# Introduction

**2009. 3. 3.**

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School of Electrical Engineering and Computer Science
Seoul National Univ.
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## Syllabus

• **Professor:** Changhee Lee, 880-9093, chlee7@snu.ac.kr

• **Text & References**

**Text** :
- Physics of Organic Semiconductors, Edited by W. Brutting, Wiley-VCH, Weinheim, 2005.
- 디스플레이공학 II (청범출판사, 2009년 2월 발간 예정)

**References:**
- M. Pope and C. E. Swenberg. Electronic Processes in Organic Crystals and Polymers, 2nd Ed. (Oxford, NY, 1999)
- K. C. Kao and W. Hwang, Electrical Transport in Solids, Pergamon Press, Oxford, 1981)
- J. D. Wright, Molecular Crystals, 2nd Ed., (Cambridge University Press, Cambridge, 1995).
- R. Farchioni, G. Grosso Eds., Organic Electronic Materials, (Springer, Berlin, 2001).
- E. A. Silinsh and V. Capek, Organic Molecular Crystals. (AIP Press, New York, 21994).

• **Grades**
- Midterm Exam 30 %, Final Exam 40 %, Attendance 10 %, Homework (including term paper) 20 %

• **Lecture room**: 301-104

• **Lecture Hour**: Tue., Thu. 1:00-2:15pm

# Lecture Schedule



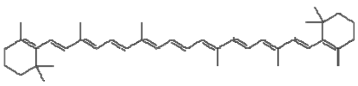
주(기간)
강의내용

| | |
|---|---|
| 1주 | Introduction, Chapter 1 Organic molecular beam deposition |
| 2주 | Electronic structure of organic semiconductors, Chapter 2 |
| 3주 | Properties of organic semiconductor/metal interfaces , Chapter 3 |
| 4주 | Optical properties of organic semiconductors |
| 5주 | Excited states of organic semiconductors and spectroscopic studies, Chapter 5 & 7 |
| 6주 | Spin dynamics of organic semiconductors, Chapter 8 |
| 7주 | Chapter 9 Phosphorescence |
| 8주 | 중간고사 |
| 9주 | Electronic states in organic semiconductors |
| 10주 | Charge carrier transport mechanism in organic semiconductors, Chapter 11 |
| 11주 | Chapter 12 Analysis and Modeling of Organic Devices |
| 12주 | Basic Principles of OLED devices, Chapter 17 & 18 |
| 13주 | Basic Principles of OTFTs, Chapter 14 |
| 14주 | Basic Principles of organic solar cells, Chapter 15 |
| 15주 | 기말고사 |



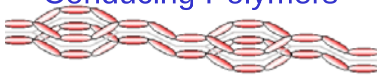
# Organic materials: new class of electronic materials





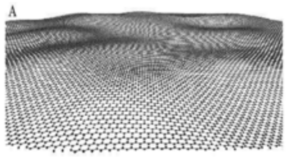
**β-Carotene**: can be found in yellow, orange, and green leafy fruits and vegetables such as carrots, tomatoes, sweet potatoes, oranges, etc..

## Conducing Polymers



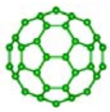
Nobel Prize in Chemistry 2000
Alan J. Heeger, Hideki Shirakawa, Alan G. MacDiarmid

**Graphene sheet**



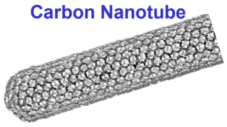

*K. S. Novoselov*, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, and A. A. Firsov, *Science 306*, 666 (*2004*)

**Fullerene, $C_{60}$**

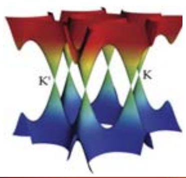


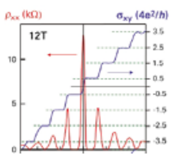
Nobel Prize in Chemistry 1996
Robert F. Curl Jr.
Sir Harold W. Kroto
Richard E. Smalley

**Carbon Nanotube**



Discovered in 1991 by Sumio Iijima



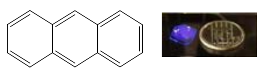

Left: Band structure of graphene. The conductance band touches the valence band at the K and K' points .Right: Resistivity (red) and Hall conductivity (blue) as a function of carrier concentration in graphene.
M.I. Katsnelson, Mater. Today 10, 20 (2007)

# Research on organic semiconductors



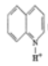
1906. Photoconductivity in anthracene:
A. Pochettino, *Acad. Lincei Rendic*. 15, 355 (1906).

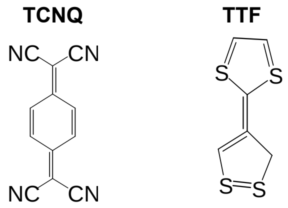
**Anthracene**



1960. TCNQ: R. G. Kepler, P. E. Bierstedt, R. E. Merrifield, Phys. Rev. Lett. 5, 503 (1960).

Table I. Electronic properties of representative radical-anion salts.

| Material | Electrical conductivity: Value at 300°K (ohm⁻¹ cm⁻¹) | Electrical conductivity: Activation energy (ev) | Magnetic susceptibility: Value at 300°K (emu-mole⁻¹) | Magnetic susceptibility: Temperature dependence |
|---|---|---|---|---|
|  $[TCNQ\cdot]^-[TCNQ]^a$ | $100^a$ | <0.01 | $+2.2\times10^{-4}$ | Decreases gradually to $+1.0\times10^{-4}$ at 77°K |
| $[(C_2H_5)_3NH]^+[TCNQ\cdot]^-[TCNQ]^a$ | $4.0^a$ | 0.14 | $+6.4\times10^{-4\,b}$ | Eq. (1) with $J=0.041$ ev |
| $K^+[TCNQ\cdot]^-$ | $1.9\times10^{-4\,c}$ | 0.36 | $-1.3\times10^{-4}$ | Temperature independent from 77° to 450°K[d] |




1973. TTF-TCNQ: L. B. Coleman, et al, Solid State Comm. 12, 1125 (1973).
σ~8,000 S/cm

1977. Doped $(CH)_x$: C. K. Chiang, C. R. Fincher, Jr., Y. W. Park, A. J. Heeger , H. Shirakawa, E. J. Louis, S. C. Gau, and Alan G. MacDiarmid, Electrical Conductivity in Doped Polyacetylene, Phys. Rev. Lett. 39, 1098 (1977).



