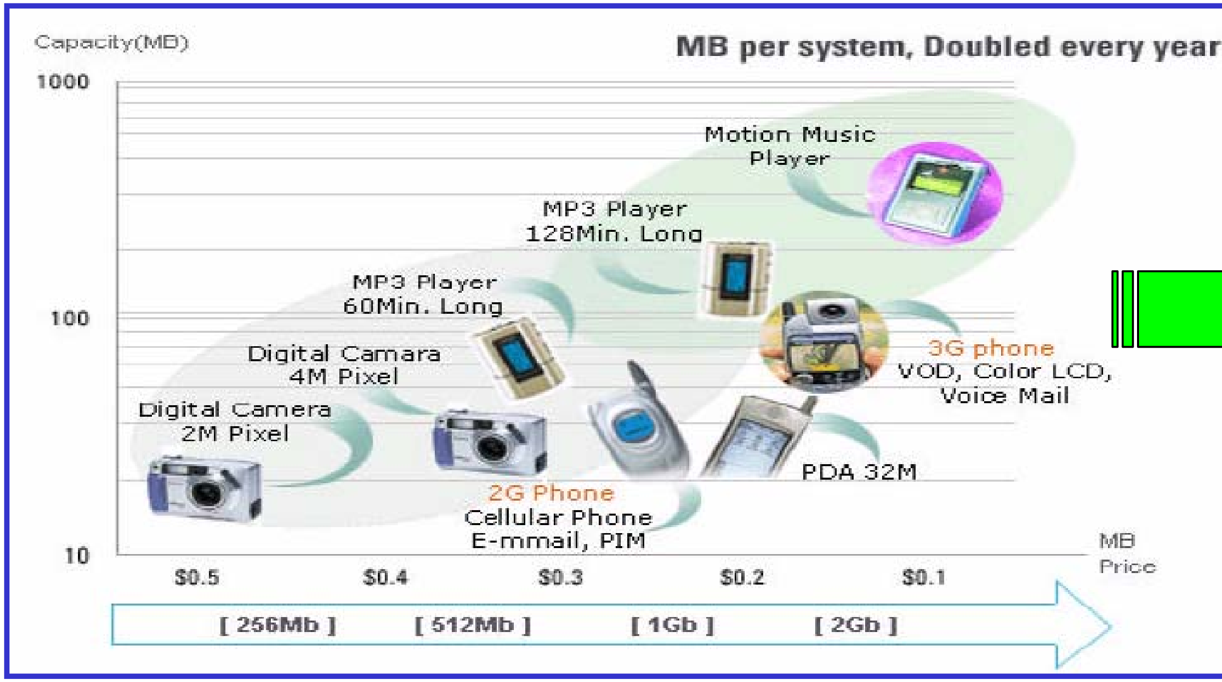
# Nanostructured molecular switch and memory

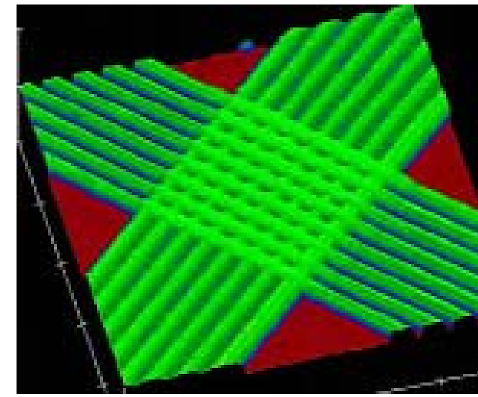
Hyoyoung Lee

US-Korea NanoForum, 27-30Apr2009

# Why working on molecular memory?




**Tera-bit**
**Molecular Memory Device**

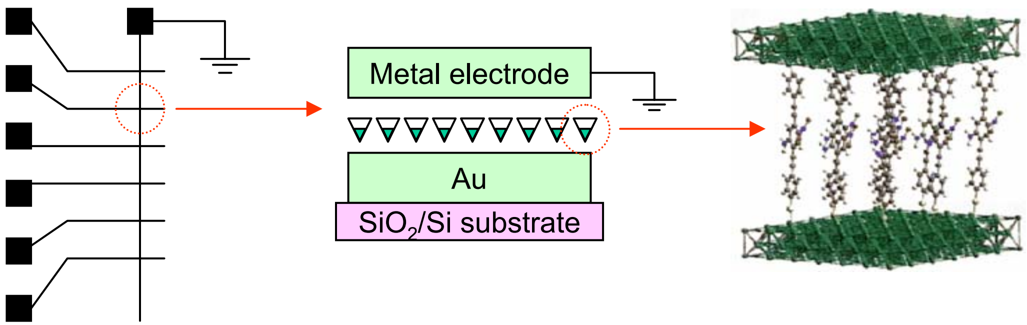


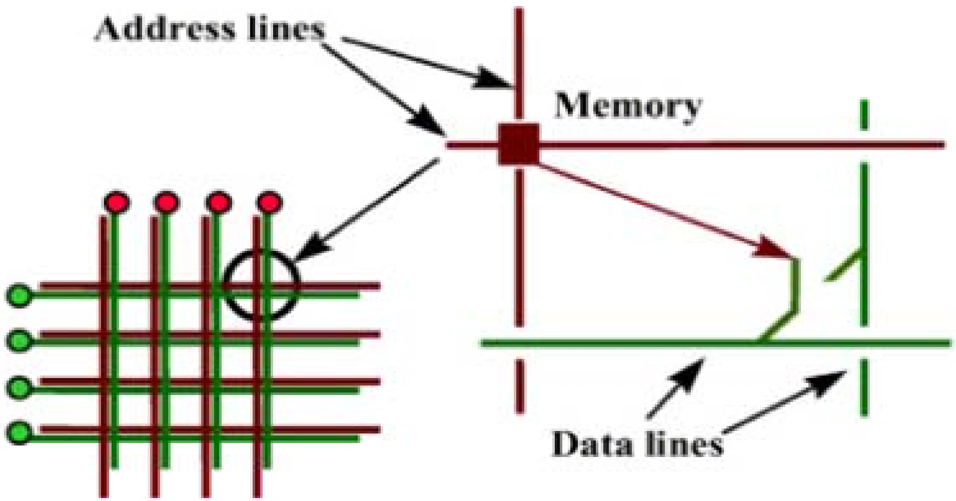
**Current Commercial Memory** → **ME, High Density**

**- Digital-Camera, mp3, Cellular phone, Hand-held PDA, Notebook**

2009. 02. 04, 500G, $170

# Possible applications of the molecular memory




**Molecular Memory**

**Random Access Memory (RAM)**

- Volatile Memory
- Non-Volatile Memory

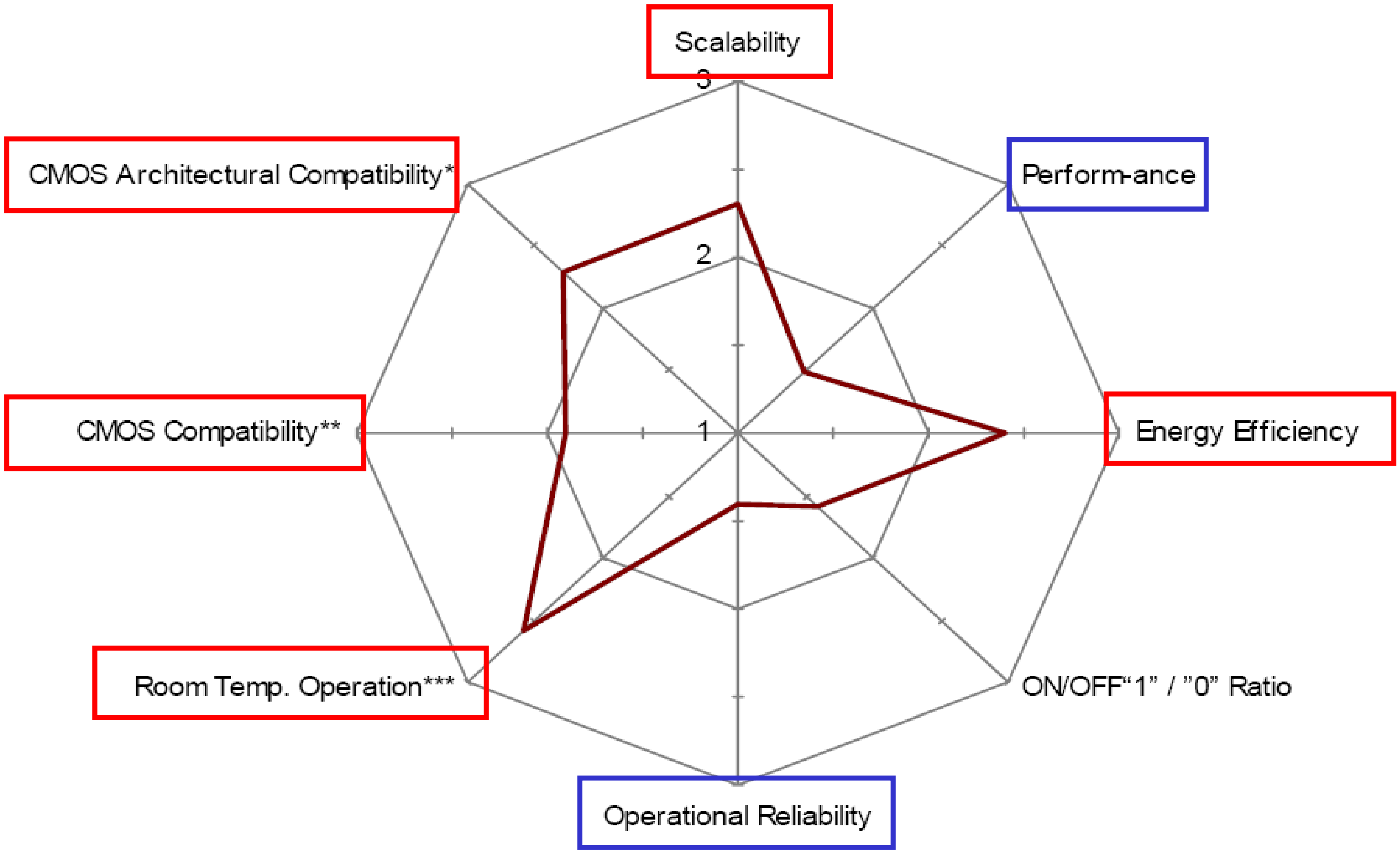
**D-, S-RAM**

**Molecular Computer**

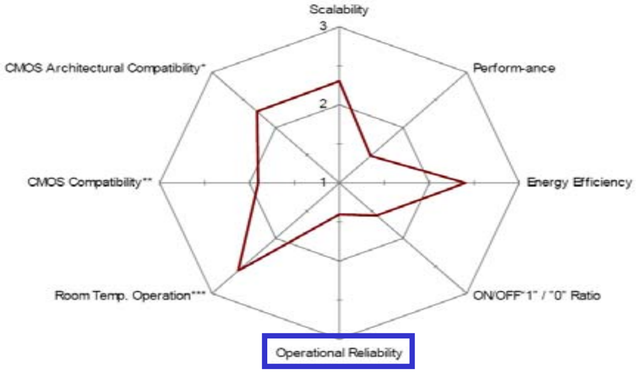
**Flash Memory**

- Highly density memory
- Cheap (Low-end product)
- Various and flexible

2007 년 ITRS Roadmap



# What is the major drawback?




Operational reliability!

What is the major issue for improving a reliability?

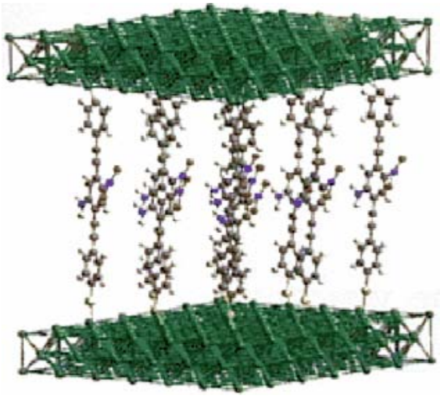
That is directly related to......device yield!

Summary of results for the fabricated devices. (Note: working and non-working devices were defined by statistical analysis with Gaussian fitting on histograms)

| | # of fabricated devices | Fab. failure | Short | Open | Non-working | Working | | | | Device yield |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | DC8 | C8 | C12 | C16 | |
| Monothiol | 13 440 (100%) | 392 (2.9%) | 11 744 (87.4%) | 1103 (8.2%) | 45 (0.3%) | | 63 (1.41%) | 33 (0.69%) | 60 (1.44%) | 156 (1.2%) |
| Dithiol | 4800 (100%) | 192 (4%) | 4080 (85%) | 428 (8.9%) | 16 (0.3%) | 84 (1.75%) | | | | 84 (1.75%) |

Tae-Wook Kim, Gunuk Wang, Hyoyoung Lee, and Takhee Lee*, Nanotechnology 18 (2007) 315204

# What are the major issues when using SAMs?



Metal electrode

SAMs, thin films of molecules

Metal electrode

1. Stability of SAMs, thin films of organic molecules

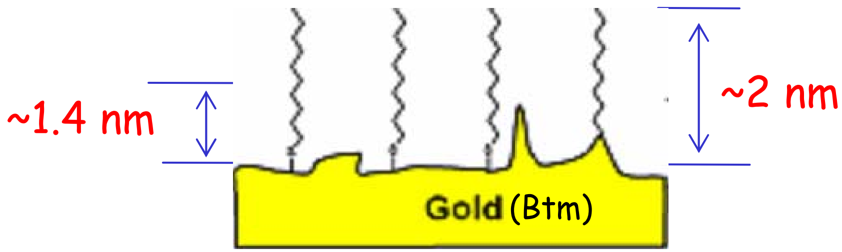
- Compactness, robustness, and **film thickness of the SAMs**
- Stability of SAMs having functional groups vs only alkane (di)thiol

2. Bottom/top Electrodes (metal)

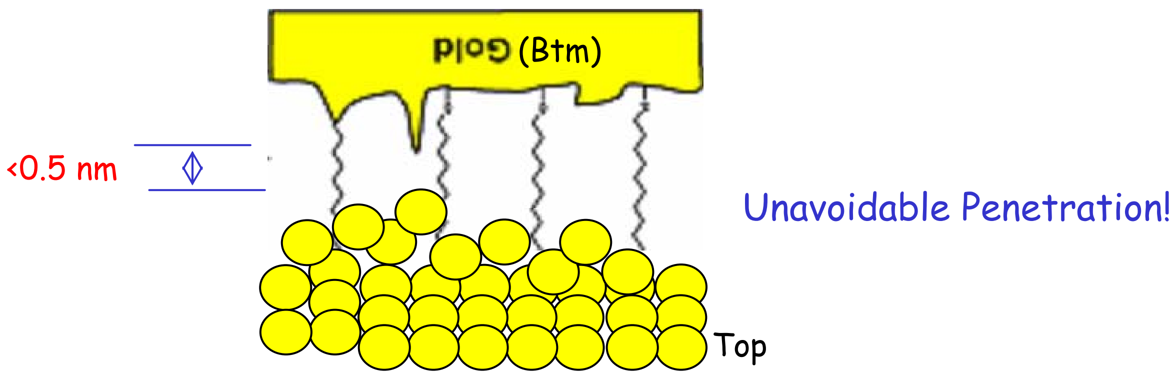
- **Surface roughness of bottom metal electrode (btm)**
- Penetration of metal particles into the SAMs (top)
- Surface area contacted on metal electrode

