

February 2015

Nanotechnology and Display Applications

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Outline

- The relation between nanotechnology and display industry
- The colorful world of quantum dots
- Quantum confinement and properties of nanoparticles
- Si nanocrystals LEDs and lasers
- Photonic crystals
- The modern display industry always used nanotechnology!
 - LC alignment layers
 - PDLC
 - PSCT
 - Metal nanoparticles in liquid crystal
 - Nanochromics
 - Electrophoretic
 - Discotic polarizers

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- FEDs
 - CNT FEDs
 - HyFED
 - Metallic nanowires FEDs
 - Discotic liquid crystal FEDs?
 - Carbonaceous mesophase FEDs?
 - SED TV versus CNT FED TV
 - iMoD from Qualcomm
 - A “flexible” revolution and nanotechnology impact
 - OLED
 - Gyricon
 - E-Ink
 - Cholesteric
 - Self-assembled displays?
 - Conclusions



Nanotechnology definition (original)

Nanotechnology is a new scientific field evolving from material-specific peculiarities of present elements when their sizes become nanometric (one nanometer corresponds to the millionth part of one millimeter).

Alternative nanotechnology definition (1)

Nanotechnology describes the creation and utilization of functional materials, devices and systems with novel functions and properties that are based either on geometrical or on material specific peculiarities of nanostructure.

Alternative nanotechnology definition (2)

Nanotechnology is the scientific field encompassing the mastery of understanding and manipulating atomic and molecular matter and interactions as prerequisite for the optimization of existing products and the creation of new ones.

The vast interdisciplinary nature of nanotechnology will...

- ❑ Improve characterization and imaging (visualization)
- ❑ Increase capabilities of chemical/biological analysis
- ❑ Facilitate manipulation of nanostructures
- ❑ Enhance theory and modeling
- ❑ Reveal the role of surfaces and interfaces
- ❑ Control size distribution, composition and self-assembly of nanostructures
- ❑ Solve concerns of thermal and structural stability
- ❑ Achieve reproducibility and scalability in synthesis and manufacturing
- ❑ Create a new type of researchers that can work across traditional disciplines and think out of the box
- ❑ Induce the congregation of all disciplines from Physics to Chemistry and Biology to essentially all other engineering disciplines
- ❑ Generate self-assembled organic (even life matter) material that can form a template of scaffolding for organic and inorganic additives

What is needed to succeed?.. Creativity!

- New techniques must be discovered to organize, characterize and manipulate these nanoscale individual elements.
- Insights into self-organization principles of these nanoelements are necessary.
- Implementation of nanoscale architectures with new microscopic and macroscopic functions.
- Nanotechnology will catalyze the unification of processes from the living to the non-living worlds.
- Nanotechnology is revolutionizing materials' understanding and offers the capability to create new artificial materials (stronger, lighter, with pre-defined optical and electronic properties, etc.).

The building blocks of nanotechnology

- Ultra–thin layers
- Top down nanostructures
- Bottom up structures
- Ultra–precise surface preparation
- Analytical instrumentation for nanostructures
- Integration of nanomaterials and molecular structures
- Nanotechnology and biotechnology convergence

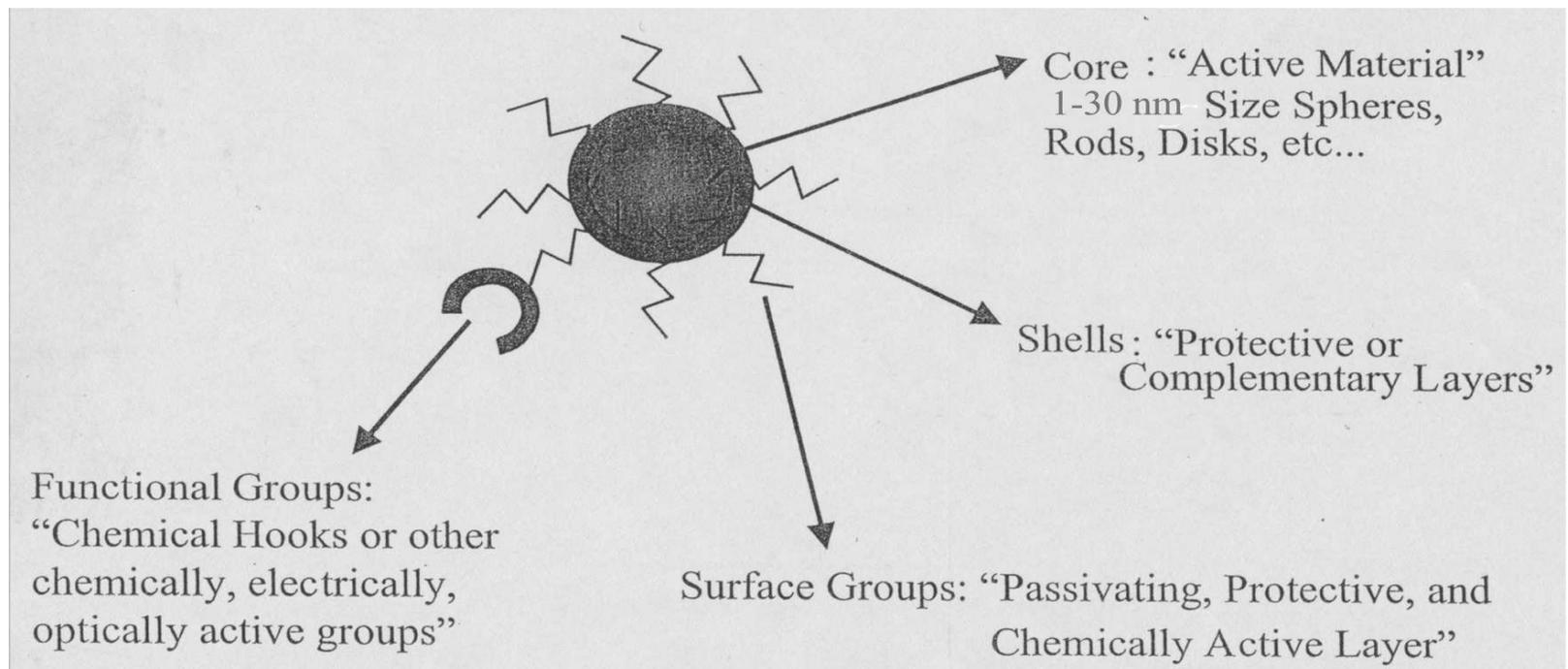
Alternative nanotechnology definition (3)

Nanotechnology is the “perfect scientific storm” in a place where all natural sciences congregate and intersect each other at the nanoscale. Nanotechnology is a creative and transformational technology.

Nanotechnology opportunities

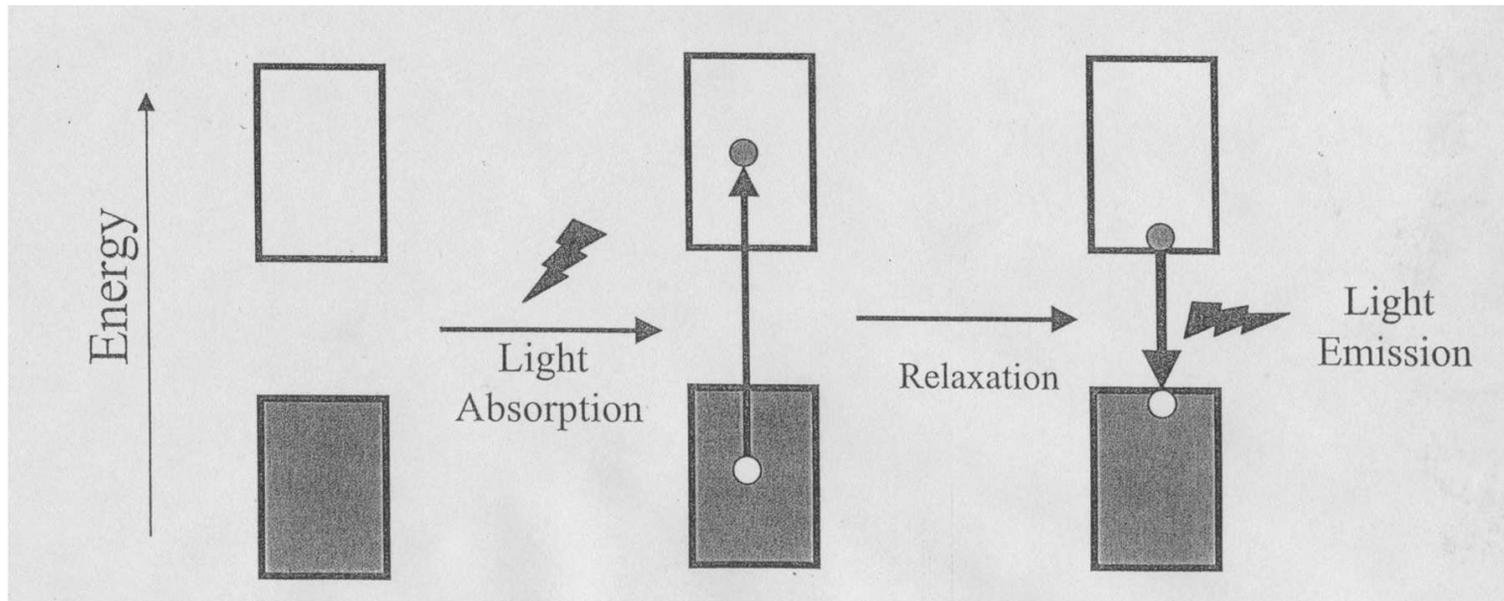
- Medicine/biology
- Chemistry
- New materials
- New nanoelectronic technology integrated with current microelectronics
- Optics and displays
- Applied research commercialization
- Defense and security

Basic nanocrystal QD architecture



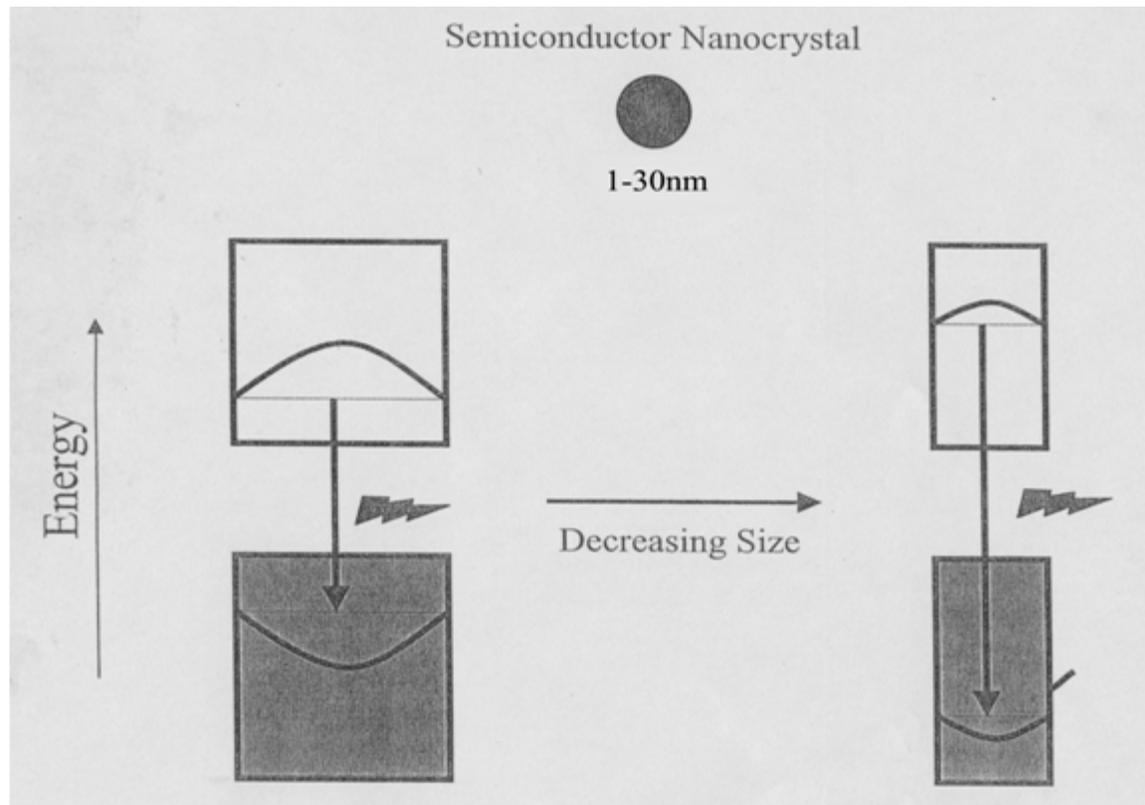
-- from Merrill Lynch presentation

Bulk semiconductor



-- from Merrill Lynch presentation

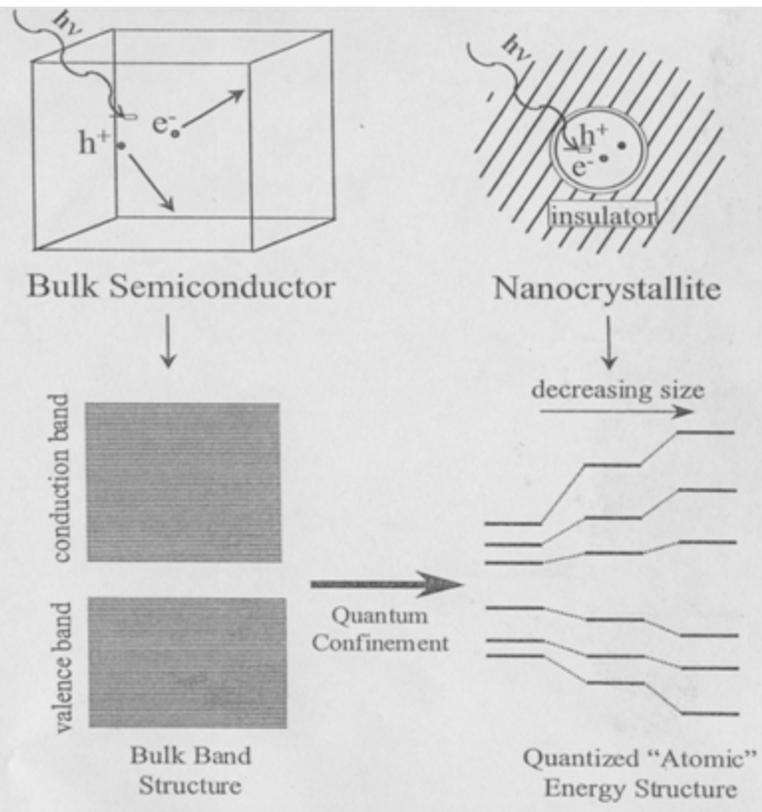
Why nanocrystals? Quantum confinement!



-- from Merrill Lynch presentation

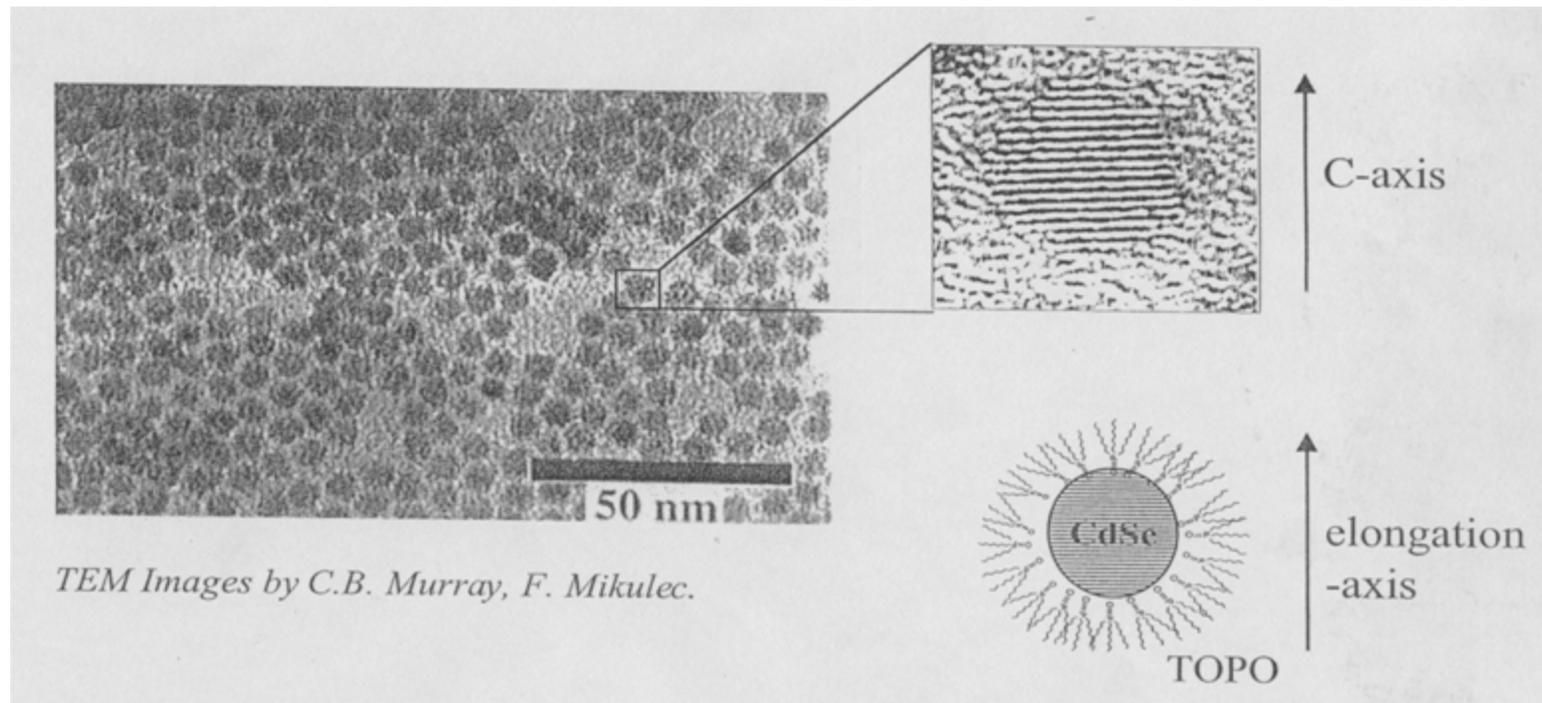
Quantum confinement

- Bulk Semiconductor
 - Free e^- and h^+ wavefunctions
 - Continuum of energy levels
 - Continuous absorption above the band-gap
- Nanocrystallite
 - Confined e^- and h^+ wavefunctions (particle in a box)
 - Quantized energy levels
 - Energy spacing dependent on nanocrystallite size
 - Tunable absorption spectrum w/discrete “atomic-like” peaks



-- from Merrill Lynch presentation

CdSe quantum dots



Si nanocrystals (quantum dots) produced by ANI

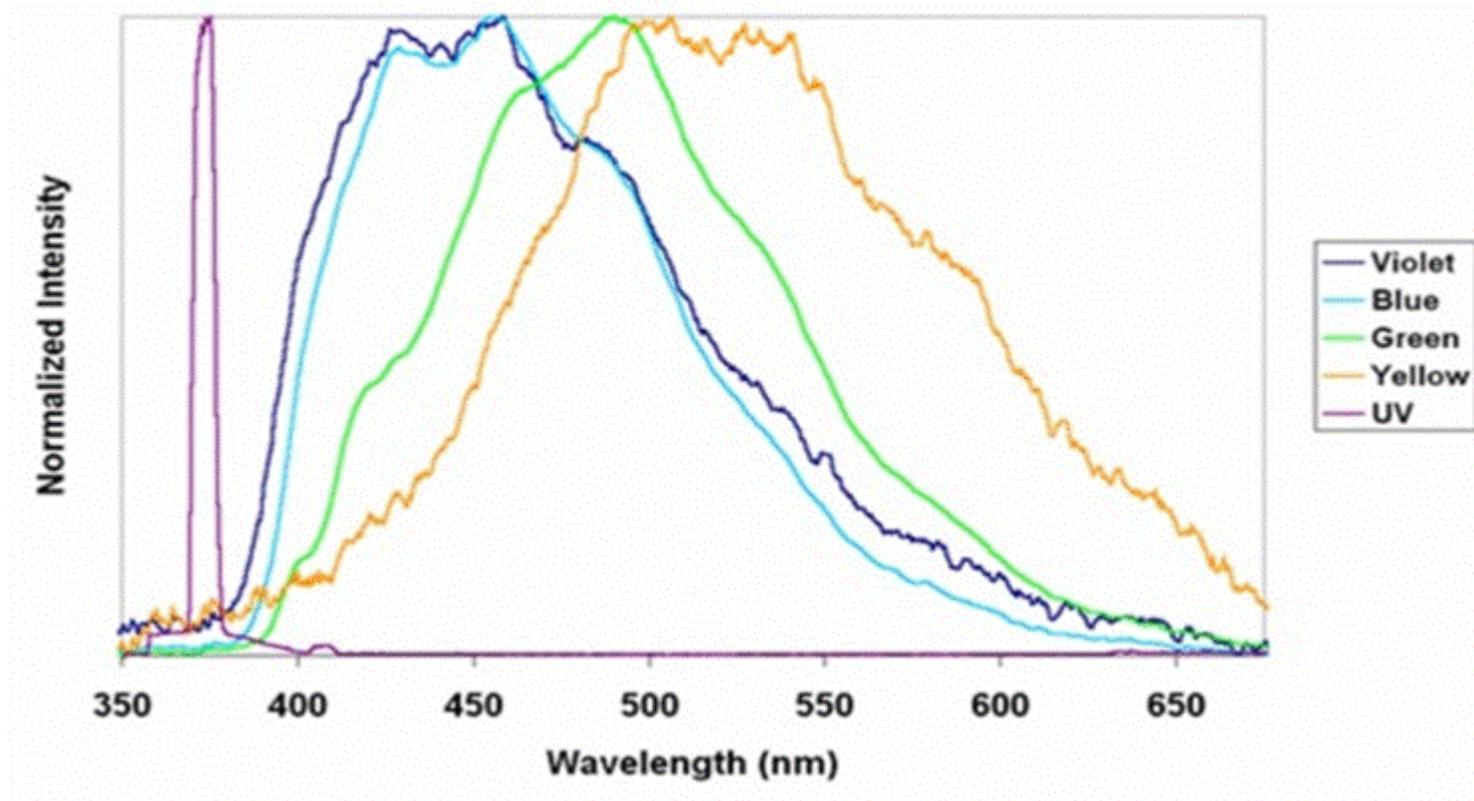


Visible Light



UV Light

Si nanocrystals photoluminescence



Heisenberg principle works!

