Organic electronics: case studies in commercialization

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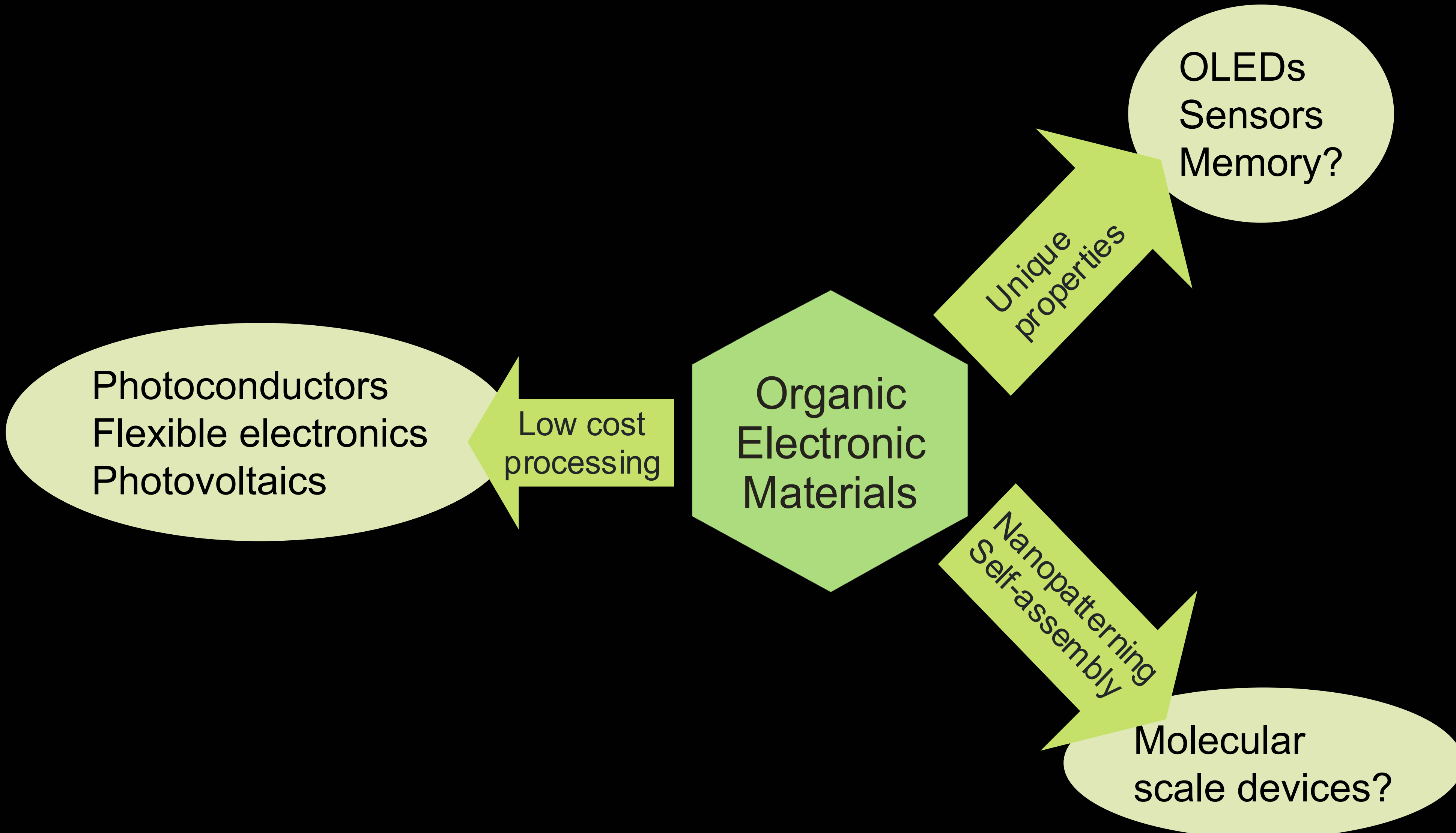
Outline

1. Organic photoconductors – an historical perspective
2. Organic light-emitting diodes
   – the view from within a large company
3. Nanotrap memory – a new application?