# Energy Band Structure of π-conjugated polymers

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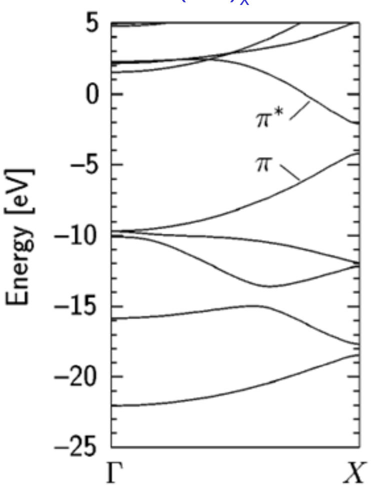
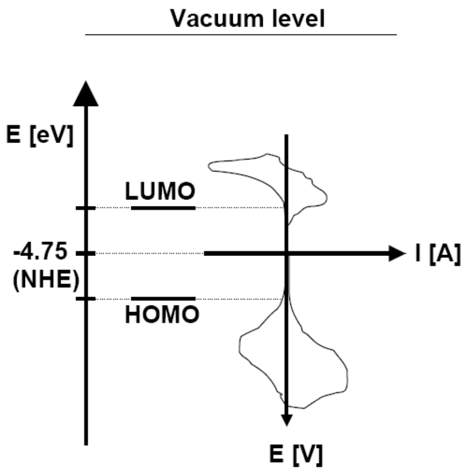
*EE 4541.617A*
*2009. 1st Semester*

$(CH)_x$




M. Rohlfing and S. G. Louie, *Phys. Rev. Lett*. 82, 1959 (1999)

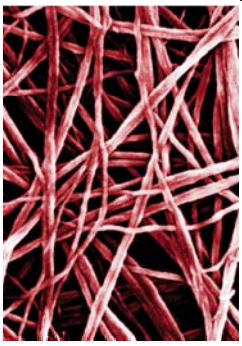



Connection of Fermi energy scale and electrochemistry: the onset potentials for oxidation and reduction correspond to the HOMO and LUMO level

David Mühlbacher, Ph.D. Thesis, Johannes Kepler Universität Linz (2002)

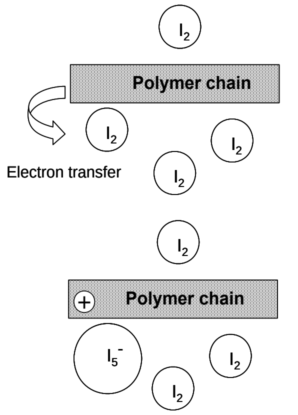
# Chemical Doping



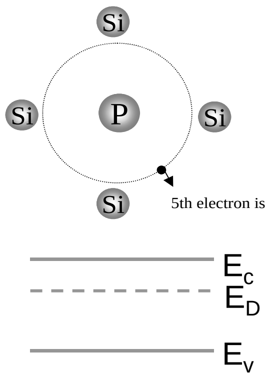


SEM of polyacetylene fibrils. (From K. Araya, A. Mukoh, T. Narahara, H. Shirakawa, Synth. Met., 1986, 14, 199, Fig. 3b)

## Organic Semiconducor




## Inorganic Semiconducor






# Chemical Doping

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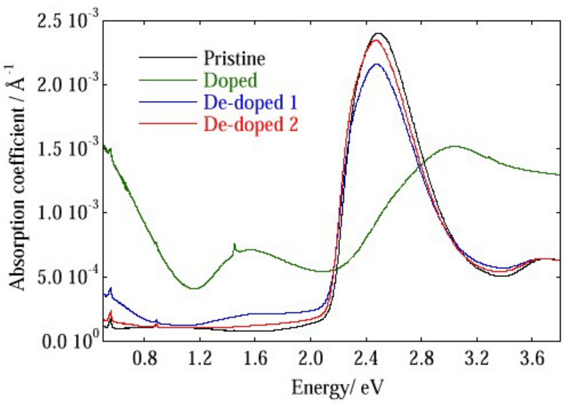
*2009. 1st Semester*

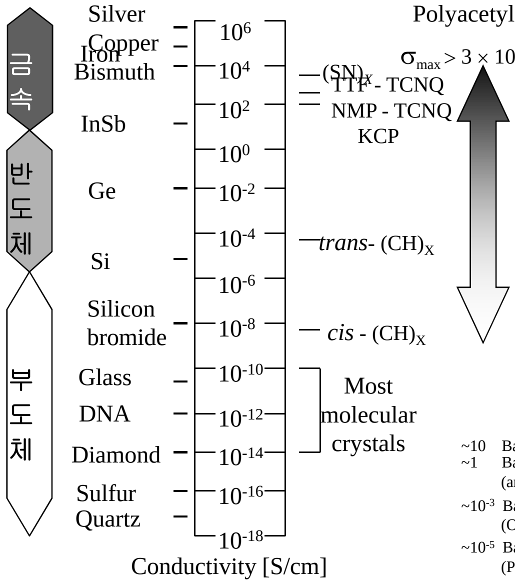
## Change in Absorption Spectrum

- **Main $\pi\pi^*$ transition blue-shifted and reduced in strength**
- **Additional peaks appear in the red and IR**

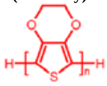



# Conducting Polymers

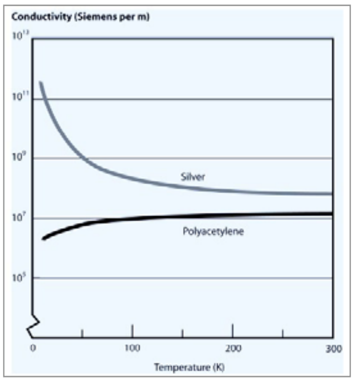





**PEDOT:PSS**
**H. C. Starck**
**(Germany)**



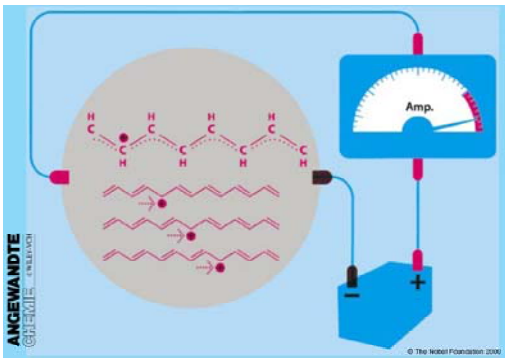
~10 Baytron® P HC
~1 Baytron® P
(antistatic applications)
$\sim 10^{-3}$ Baytron® P VP Al4083
(OLED)
$\sim 10^{-5}$ Baytron® P VP CH8000
(PMOLED)