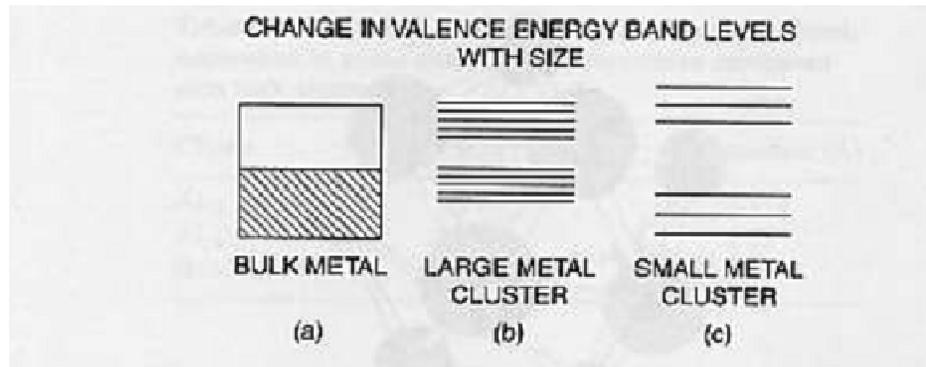
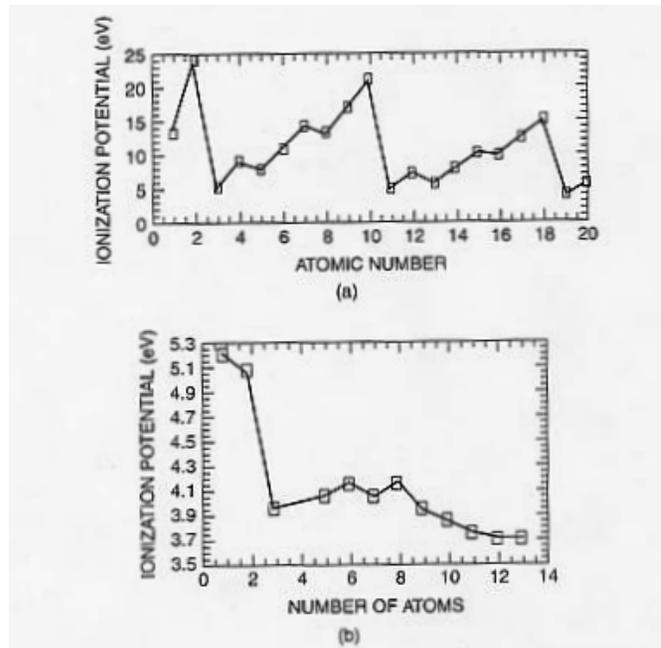


Illustration of how energy levels of a metal change when the number of atoms of the material is reduced: (a) valence band of bulk metal, (b) large metal cluster if 100 atoms showing opening of a band gap; (c) small metal cluster containing three atoms.

Metallic clusters behave as “super atoms”

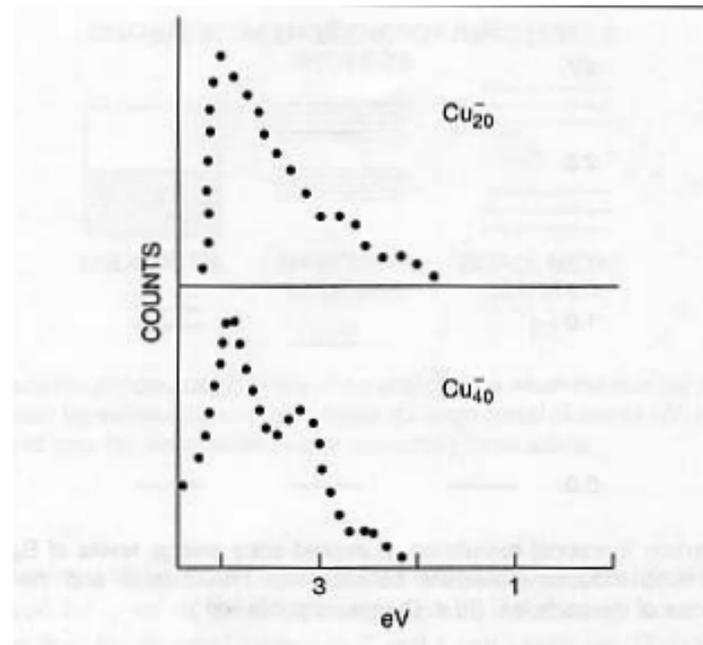


- (a) A plot of the ionization energy of single atoms versus the atomic number.
- (b) (b) plot of the ionization energy of sodium nanoparticles versus the number of atoms in the cluster. [A. Herman et al., J. Chem. Phys. 80, 1780 (1984).]



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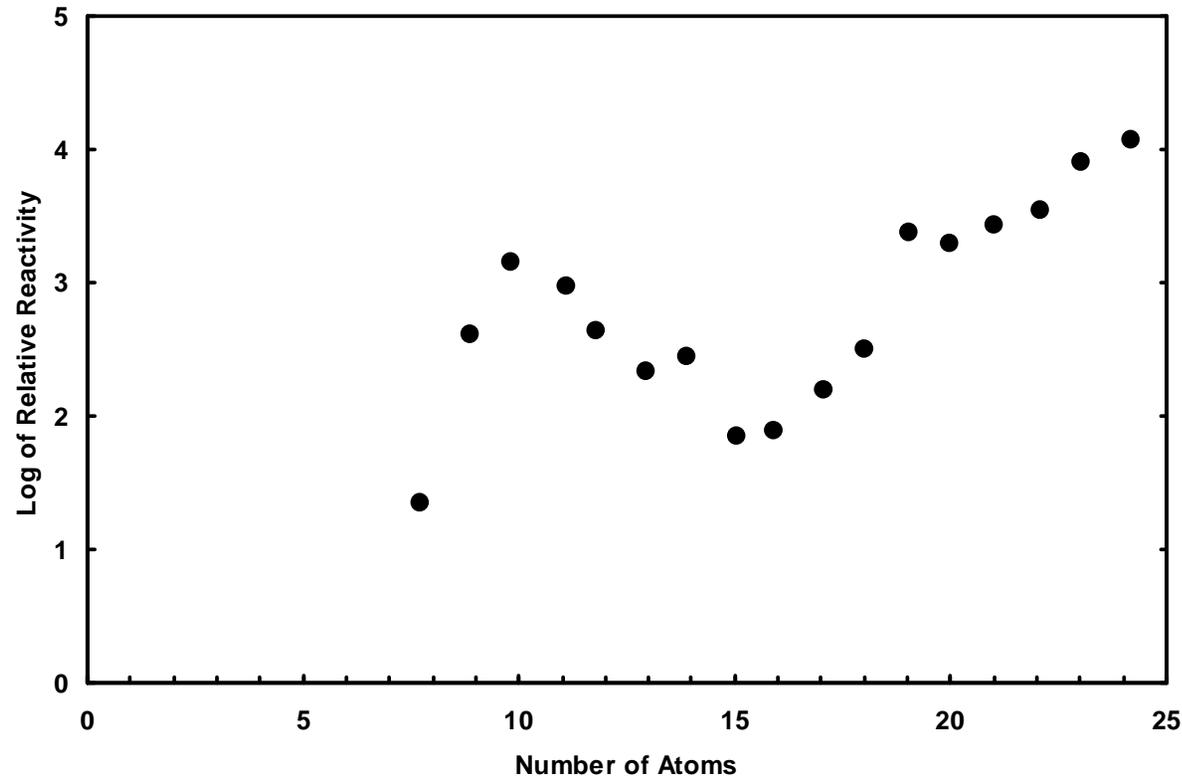
Properties of a cluster depend on the number of atoms



UV photoelectron spectrum in the valence band region of copper nanoparticles having 20 and 40 atoms.

C.L. Pattieta et. Al., J. Chem. Phys. 88, 5377 (1988).

Chemical reactions depend on a number of atoms in the cluster



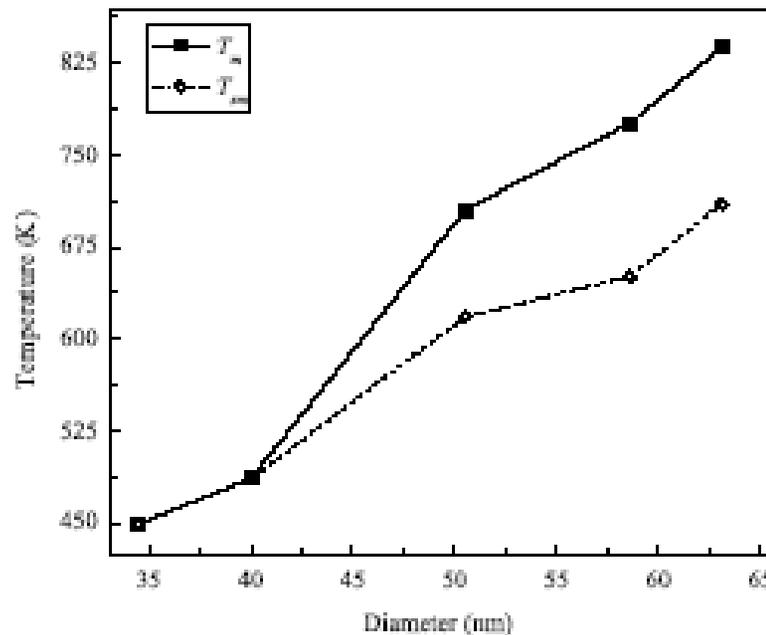
Reaction rate of hydrogen gas with iron nanoparticles versus the particle size.

R.L. Whetten et al., Phys. Rev. Lett. 54, 1494 (1985).



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Size dependent melting of Cu nanoparticles



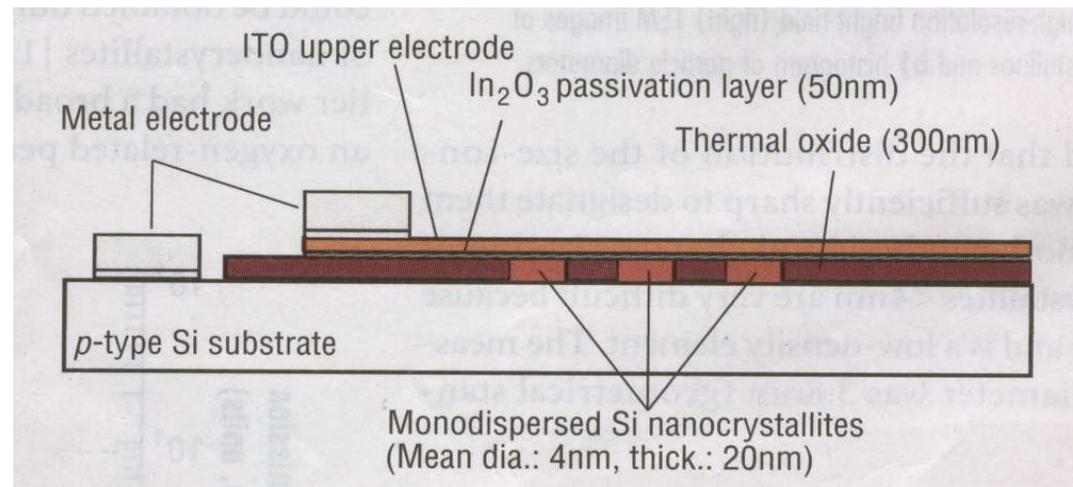
Dependencies of the temperature of melting and surface melting of copper nanoparticles on their diameter.

O.A. Yeshchenko, et al,

arXiv:cond-mat/0701276v1 12 Jan 2007

Near IR and visible LEDs fabricated from Si nanocrystals

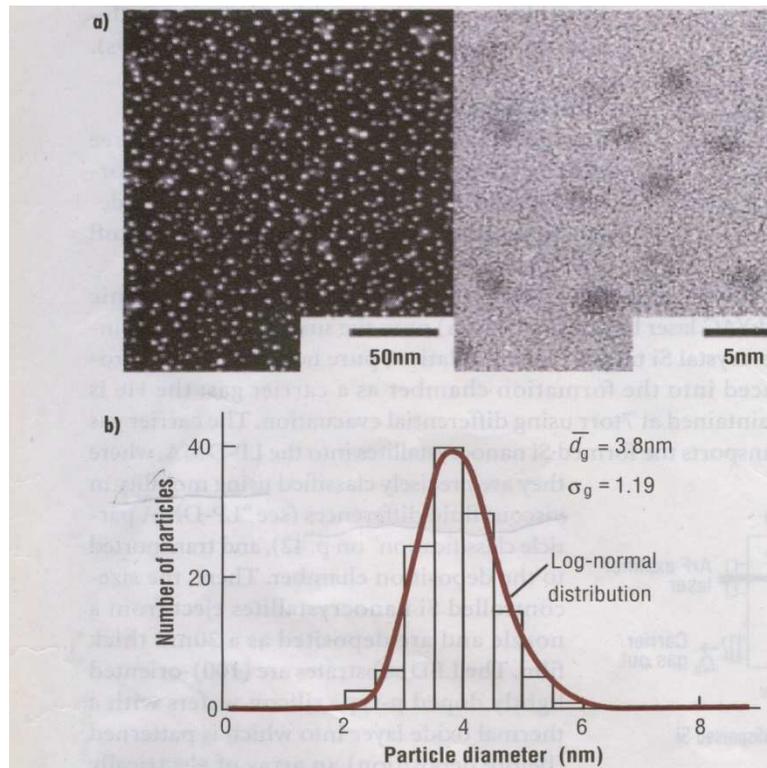
- Si nanocrystals by laser ablation
- Separation technique by differential mobility in a viscous fluid



T. Yoshida, N. Suzuki, T. Makino, Y. Yamada

Matsushita, Japan

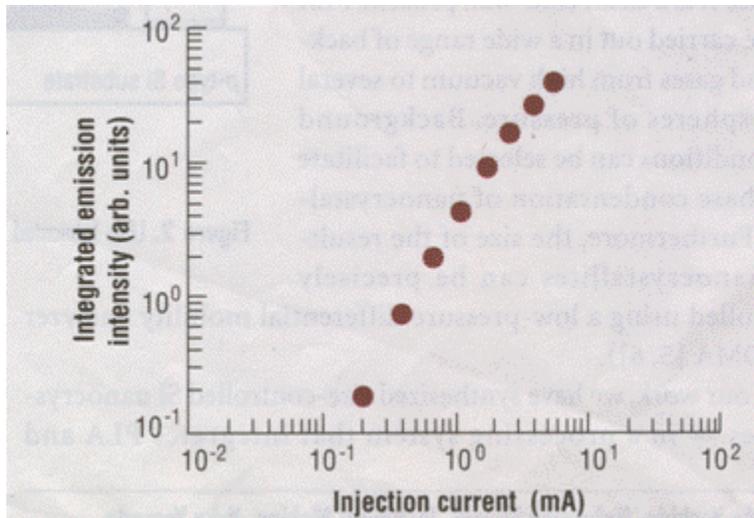
Monodispersed Si nanocrystals



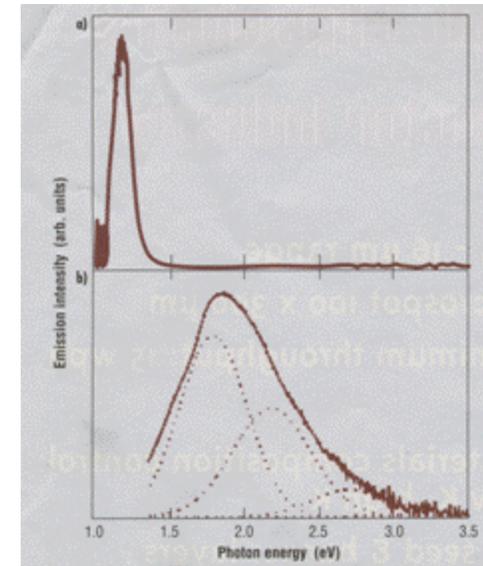
- a) Dark field (left) and high-resolution bright-field (right) TEM images of deposited monodispersed Si nanocrystallites
- b) Histogram of particle diameters

Solid State Technology, APR. 2002, pg. 41

Characteristics of Si nanocrystal LEDs



Integrated emission intensity as a function of forward injection current



Light emission spectra of LEDs at room temperature from:

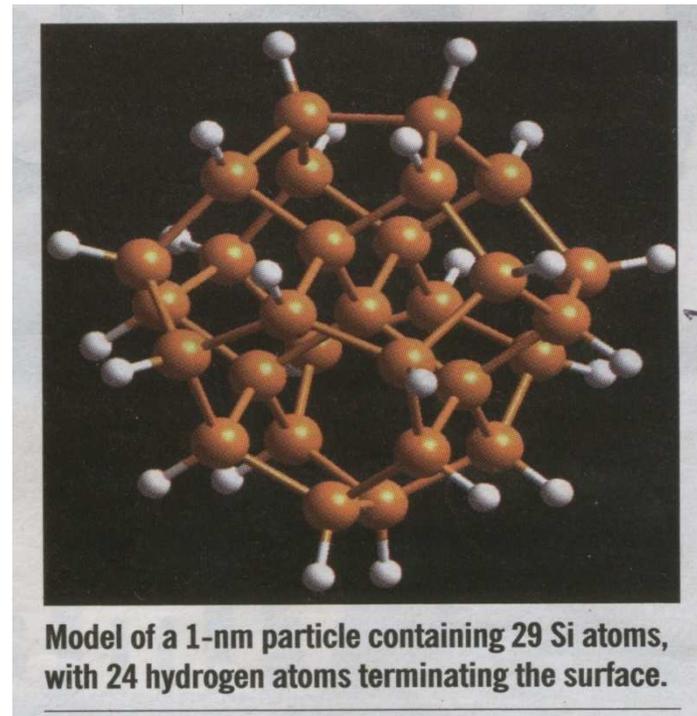
a) the clean sequential process without exposure to air after Si nanocrystallite deposition and

b) with exposure to air and thermal oxidation before In₂O₃ deposition. Dissipation power = 84mW

Solid State Technology, APR. 2002, pg. 41

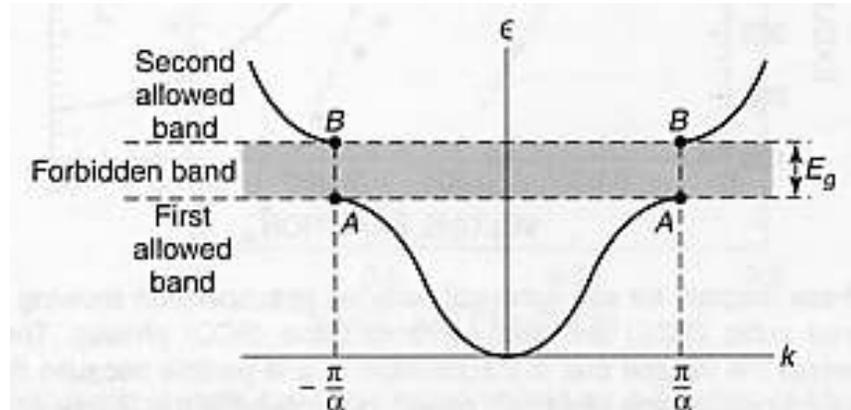
Microscopic lasers of Si nanoparticles

- In aggregates Si nanoparticles lased in response to a green mercury lamp
- In 6 μm aggregates Si nanocrystals can stimulate each other until a higher energy state is achieved resulting in laser action (blue and red lasers were demonstrated).