Applications of Organic and Molecular Electronics



Organic Photoconductors – since 1966

United States Patent Office

3,484,237

Patented Dec. 16, 1969

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3,484,237

ORGANIC PHOTOCONDUCTIVE COMPOSITIONS AND THEIR USE IN ELECTROPHOTOGRAPHIC PROCESSES

Meredith D. Shattuck and Ulo Vahtra, San Jose, Calif., assignors to International Business Machines Corporation, Armonk, N.Y., a corporation of New York

Filed June 13, 1966, Ser. No. 556,982

Int. Cl. G03g 7/00

U.S. Cl. 96—1.5 — 8 Claims

ABSTRACT OF THE DISCLOSURE

An organic photoconductive composition comprising from about 0.49 to about 1.23 moles of 2,4,7-trinitro-9-fluorenone per monomeric unit of a polymerized vinylcarbazole compound.

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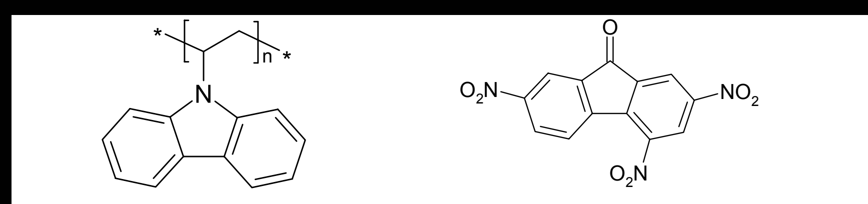
the dark conductivity to become too high and the photoconductive composition will no longer accept sufficient electrostatic charge to be useful in electrophotography.

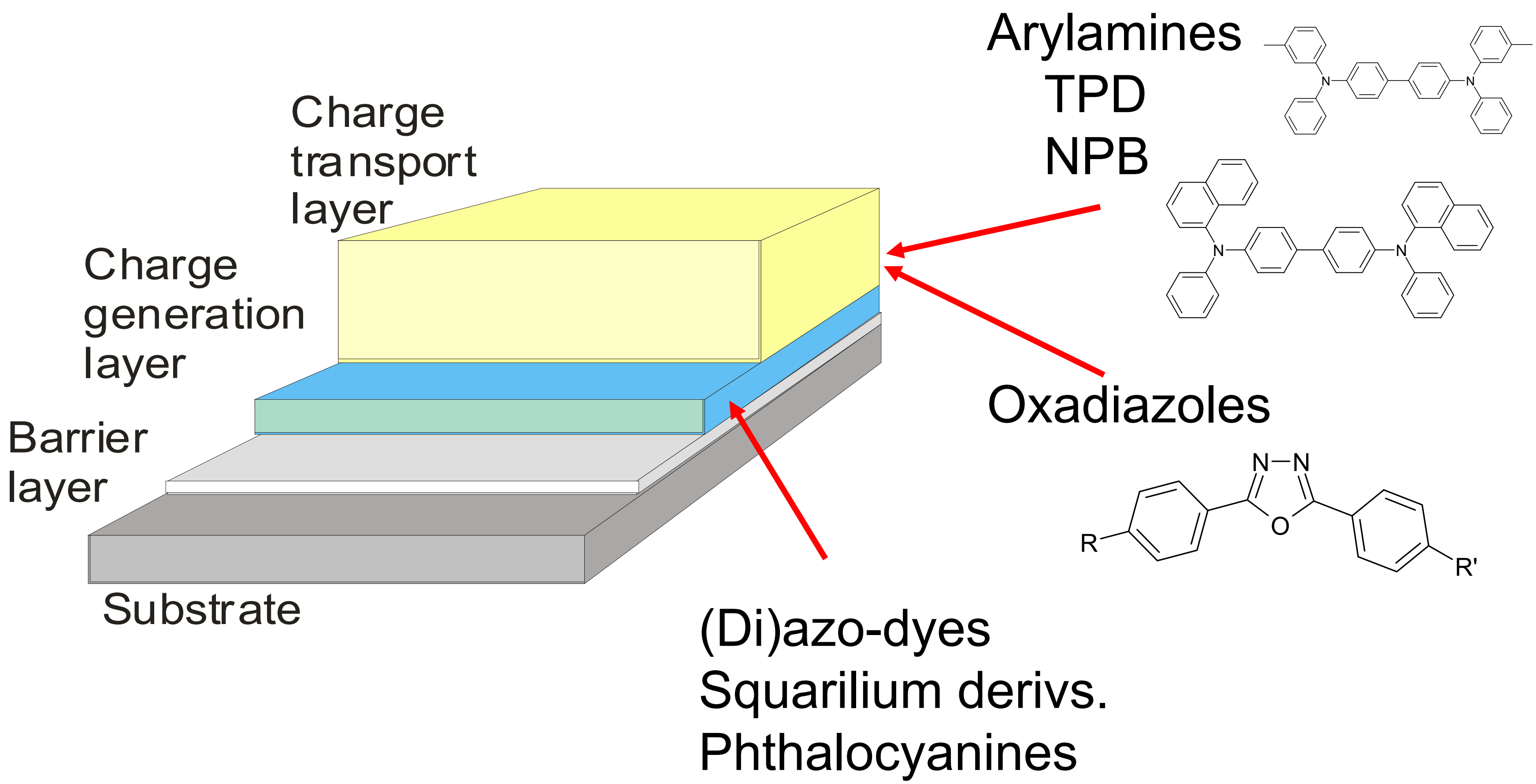
Because of the combination of lack of stability and low sensitivity, organic photoconductive compositions have been competitively unfit for use in a high speed optical xerographic copier in which the photoconductor is reused thousands of times. That is, the known organic photoconductive compositions have not compared favorably with the sensitivity or exposure speed and stability of commercial selenium presently being used in xerographic copiers. To be competitive with selenium, an organic photoconductive composition has to have a sensitivity or exposure speed not less than two times slower than the exposure speed of selenium.