# Real world in small, tiny land!

Surface roughness , RMS of bottom electrode: ~1.4 nm




The length of SAM molecules, film thickness of SAMs: ~2 nm

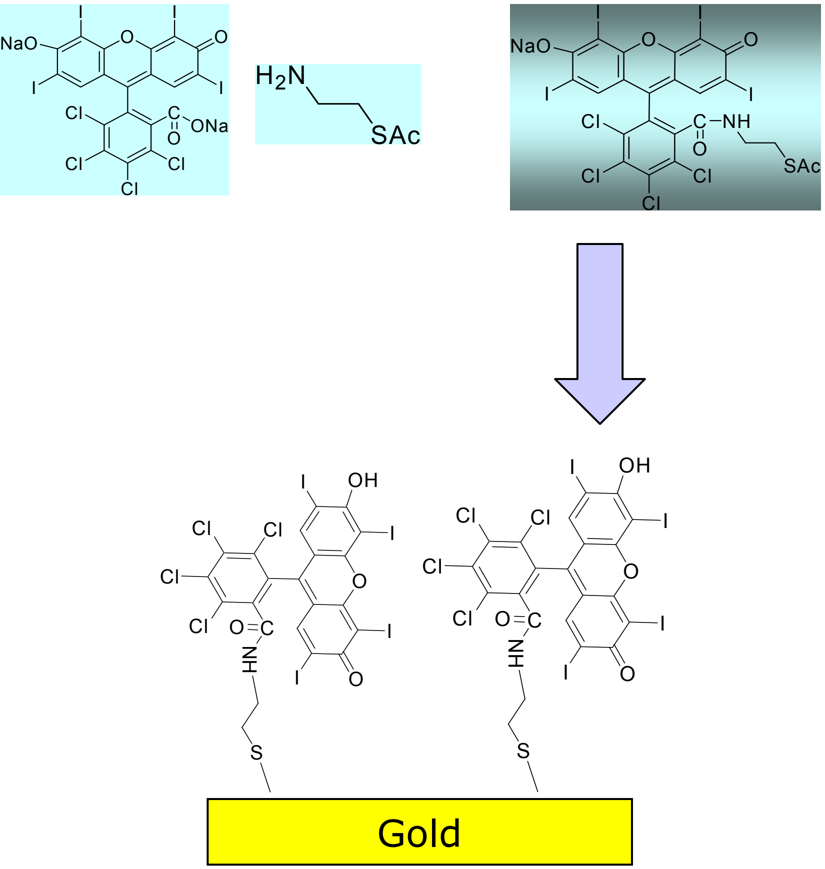



Vapor deposition

**What is your suggestion to improve our device yield?**

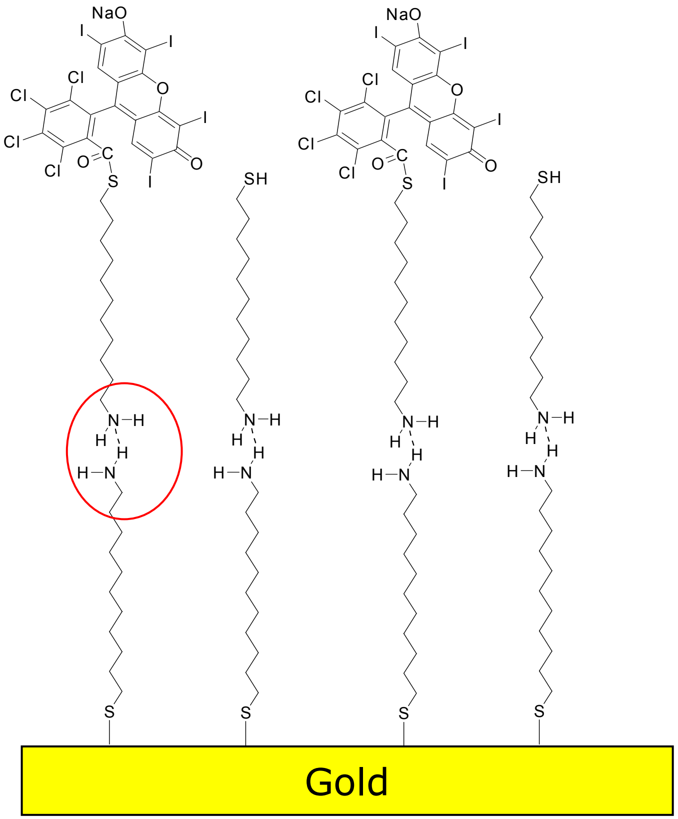
**What do you say about film thickness?**

# Self-Assembled Monolayer of RB




**RB-$(CH_2)_2$SH**

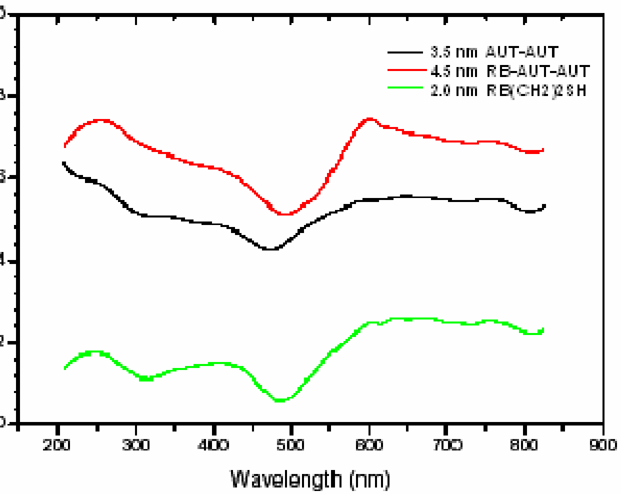
*Bi-layer*

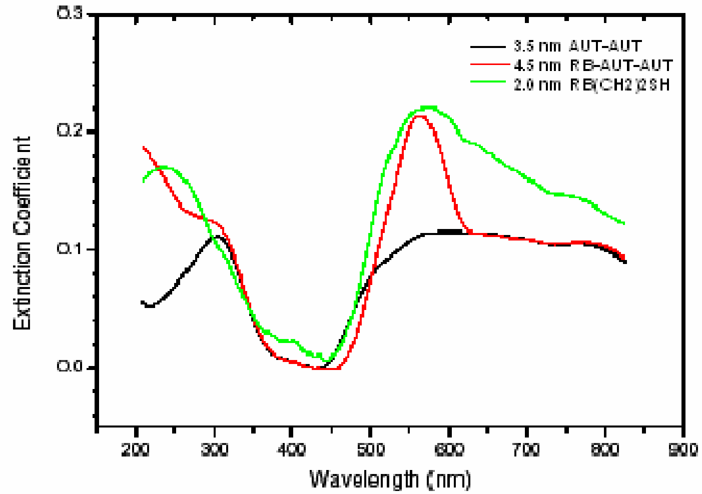


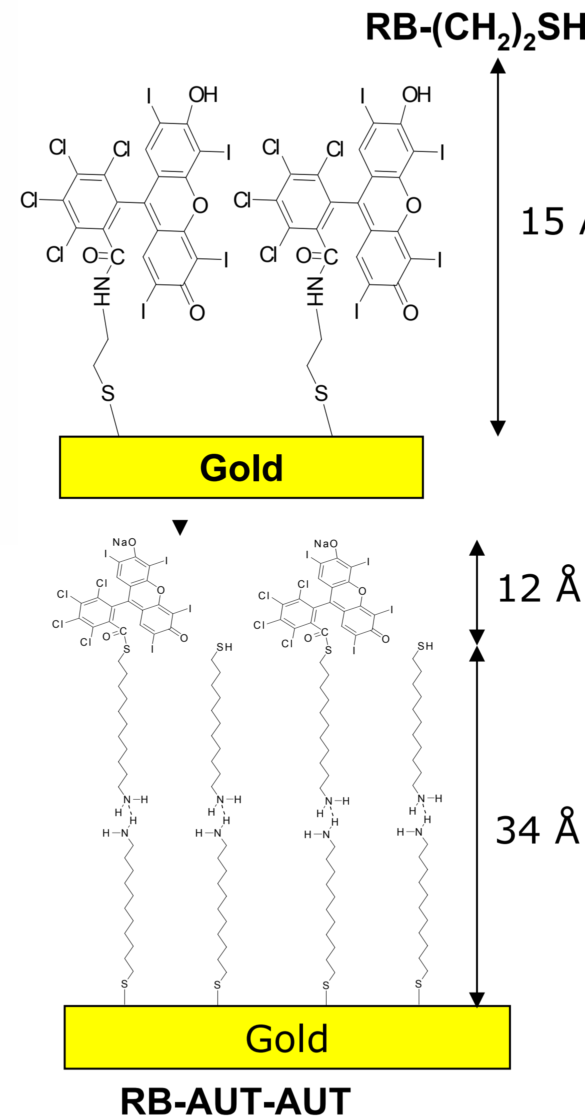

**RB-TUA-AUT**

Surface : Au(800 Å)/Ti(50 Å)/Si

# Thickness of RB-$(CH2)_2$SH, AUT-AUT and RB-AUT-AUT using Ellipsometer

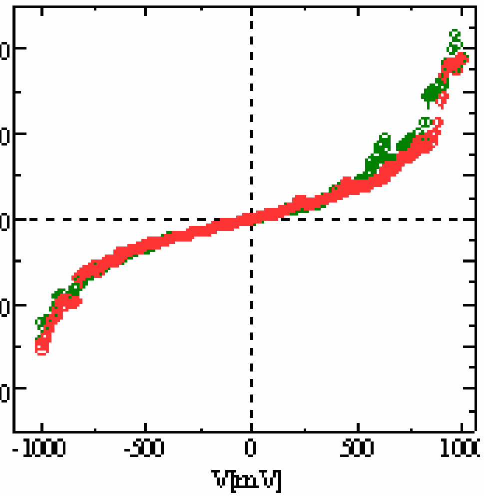


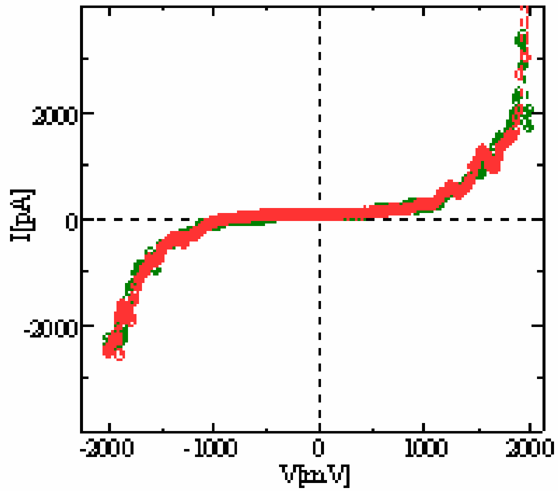




| SAMs | Theoretical value/ Å | Observed value/ Å |
|---|---|---|
| RB−$(CH_2)_2$SH | 17 | 20 |
| AUT−AUT | 34 | 35 |
| RB−AUT−AUT | 46 | 45 |

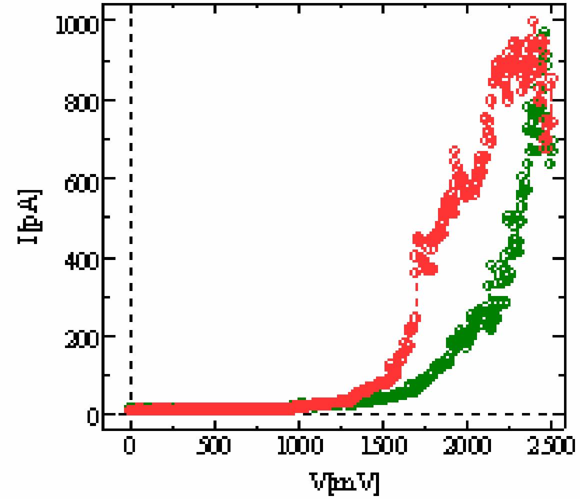
# *I-V* curves by using CP-AFM




**RB-(CH$_2$)$_2$SH**




**AUT-AUT**

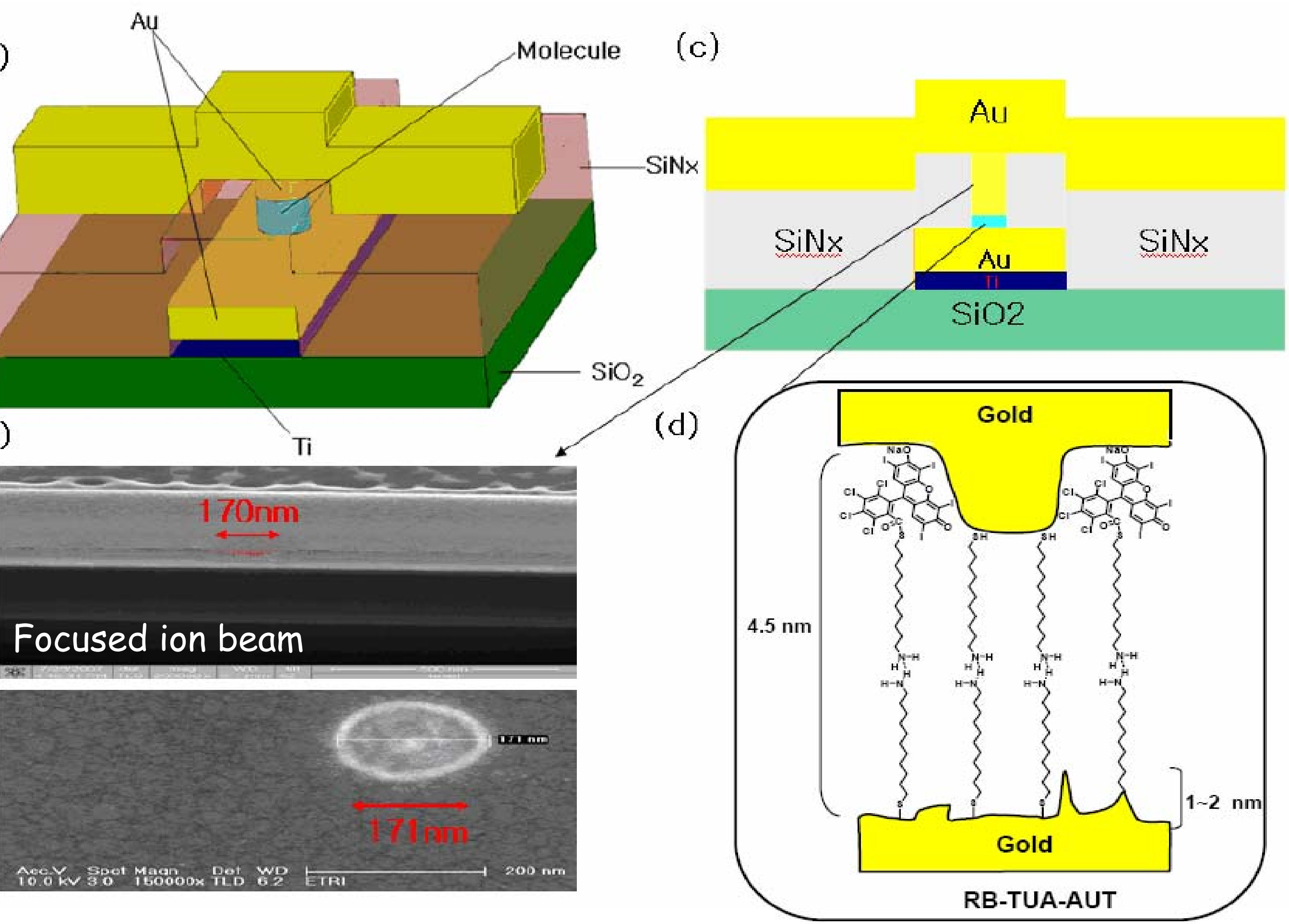



**RB-AUT-AUT**

1. *RB-(CH$_2$)$_2$SH film show ohmic behavior*
2. *AUT-AUT film show insulating behavior*
3. *RB monolayer on the bilayered AUT exhibit hysteresis.*