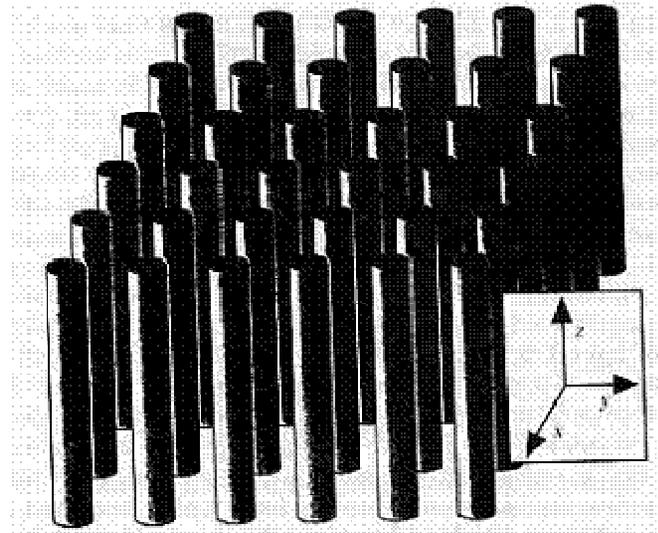
**University of Illinois, EE
Times, March 4, 2002, pg. 61**

Macrocrystals with photonic gap



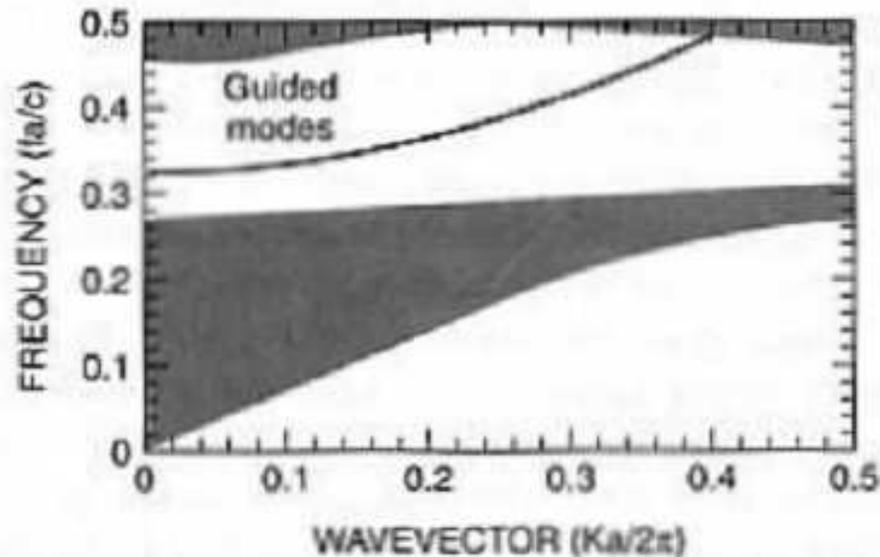
Curve of energy E -plotted versus wavevector k for a one-dimensional line of atoms.

Photonic crystals



A two-dimensional photonic crystal made by arranging long cylinders of dielectric materials in a square lattice array.

Guided modes in photonic crystals



Effect of removing one row of rods from a square lattice of a photonic crystal, which introduces a level (guided mode) in a forbidden gap.

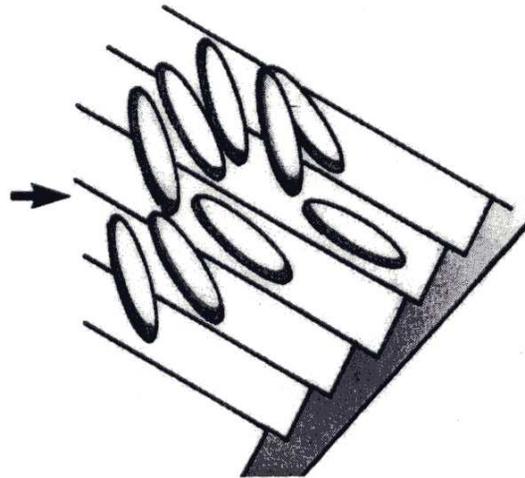
J. D. Joannopoulos, Nature 386, 143 (1970)

The LC nematic phase and molecular alignment

Natural state



Molecules are arranged in a loosely ordered fashion with their long axes parallel.



When flowing on a finely grooved surface (alignment layer)

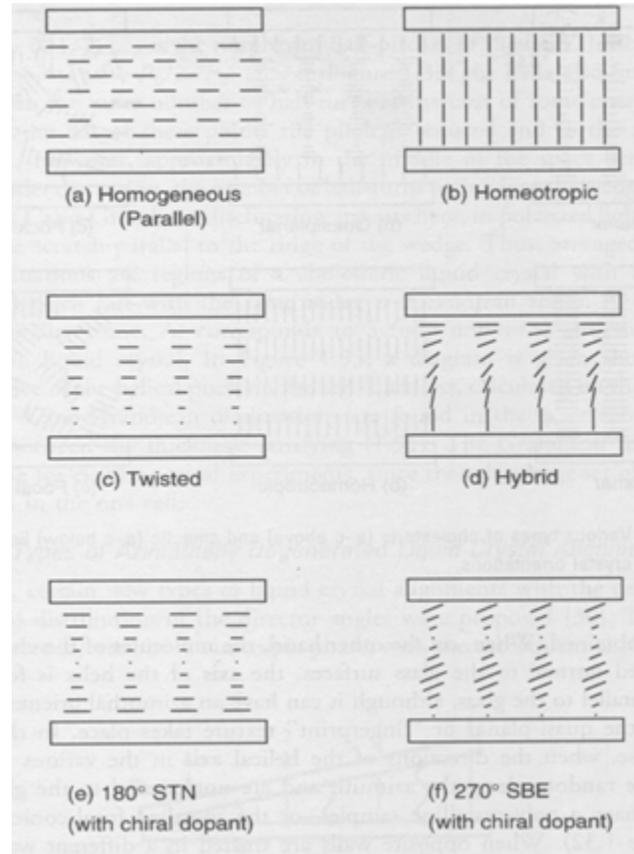


Molecules line up parallel along the grooves.



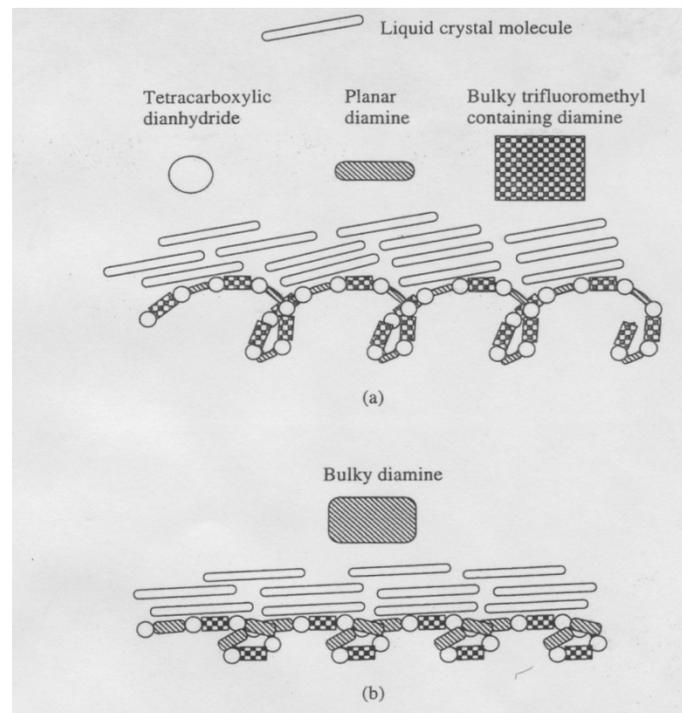
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Different types of nematic liquid crystal orientation



After V.G. Chigrinov

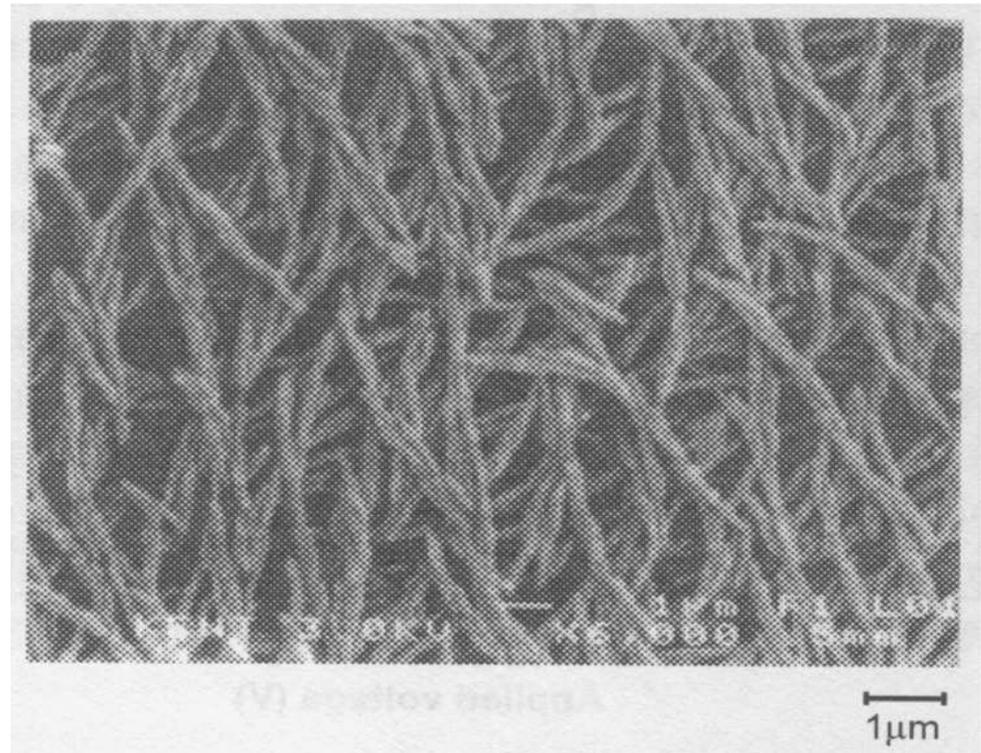
Influence of PI molecular shape



The role of the molecular shape of determining the surface molecular undulations

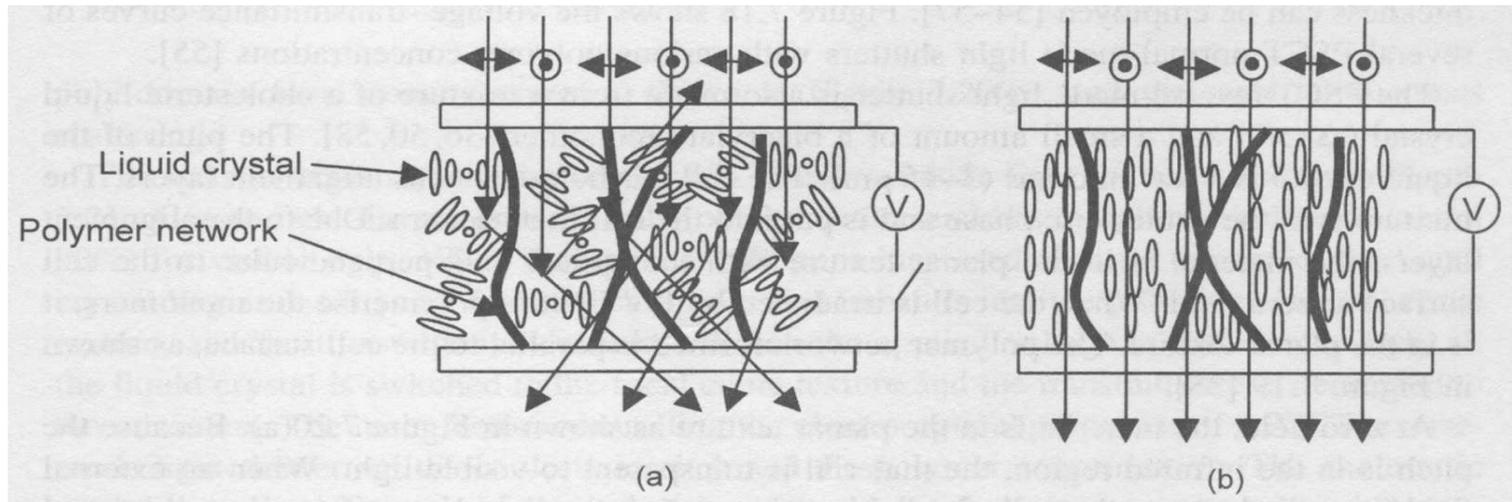
PSCT

SEM Photograph of
the polymer network
in PSCT reverse-
mode light shutter.



After Wu and Yang

PSCT



Schematic diagram showing how the polymer-stabilized cholesteric texture normal-mode light shutter works.

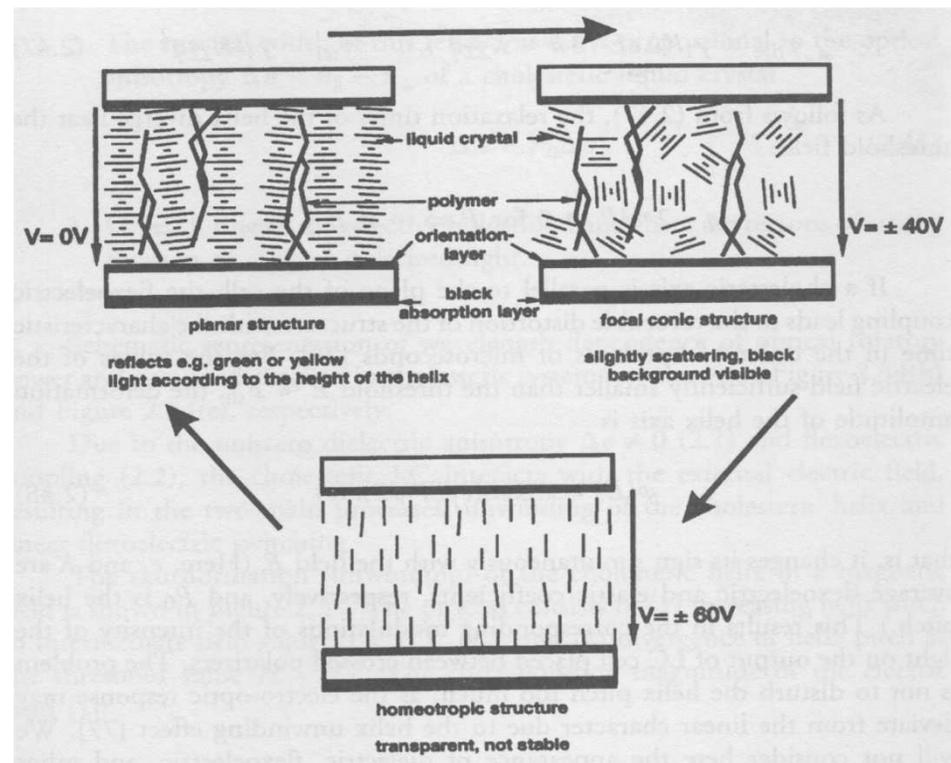
After Wu and Yang



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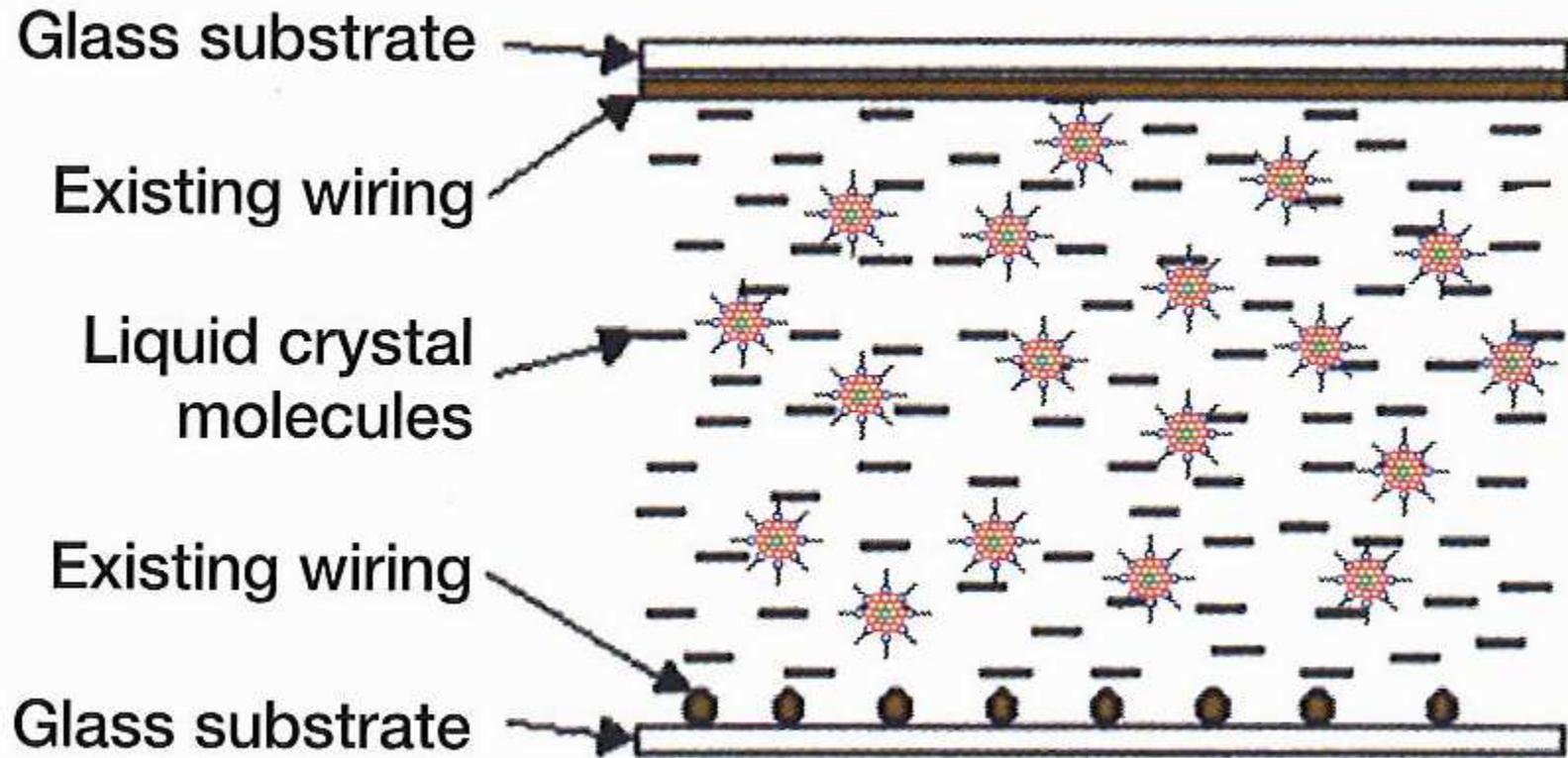
PSCTD

Switching between three cholesteric textures in PSCT configuration.

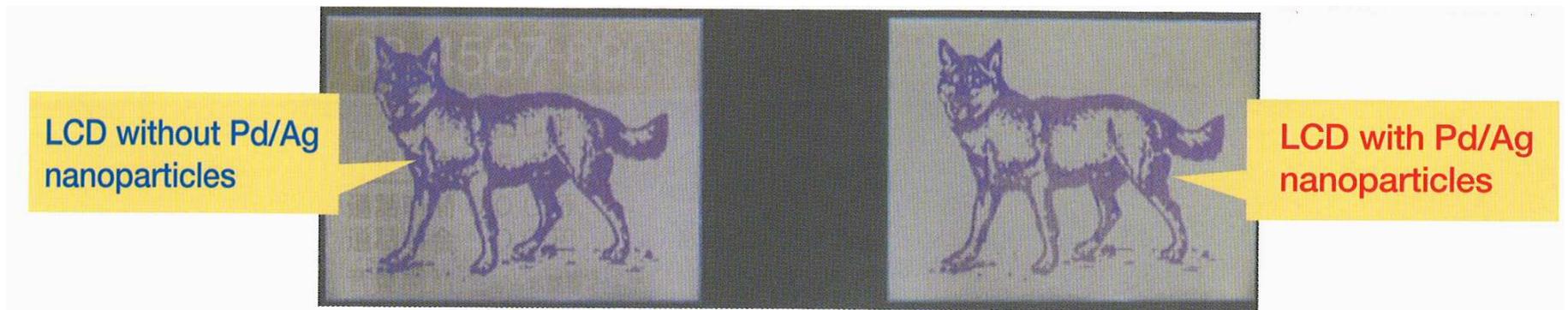


After V.G. Chigrinov

Metal nanoparticle doped liquid crystal



Metal nanoparticle dopped liquid crystal



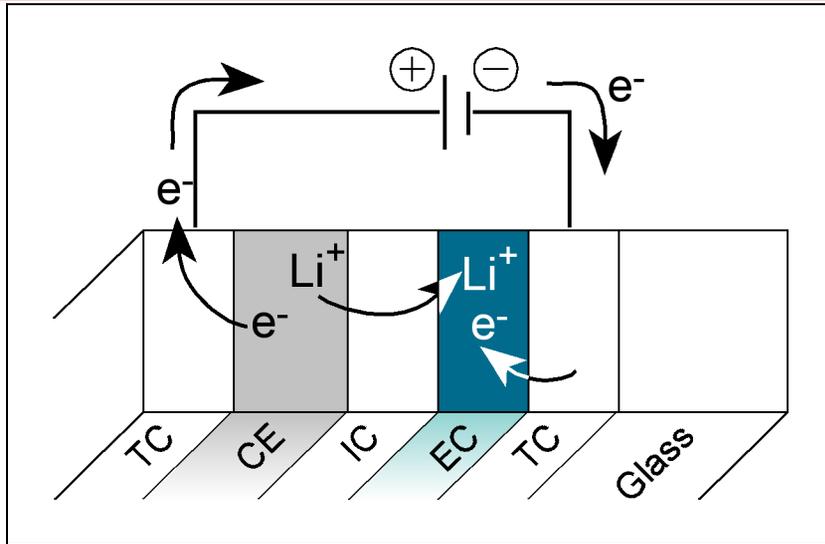
LCD response time and CR improved at -15°C

NanoChromics™ paper quality display technology

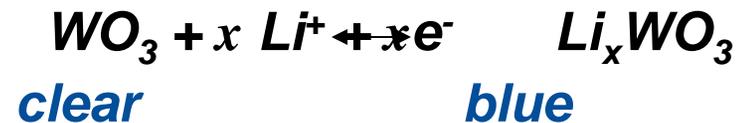
Electrochromic materials change their color under the influence of electricity