It has now been discovered that organic photoconductive compositions, comprising from about 0.49 to about 1.23 moles of 2,4,7-trinitro-9-fluorenone per mole-

PVK-TNF



Materials for Organic Photoconductors



A brief history of OPC

- Original motivation (1965)
  - Circumvent Xerox Se patent
- Ultimate drivers (Canon 1984)
  - Cost, reduced toxicity, spectral sensitivity (840nm)

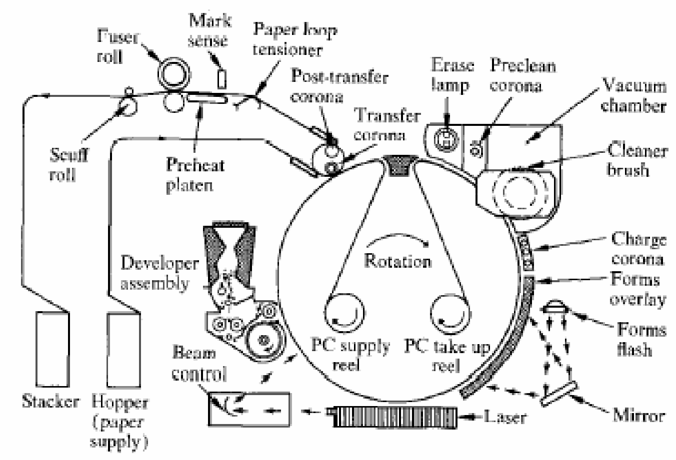


Figure 1 Configuration of the electrophotographic printing process.

Vahtra and Wolter
IBM J. Res. Dev. 1978

- Original format
  - Web, reel-to-reel coating
- Ultimate format
  - Drum, dip-coating

From AEG website

Lessons from OPC

Trickles flow both down and up

Organics started at high end (no low end EP)