G. S. Bang, …**H. Lee***, *Langmuir* (IF. 4.0) **23**, 5195-5199 (2007)

# What do you say about…in device?



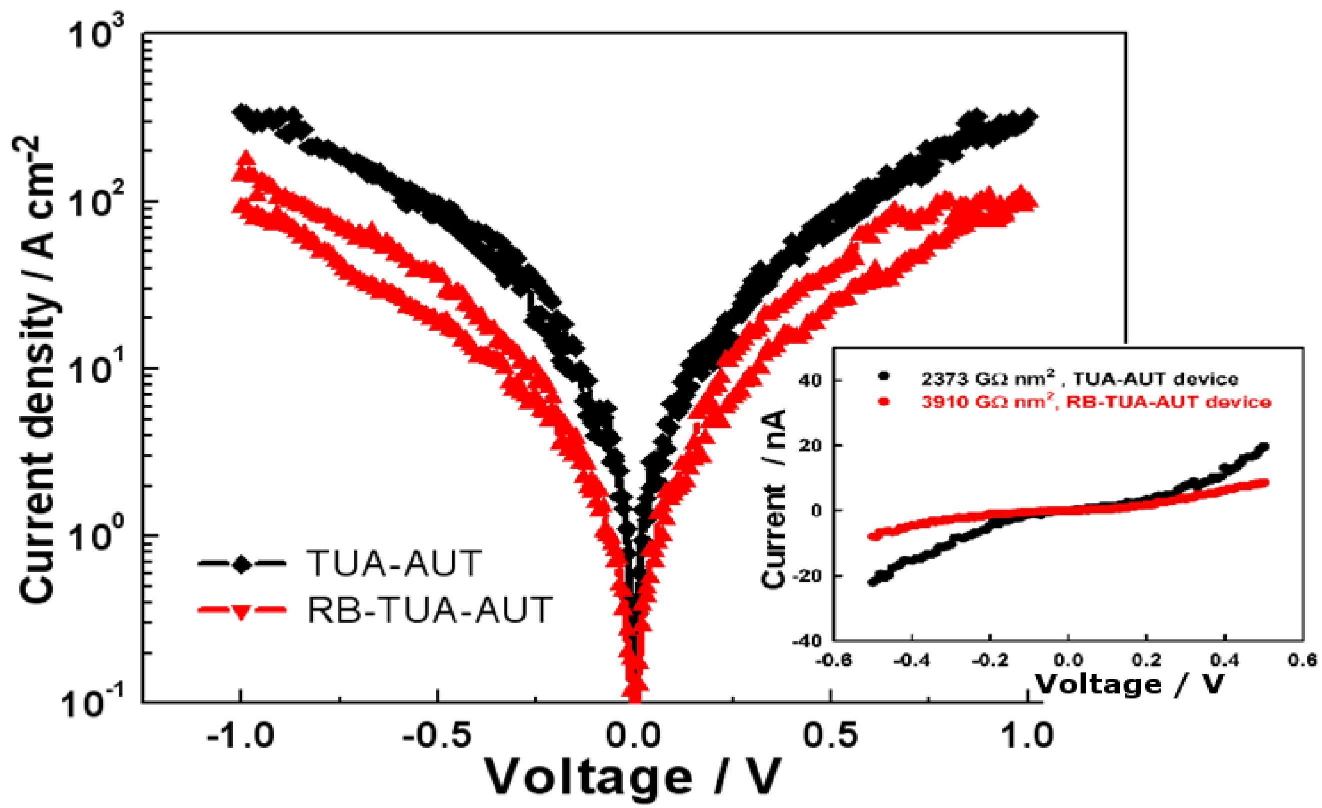

- Preventing the penetration of Au NPs

- Increasing the film thickness
- Introducing H boning

to overcome the RMS of Au btm

# Current density-voltage (J-V)

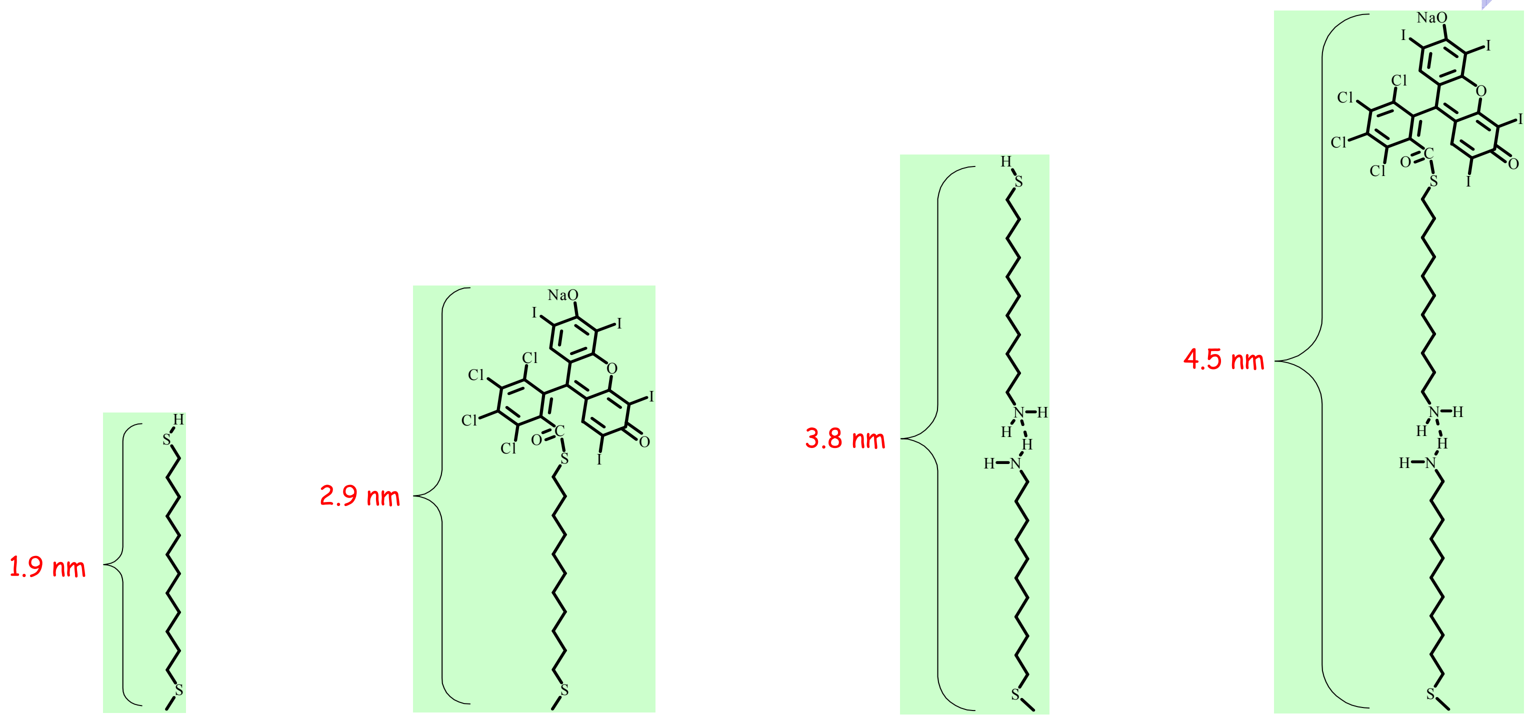
- Current density-voltage (*J-V*) characteristics of semi-log scale



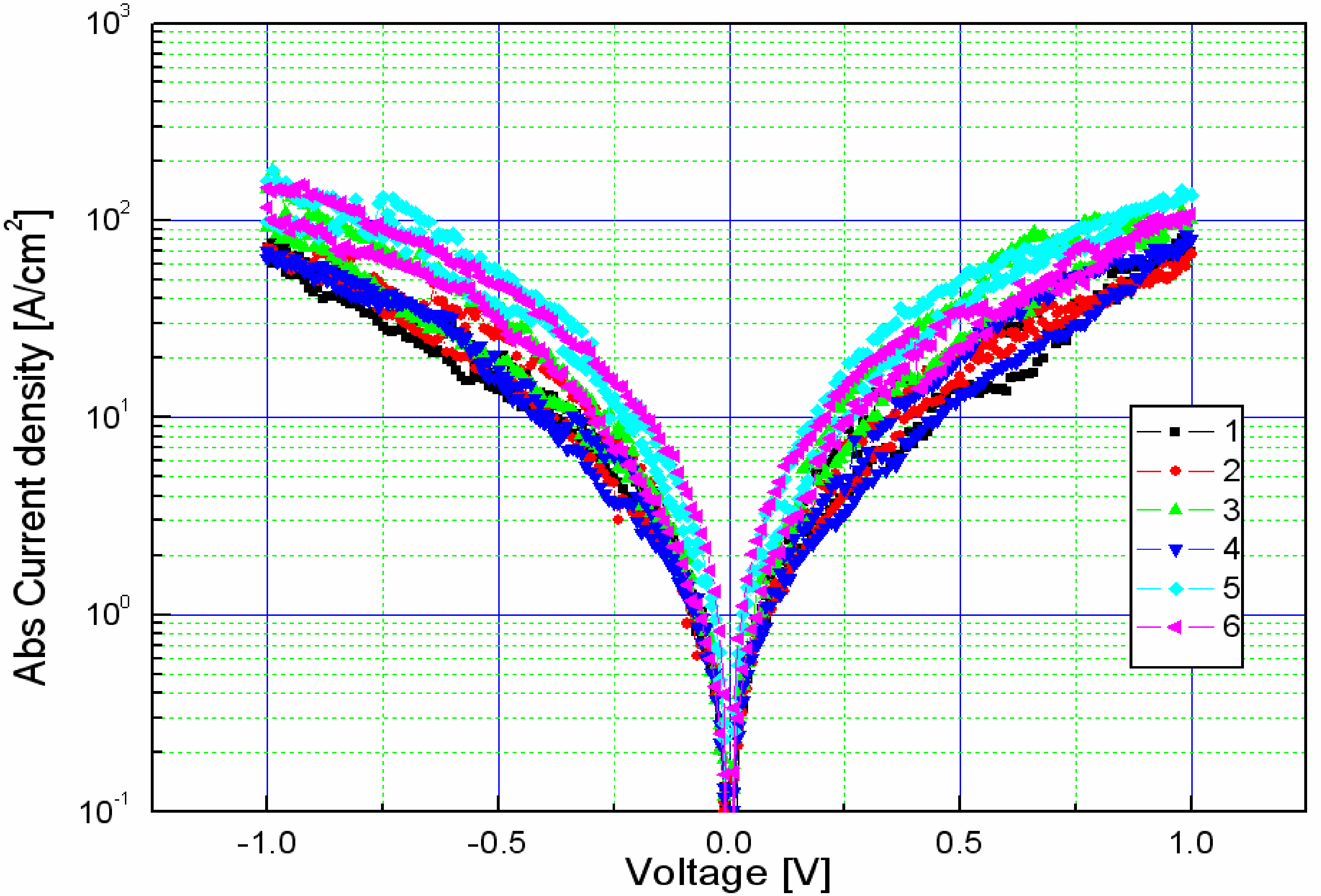

Current density-voltage (J-V) characteristics; Normalized I-V curves between – 0.5 V and + 0.5 V (the inset) for the TUA-AUT device (black line) and the RB-TUA-AUT device (red line) in the nano via-hole with 170 nm diameter.

# Device yields depending on the length of molecules

| | DDT SAM | RB-DDT SAM | TUA-AUT Bilayer SAM | RB-TUA-AUT Bilayer SAM |
|---|---|---|---|---|
| Nano via hole | 0% | 0% | > 11% | 94% |
| | - | - | 18 out of 160 | 102 out of 108 |



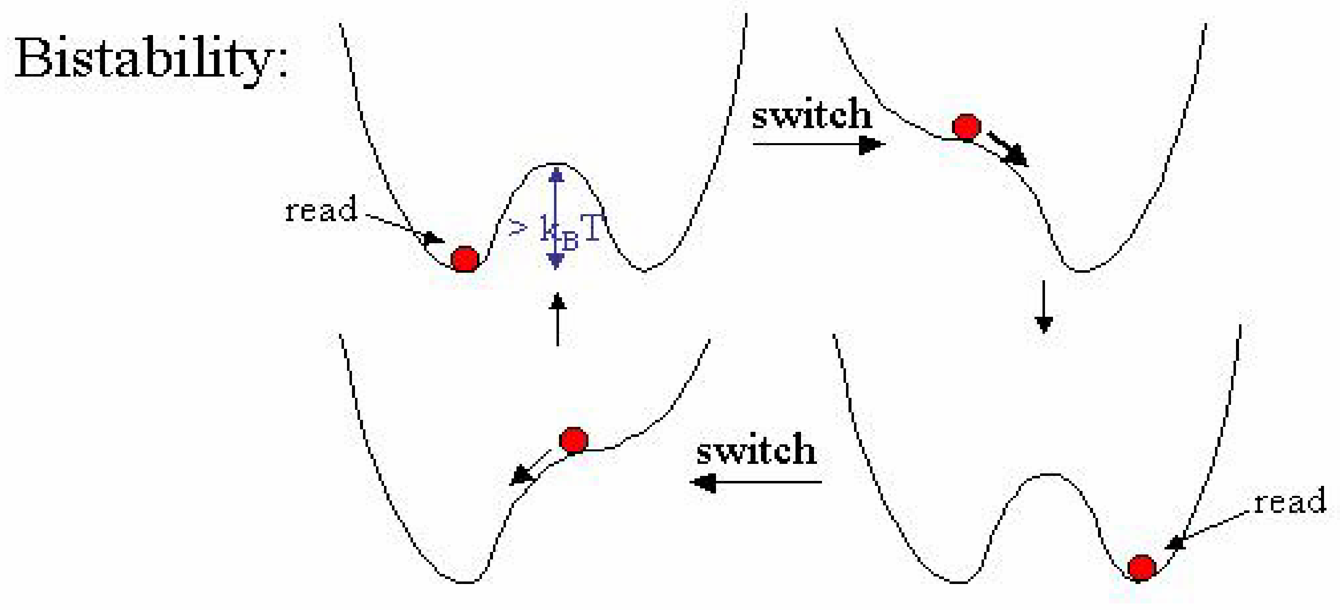
# High Reproducibility

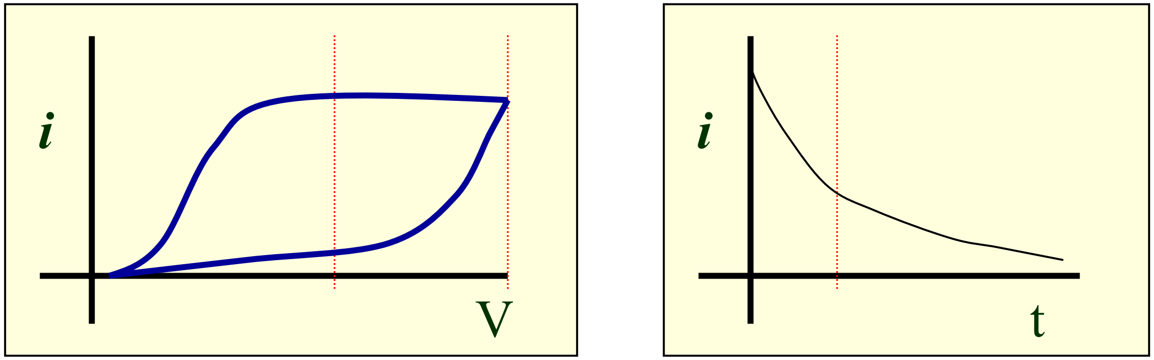



Current density-voltage (*J*-*V*) characteristics for the RB-TUA-AUT device

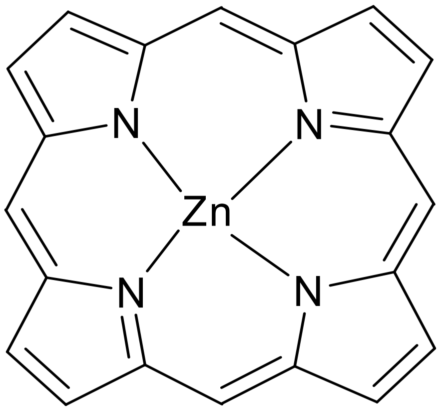
G. S. Bang, …,…**H Lee***, *Small (IF 6.4)*, 4, 1399-1405 (2008).