- Current areas of commercial applications
 - Anti-glare rear view mirrors (for over 10 years)
 - Smart windows (first products entering market)
- Electrochromic displays not currently on market
 - Slow switching speed and power consumption are listed as issues

Li Based EC Device (Sage Glass)



- **Based on reversible lithium insertion into EC layer, e.g.:**



- **State of coloration determined by x**
- **Lithium stored in CE in clear state**

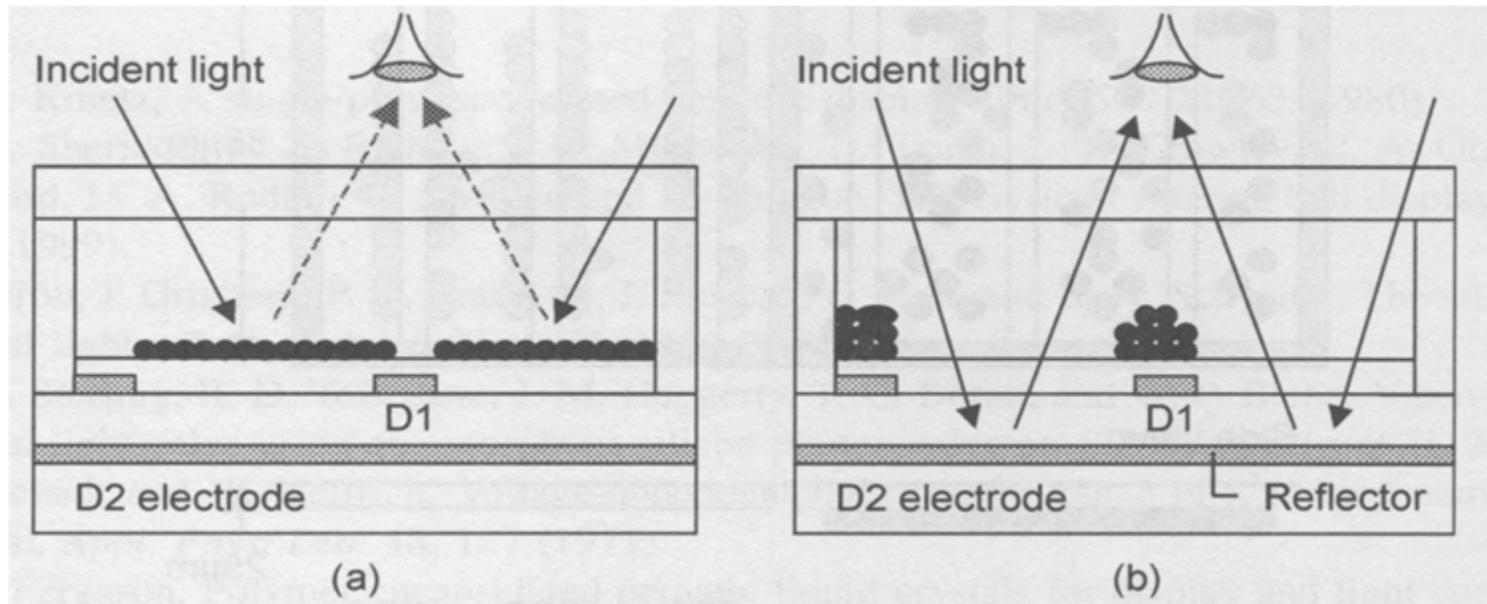
TC - transparent conductor - provides conductive path for electrons

CE - counter electrode - stores Li ions

IC - allows conduction of Li^+ ions & prevents conduction of electrons

EC - electrochromic electrode

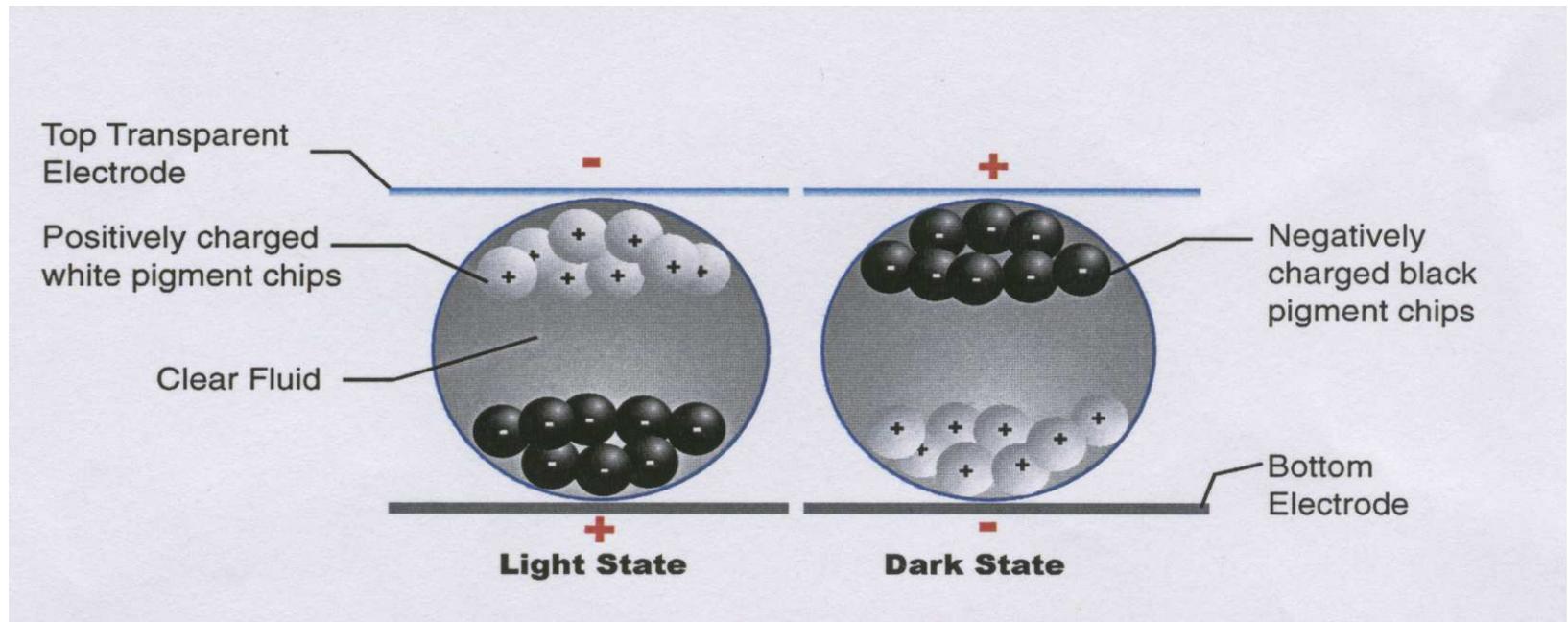
Electrophoretic display



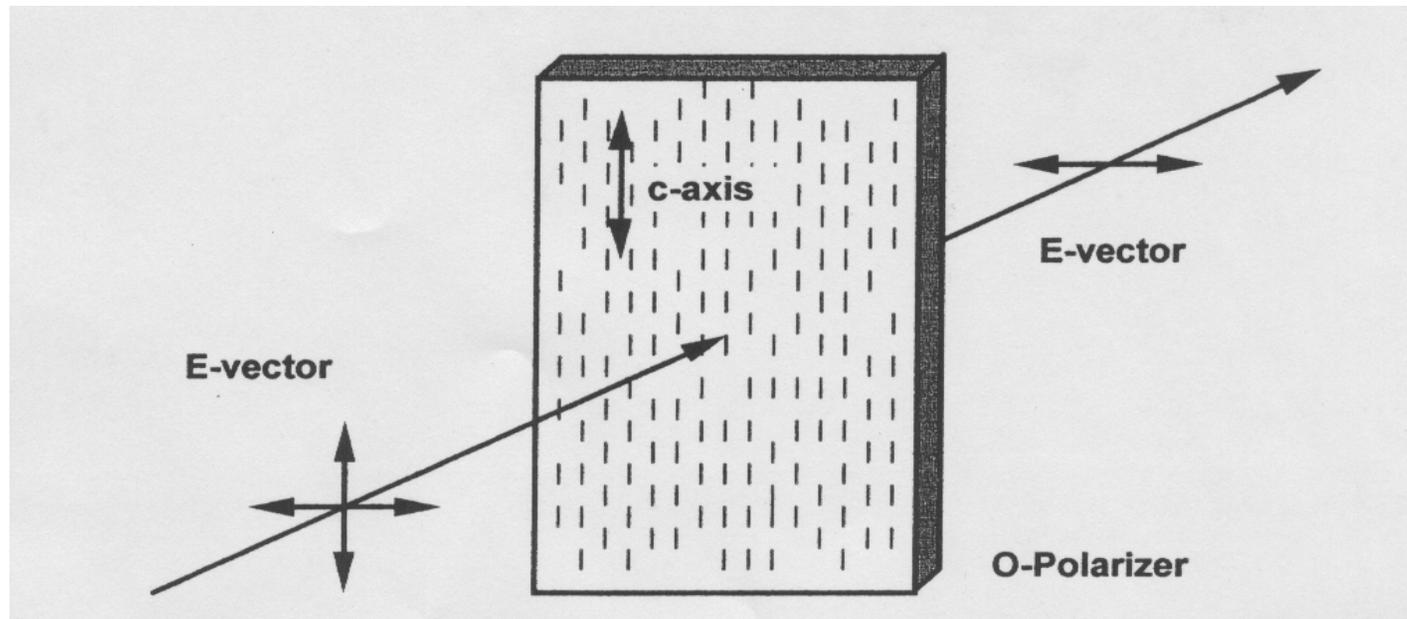
Device structure of an in-plane electrophoretic display:
(a) black state, (b) bright state.

After Wu and Yang

E-Ink



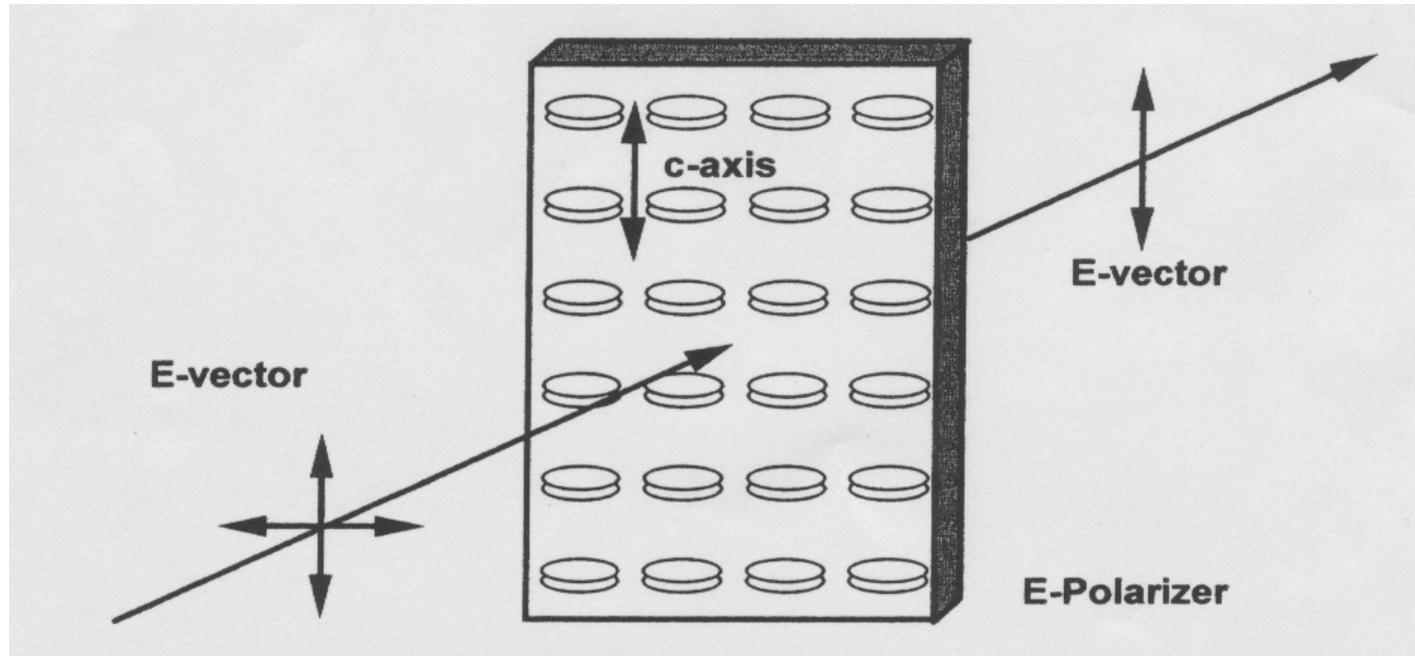
O-type sheet polarizers



Schematic drawing of an O-type sheet polarizer which transmits polarization component with E-vector perpendicular to the direction of alignment and absorbs polarization component with E-vector parallel to the directions of alignment.

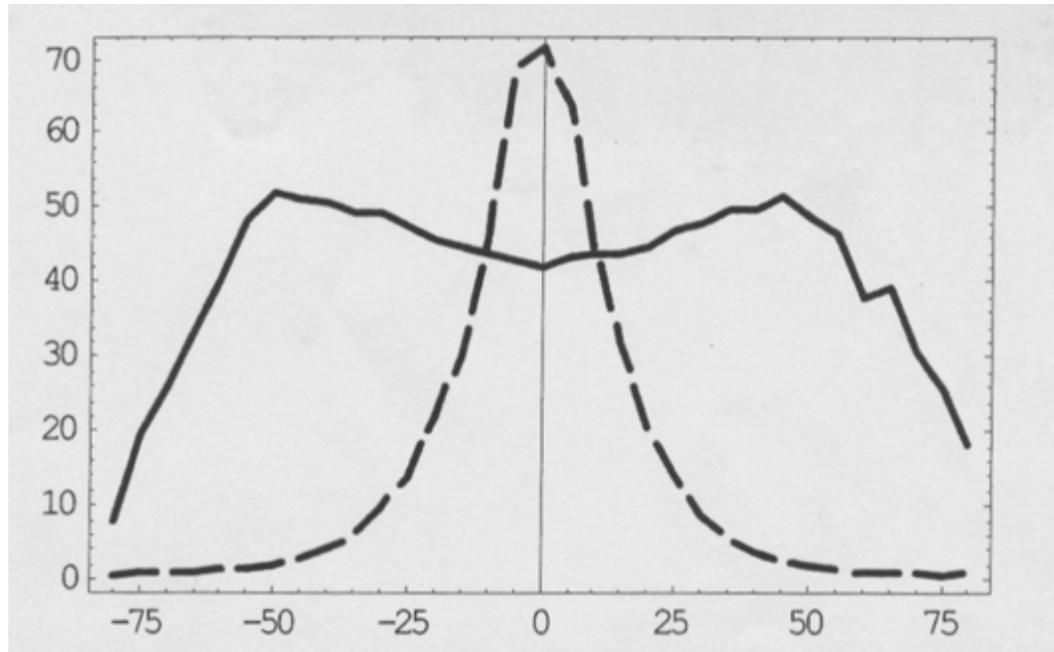


E-type sheet polarizers



Schematic drawing of an E-type sheet polarizer which transmits polarization component with E-vector parallel to the direction of alignment and absorbs polarization component with E-vector perpendicular to the direction of alignment.

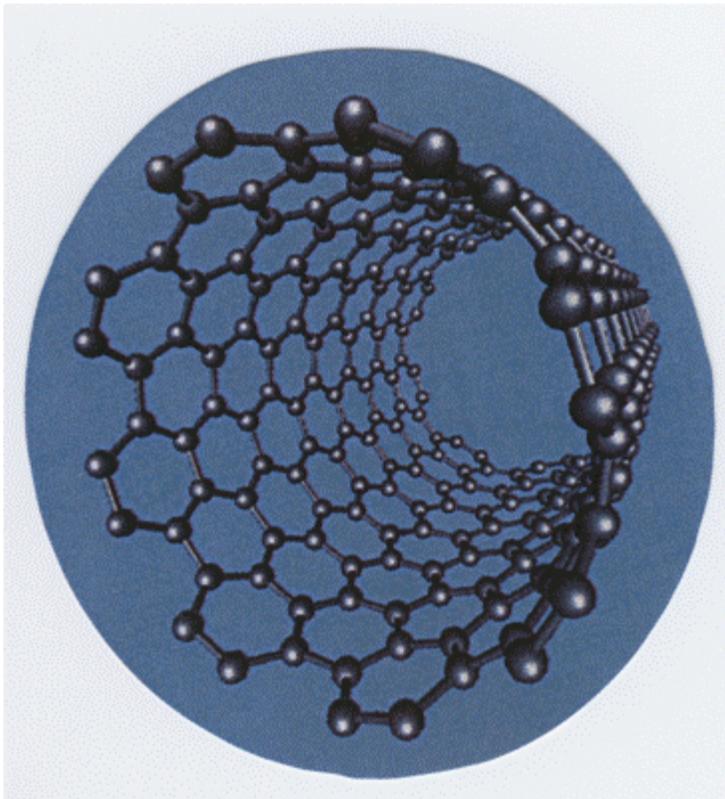
The contrast ratio dependence



The contrast ratio dependence of viewing angle in the range (-80°, 80°). The continuous curve is the contrast ratio for N600 OPTIVA polarizer. The dashed curve is the contrast ratio for the conventional (O-type) polarizer.



CNTs for FEDs



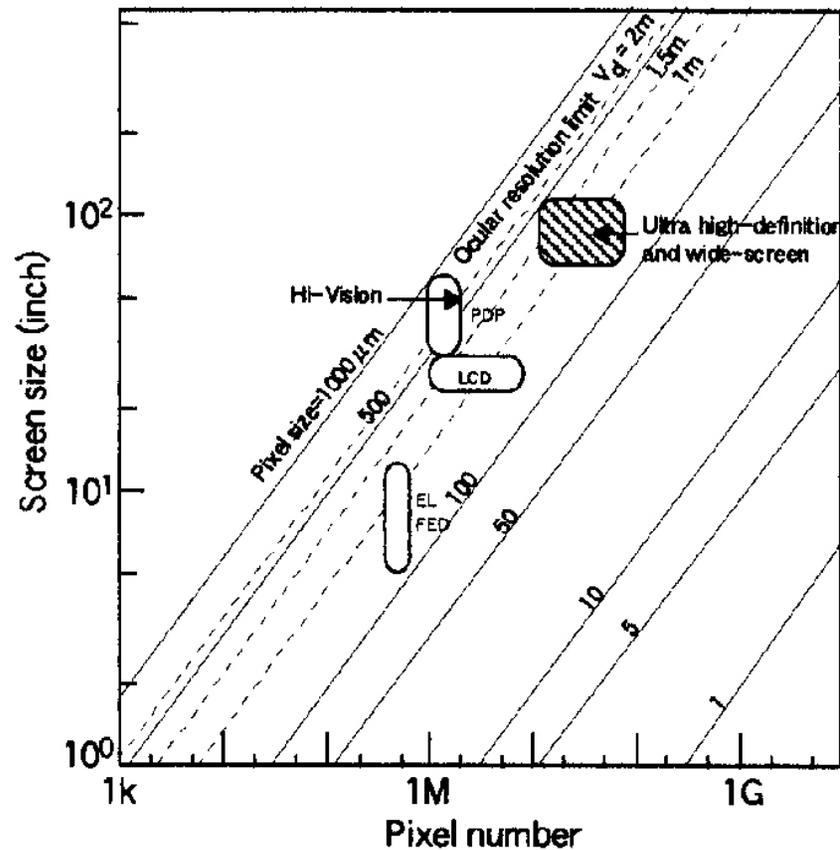
Why CNTs?

- The high current carrying capacity, huge thermal conductivity, length independent resistance and mechanical stability of metallic nanotubes suggests applications for microelectronic interconnects;
- The reasonably large band gap of narrow single-walled nanotubes suggests nanoscale transistors and diodes;
- The small radius of curvature at the tips of nanotubes suggests low-voltage field emission devices for flat-panel displays.