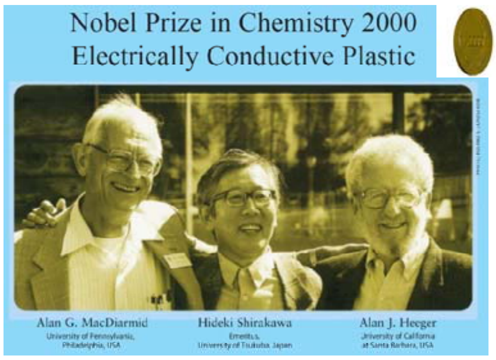





# Nobel Prize in Chemistry 2000






Homework 1: Read the following papers.

1. CHEM. COMMUN., 1 (2003)
2. Hideki Shirakawa, The Discovery of Polyacetylene Film: The Dawning of an Era of Conducting Polymers (Nobel Lecture), Angew. Chem. Int. Ed. 40, 2574 (2001).
3. Alan G. MacDiarmid, "Synthetic Metals": A Novel Role for Organic Polymers (Nobel Lecture), Angew. Chem. Int. Ed. 40, 2581 (2001).
4. Alan J. Heeger, Semiconducting and Metallic Polymers: The Fourth Generation of Polymeric Materials (Nobel Lecture), Angew. Chem. Int. Ed. 40, 2591 (2001).

# Molecule-Based Magnets



- New phenomena observed, not in conventional magnets
- Tunable properties ('magnets by design')
- Light-weight, bio-compatible alternative to conventional magnets
- Low-cost, low-temperature, flexible syntheses

***Possible Future: lightweight "plastic" electric generators and transformers***

**Solution made $V[TCNE]_x$:Manriquez et al Science 252, 1415(1991)**

**Shielding, Inductor: Morin et al, J Appl. Phys. 75, 5782 (1994)**




# High Tc (> 350 K) Organic-based Magnet

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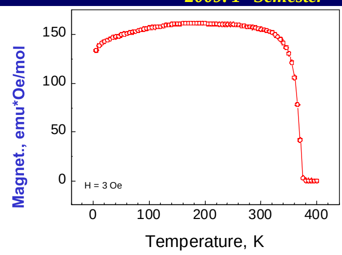
*2009. 1st Semester*

**Electron transfer salt:**

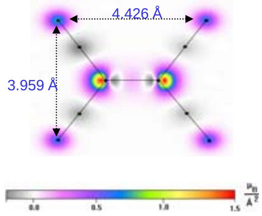
S = 3/2, donor: $[V]^{++}$
S = ½, acceptor: $[TCNE]^{-}$

**Magnetic order is due to antiferromagnetic coupling spins of $V^{2+}$ s and $[TCNE]^{-}$s.**
The net spin per "repeat" cell is 3/2 - 2(1/2) = 1/2.

Pokhodnya et al., *Adv. Mater.* **12**, 410 (2000)

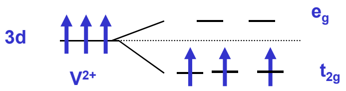



**$[TCNE]^{-}$ : S = 1/2**
unpaired electron in $\pi^*$ state




**Spin density distribution in** $[TCNE]^{-}$
Schweizer, et al, *J. Am. Chem. Soc.* ***116***, *7243 (1994)*

Octahedral coordination of **V** with **N**s splits 3d-level of $V^{2+}$
(EXAFS, ANL)




Large Hund's pairing energy keeps all three spins parallel providing high spin state

**$V^{2+}$: S = 3/2**

# Organic Electronics: Advantage



- Organic semiconductors can not outperform Si electronics in speed, stability, and robustness.
- Advantage: extreme price advantage for the printed electronics (low cost electronics)
- Organic electronics can compete with silicon electronics where performance can be traded for the price break.
- Organic electronics is most applicable at two extreme size scales.

(1) Very large area: ~ $cm^2$ ~ $m^2$, and over,

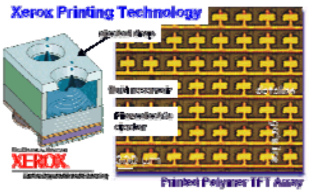
where the form factor of a component is much larger than a typical Si chip,

where the electronics needs to be distributed over that entire area (e.g., an entire wall, or a large portion of a person's body).

→ Macroelectronics

(2) Nanoregime

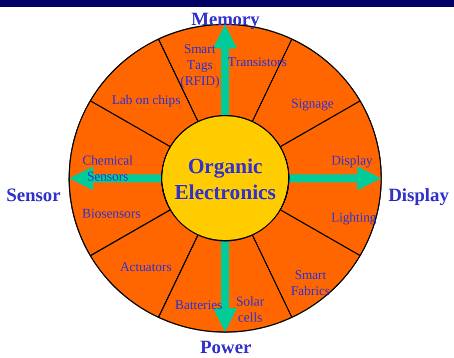
High-speed printing processes on flexible substrates

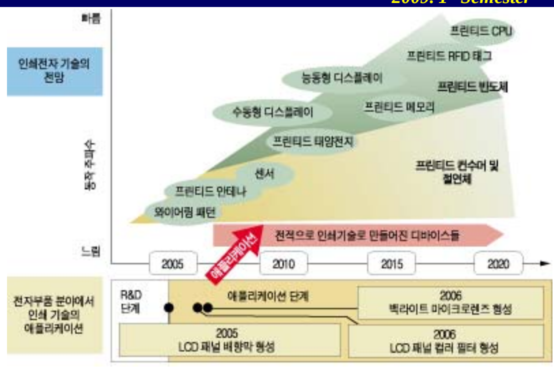





# Application of Organic semiconductors

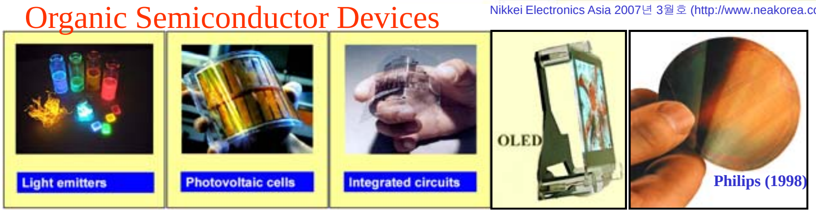





Nikkei Electronics Asia 2007년 3월호 (http://www.neakorea.co.kr/)