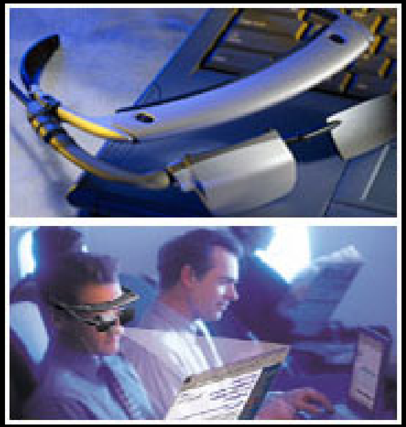
… helped to create low end

… took over all but the very top

Materials optimized after application is identified

Organic light-emitting diodes

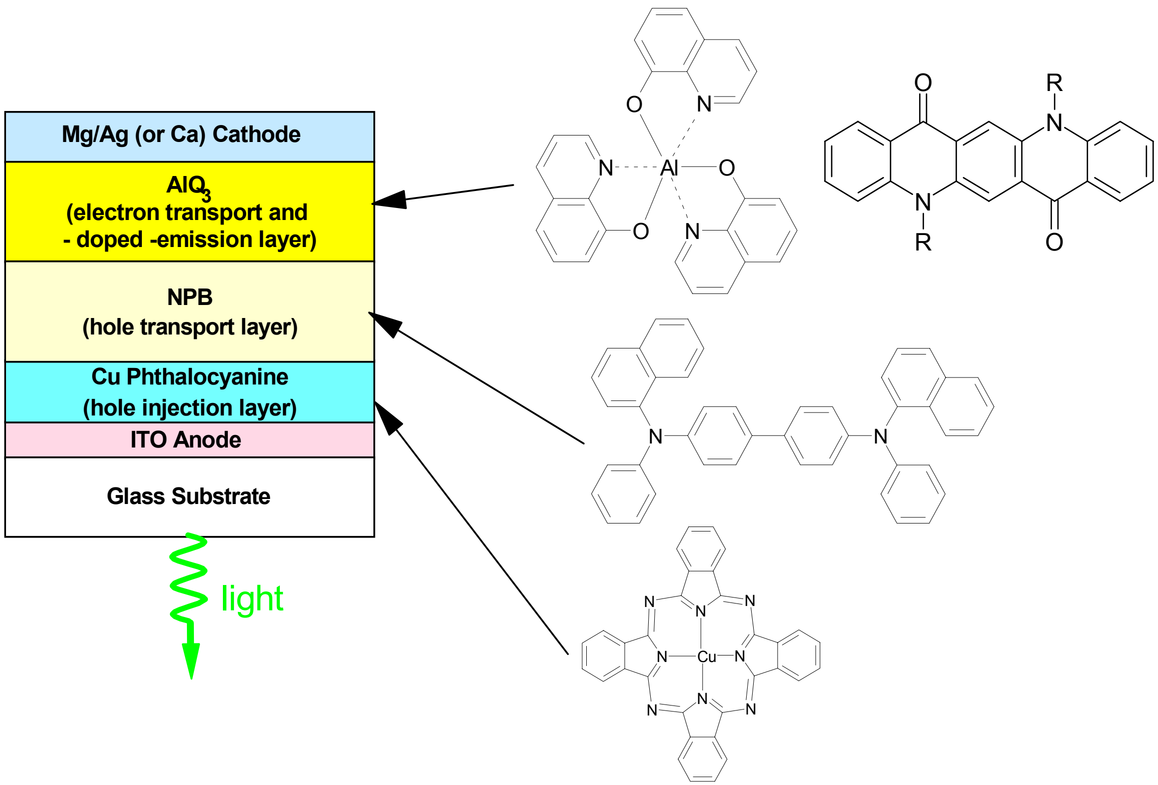
- Motivation (in a large computer company)
  - Provide an alternative to liquid-crystal flat-panel display (for laptop computers)
  - More efficient (battery life in mobile devices)
  - Better viewing angle
  - Thinner, lighter
  - Enable new applications, e.g. head-mount, virtual 3D
- Issues addressed
  - Lifetime
  - Color gamut
  - Driver electronics
  - Processing



eMagin

Materials for OLEDs

Early OLED Structure
(Kodak materials)



Later developments

Polymers for transport and emission (arylamines, fluorenes, …)

Crosslinkable polymers for multilayering

Polymeric anodes (polyaniline, polythiophene - PEDOT)

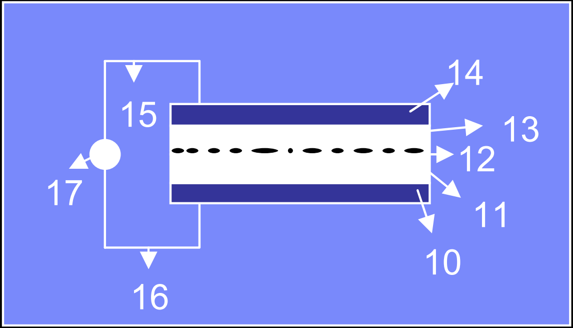
Emissive dyes (modification of laser dyes, use of triplet excitons)