The top three markets for carbon nanotube thin film technology

- Large area color TVs
- Medium resolution large area electronic billboards
- Backlights for LCDs

Target for ultra-high definition and wide screen display



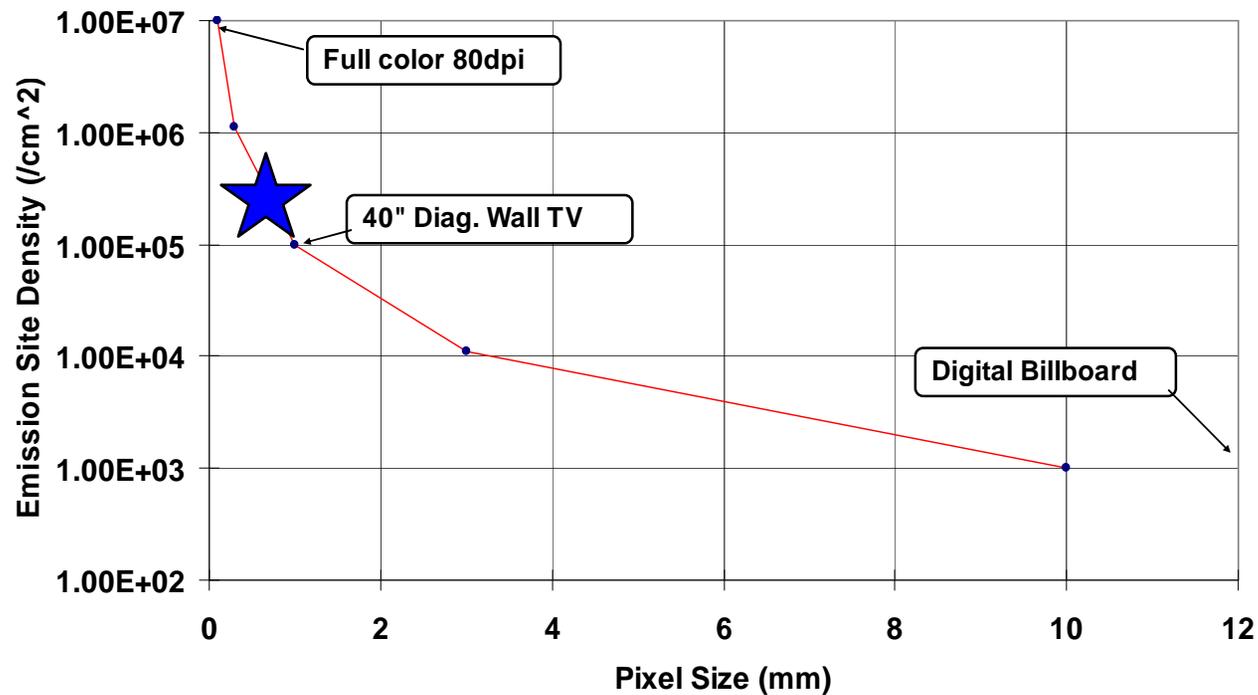
Data from F. Sato and M. Seki, IDW '01, p.1153

48

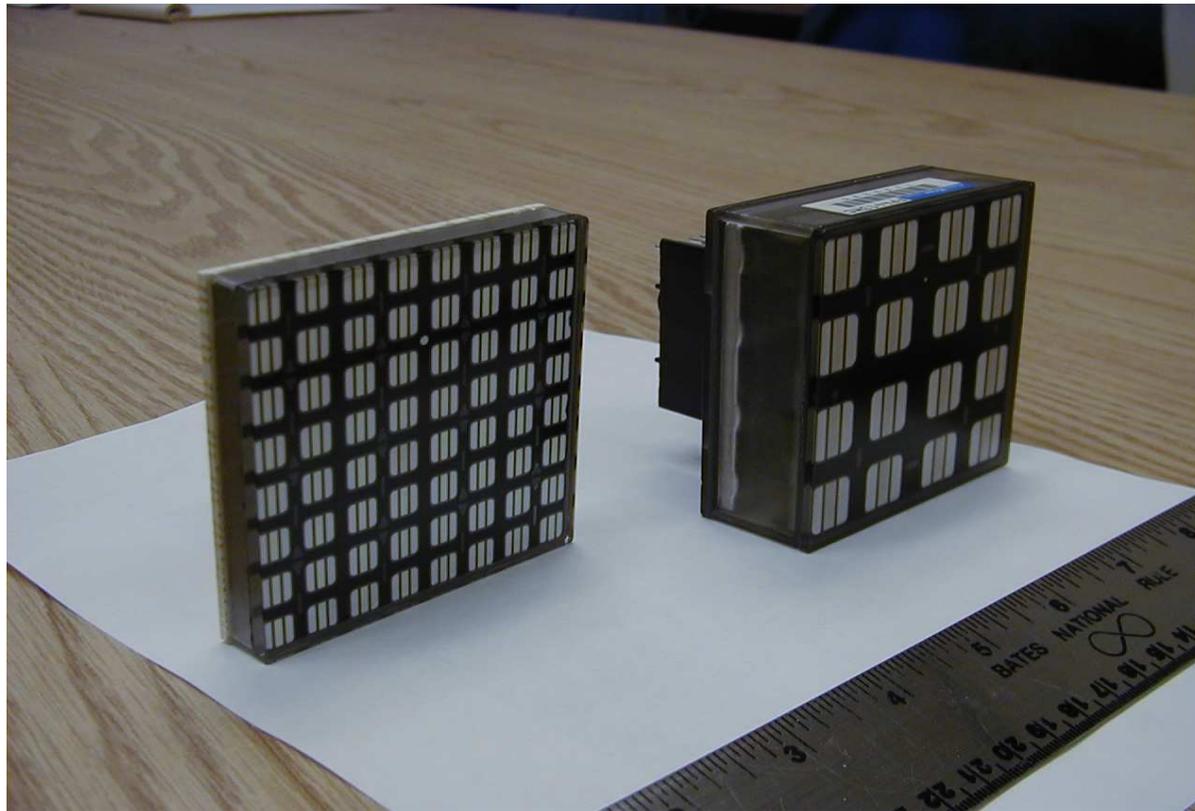


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Emission site density required for applications as a function of the pixel size



The FED PET and VFD PET (right)



SID 1997

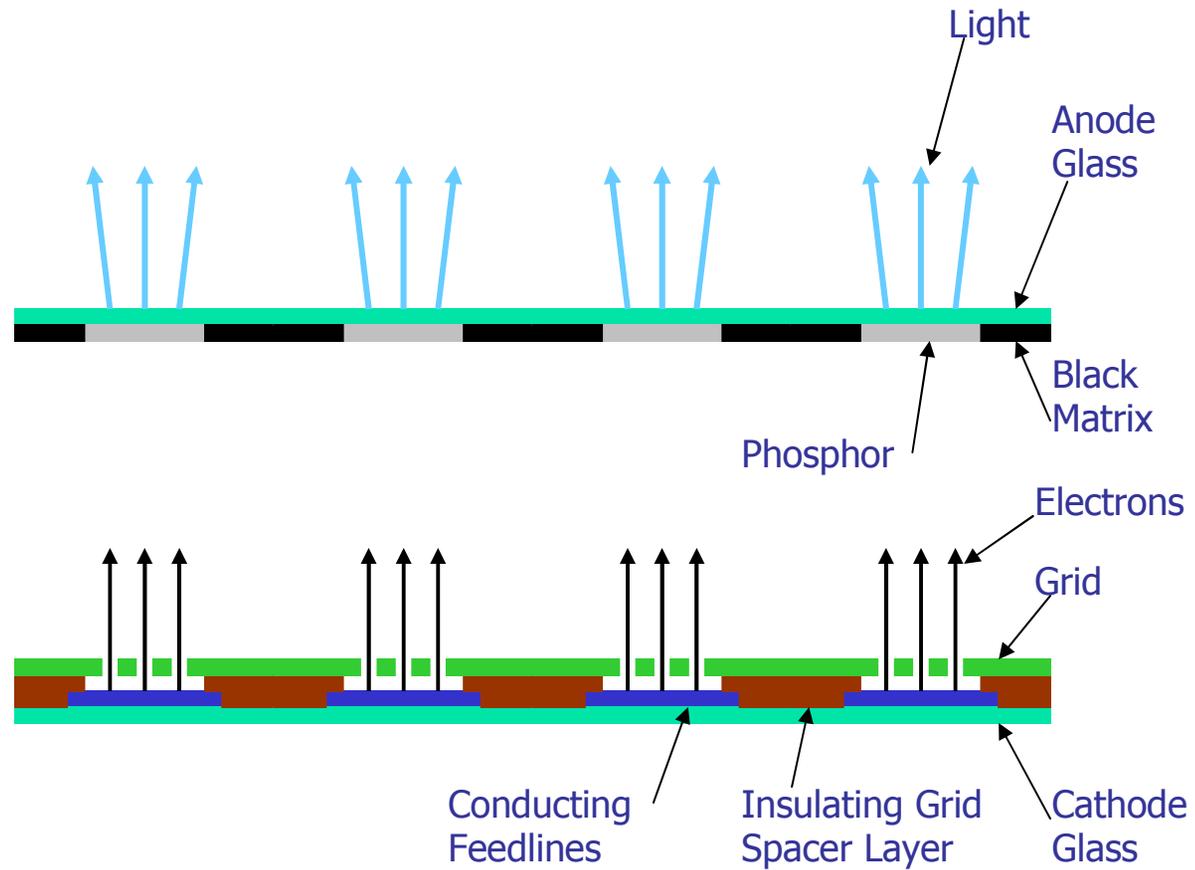


Applied Nanotech, Inc.

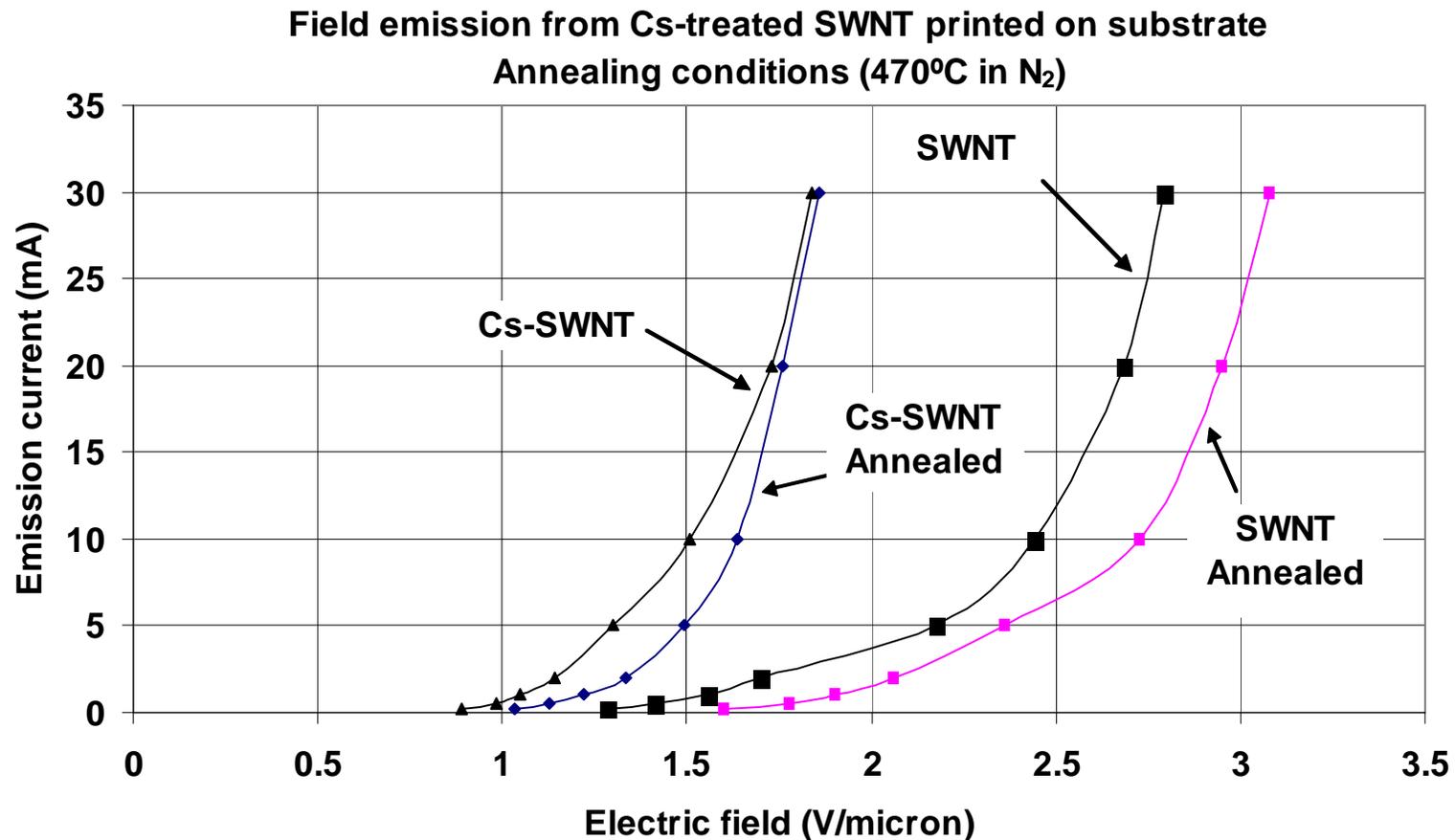
Large screen home FEDs

- Target market is 60"-80" display for home-use flat screen HDTV.
- "The field emission display (FED) is one of the most promising devices for this from viewpoints of energy efficiency, luminance, response time, etc." (F. Sato and M. Seki, NHK, IDW'01)
- Luminance $\sim 1000 \text{ cd/m}^2$
- Luminance efficiency (Lm/W) ~ 15

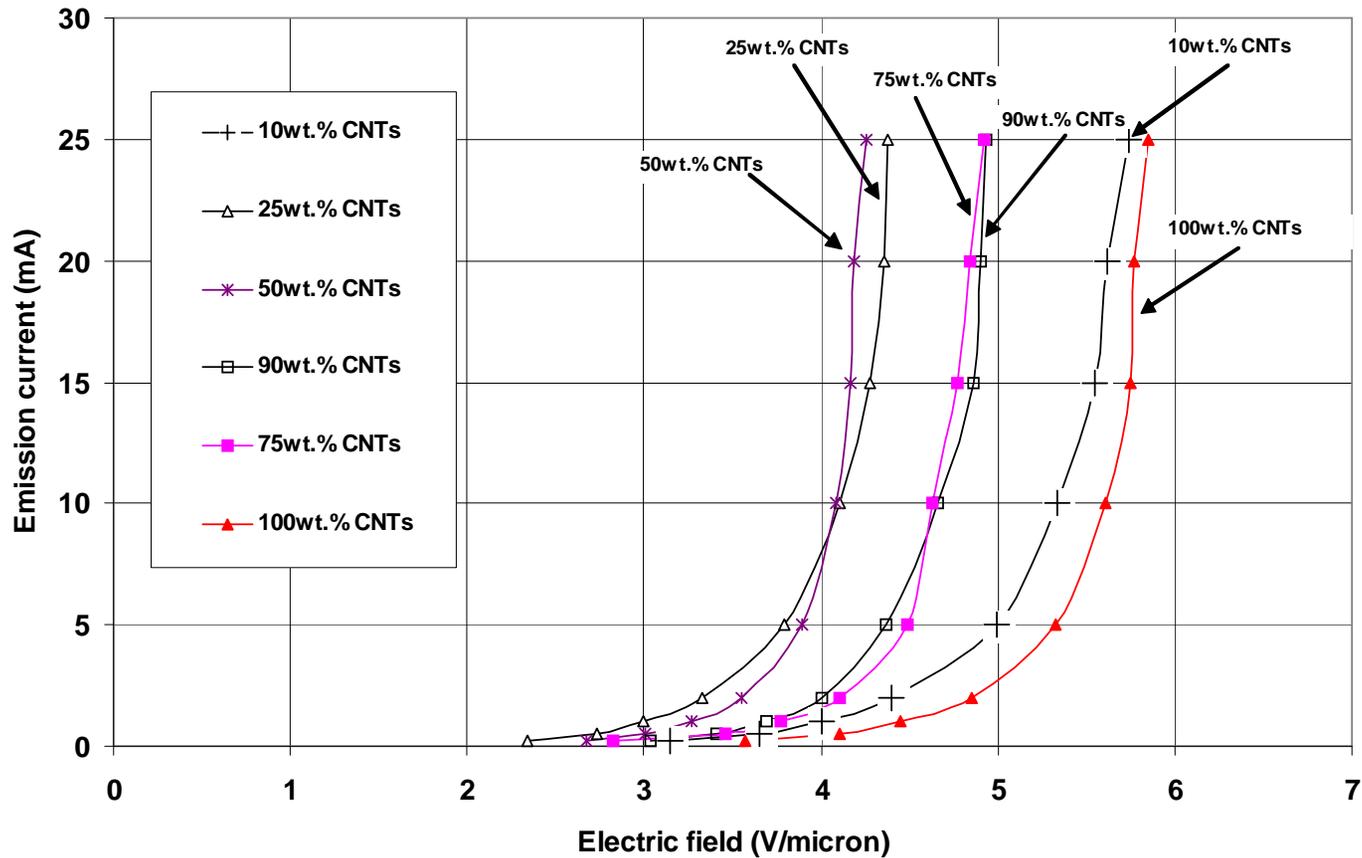
Cross-section of display structure



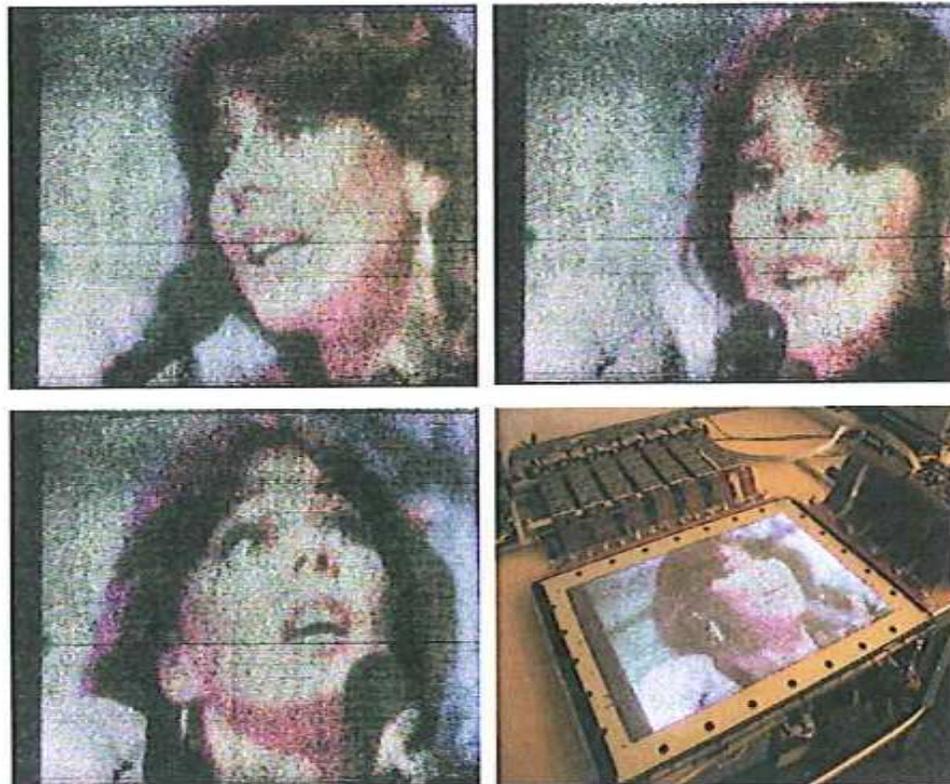
Cs treatment lowers driving voltage



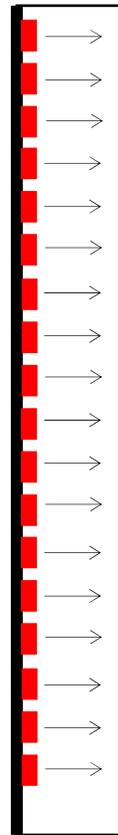
Field emission I-V of composites of various concentrations of CNT-nanoparticles



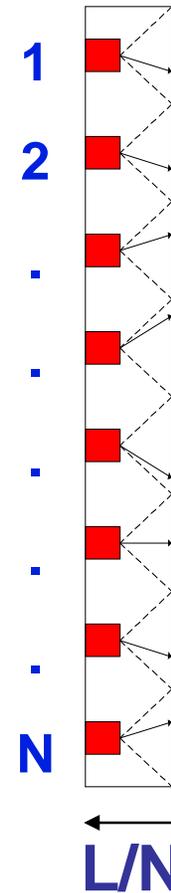
ANI's 25" color CNT TV



FED vs. HyFED™

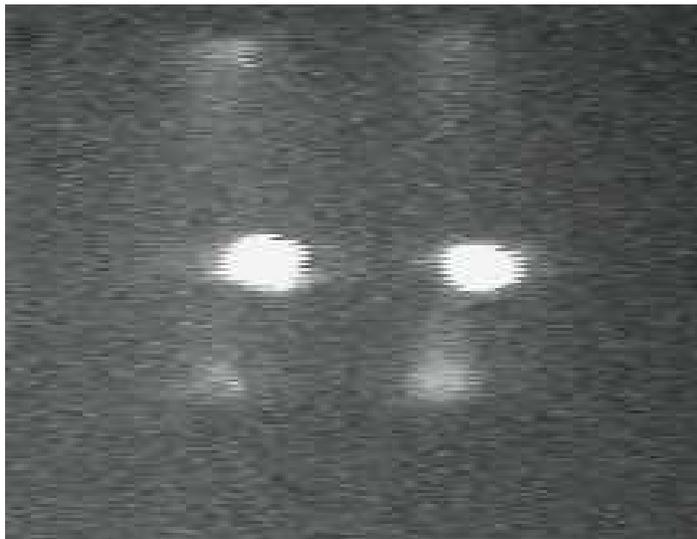


FED



HyFED™

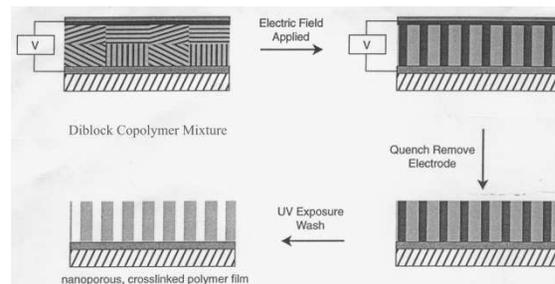
Demonstration of HyFED™



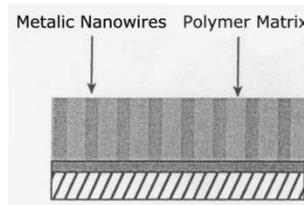
Two beams (left), each scanning 6x8 pixels at a resolution of 250 dots/inch (right).