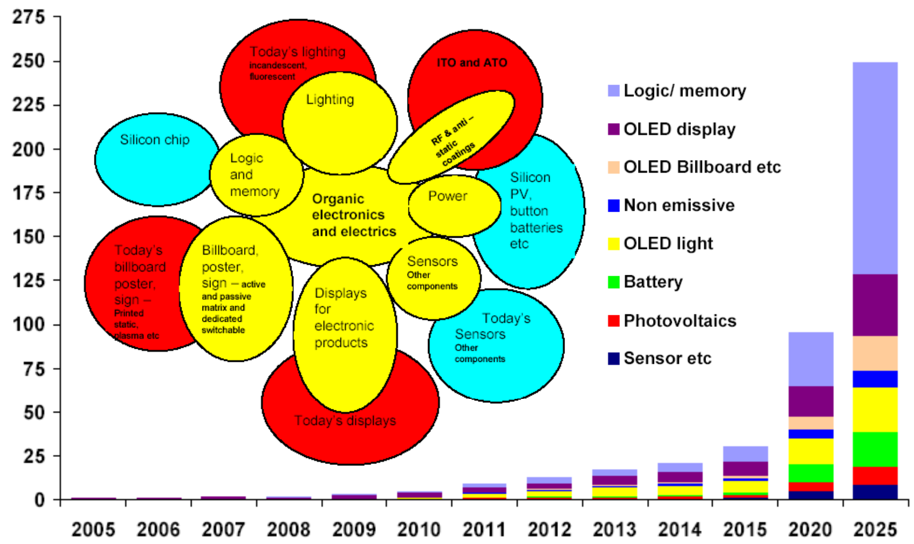
Organic Semiconductor Devices




→ integration of functionally discrete organic devices into an active integrated circuit

# Market for the organic electronic and electric products



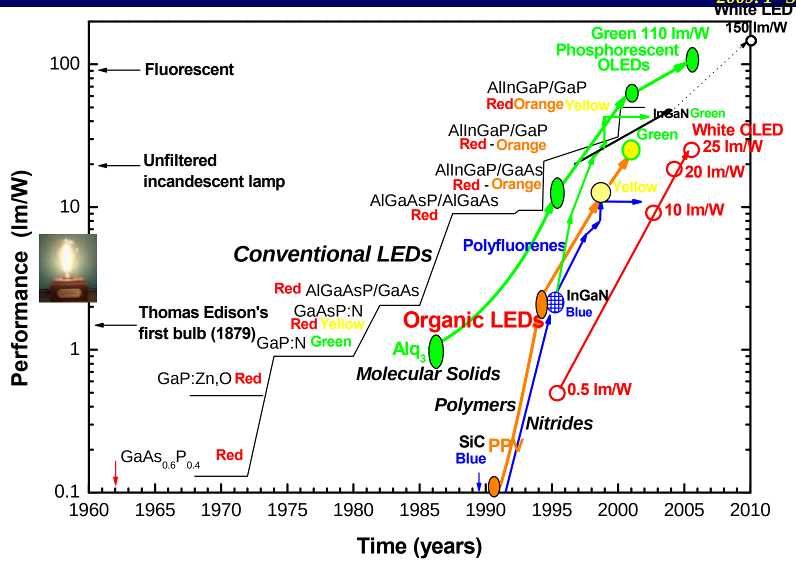



Dr P. Harrop and R. Das, Organic Electronics Forecasts, Players, Opportunities 2005-2025, IDTechEx, 2005

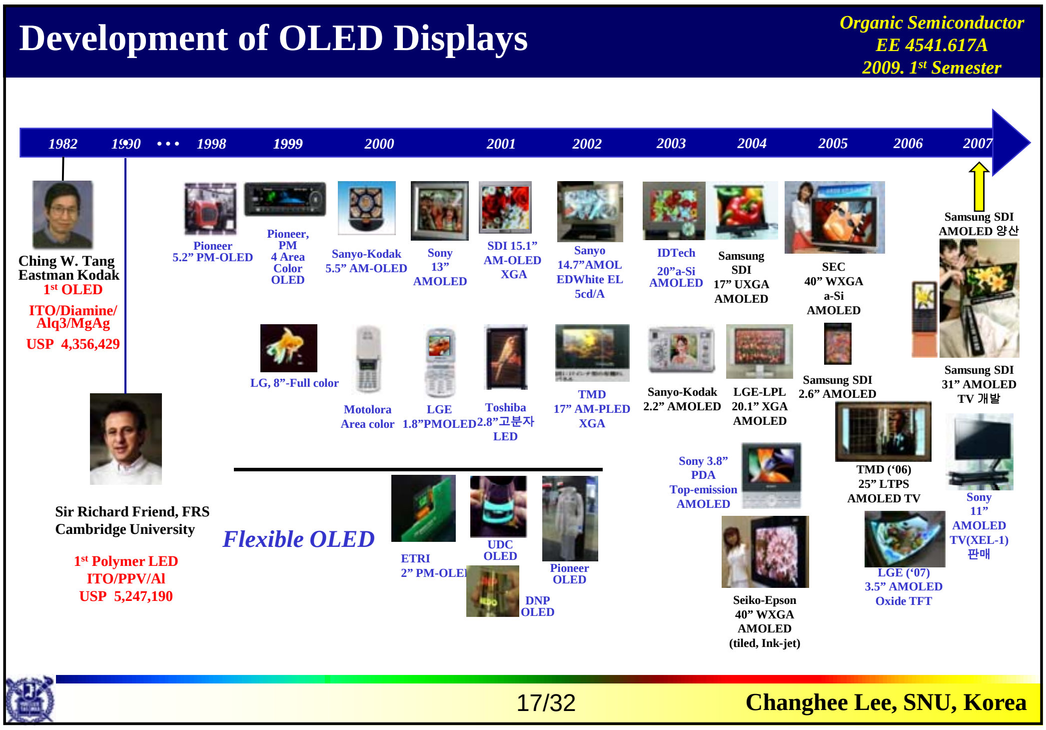


# Progress of OLED performance






Updated data in J. R. Sheats *et al.*, Science **273**, 884 (1996) and Mike Krames (Lumileds Lighting), Progress and Future Direction of LED Technology, SSL Workshop, (2003. 11. 13, Arlington, VA, USA)