# Molecular switch/memory

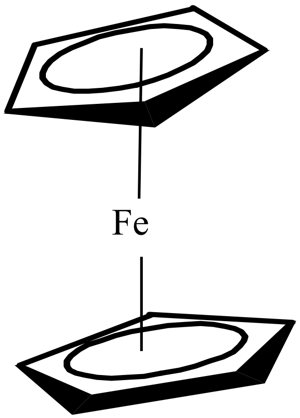


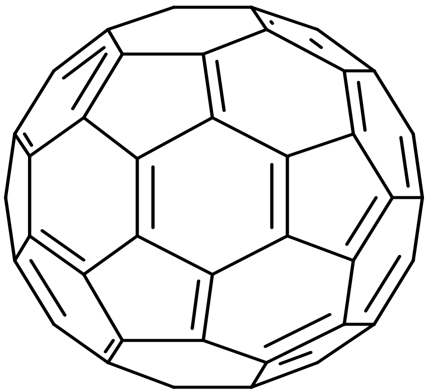
# Possible molecules for molecular switches/memory




Porphyrin



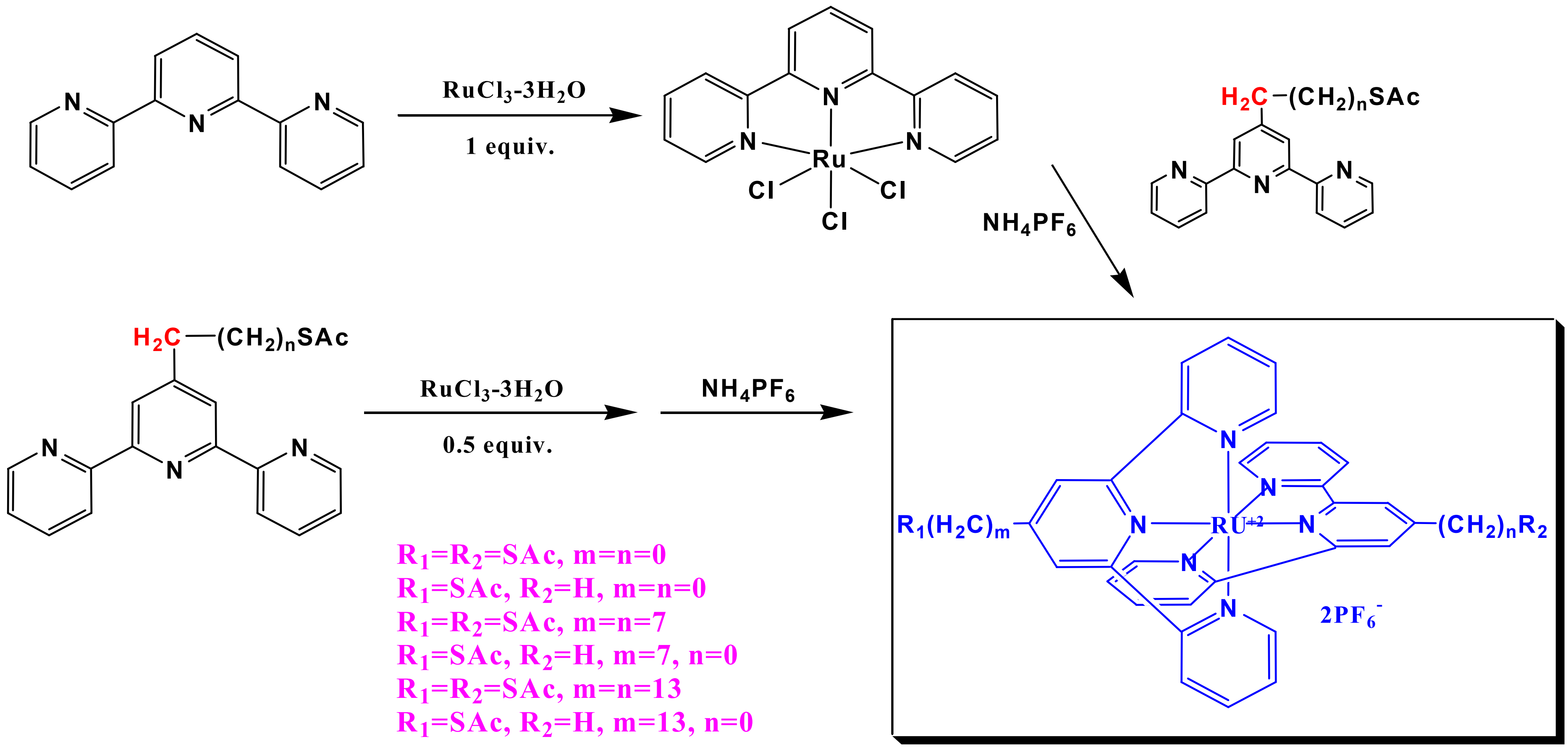

Ferrocene



Fullerene, N-type

What are other possible molecules for molecular switch/memory device?

# Synthesis of $Ru(tpy)_2$ Derivatives

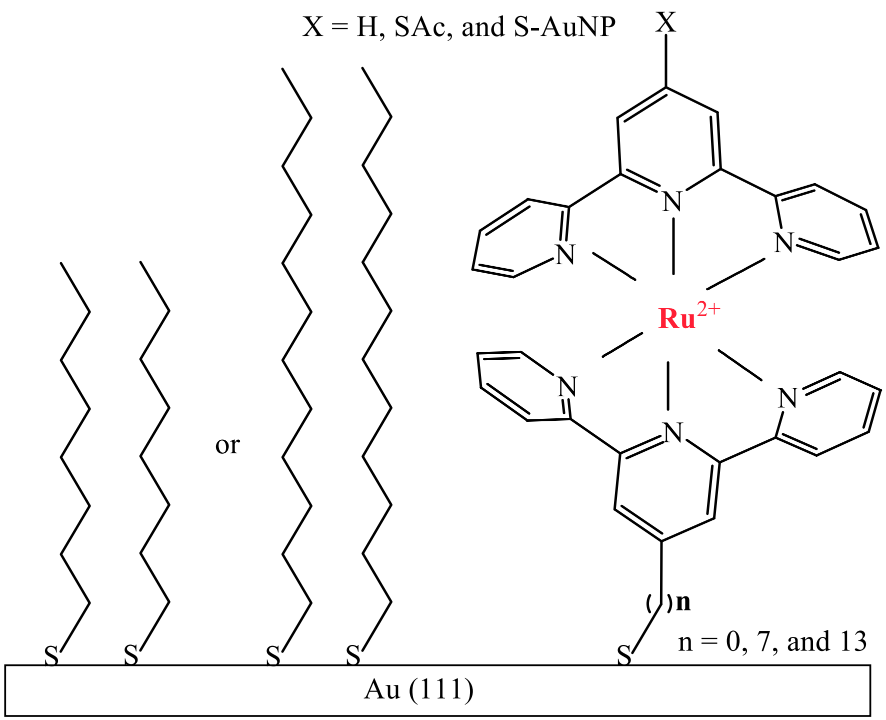


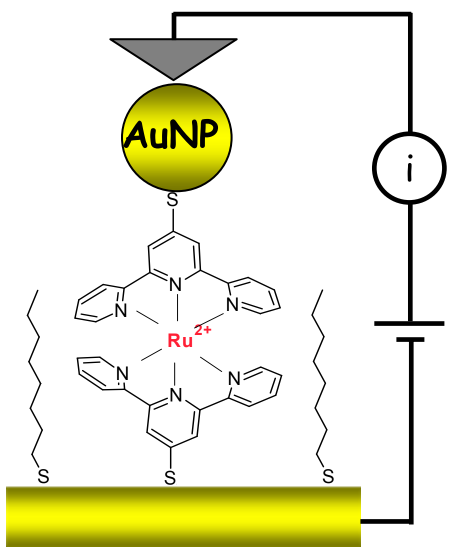

Electron Donor (metal)-Acceptor (Ligand, tpy)

$Ru^{2+}$ ---> $Co^{2+}$ , $Fe^{2+}$ (got now)

# Measurement system (STM) of the solid state

Scheme of $Ru^{II}$ complexes incorporated in an ordered *n*-alkanethiol SAM on Au(111)

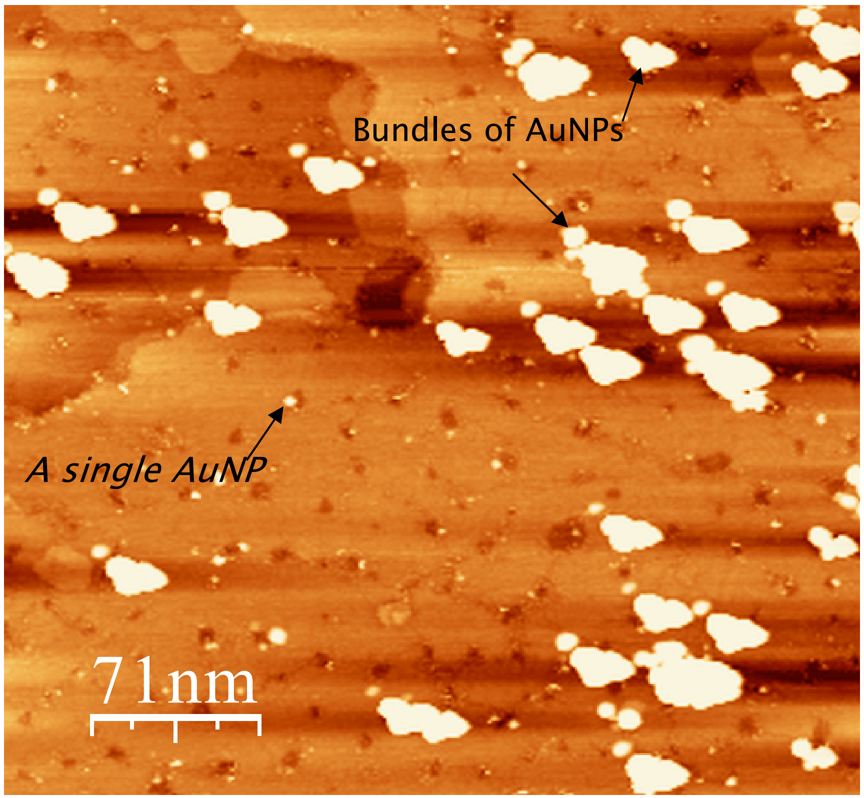


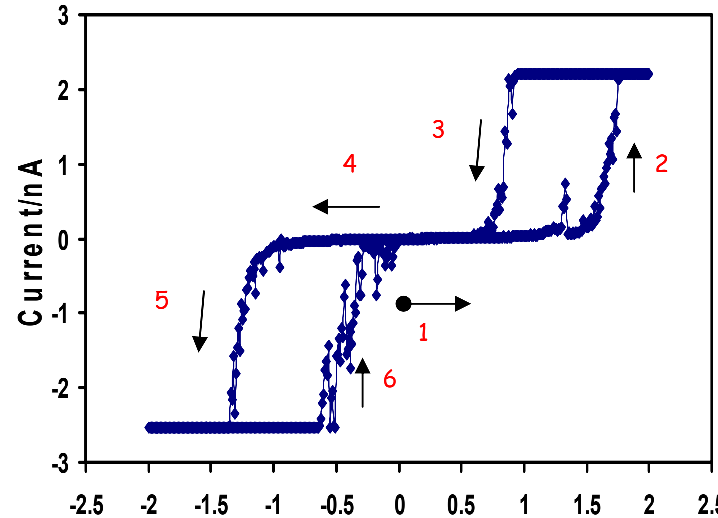

A voltage-driven molecular switch

# I-V characteristics of a Au-NP/$Ru^{II}(tpyS)_2$ incorporated 1-octanethiol (OT) SAM on Au(111), Dithiol

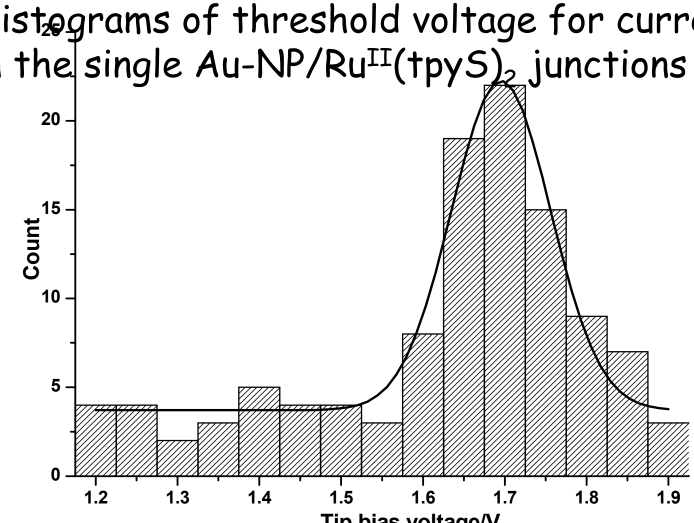
STM image at a constant tunneling current of 20 pA with a tip bias of 1.2 V




Current-voltage (*I*-*V*) characteristics

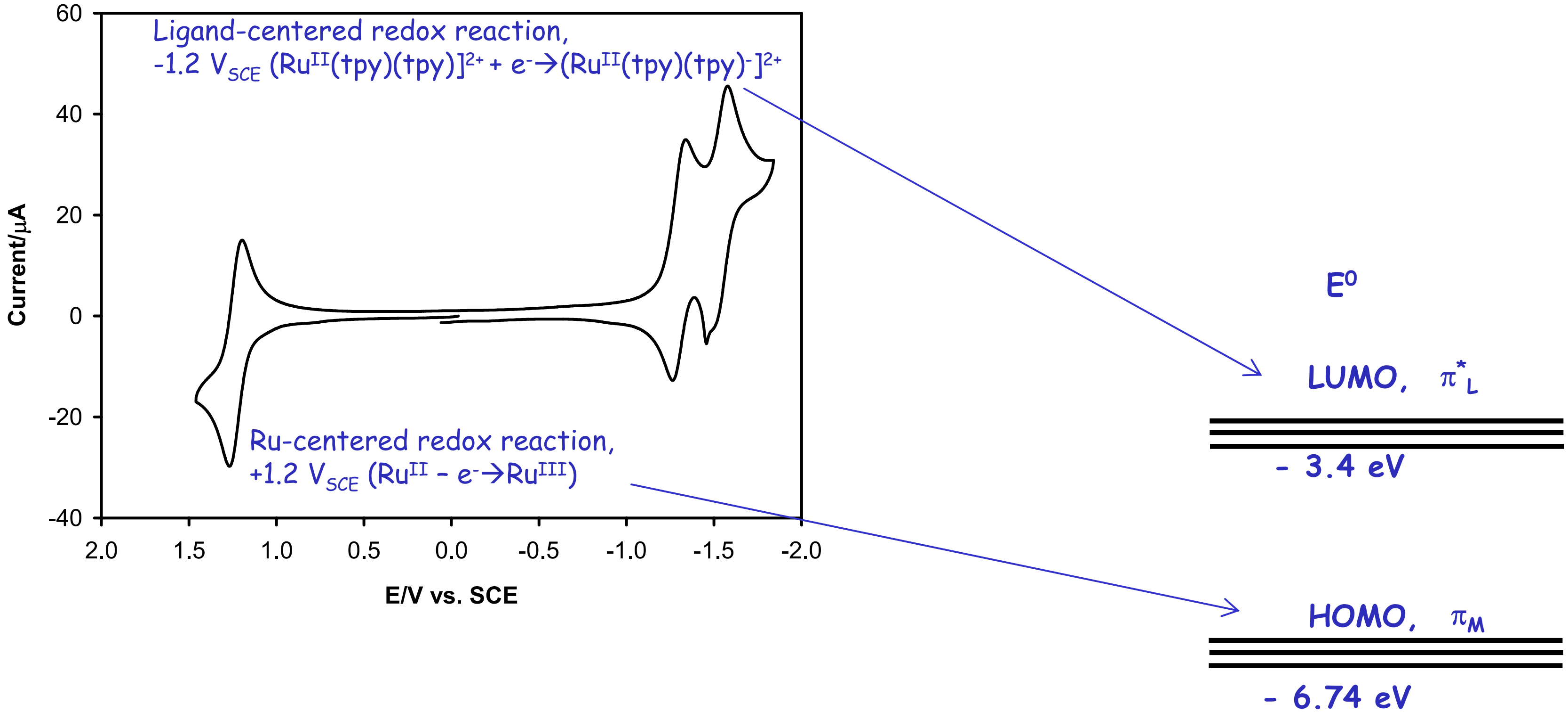



Histograms of threshold voltage for current switch-on in the single Au-NP/$Ru^{II}(tpyS)_2$ junctions