Summer, 1998

Creation of ordered nanocylinders cavities film



Electrochemical Deposition

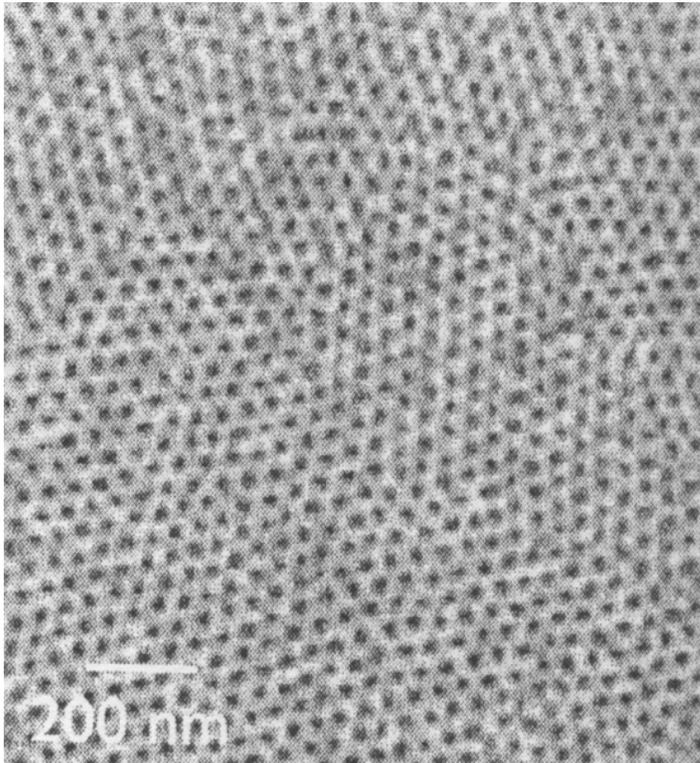


M. T. Tuominen and T.P. Russell. University of Massachusetts, USA.



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Organized metal cylinders in a polymeric matrix



Lattice: Hexagonal

PERIOD: $\approx 25\text{nm}$

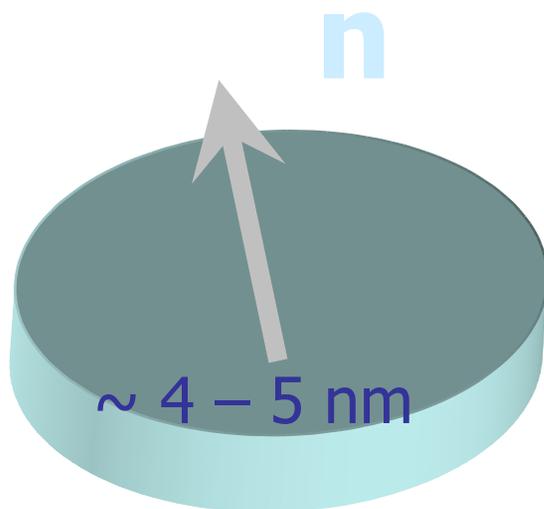
Cylinder Density $\approx 10^{12} \frac{\text{cylinders}}{\text{inch}^2}$



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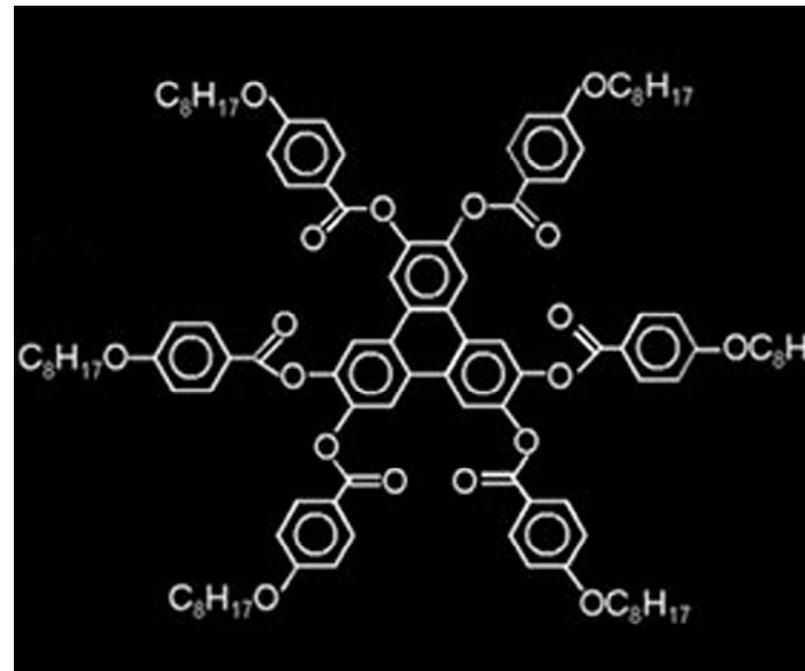
Discotic liquid crystal

Nematic Director



Physicist's view

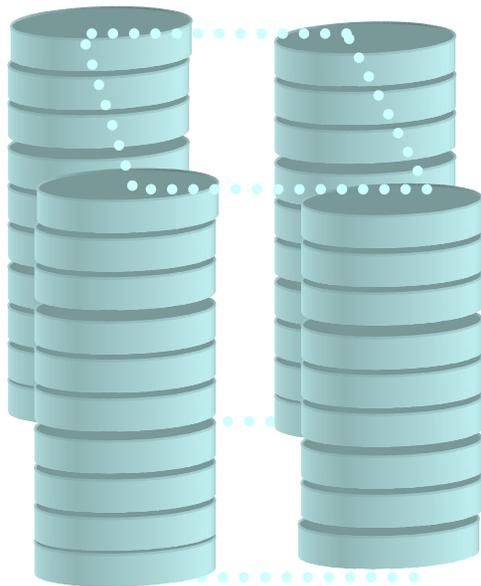
Chemist's view



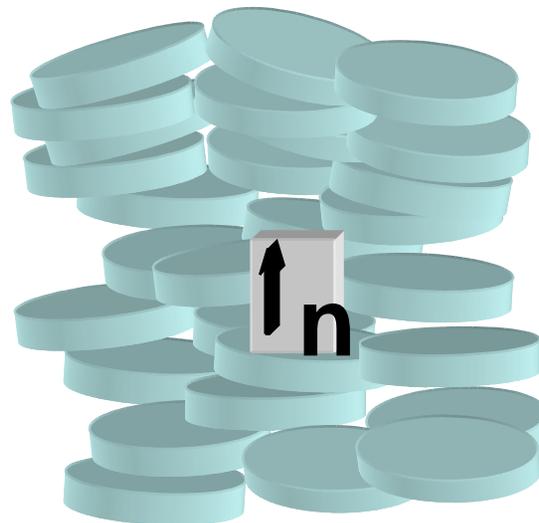
HBT8 (EM Industries) 2,3,6,7,10,11, - triphenylene hexa(octyloxy benzoate)
N. H. Tinh, H. Gasparoux, C. Destrade, *Molecular Crystal Liquid Crystal* **68**, 101 (1981)

Discotic liquid crystal

K - 152°C - Dr - 169°C - N_D - 244°C - I



Rectangular



Nematic Discotic



Isotropic

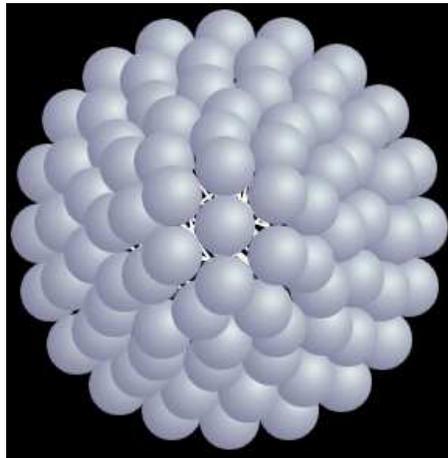
Temperature

N. H. Tinh, H. Gasparoux, C. Destrade, *Molecular Crystal Liquid Crystal* **68**, 101 (1981)



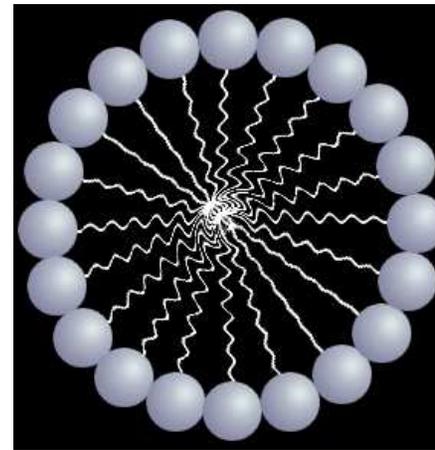
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Liquid crystals (membranes)

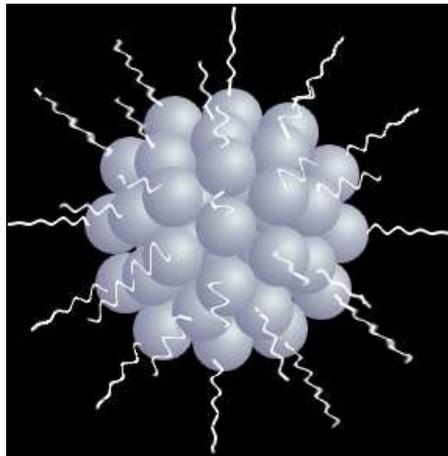


Lyotropic

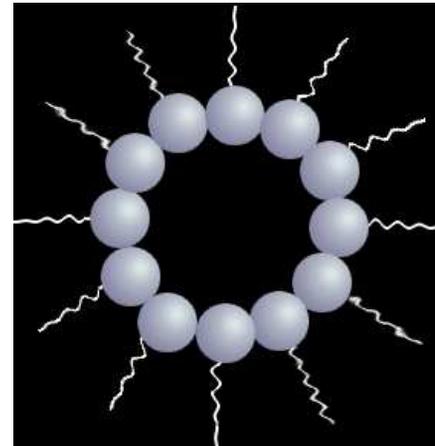
micelle



cross section

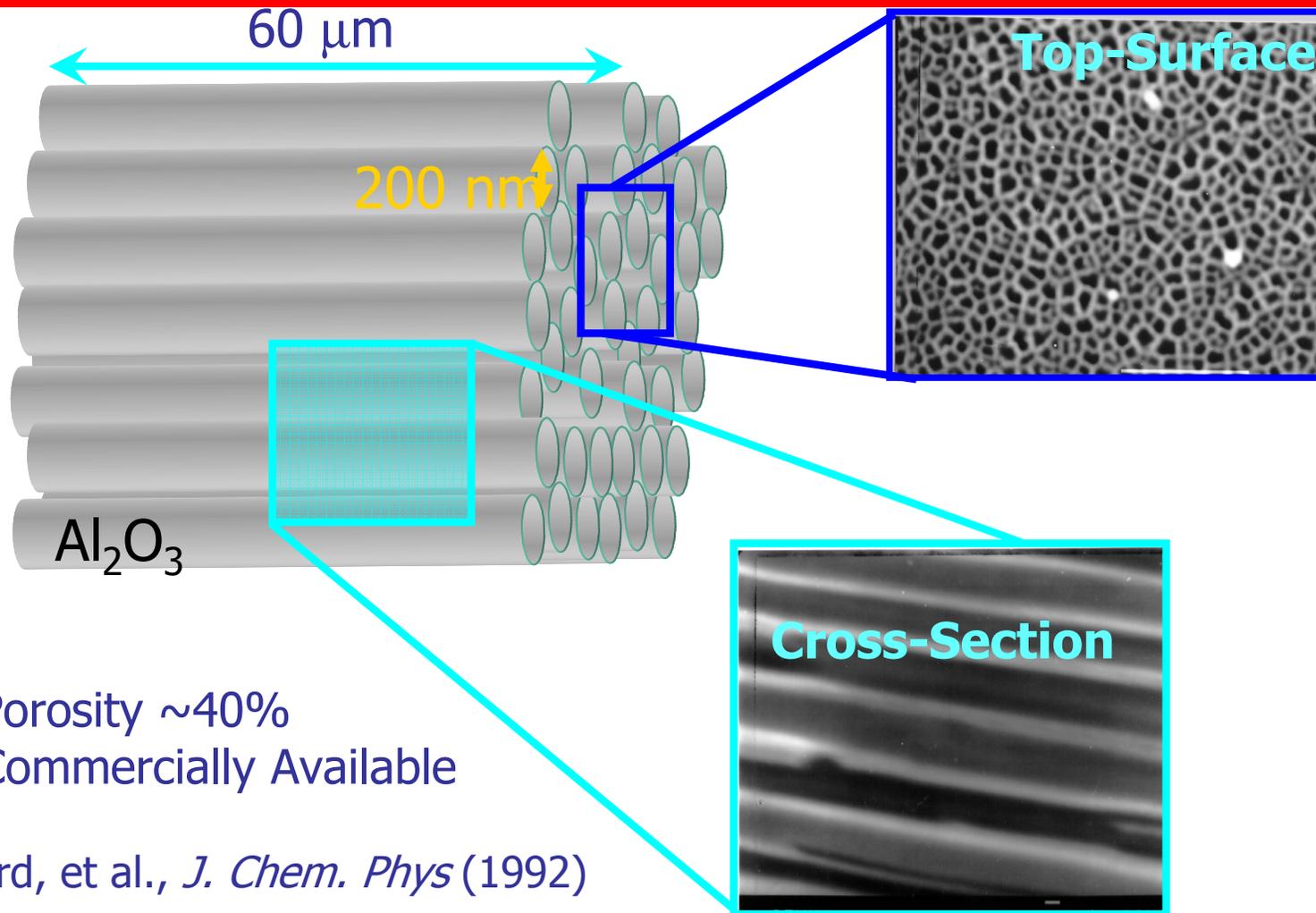


reverse
micelle



cross section

Templates Al_2O_3

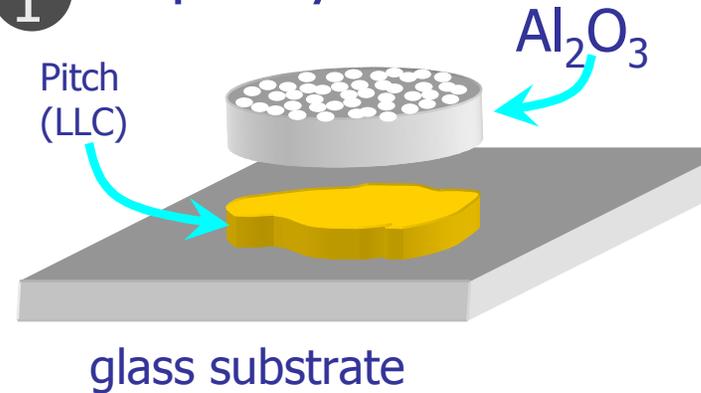


Porosity $\sim 40\%$
Commercially Available

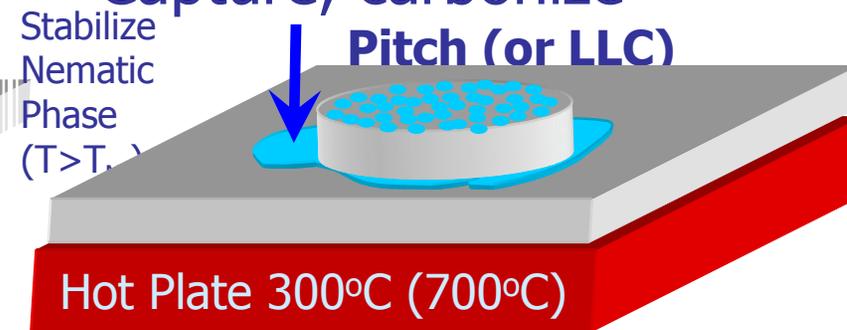
Crawford, et al., *J. Chem. Phys* (1992)

Templates processing

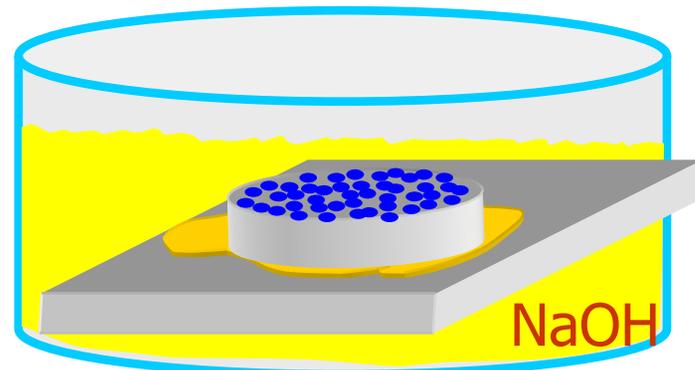
1 Capillary Fill



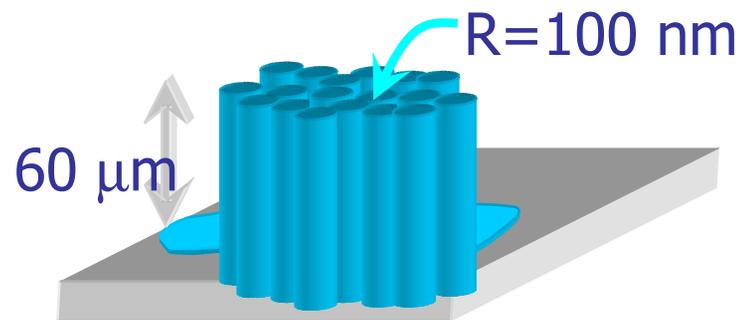
2 Stabilize LC phase, covalent Capture, carbonize



3 NaOH Etch



4 Carbon Cylinders/Posts/Tubes



Solution-deposited carbon nanotube layers for flexible display applications

- **Axel Schindler, Jochen Brill, Norbert Fruehauf**

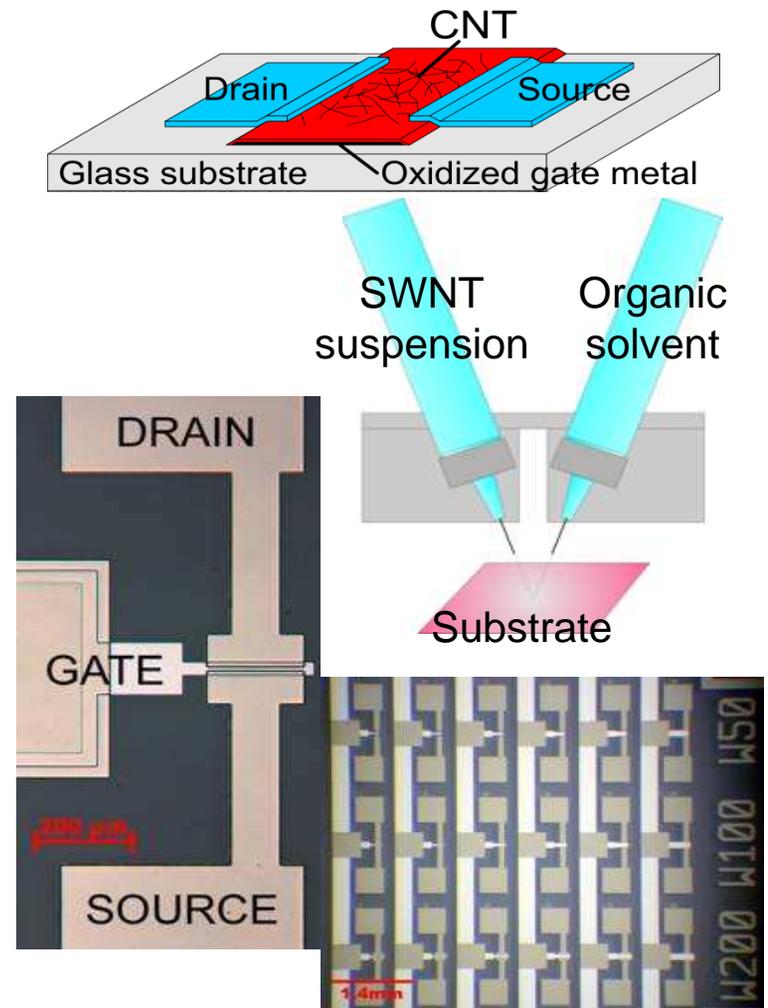
Chair of Display Technology, University of Stuttgart, Germany