Development of OLED Displays
Organic Semiconductor
EE 4541.617A
2009. 1st Semester
1982
1990
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
Ching W. Tang
Eastman Kodak
1st OLED
ITO/Diamine/
Alq3/MgAg
USP 4,356,429
Sir Richard Friend, FRS
Cambridge University
1st Polymer LED
ITO/PPV/Al
USP 5,247,190
Pioneer
5.2" PM-OLED
Pioneer, PM
4 Area
Color
OLED
Sanyo-Kodak
5.5" AM-OLED
Sony
13"
AMOLED
SDI 15.1"
AM-OLED
XGA
Sanyo
14.7"AMOL
EDWhite EL
5cd/A
IDTech
20"a-Si
AMOLED
Samsung
SDI
17" UXGA
AMOLED
SEC
40" WXGA
a-Si
AMOLED
Samsung SDI
AMOLED 양산
LG, 8"-Full color
Motolora
Area color
LGE
1.8"PMOLED
Toshiba
2.8"고분자
LED
TMD
17" AM-PLED
XGA
Sanyo-Kodak
2.2" AMOLED
LGE-LPL
20.1" XGA
AMOLED
Samsung SDI
2.6" AMOLED
Samsung SDI
31" AMOLED
TV 개발
TMD ('06)
25" LTPS
AMOLED TV
Sony 3.8"
PDA
Top-emission
AMOLED
Sony
11"
AMOLED
TV(XEL-1)
판매
Flexible OLED
ETRI
2" PM-OLED
UDC
OLED
Pioneer
OLED
DNP
OLED
Seiko-Epson
40" WXGA
AMOLED
(tiled, Ink-jet)
LGE ('07)
3.5" AMOLED
Oxide TFT
17/32
Changhee Lee, SNU, Korea


OLED Displays
Organic Semiconductor
EE 4541.617A
2009. 1st Semester
PMOLED 제품
Pioneer
카스테레오
Motorola
(Pioneer)
삼성전자
(삼성SDI)
LG
(Pioneer)
Philips 전기면도기
고분자 OLED
AMOLED 제품
Sanyo-Kodak 디지털 카메라
2.2" Full-color AMOLED
Sony 'CLIE' PDA
3.8" Full-color AMOLED
삼성SDI, 2인치급 AMOLED
(좌) 레인콤 MP3 "Clix" (2.2"); (중앙) TDDI
Media skin (2.4"); (우) Nokia 7900 (2.0")
Sony 'XEL-1' OLED TV
11" Full-color AMOLED
QHD 960x540
18/32
Changhee Lee, SNU, Korea

# OLED TV

Organic Semiconductor
EE 4541.617A
2009. 1st Semester

LG전자-LG Philips LCD (2004)
20.1" XGA (1280×800)
Poly-Si TFT AMOLED

삼성SDI (2008)
31" AMOLED TV
LTPS-TFT , Lifetime~35,000 h.

삼성전자 (2005)
40" WXGA (1280x800) HD급
a-Si TFT AMOLED

Philips (SID2004)
13" (576×324)
PolyLED TV (Injet-printing)

Seiko-Epson (2004)
40" WXGA (1280x768) tiled
AMOLED (Ink-jet printing)



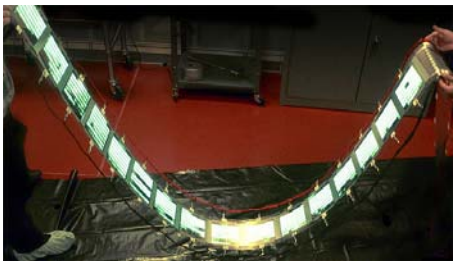
# OLED Lightings

Organic Semiconductor
EE 4541.617A
2009. 1st Semester

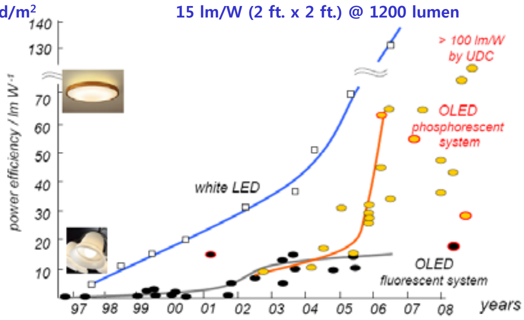
Philips Lighting/Novaled
25 lm/W @ 1000 cd/m$^2$

UDC
20 lm/W @ 800 cd/m$^2$

General Electric
15 lm/W (2 ft. x 2 ft.) @ 1200 lumen



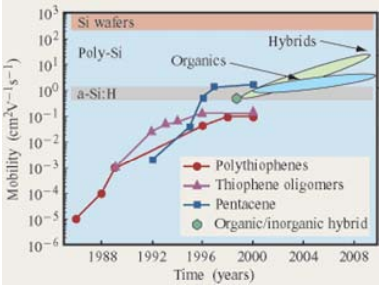
8-ft. strip comprised of 6 x 6 in. lighting panels
GE / Energy Conversion Devices / NIST the 2008. 3.