# Redox formal potentials to the vacuum levels

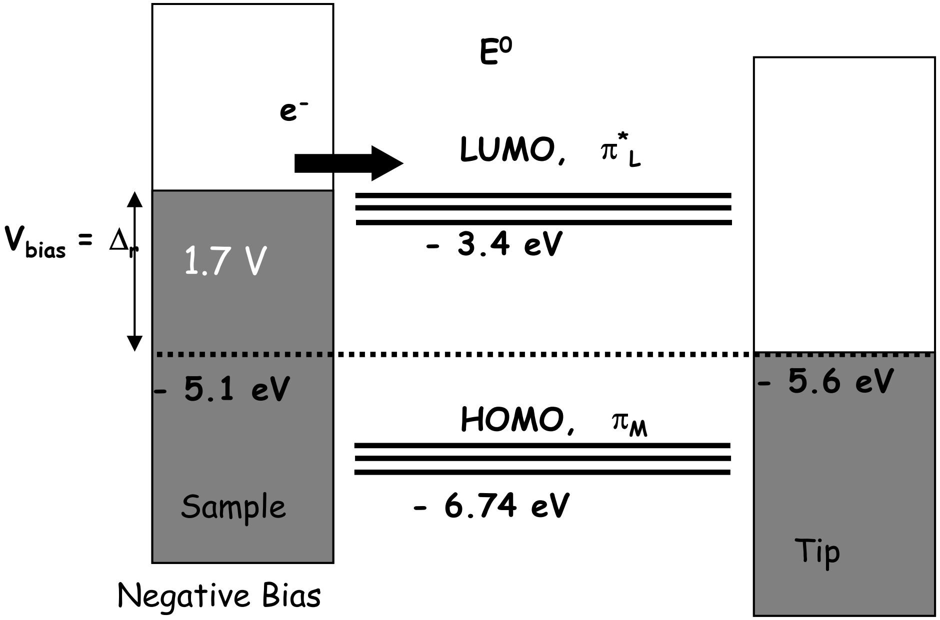
Cyclic voltammogram for a 3 mM RuII(tpy)(tpy$C_{13}$SAc) solution in acetonitrile using a glassy carbon electrode.

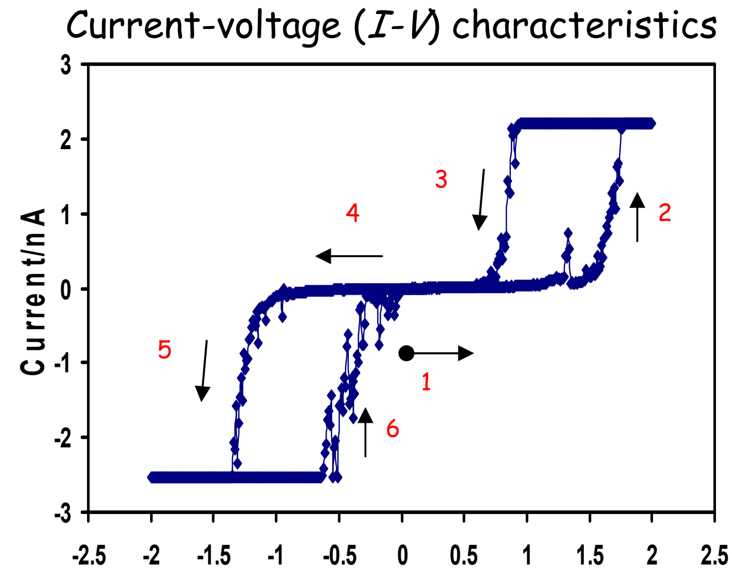



The redox formal potentials can be converted to the vacuum levels;
Hipps et al. *[4.7 eV + (1.7)$E_{ox}(SCE)_{1/2}$]* and Armstrong et al *[4.7 eV + $E_{red}(SCE)_{1/2}$]*

1.Energy levels of the first metal-centered oxidation, 6.74 (*$V_{ox}$ = 4.7 eV + (1.7) x 1.2 = 6.74 eV*)
2.Energy levels of the first ligand-centered reduction are 3.4 V (*$V_{red}$ = 4.7 eV - 1.2* = 3.4 eV) below the vacuum.

# Proposed charging process into the ligand-centered LUMO of $Ru^{II}$ terpyridine complexes




-Typical *I-V* characteristics through molecular junctions of $Ru^{II}(tpy)(tpyC_7S)$ showed significant conductance switching to a high conductance state approximately at 1.7 V.

-The threshold voltage of switch-on is comparable to the first redox formal potential of the terpyridine ligand supported on gold.

. Seo, … **H. Lee***, J. Am. Chem. Soc. (IF 7.9), 130(8), 2553-2559, 2008

**1st understanding of the charging Process of the molecules at the solid state**

lectron Tunneling through an Alkyl Chain-Tethered Metal Complex Molecular Switch Junction

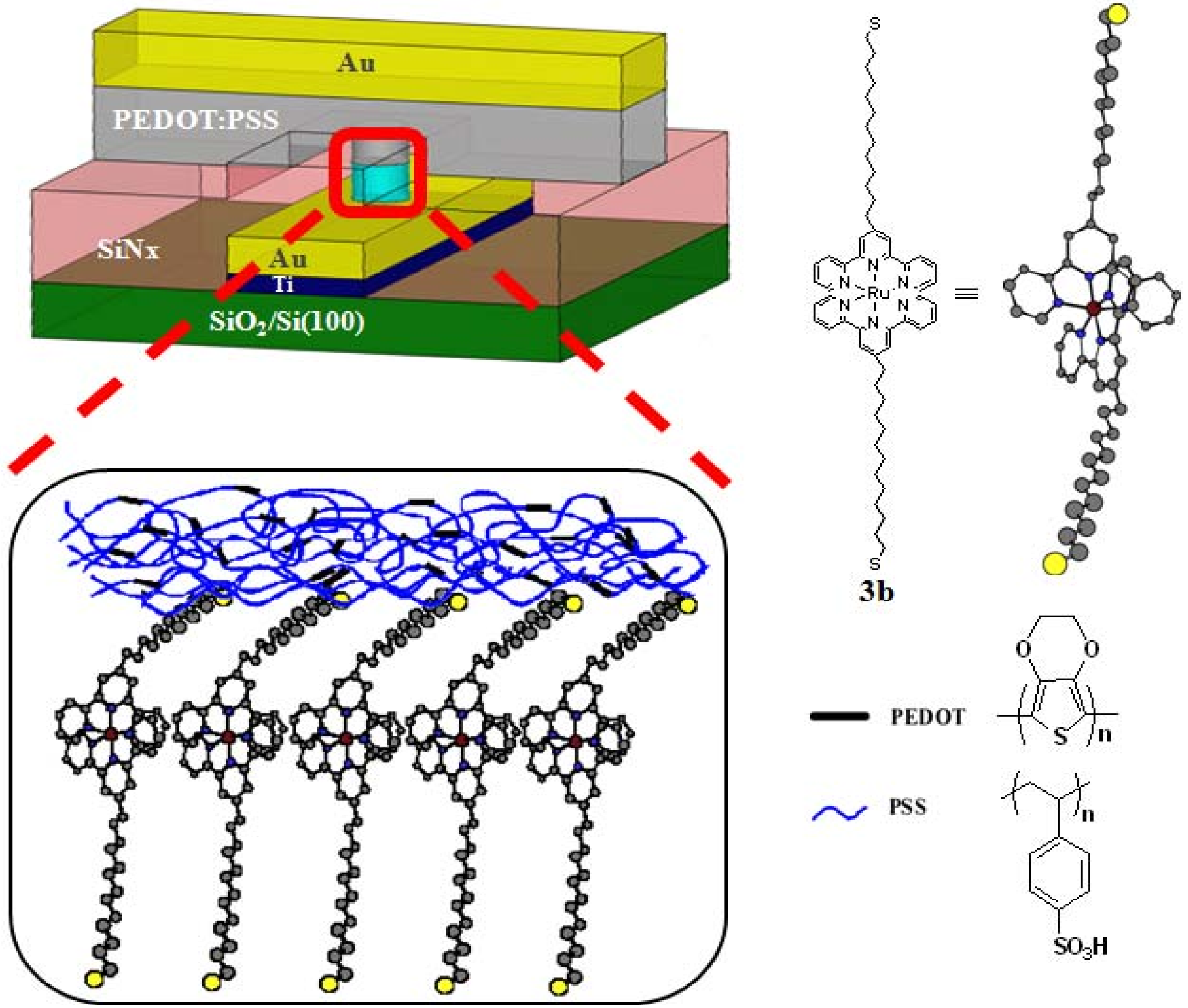
. Seo, … **H. Lee***, Chem. of Mater., submitted, 2009

olecular Electron Transport on Structural Phase Transition in a Large Area Junction

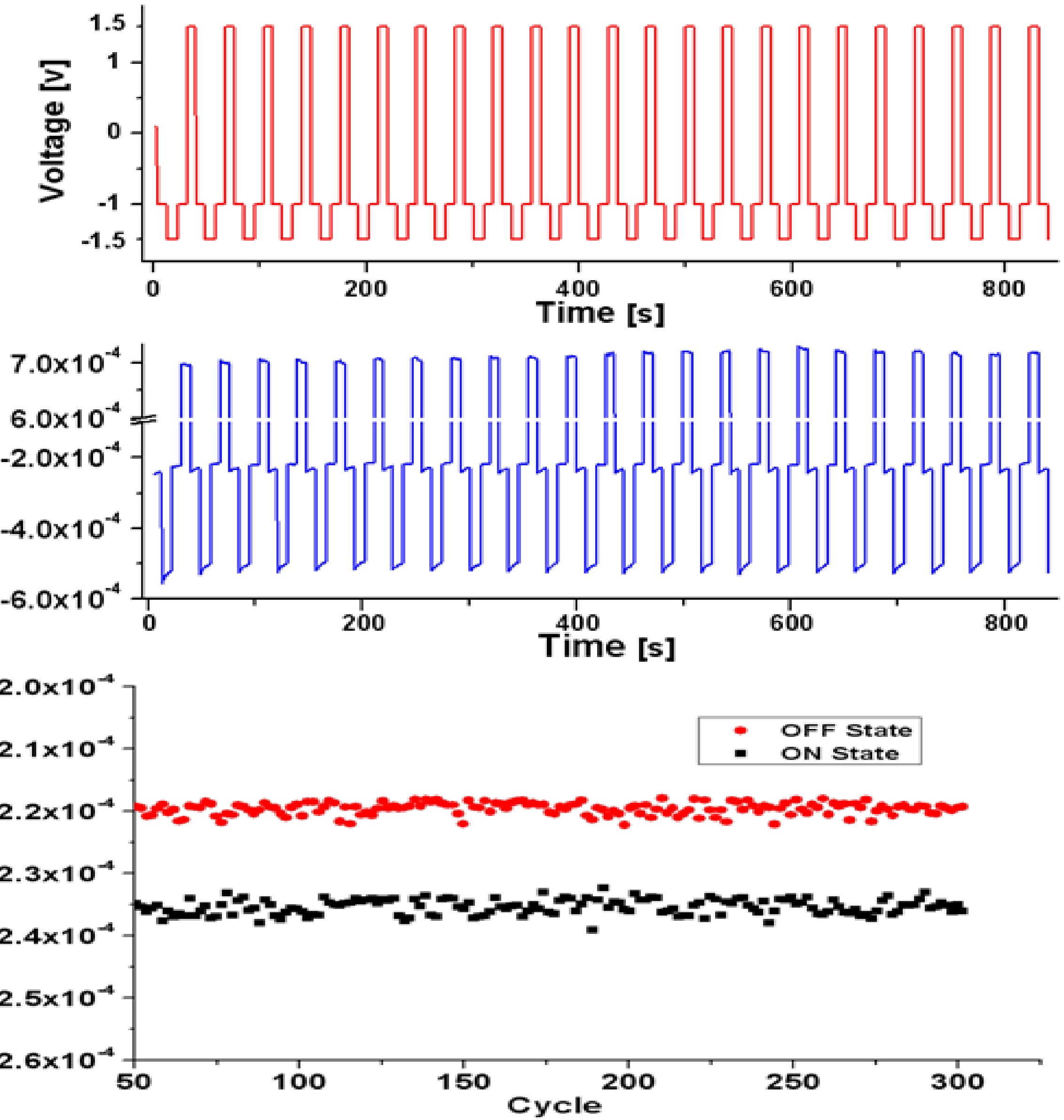
. Seo, **H. Lee***, ACS Nano., accepted, 2009

# Fabrication of Molecular Monolayer Non-Volatile Memory (MMMVM)

단분자막



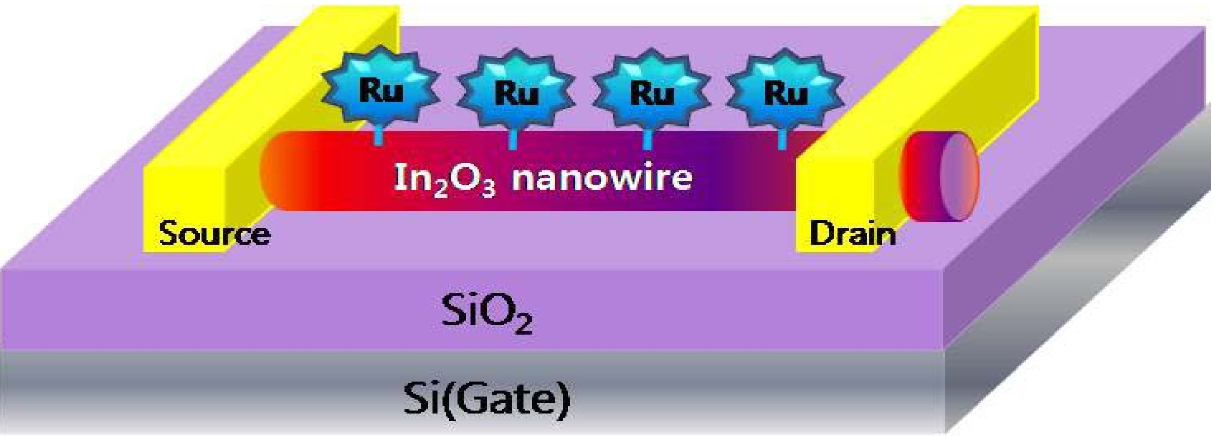
# Write-multiple read-erase-multiple read (WRER) cycles