- **James P. Novak, Zvi Yaniv**

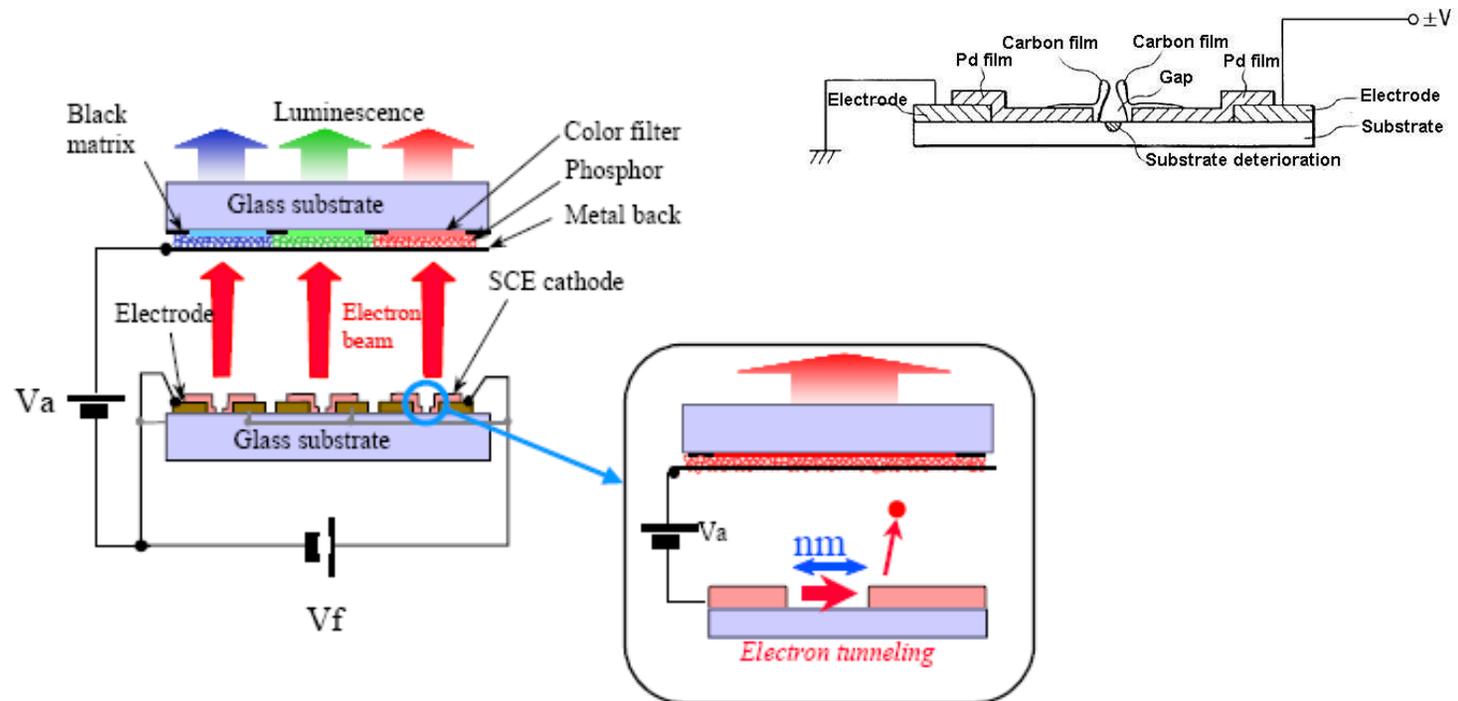
Applied Nanotech Inc., Austin, TX 78758 USA

Device fabrication

- Glass substrate with patterned Al gate
- Formation of Al_2O_3 gate dielectric by anodic oxidation
- SAM of 3-amino-propyl-triethoxy-silane as adhesion promoter
- Spin coating SWNT suspension plus organic solvent
- Rinse to remove residual surfactant
- Forming Palladium or Titanium S/D contacts
 - E-beam evaporation and Lift-off
- Removal of unnecessary CNTs with CO_2 snow-jet

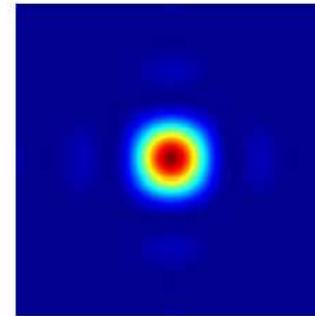


SED TV structure

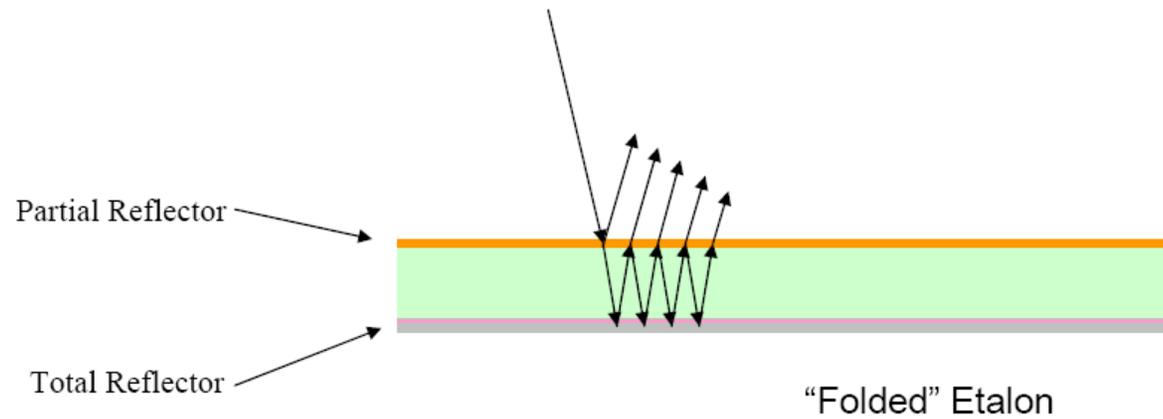
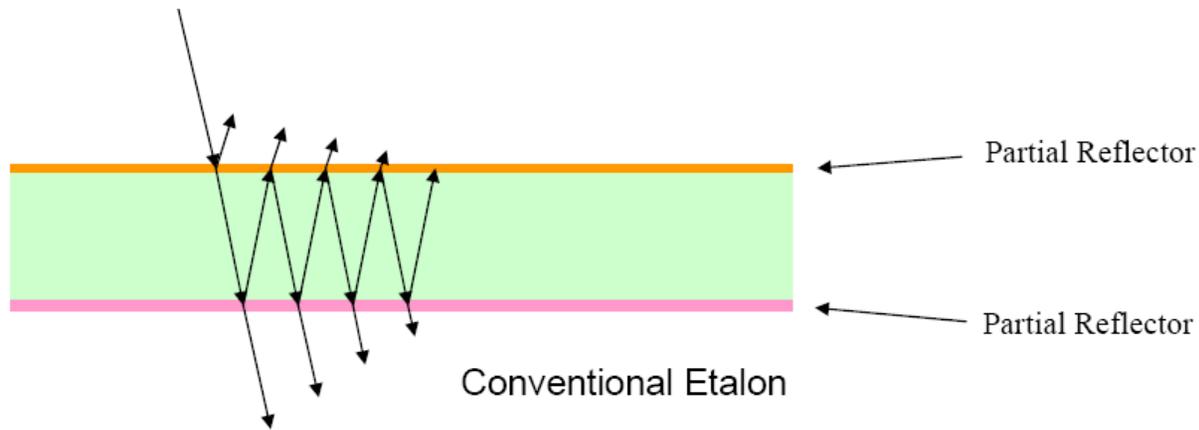


Structure of SED. Each sub-pixel has a unique pair of electrodes that supplies an electron current.

Color without filters?

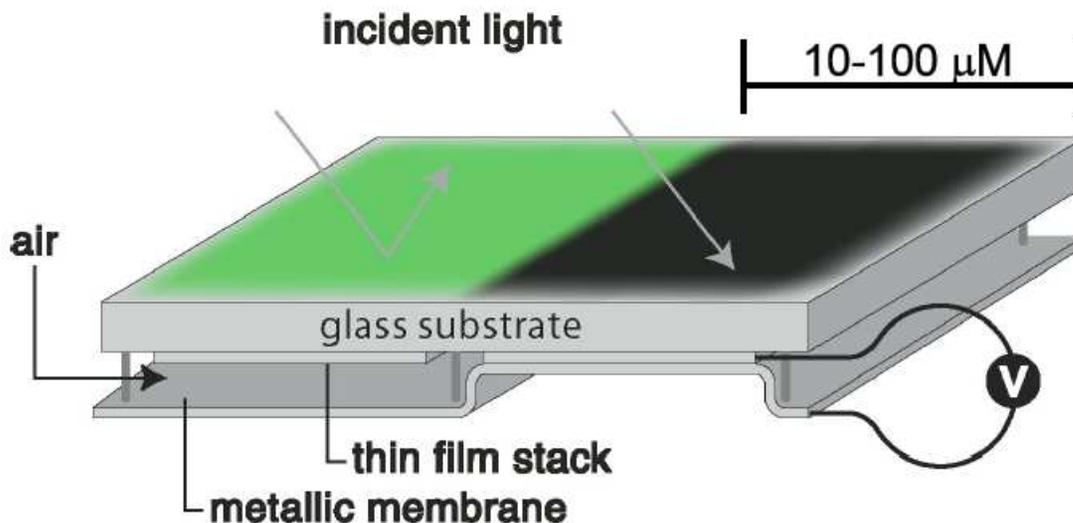


Etalons



iMoD concept

- Interferometric modulator operation
 - Microsecond response
 - Low voltage (<10V) operation
 - Simple, PVD (or CVD) thin film structure

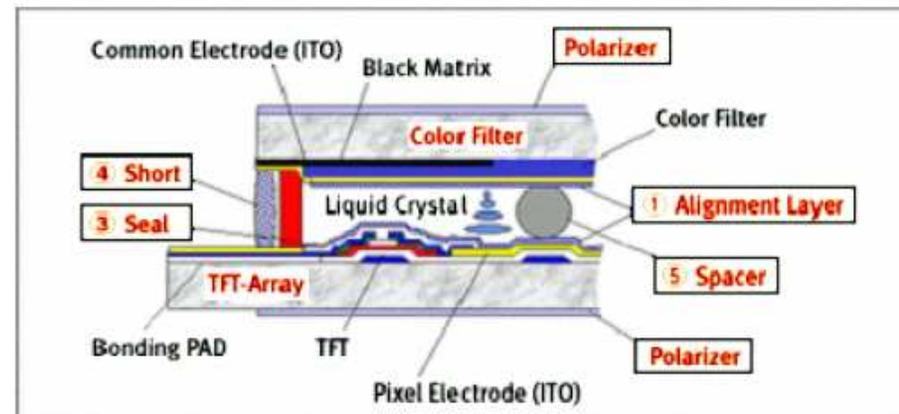
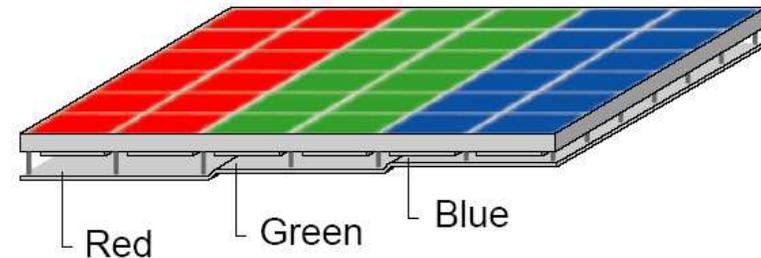


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⁷¹Courtesy of Jeff Sampsel, Qualcomm

iMoD technology advantage

- Modulator, color control and memory in one structure
- Simpler than TFT LCD
 - No transistors
 - No organic material
 - No color filters
 - No polarizers

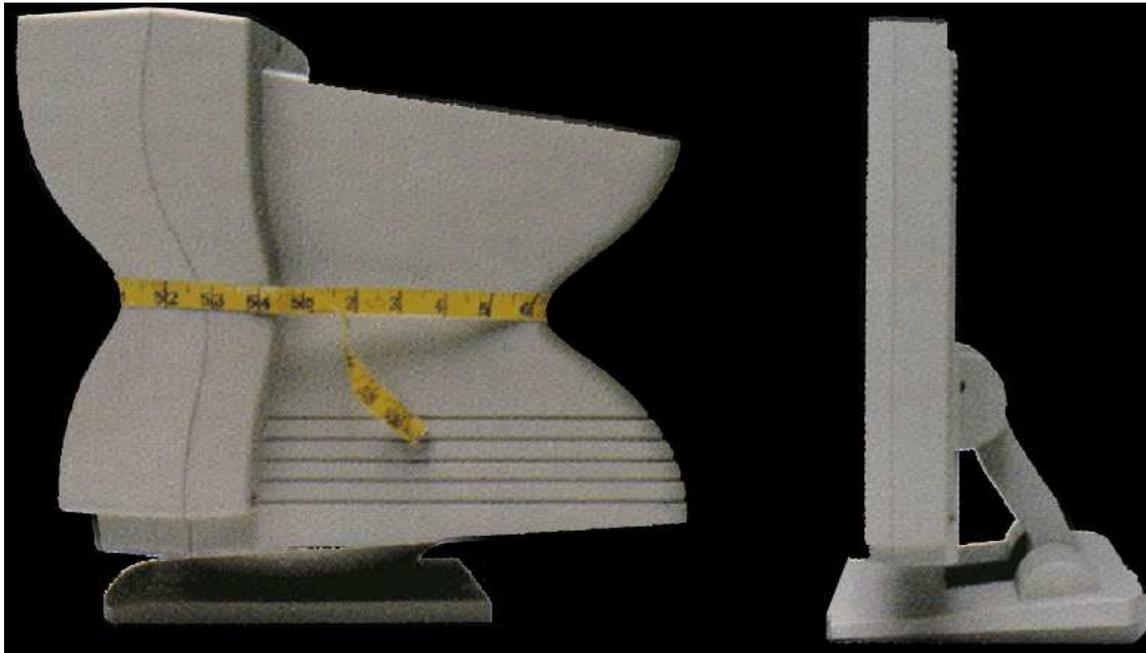




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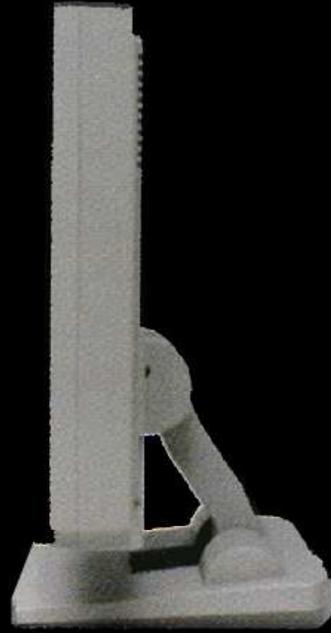
A "flexible" revolution and nanotechnology impact

CRT



~ 100 years old

LCD



~ 25 years old

?



Future



Applied Nanotech, Inc.

Courtesy of Dr. Gregory Crawford,
Brown University, Providence, RI

Flexible flat panel displays

- What is the definition of a flexible flat panel display?
- What applications will FFPDs enable?
- What are the issues for FFPDs?
- Who believes we will have FFPDs in the next 3 years? 5 years?

Flexible flat panel displays

“Defining a flexible flat panel display is a bit like defining modern art” [Slikkerveer, *Information Display* **19** (2003)]

It is also a bit like religion –

There are believers and non-believers

It is also a bit like politics-

Everyone has a different opinion

Technology convergence

Flexible Substrates

Flexible glass or plastic

Barrier Layers

Multi-layer films

Conducting Layers

Conducting polymer or ITO

Other Components

Polarizers, retarders

Electro-Optic Materials

LC, EP, Gyricon, OLED

Active Matrix

Organic, inorganic

Manufacturing

Roll-to-Roll, Sheet



Flexible display designs

- **Flat, thin, lightweight, and robust displays**
(use plastic substrates for these features)
- **Curved or conformed displays**
(permanently curved or bent)
- **Flexible displays**
(continuous or casual flexing throughout life)
- **Foldable displays**
(fold away when not in use)
- **Rollable displays**
(roll away when not in use)
- **Wearable displays**
(in clothing for example)
- **Irregular shaped displays**
(circular and odd shapes for example)

Applications

Permanently Conformed Display



- Little/no degradation after process
- Issues arise during processing
- Delaminating over time

Rollable Display



- Continuous rolling/unrolling
- Issues can arise over time
- Fatigue

Essential technologies

- Substrates (plastic and glass)
- Barrier layers (keep out oxygen and water)
- Conductors (organic and inorganic)
- Active matrix (organic, inorganic, liftoff methods, a lot of activity)
- Materials (LCD, OLED, electrophoretics, gyricon, fabric)
- Manufacturing (Roll-to-roll or sheet-wise)

Flexible glass

Make glass behave like plastic (Schott, NSG) – coat with polymers
Thin glass can go down to 30 mm in thickness

	Polymer foils	Thin glass		Polymer coated ultra thin glass
Water permeation	X	✓	→	✓
Oxygen permeation	X	✓	→	✓
Thermal stability	X	✓	→	✓
Chemical resistance	X	✓	→	✓
Mechanical Stability	✓	X	→	✓
Flexibility	✓	X	→	✓
Standard manufacturing	X	✓	→	✓

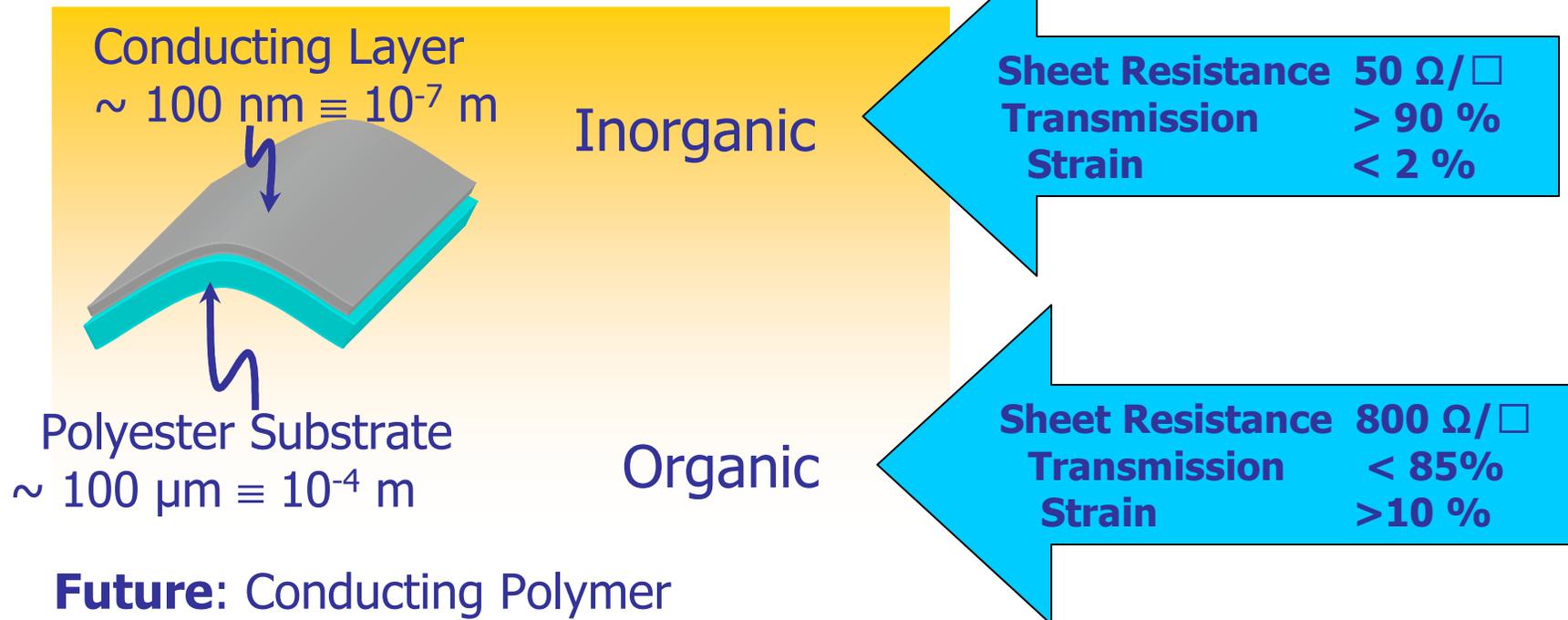
Presented at USDC Flexible Conference (2003), Norbert Hildebrand

Courtesy of Dr. Gregory Crawford,
Brown University, Providence, RI

Conductor technology

Today's Solution: Indium-Tin-Oxide (ITO)

- Great properties, but
- Cracks under strain (tension, compression)



Future: Conducting Polymer

- Poor performance, but
- Does not crack, very robust, flexible

Flexible flat panel displays

- Organic Light Emitting Diodes (OLED)
- Emissive Technology
- Gyricon
- Electrophoretic
- Cholesteric Liquid Crystal
- Liquid Crystal Paintable Displays
- Polymer Dispersed Liquid Crystals

See Chapters in *Flexible Flat Panel Displays* by Sheridan, Amundson, Doane, Broer, Crawford, and Hildner.

Howard, *Scientific American*, **290**, 64-69 (2004).

Penterman, et al., *SID Digest XXXIII*, 1020-1023 (2002).

Gorkhali, et al., *SID Digest XXXIII*, 1004-1007 (2002).

Slikkerveer, et al., *SID Digest of Technical Papers XXXIII*, 27-29 (2002).

Crawford, *IEEE Spectrum*, October, 40-46 (2000).

West, et al., *IDW Proc. 99*, 235-238 (1999).

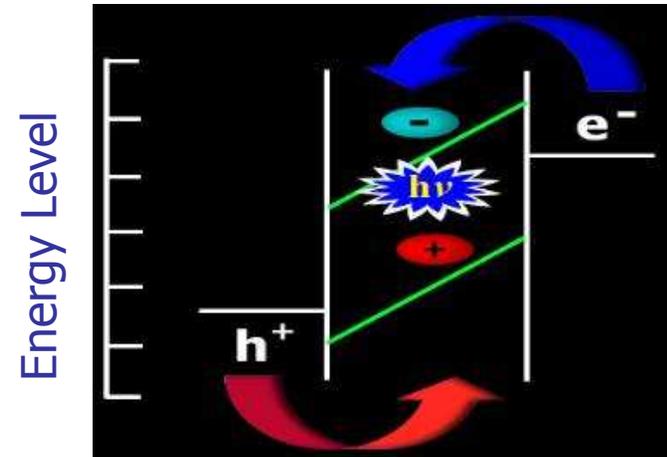
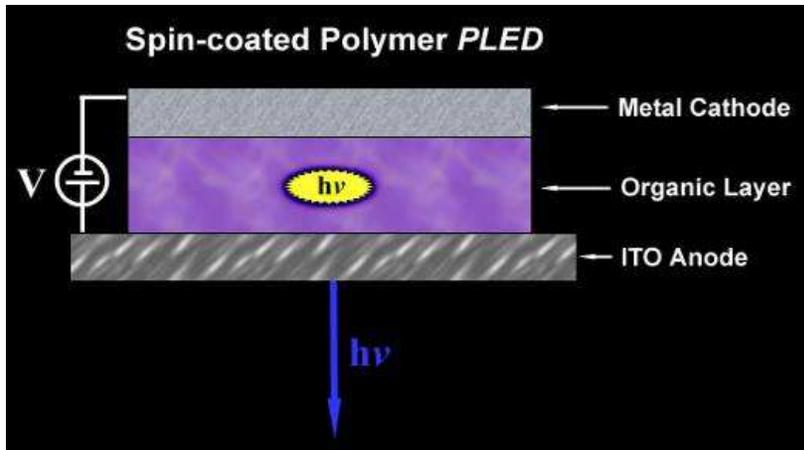
Sheridan, *J. SID* **7**, 141-144 (1999).