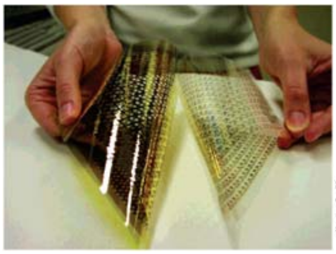

N. Ide (Matsushita Electric Works, Ltd.), et al., SPIE (2008)

# Progress of organic TFT performance






J. M. Shaw, P. F. Seidler, *IBM J. Res. & Dev.*, **45**, 3 (2001)



T. W. Kelley, et al. (3M), *Chem. Mater.* ***16***, 4413 (2004).

**low-thickness gate insulator using SAM**

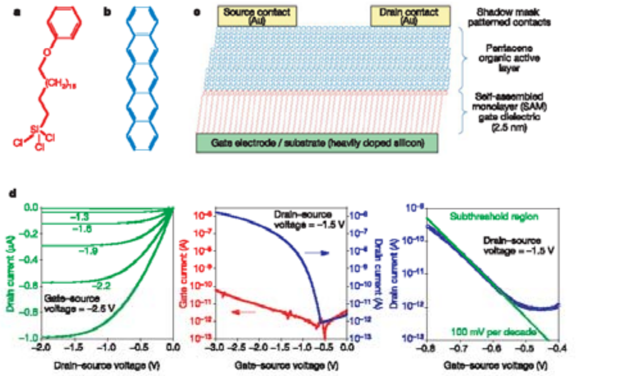



**Figure 1** Chemical structures of organic materials, and cross-section and electrical characteristics of a TFT with molecular SAM gate dielectric. **a**, Structure of (18-phenoxyoctadecyl)trichlorosilane (PhO-OTS). **b**, Structure of the organic semiconductor pentacene. **c**, Cross-section of a pentacene TFT with SAM dielectric and source/drain contacts deposited through a shadow mask. **d**, Output characteristics; **e**, transfer characteristics; **f**, subthreshold region, showing a subthreshold swing of 100 mV per decade.

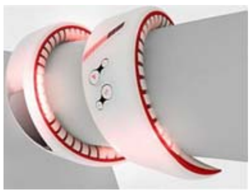
Marcus Halik, et al. (Infineon Technologies), Nature **431**, 963 (2004)