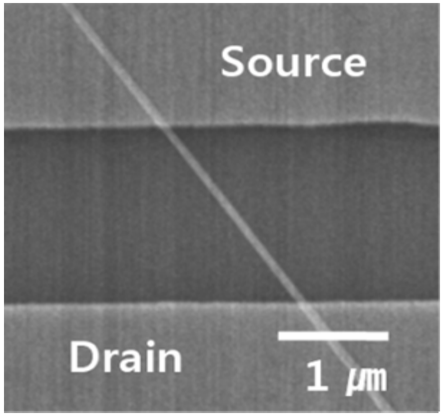

1st Molecular Monolayer Non-Volatil
Memory **(MMMVM)** w/ voltage-driven

J. Lee, …**H. Lee***,
will be submitted to Adv, Func. Mater, , 20

# Intrinsic Properties of Ru complexes and memory w/NW




Schematic diagram of the $In_2O_3$ nanowire FET device

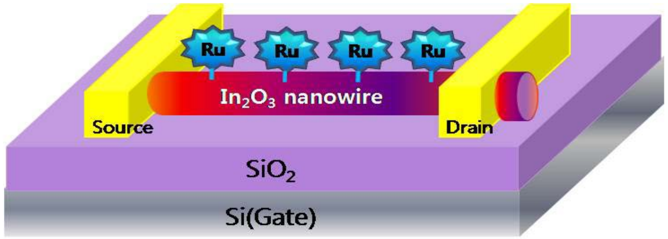


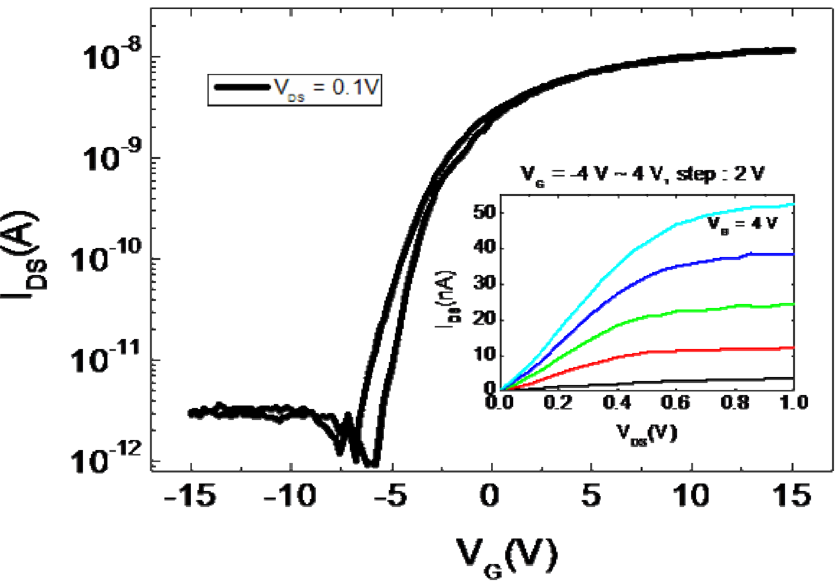

SEM image of an $In_2O_3$ nanowire FET

1. M. Jung …**H Lee*** and J. Kim*, Quantum interference in radial heterostructure nanowires, *Nano Letters*, *8*, 3189, **2008**

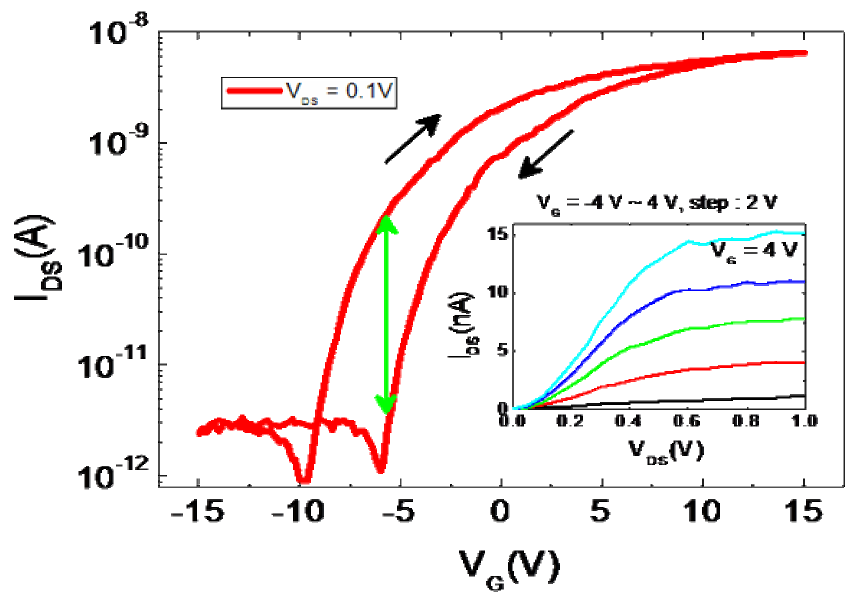
2. M Jung, **H Lee***…, Short-channel effect and single-electron transport in individual indium oxide Nanowires, *Nanotechnology*, 18, 435403, **2007**.

# Electron Transport through Individual Indium Oxide Nanowire



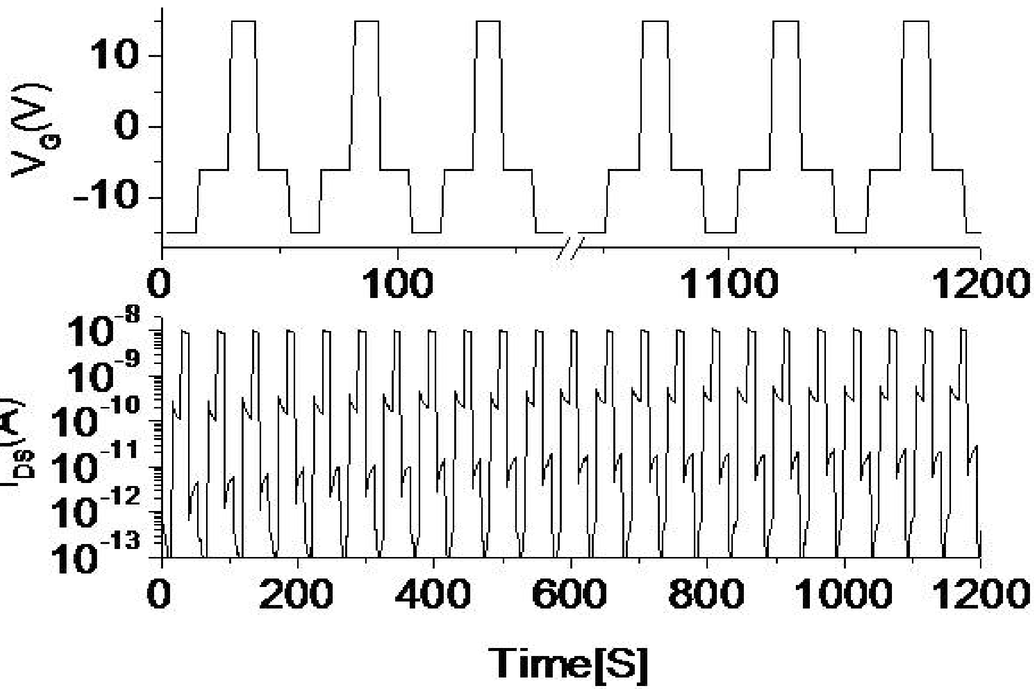




$I_{DS}$- $V_G$ characteristics of the $In_2O_3$ nanowire FET device

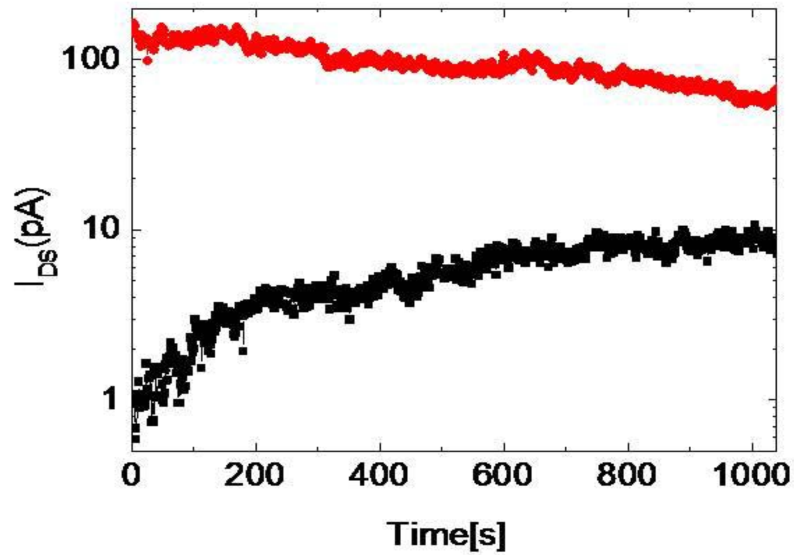



$I_{DS}$- $V_G$ characteristics of the $In_2O_3$ nanowire FET device modified with Ru SAM

# Electron Transport through Individual Indium Oxide Nanowire




Reversible switching operations in the write, read, erase and read voltage cycles; writing, reading and erasing voltages ($V_G$ pulses for 1 s) are −15 V, −6 V and 15 V, respectively.

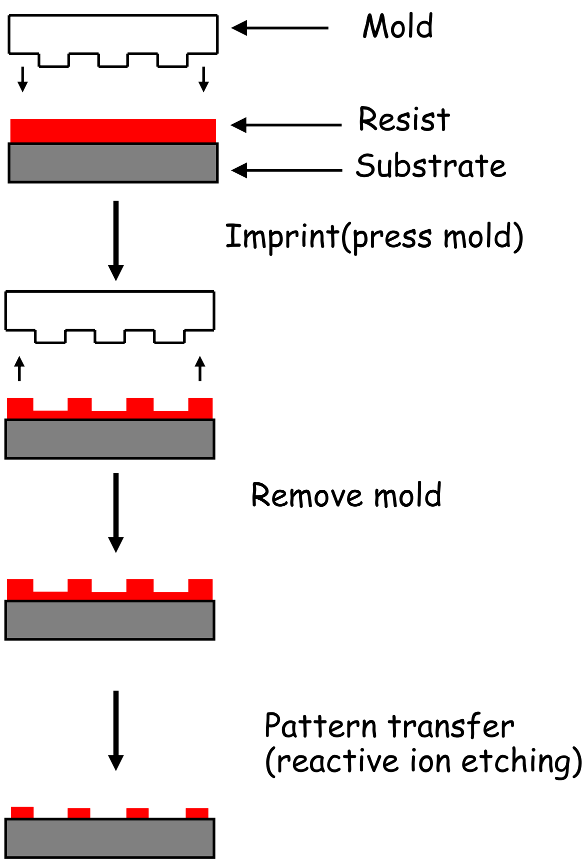



$I_{DS}$ versus retention time for the $In_2O_3$ nanowire FET in an ON current state (red line) and an OFF current state (black line).

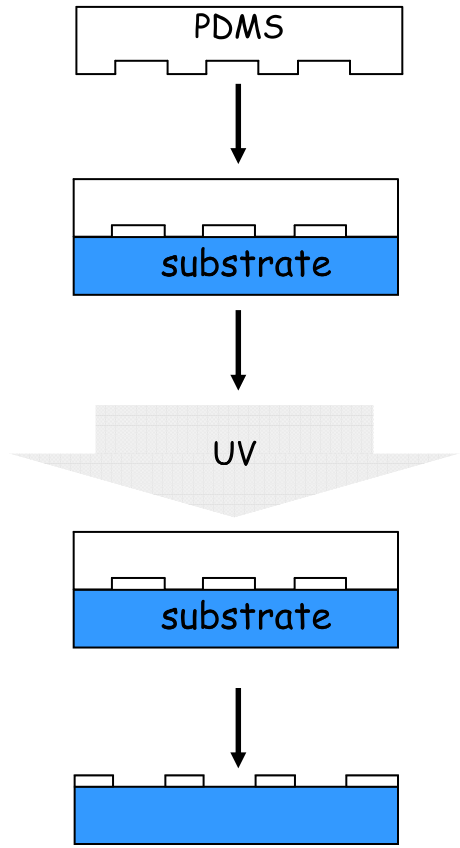
I, Choi, …**H Lee***, Charge Storage Effect on $In_2O_3$ Nanowires with Ruthenium Complex Molecules, Applied physics express, 2, 015001, 2009