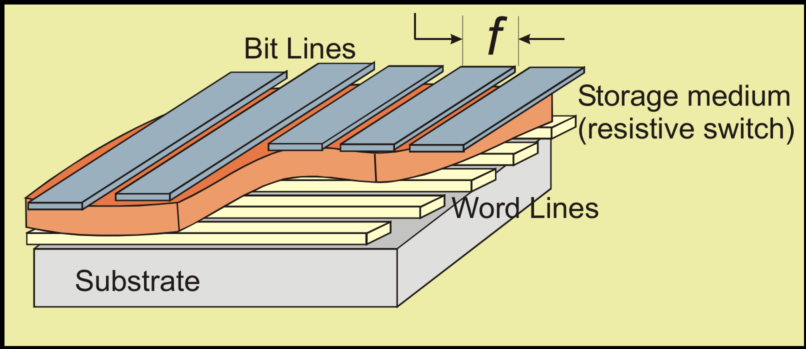
Lessons from OLED

- A completely new technology
  - Not a replacement component
- Initial commercialization at the low end
  - Cell phones
  - Automotive (radio, navigation)
  - Small alphameric displays
  - Cameras
  - Computer screens much later?
- Entrenched technologies generate $ to improve
  - LCD viewing angle
  - LCD Efficiency / Brightness
  - Cost

Nanotrap memory – nonvolatile, solid-state

- Metallic nanoparticles imbedded in organic semiconducting matrix
- Data stored as charges on nanoparticles
- Two-terminal bit-cell
- $4f^2$ in crosspoint architecture
- Thin film processing on flex substrate?





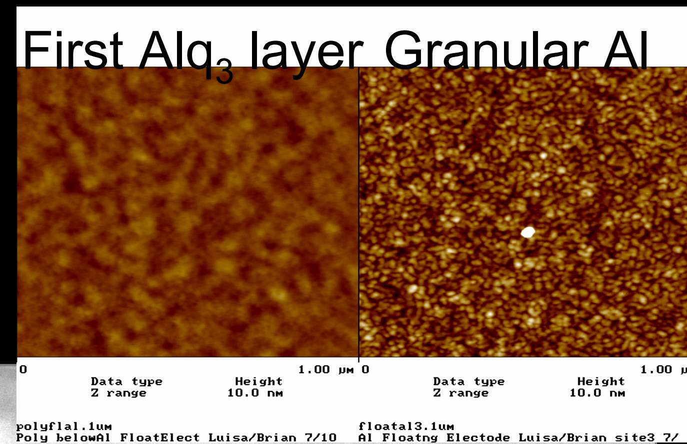
Motivation

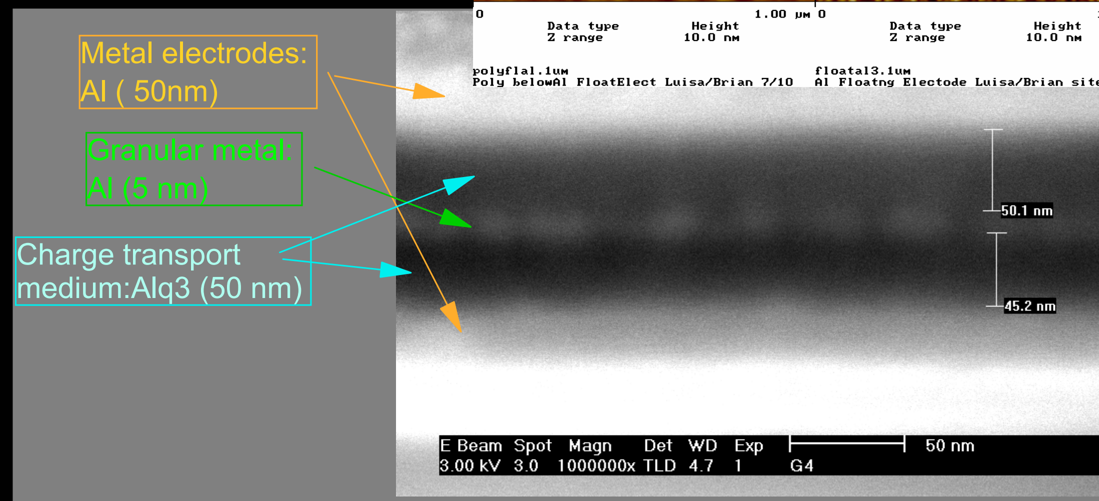
- Weaknesses of HDD
  - Reliability of moving parts
  - Long access times
  - High standby power
  - Poor granularity (higher cost/GB at lower capacity)
- Weaknesses of Flash
  - Relatively low endurance (10^5 – 10^6 write/erase cycles)
  - Long write times (2 ms erase, 200 μs write)
  - Scaling (45 nm or 32 nm?)