Drzaic, et al., *SID Digest XXIX*, 1131-1134 (1999).

Liquid Crystals in Complex Geometries (Taylor & Francis, 1996), editor Crawford

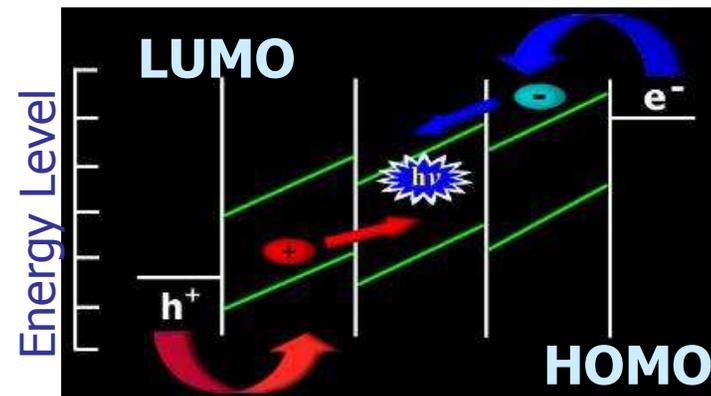
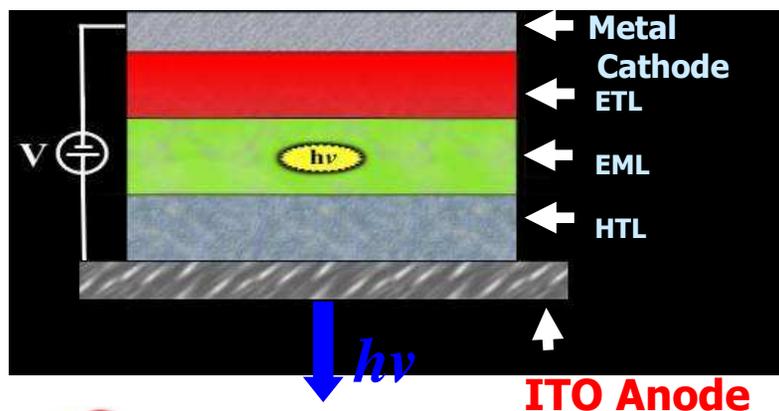
Organic light emitting diodes

See Howard, *Scientific American*, **290**, 64-69 (2004).



ITO/Polymer/Metal

Vapor Deposited Molecule OLED

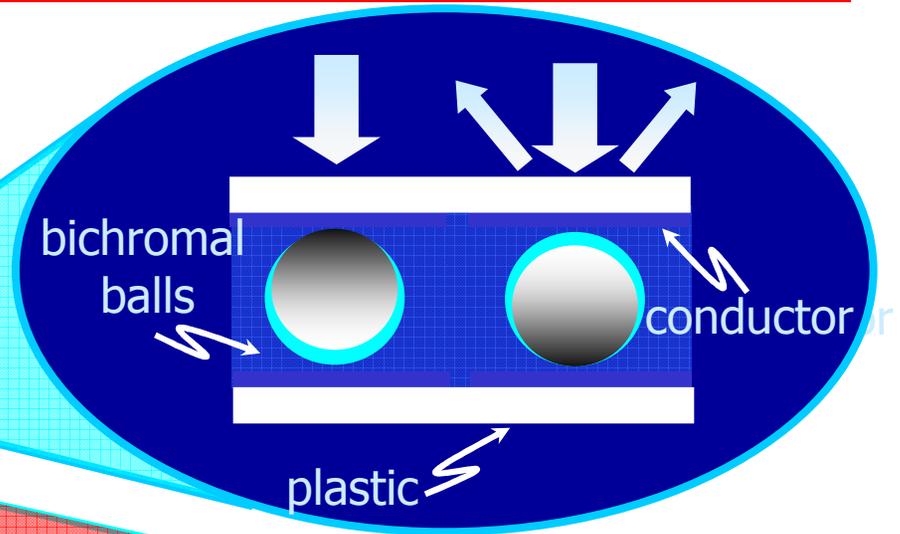


ITO/ HTL/ EML/ ETL/ Metal

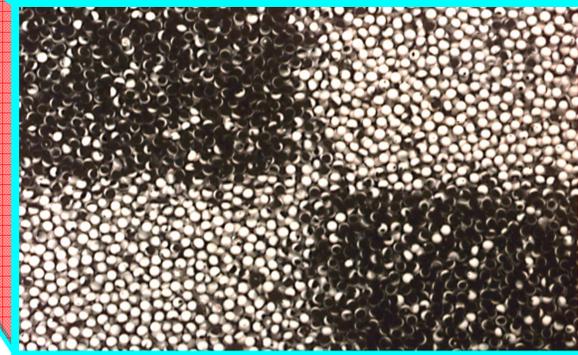
Gyricon technology

Developed at Xerox PARC

(photo courtesy of Dr. Nick Sheridan)



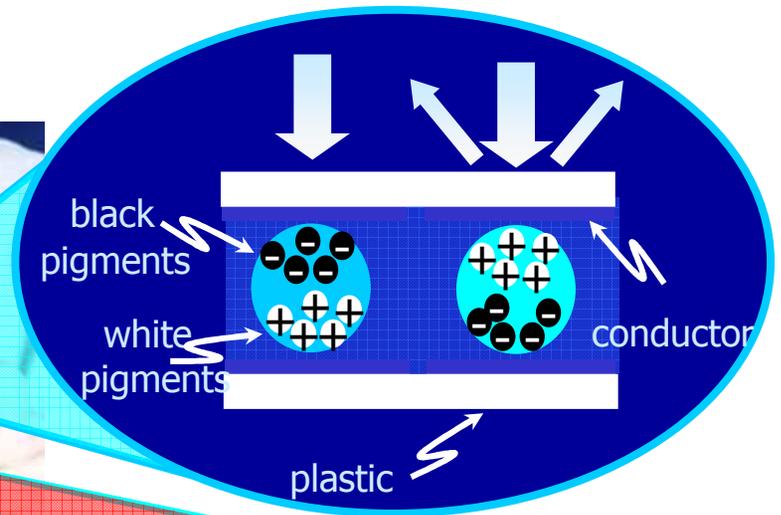
- ✓ Black on white
- ✓ Color Possible
- ✓ Contrast 5-10:1
- ✓ Reflectance 25-30 %
- ✓ < 100 volts
- ✓ Bistable memory, thresholdless



Electrophoretic technology

Developed at e-Ink

(photo courtesy of Dr. Karl Amundson)



- ✓ Black on white
- ✓ Color possible
- ✓ Contrast >10:1
- ✓ Reflectance 40 %
- ✓ < 20 volts
- ✓ Bistable memory, thresholdless



Reflective E-Ink electrophoretic smart card



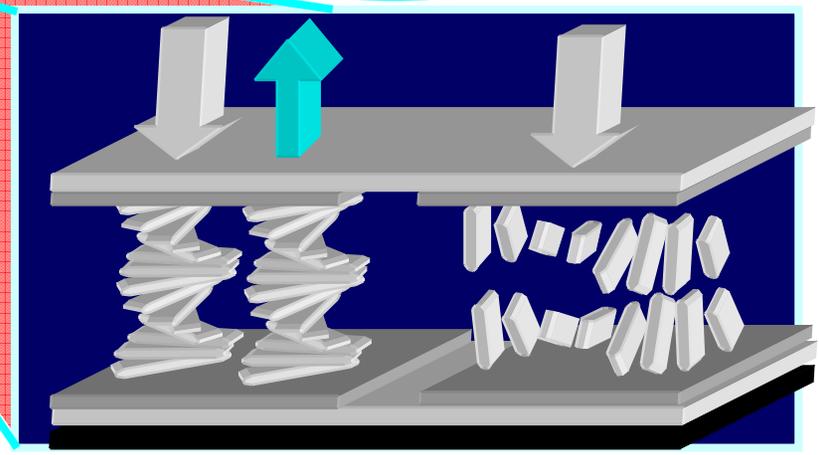
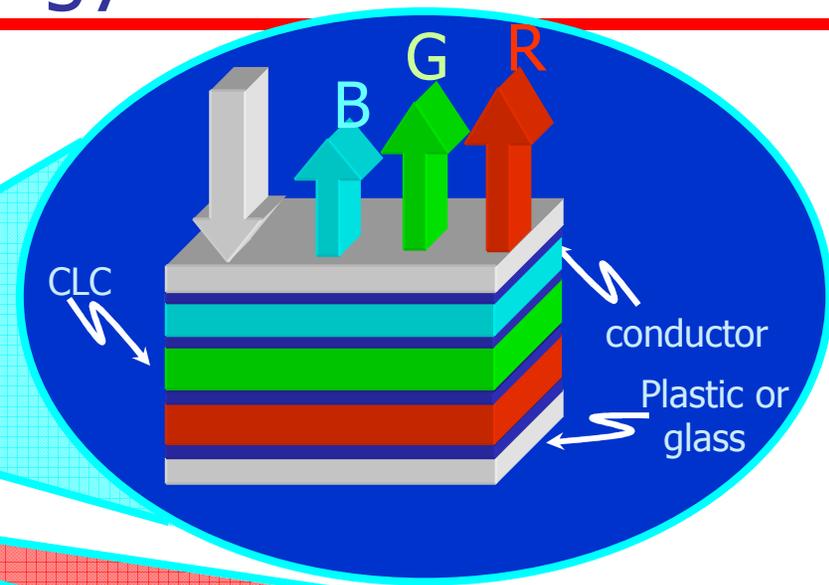
Courtesy of Dr. H. Jacht, Philips



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Cholesteric technology

Developed at *Kent Displays*
(photo courtesy of Dr. Bill Doane)



- ✓ Color Monochrome
- ✓ Color Demonstrated
- ✓ Contrast 50:1
- ✓ Reflectance 25-30 %
- ✓ < 35 volts
- ✓ Bistable memory, threshold

Reflective cholesteric electronic book

Presented at Symposium (Shiyanovskaya, et al.)



Coated cholesteric LC displays by Kent Displays

Courtesy of Dr. A. Khan, Kent Displays, 2005

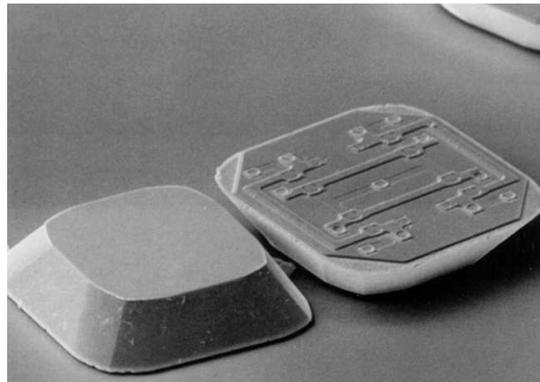


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TFTs on plastic

Raise Process

Temperature of plastic *e.g.* PCO, PAR, PI
(inorganic TFTs)

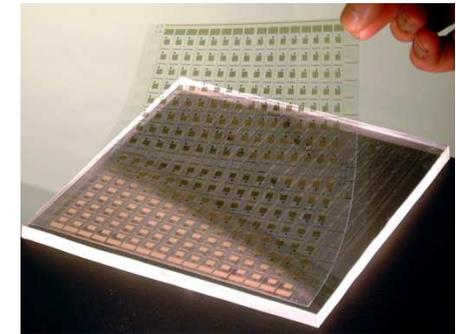
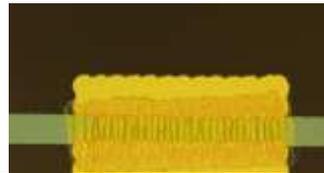


Self Assembly



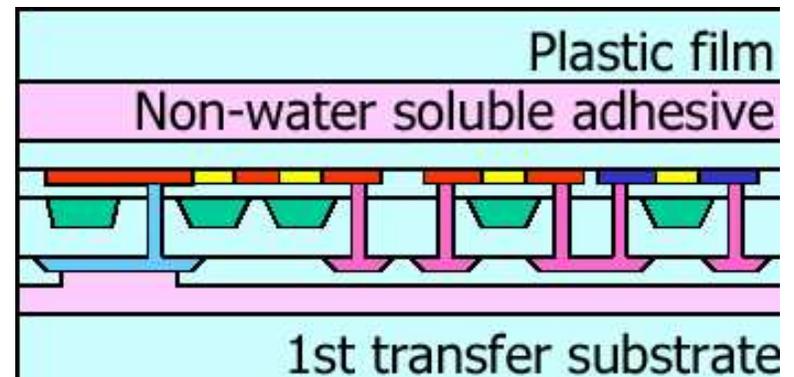
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Lower Processing Temperatures
(stamping/printing) (organic TFTs)



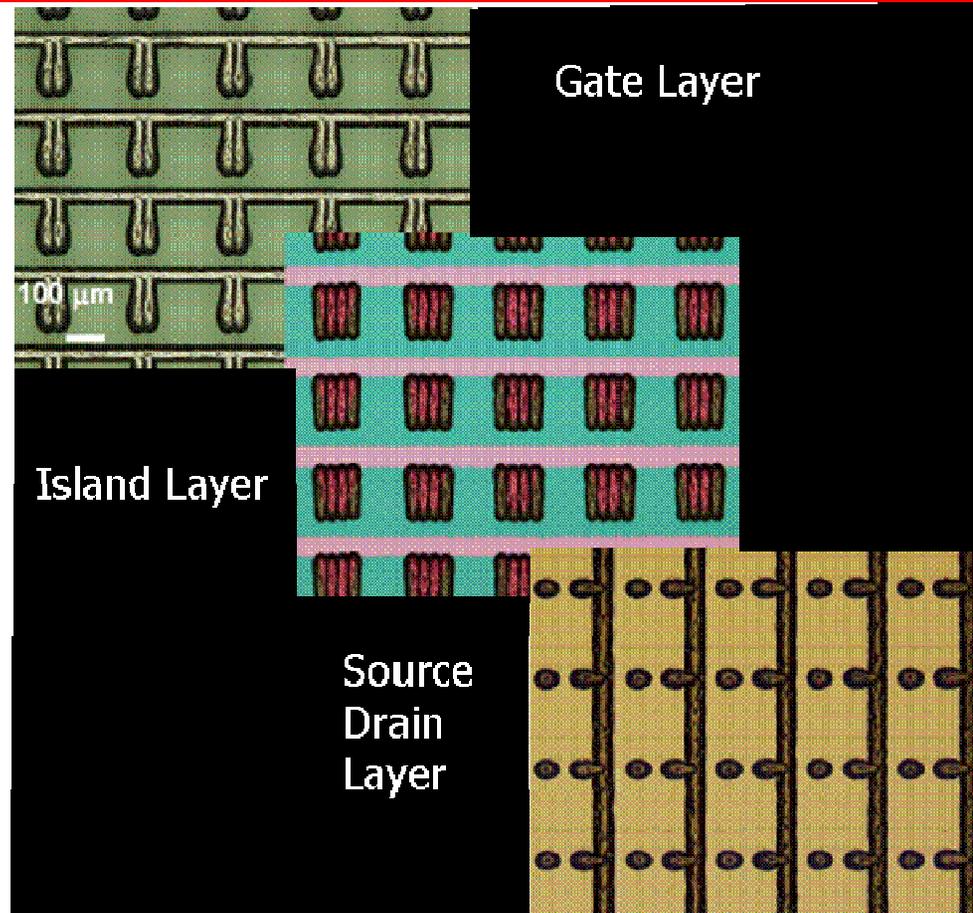
Schools of Thought

Transfer Process



Courtesy of Dr. Gregory Crawford,
Brown University, Providence, RI

Printing TFTs



Courtesy of Raj Apte (*PARC*): Street, USDC 2005



Courtesy of Dr. Gregory Crawford,
Brown University, Providence, RI

LTPS TFT LCD



Sony



Adapted from *Flexible Flat Panel Displays*, Chapter 23, Asano et al (John Wiley & Sons, Ltd., 2005, Chichester), G. P. Crawford, Editor

Market opportunity

Can flexible (plastic) displays replace glass displays in conventional display applications?



Not right now???

Performance driven market: At time of market entry, flex display would have to compete with full color, active matrix, high resolution, power consumption, etc.

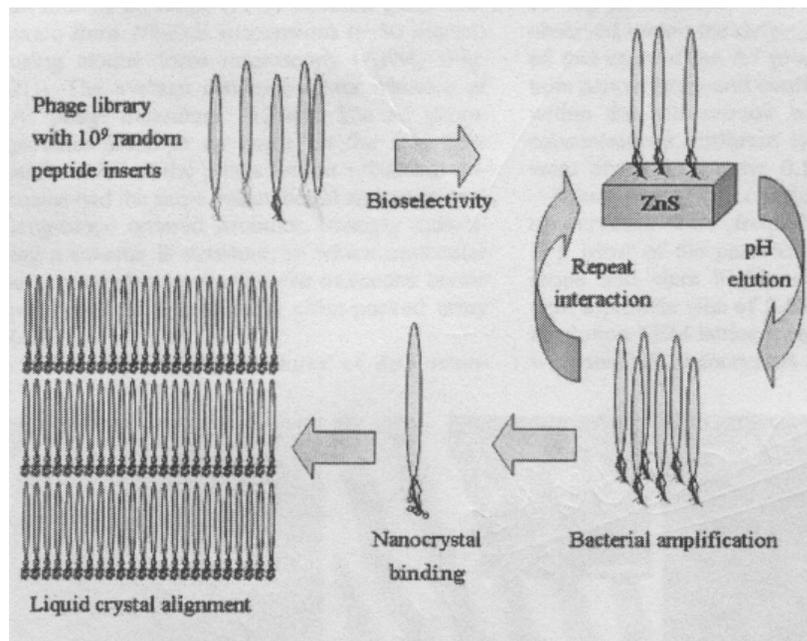
Cost Driven Market: At time of market entry, flex displays would have to be less expensive than small, low quality but functional displays (e.g. STN displays can be really cheap). Today's optimistic estimates put flex displays at 2 times higher cost

Liquid crystalline phases of genetically engineered viruses

- Using phagocyte bacteria
- Bacteria with specific recognition moiety for crystalline surfaces
- Self-ordering process through biomultiplication
- Lyotropic phases were obtained

Angela M. Belcher, *et al*, Science, Vol. 296, May 3, 2002.

Liquid crystal order self-assembly



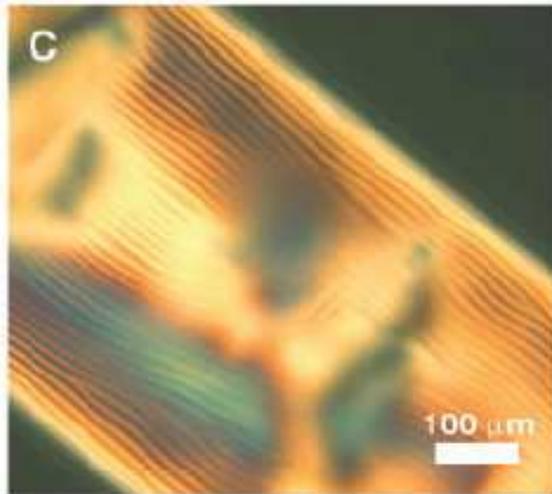
Schematic diagram of the process used to generate nanocrystal alignment by the phage display method.

Angela Belcher group, The University of Texas and MIT



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Characterization of the liquid crystalline suspension of A7-phage –ZnS nanocrystals (A7-ZnS) and cast film



(C) The characteristic fingerprint texture of the cholesteric phase of an A7-ZnS suspension (76 mg/ml).

DNA electronics

The molecules in our bodies in order to perform their functions must:

- Self-assemble
- Recognize
- Bind in specific ways
- Form complex polymers

How can we learn and apply the same techniques?

Nanolithography today!

(i) RecA Polymerization



(ii) Homologous recombination



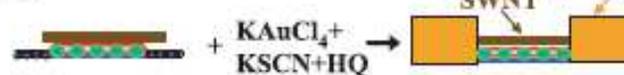
(iii) Localization of a SWNT using antibodies



(iv) RecA protects against silver reduction



(v) Gold metallization



DNA-templated carbon nanotube FET

K. Keren, R. Berman, E. Buchstab, U. Sivan, E. Braun, Science, Vol. 302, November 21, 2003, 1380.



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Display industry & nanotechnology are multidimensional

- Constantly revising (processes, products,...)
- Constantly enhancing (process, products,...)
- Constantly interacting (society, culture,...)
- Constantly inventing (processes, products,...)
- Constantly influencing (economy, society,...)
- Constantly changing (regions, fields,...)
- Constantly vastly interdisciplinary