# Electrode patterning w/soft Lithography

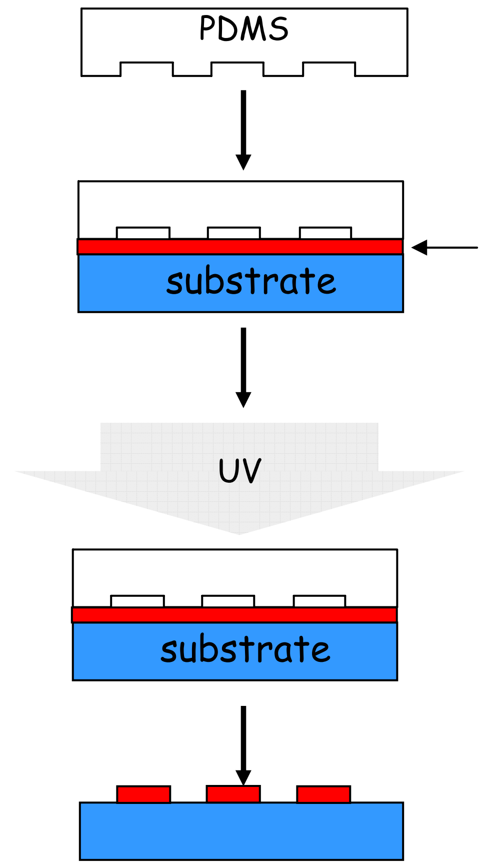
## Nanoinprinting




## Decal Transfer μ-Contact Printing

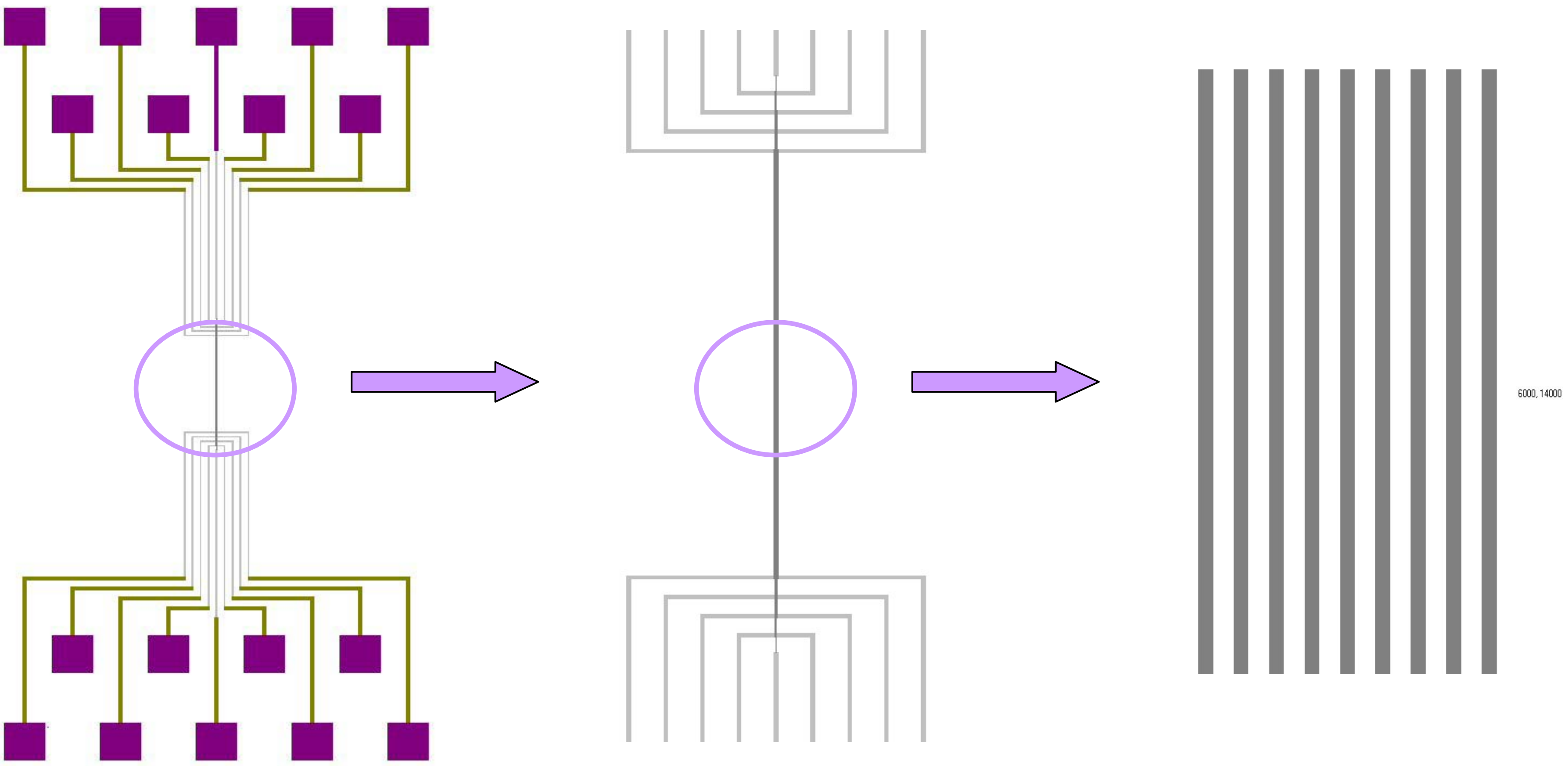



## Light Stamp



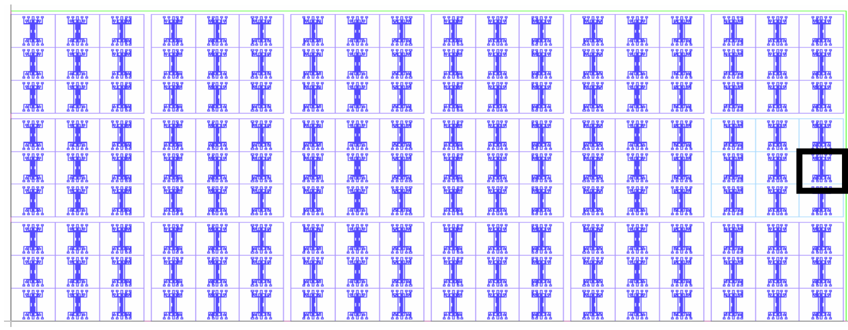
# Nano-Imprint Lithography: Stamp Design

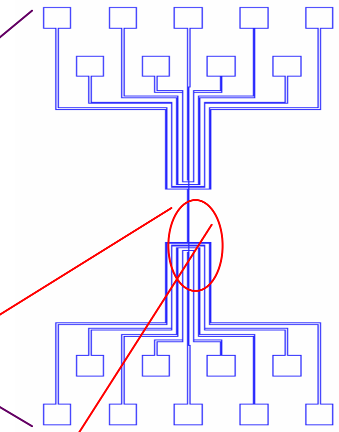
Unit cell size : 1180X1180um$^2$
Main pattern : line width/line space 40/75, 50/75



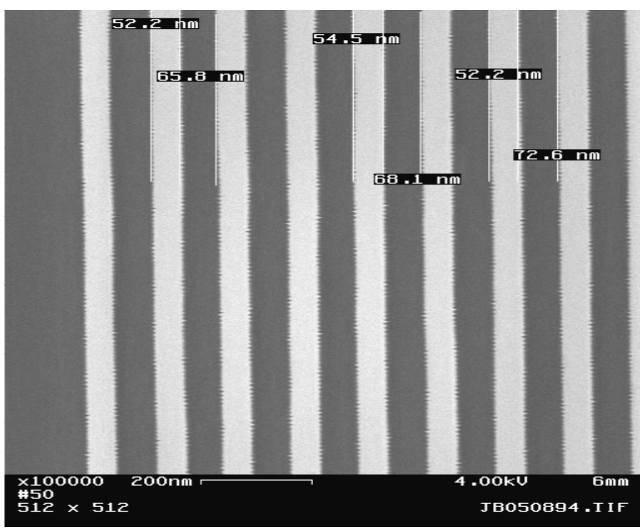
# Nano-Imprint Lithography: Stamp

1. Stamp or Mold (on a quartz)

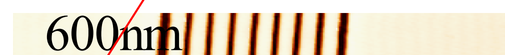


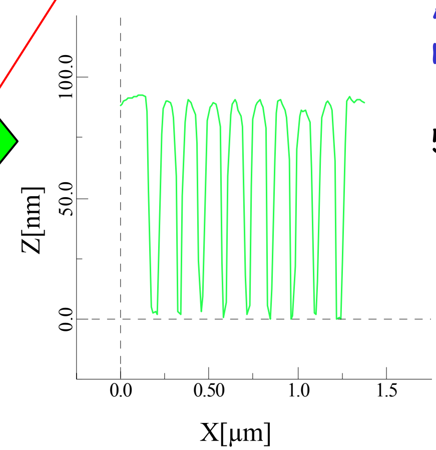


Dimension : 1180*1180um²
Pad Size : 50um²




SEM image

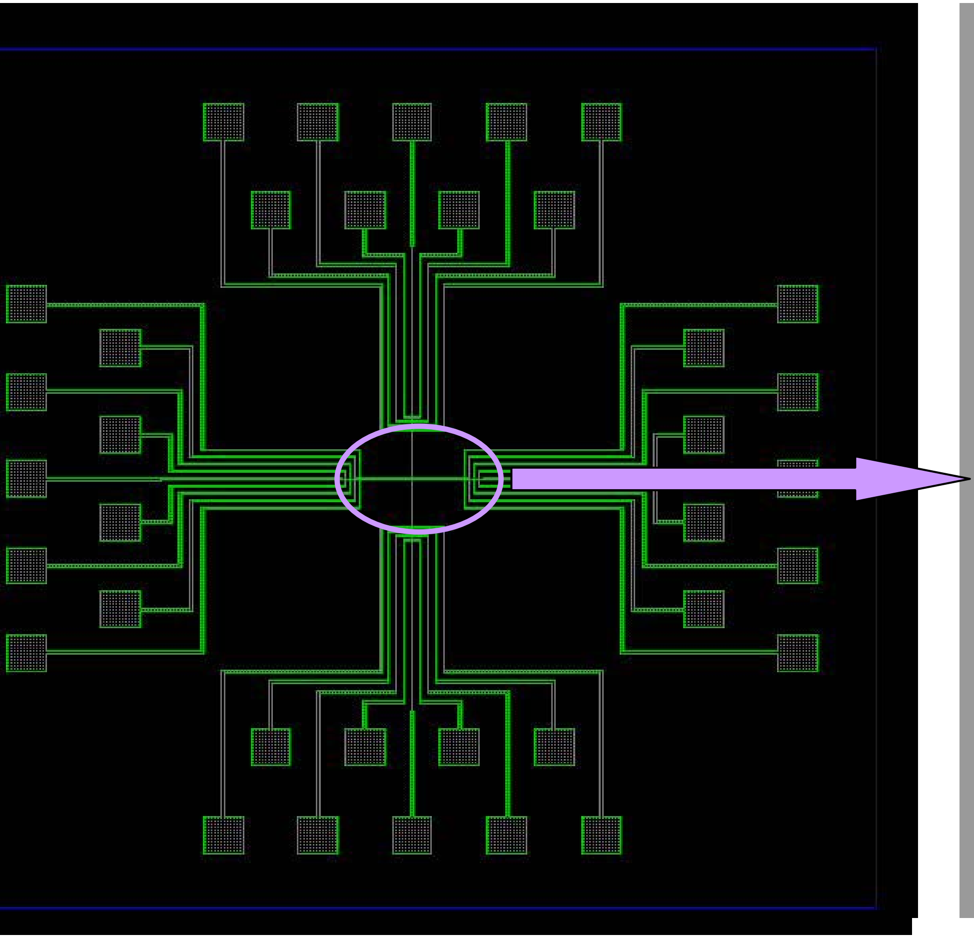


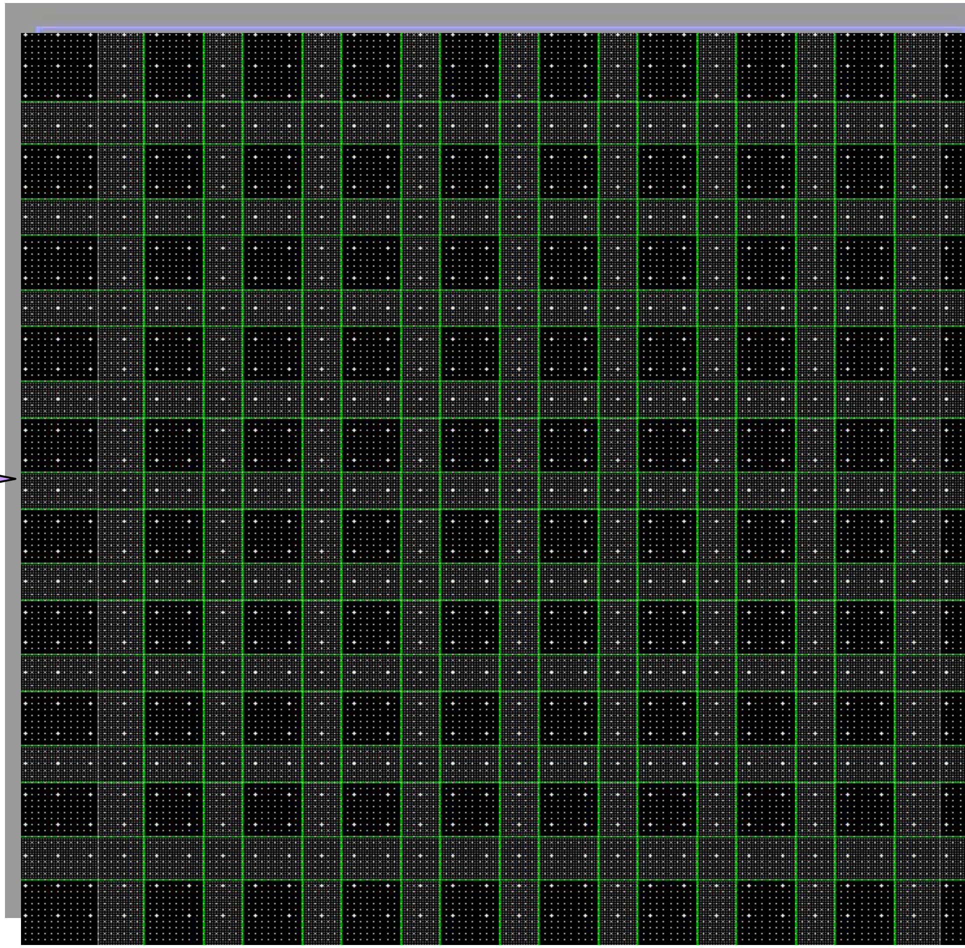




*AFM morphology of quar mold*

50 (Width)/75 (Space) nm

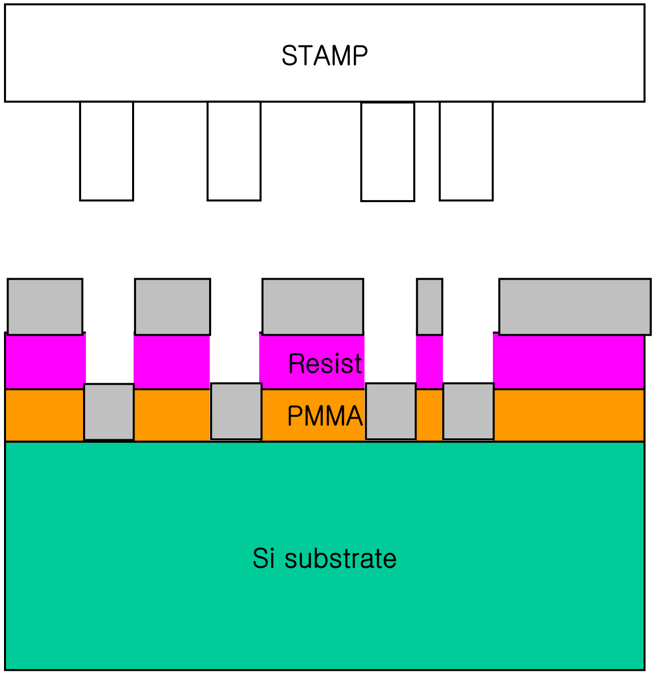
# Nano-Imprint Lithography: Stamp Design II