Device structure

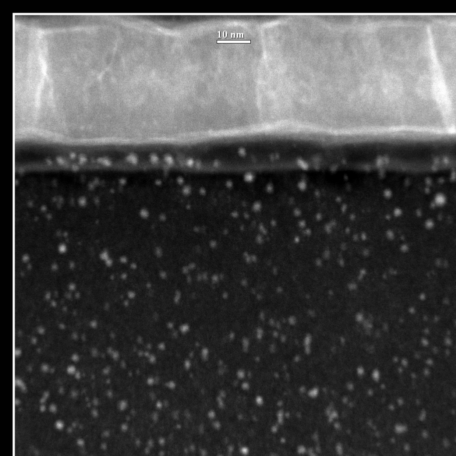
- Metallic nanoparticles imbedded in semiconducting host matrix
- Sandwich between metal electrodes
- Fabrication:
  1. Thermal evaporation
     Island growth of metallic layer
  2. Spin coating of polymer/NP blend
     NP (~ 1 – 10 nm) dispersed throughout polymer layer
     Multiple layers w/wo NP

AFM
Jane Frommer





FIB SEM by V. Deline



TEM
Phil Rice

L. D. Bozano et al.
Appl. Phys Lett., 2004

Materials

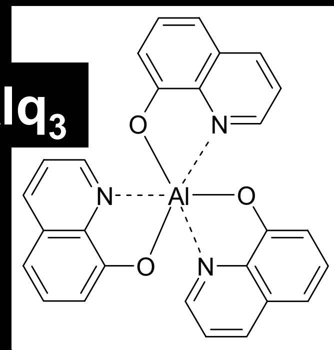
Semiconducting host

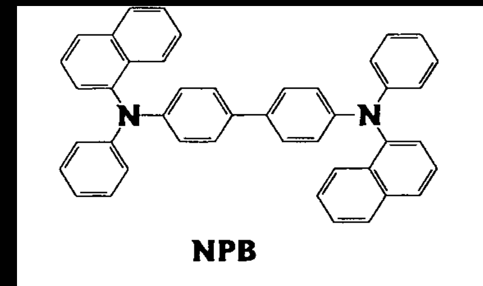
- Small Organic Molecule
  - Alq_3 - Electron transporting material
  - NPB - Hole transporting material
- Wide bandgap inorganic
  - SiO, ZnSe
- (X-linkable) Polymer
  - Arylamine - X-HTPA
  - Conjugated polyfluorene - X-DHF
  - Poly(biphenylmethylene) e.g. xBPF6

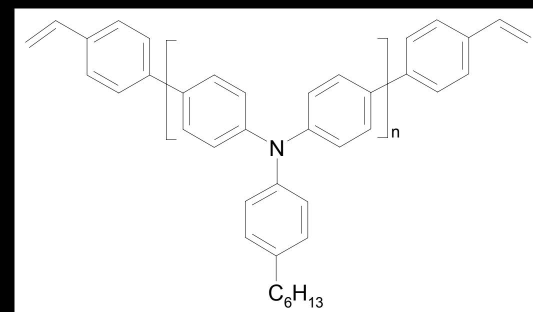
Metal electrodes and NP

- NP: Au
- Evaporated islands: Cu, Cr, Al, Ag, Au, Mg
- Electrodes:
  - Anode: Au, Al, Ag, ITO, Cu, Cr, Ni
  - Cathode: Ca, Al, Cr, Au, Ag