# Concept phones and Smart card



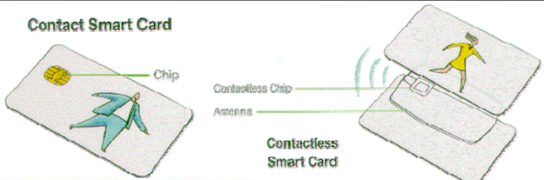
Nokia 888 Concept Phone

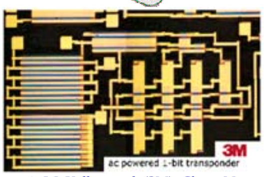


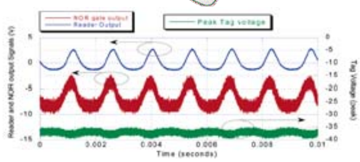
BenQ Siemens Snake phone

NEC Tag concept phone

RFID

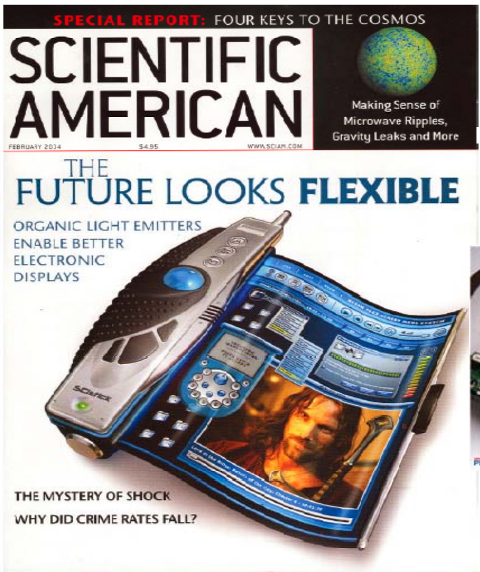



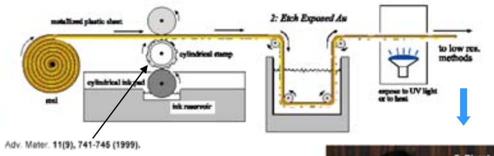



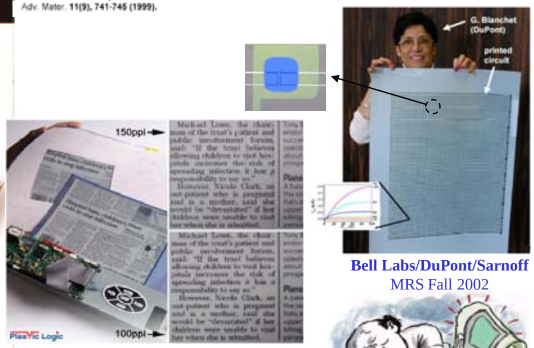

Tommie W. Kelley, et al. (3M), *Chem. Mater.* **2004,** *16*, 4413-4422

# Future displays






Bell Labs/DuPont/Sarnoff
MRS Fall 2002

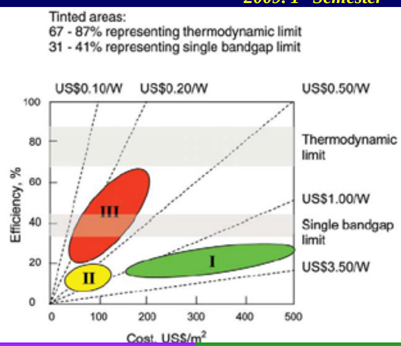


# Solar cell efficiency

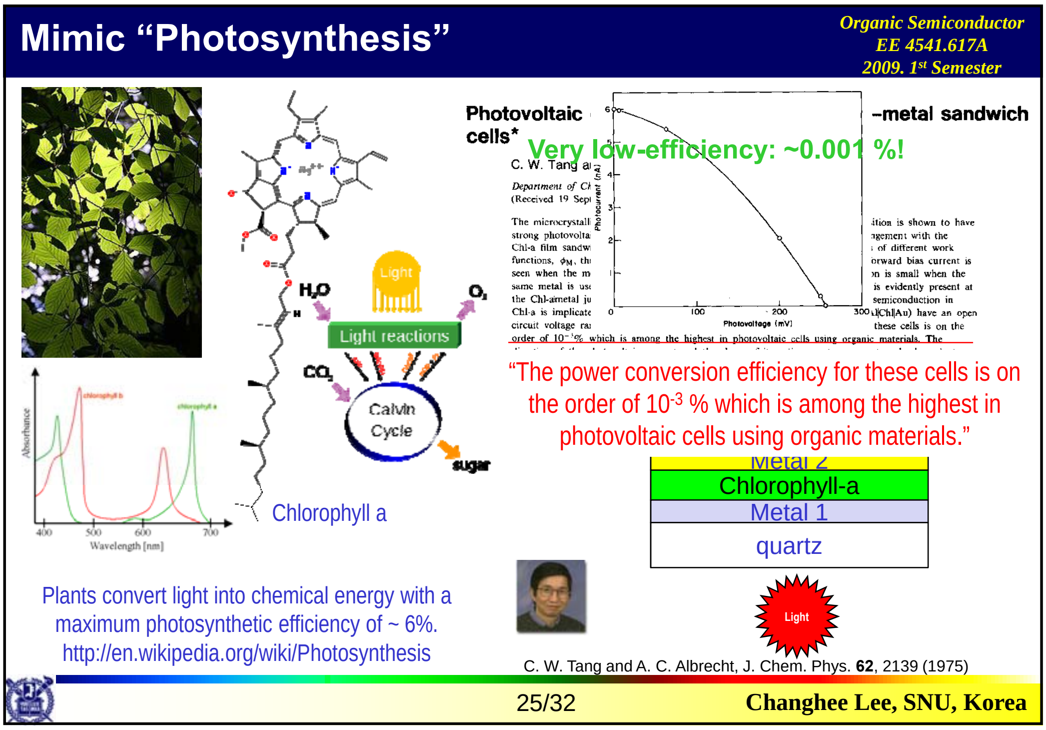


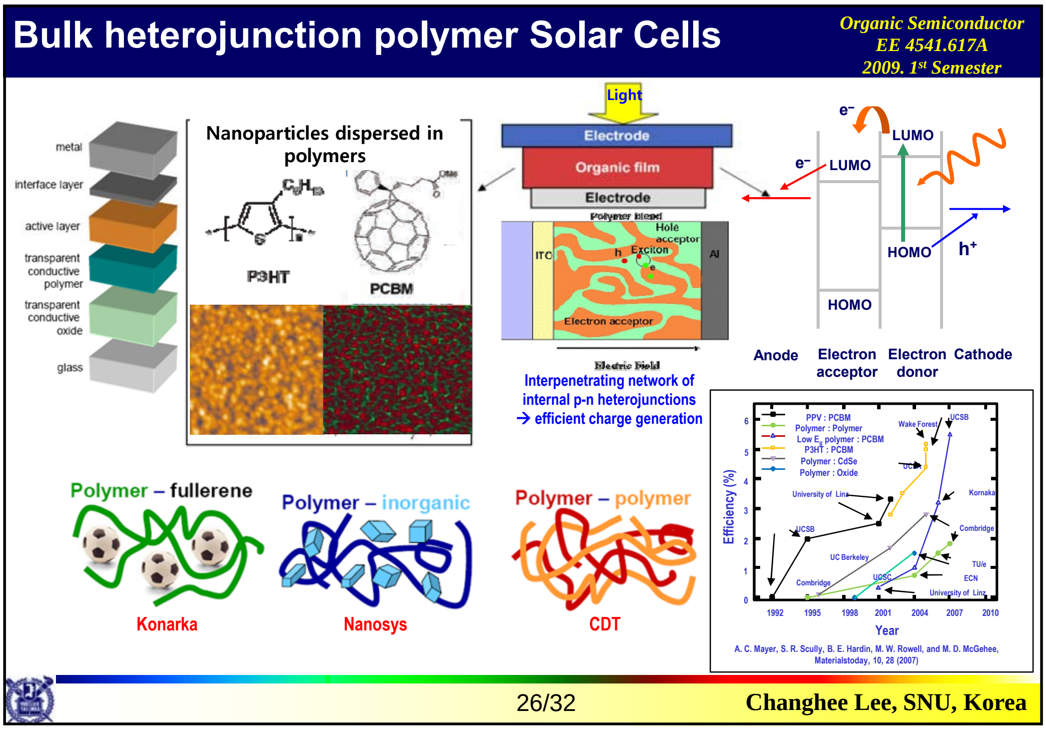
- **Si**
  - **Crystalline-Si**
    - Single Crystal: 24.7% (UNSW PERL)
    - Multi-Crystal: 20.3% (Fraunhofer)
  - **a-Si/μc-Si thin film**: 11.7% (Kaneka)
- **Compound Semicond.**
  - **III-V Cells**: 25.1% (Kopin, AlGaAs window)
  - **Multi-junction**: 32.0% (Spectrolab), 40.7%(240sun)
  - **Thin film chalcogenide**: 18.8% (CIGS, NREL) 16.5% (CdTe, NREL)
- **Organic**
  - **Dye-sensitized**: 10.4% (Sharp)
  - **Organic**: 5.15% (Konarka)

* Solar cell efficiency data from M. A. Green, K. Emery, Y. Hishikawa and W. Warta, *Prog. Photovolt: Res. Appl*. **16**, 61-67 (2008)




| Traditional PV | OPV |
|---|---|
| Expensive (3~4 $/Wp, 50 cents/kWh) | *Lower* cost (simple device structure, process, production facilities) |
| High module prices, high spec. (long life time) | Low unit costs enable use *even for shorter lifecycles* |
| Materials characteristics limit application field (rigid, heavy) | *New* applications (Light, Flexible, Semi-transparency) |

