagents
   - Glass
   - Exhaust
   - Heat source

3. **Collapse**
   - Heat source

4. **Fiber Drawing**
   - Heat source
Drawing Fiber from Preform
Plastic Optical Fiber (PMMA based)

Preform Production of PMMA GI-POF

- For PMMA graded-index preforms, interfacial gel process is very desirable. (Y. Koike, 1)
- Start with uniform mixture of MMA monomer and dopant molecules
- Index profile formed by preferential exclusion of dopant molecules from gel phase as gelation front propagates inward
- Profile controlled by adjusting polymerization rate, temperature, etc.
- Approximate power-law profiles with $g = 2-5$
- Demonstrated near-intrinsic attenuation, 500 Mhz-km bandwidth at 650 nm

Interfacial gel was first effective graded-index POF technology
Recently commercialized by Fuji Film
Process has not been demonstrated with perfluorinated materials
Plastic Fiber Manufacture

Silica preform processes are scalable to large volumes

- Draw temperature ~2000° C
- Fast, uniform radiative heating
- Negligible material absorption a furnace wavelengths
- Tens of meters/second line speeds

Polymer preform processes are NOT scalable

- Draw temperature ~200° C
- Mixture of convective, radiative heating, low heat flux
- Significant material absorption a furnace wavelengths
- Heat transfer and thermal uniformity set limits
- Tenths of meters/second line speeds

5 cm PMMA Preform
**Production of Perfluorinated GI-POF Preforms**

- Pioneered by Asahi Glass Co in late 1990’s

- CYTOP polymer, small-molecule dopant

- Lowest-attenuation process for making POF (15 dB/km)

- 300 MHz-km bandwidth specification

- Commercial production volumes (megameters/yr)

![Graph showing attenuation vs wavelength](image)

*Typical Installation Ginza Tower*
Low Loss Perfluoropolymer Fiber

Cytop™
New POF Technology

Graded-index POF Extrusion

- High Line Speed
- Continuous Production
- Much Lower Cost
- Flexible

Materials Chemistry LLC
Bowling Green June 2005
Real Engineering Challenges!

Technical Challenges of Extruding GI-POF

Structural Complexity

Perfluorinated POF needs 3 or more layers composed of very different materials.

Core and cladding layers -- perfluorinated
Reinforcement (overcladding) layer -- non-fluorinated

Multilayer, heterogeneous fibers are simple in principle, but difficult in practice

- Compatible processing temperatures
- Good interfacial adhesion
- Comparable thermal expansion for low microbending loss
- Control of diameter and other geometric properties for all layers
- Tight tolerances for gigabit applications (e.g. +/-5 μm OD variation)

Ultrahigh Purity

In a fiber with 100 μm core diameter, a 5 μm particle will scatter ~0.25 % of incident optical power
For attenuation within 10 dB/km of intrinsic, there must be less than 1 such particle per meter
This corresponds to about 8 parts per billion by volume (less for smaller particles)

So, the material must be dried from solution, transferred into the extruder, and processed without adding more than a few ppb of contaminants. Since in-situ polymerization is not feasible, all of this must be done after polymerization.

Surprisingly, this is both possible and manufacturable
Success!

Chromis Fiber Optics

Properties of Extruded Perfluorinated GI-POF

Geometry

Geometry controlled by flow ratios
Easy, rapid shift between fiber types
OD variation < +/- 3 μm (500 μm OD)

Attenuation

Attenuation typically 25-35 dB/km at 850 nm