Alq_3

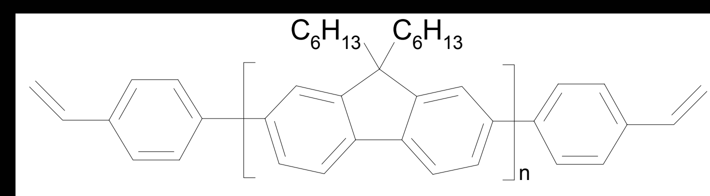




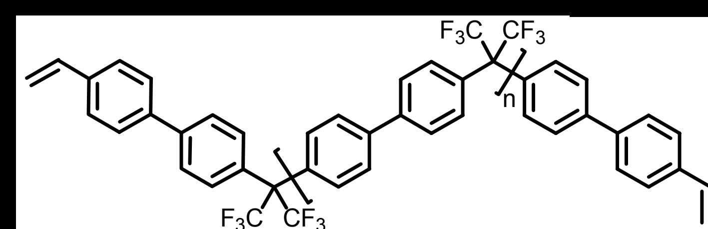


X-HTPA

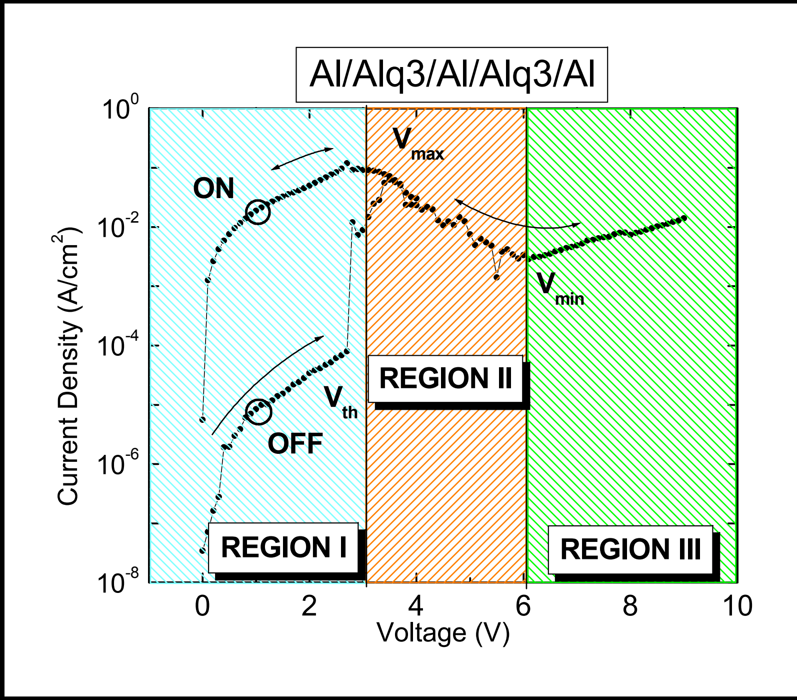
X-DHF

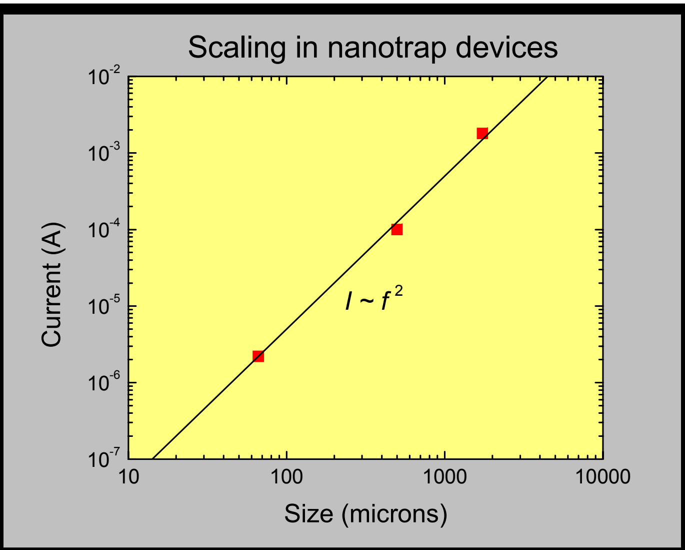


BPF6



Features of dc electrical response





- "N-shaped" current-voltage
  Negative quadrant similar
- Region I
  $V < V_{max} \sim V_{th}$: bistable region, current depends on history
- Region II
  $V_{max} < V < V_{min}$: negative differential resistance, noisy, irreproducible
- Region III
  $V_{min} < V$: monotonic
- Turn on with pulse near V_{max}
  Turn off with pulse near V_{min}
- (On) Current scales with device area

Nano-trap memory - Summary

- Good
  - On-off resistance ratio (> 100)
  - Switching time (< 1 μs)
  - Operating voltage (< 8 V)
  - Power consumption to switch (< 1 $\mu J/cm^2$)
  - Understand basic mechanism
- Promising
  - Retention time (> 1 y)
  - Cycling endurance (> 10^4)
  - On-state resistance, read time (high but getting lower)
- Poor
  - Rectification ratio (too low)