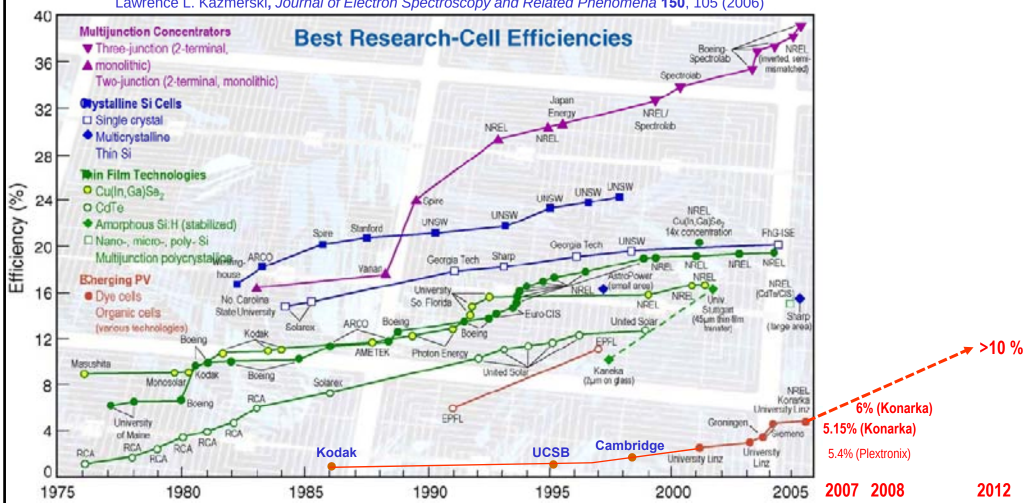

Mimic "Photosynthesis"
Organic Semiconductor
EE 4541.617A
2009. 1st Semester
Photovoltaic cells*
–metal sandwich
Very low-efficiency: ~0.001 %!
Light
H2O
O2
Light reactions
CO2
Calvin Cycle
sugar
Chlorophyll a
"The power conversion efficiency for these cells is on the order of 10-3 % which is among the highest in photovoltaic cells using organic materials."
Metal 2
Chlorophyll-a
Metal 1
quartz
Light
Wavelength [nm]
Plants convert light into chemical energy with a maximum photosynthetic efficiency of ~ 6%.
http://en.wikipedia.org/wiki/Photosynthesis
C. W. Tang and A. C. Albrecht, J. Chem. Phys. 62, 2139 (1975)
25/32
Changhee Lee, SNU, Korea


Bulk heterojunction polymer Solar Cells
Organic Semiconductor
EE 4541.617A
2009. 1st Semester
metal
interface layer
active layer
transparent conductive polymer
transparent conductive oxide
glass
Nanoparticles dispersed in polymers
P3HT
PCBM
Light
Electrode
Organic film
Electrode
Polymer blend
Hole acceptor
Exciton
ITO
Al
Electron acceptor
Electric field
Interpenetrating network of internal p-n heterojunctions
→ efficient charge generation
LUMO
HOMO
Anode
Electron acceptor
Electron donor
Cathode
Polymer – fullerene
Polymer – inorganic
Polymer – polymer
Konarka
Nanosys
CDT
Efficiency (%)
Year
A. C. Mayer, S. R. Scully, B. E. Hardin, M. W. Rowell, and M. D. McGehee, Materialstoday, 10, 28 (2007)
26/32
Changhee Lee, SNU, Korea

# History for the development of OPVs



Lawrence L. Kazmerski, *Journal of Electron Spectroscopy and Related Phenomena* **150**, 105 (2006)





Dr. Ching W. Tang
Eastman Kodak


Prof. Alan J. Heeger
(Nobel Laureate Chemistry 2001)
UCSB


Sir Richard Friend,
Univ. of Cambridge


Prof. N. Serdar Sariciftci
Johannes Kepler
Universität Linz



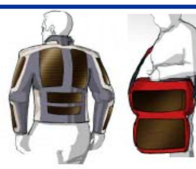
# Applications of organic solar cells






*Initial applications*

Consumer

Off-Grid

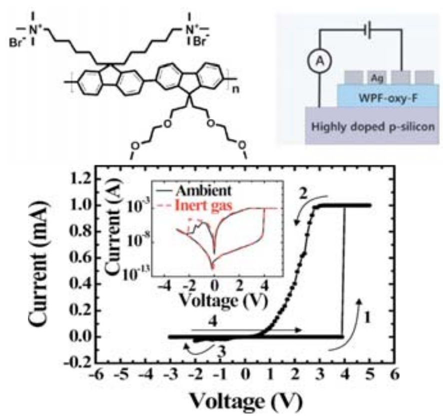

On-Grid


Current lifetime and performance allow to address
consumer electronics and selected off-grid markets

# Organic memory

*Organic Semiconductor*
*EE 4541.617A*
*2009. 1st Semester*

❖ **Switching behavior**

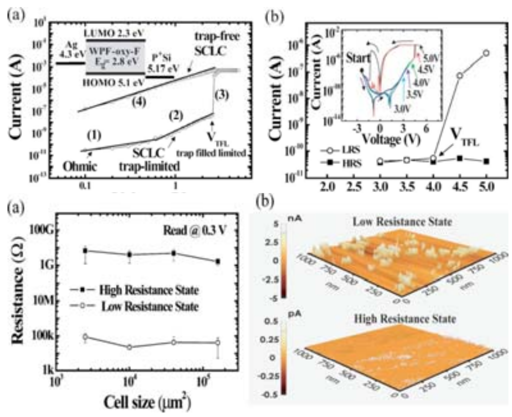



• WPF-oxy-F memory device showed bipolar switching behavior

• More than 3 orders of magnitude of on/off ratio

• Low operation voltage ( -3V ~ 5V )

❖ **Memory mechanism**




• Space-charge limited conduction

• Localized conduction paths in current image of LRS

Kim et al, *Appl. Phys. Lett.* 92, 253308 (2008)
Kim et al, *IEEE Electron. Device Lett.* 29, 852 (2008)



# Applications of Organic electronics

*Organic Semiconductor*
*EE 4541.617A*
*2009. 1st Semester*

## Applications:

• OLED displays

• White OLEDs: Large area smart lighting (rooms and vehicles)

• Solar cells, photodetectors, x-ray detectors

• Organic memory

• Smart cards, RFID tags : pixilated antennas and other wireless electronic elements

• Chemical sensors and biosensors

## Future applications:

• Organic spintronics

• Organic lasers

• Medical applications – test speed, sensitivity and selectivity : capability for covalent attachment to biological molecules and distribution over medically relevant materials. The ability to fabricate chemically sensitive OFETs is useful for medical applications.

## Organic electronics: Issues

Several issues continue as barriers to the implementation of organic electronics as a robust technology.

- Lower mobilities of organic semiconductors
- Possible contact resistance
- A dense organic circuit is expected to generate considerable heat.
- Stability and reliability of devices and circuits have yet to be adequately demonstrated.





HW2. Read the following review articles:
Stephen R. Forrest, “The path to ubiquitous and low-cost organic electronic appliances on plastic”, Nature **428**, 911 (2004).

Nitzan and Ratner, “Review: Electron transport in Molecular Wire Junctions,” Science **300**, 1384 (2003).

H.-S. Philip Wong, “Beyond the conventional transistor”, Solid-State Electronics **49**, 755 (2005).

M.I. Katsnelson, “Graphene: carbon in two dimensions”, Materials Today **10**, 20 (2007).