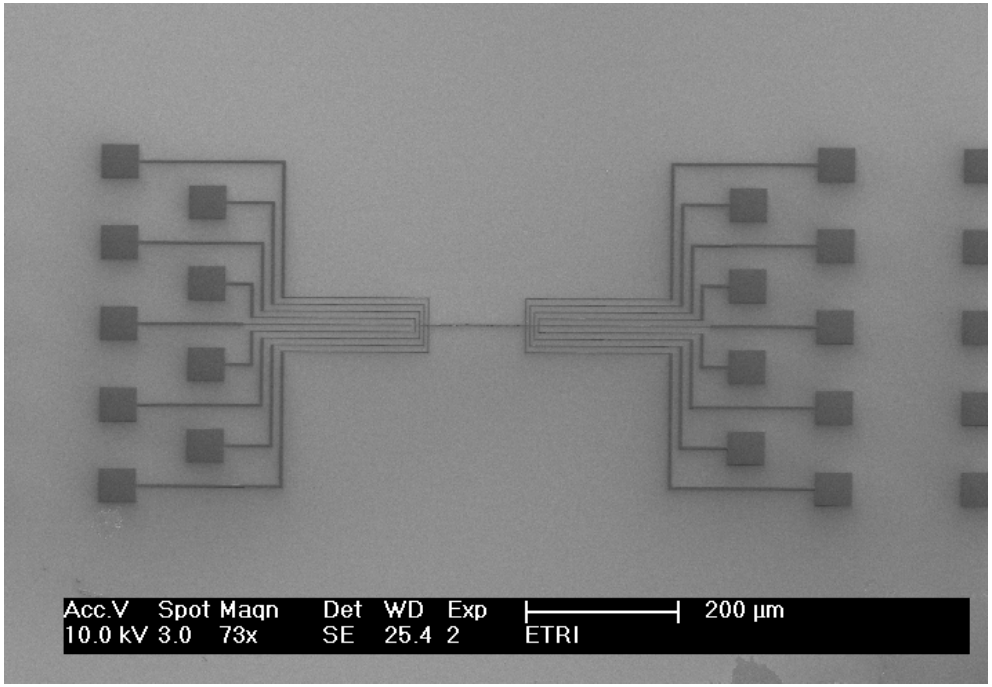




# Fabrication Process for Bottom Layer

7. Lift off

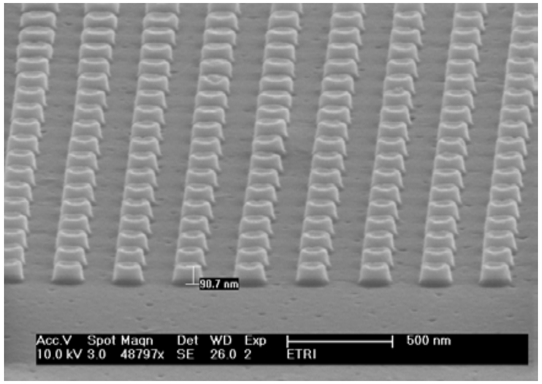


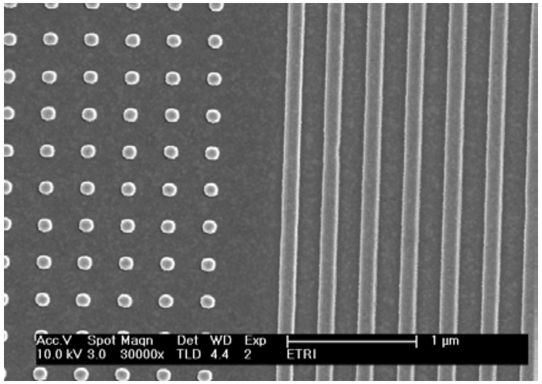



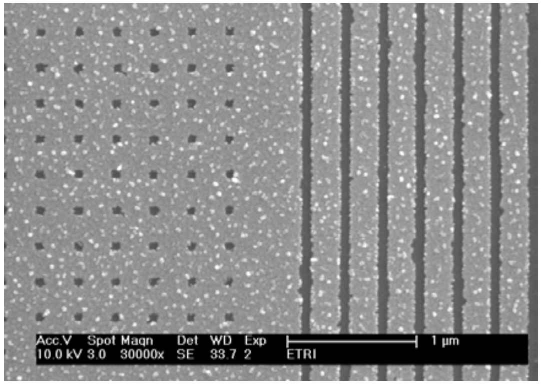
# Pictures in Etching Process

**1. After Imprinting** | **2. After RIE** | After Lift-Off

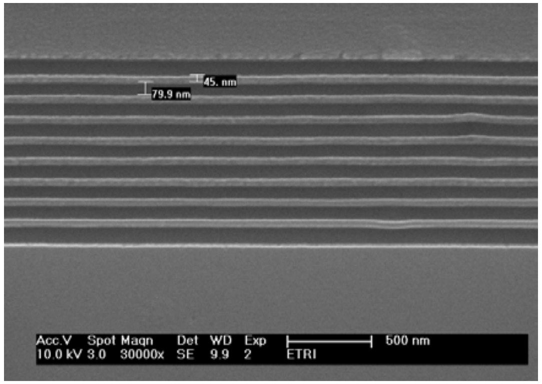
ositive

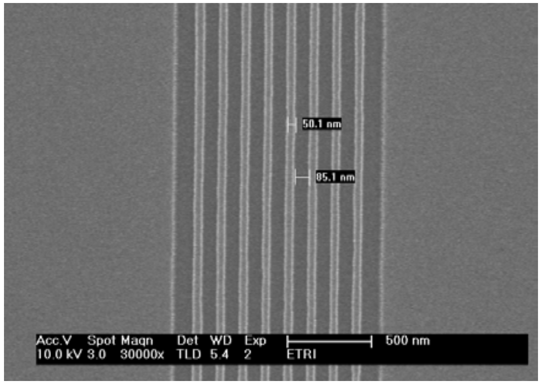


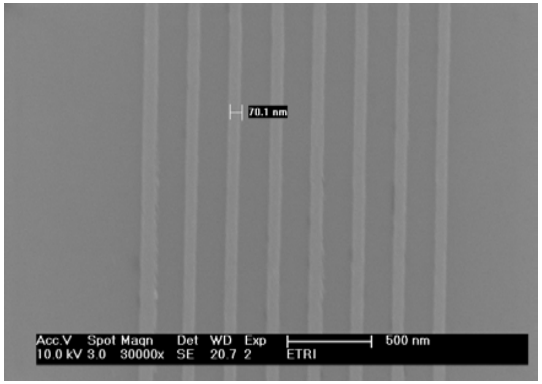



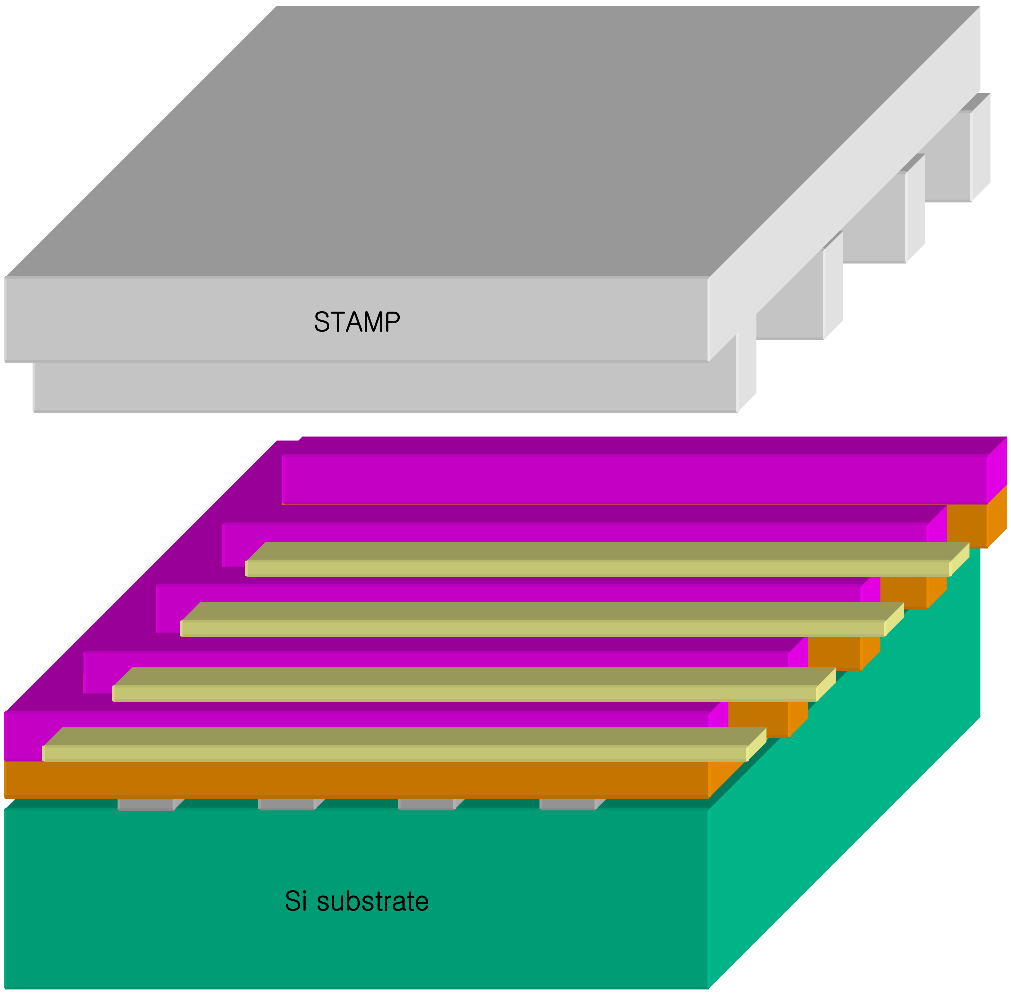

egative

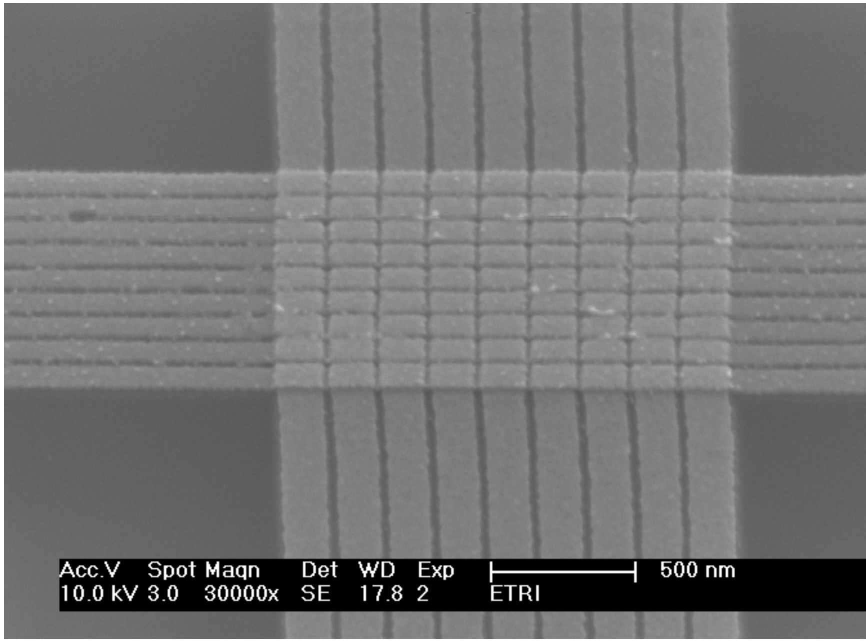


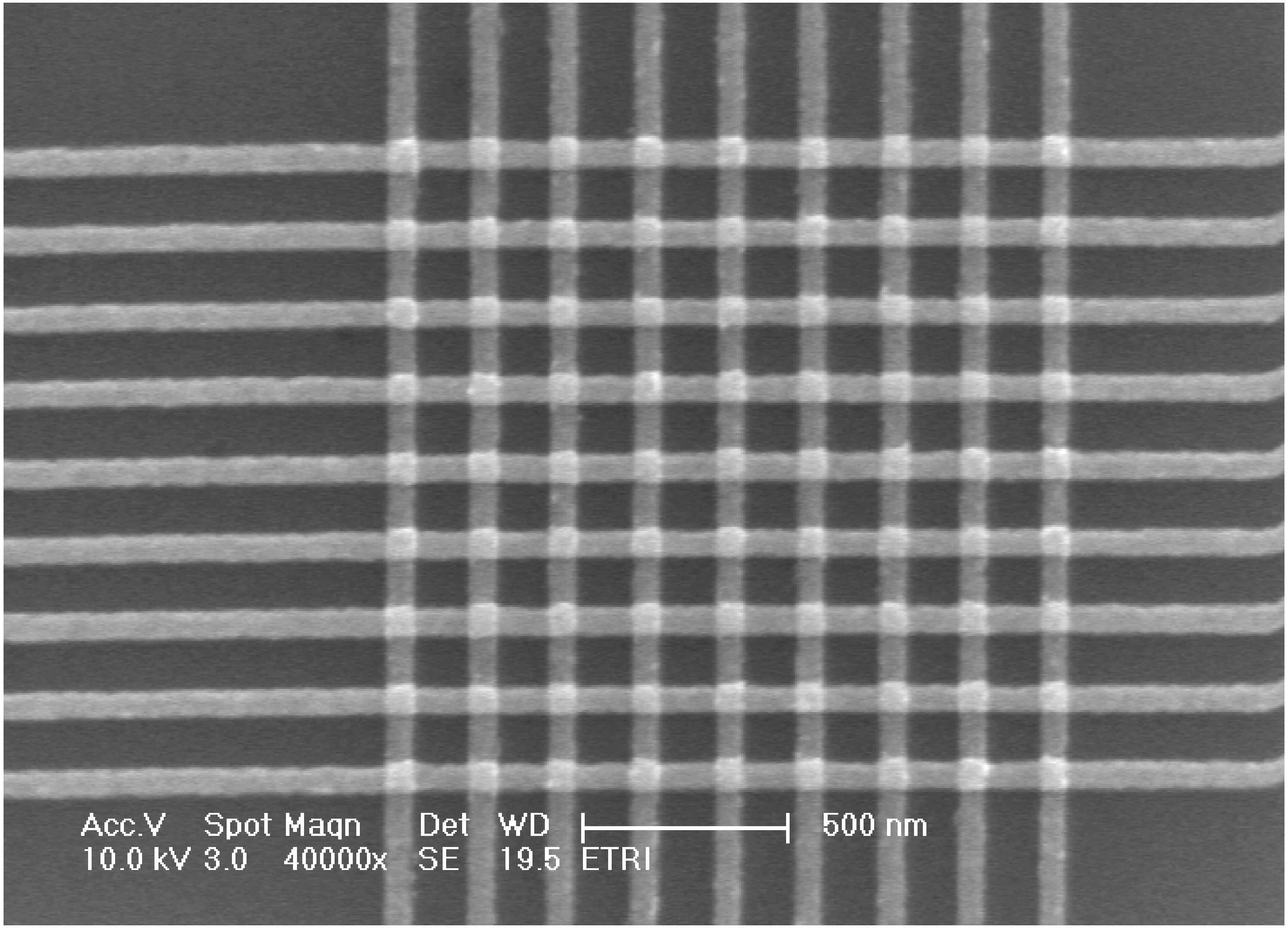



# Fabrication Process for Top Layer

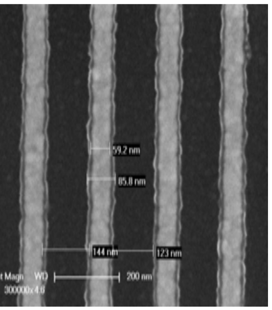


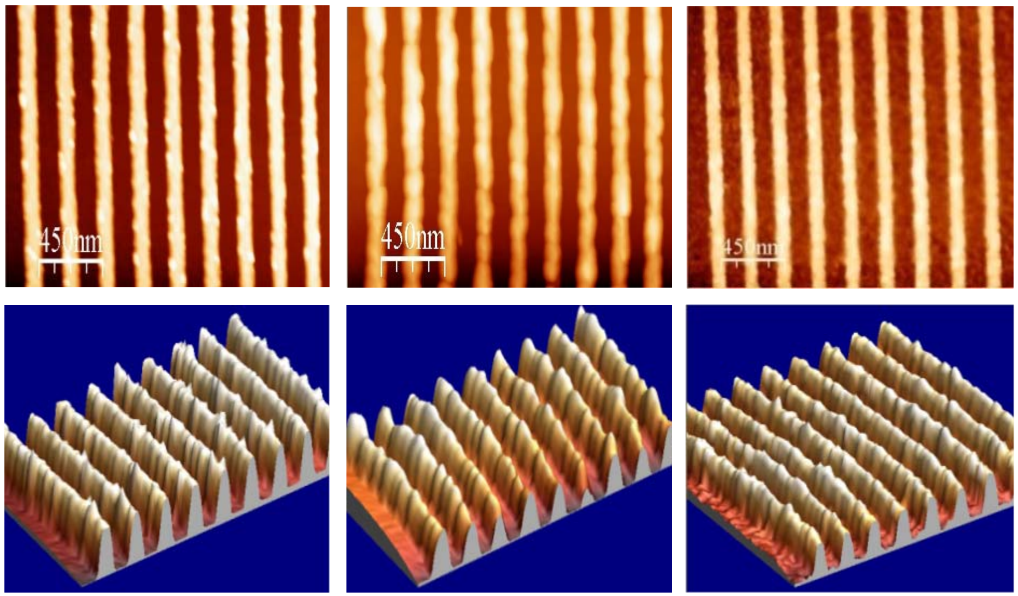
# 60 nm (width)/130 nm (space)

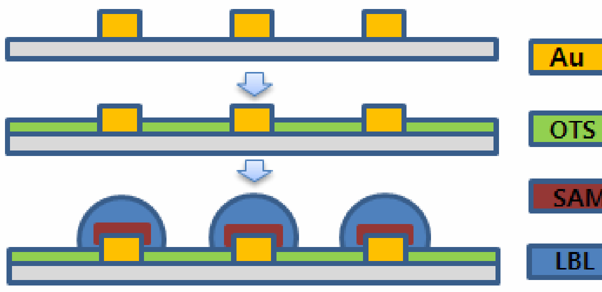


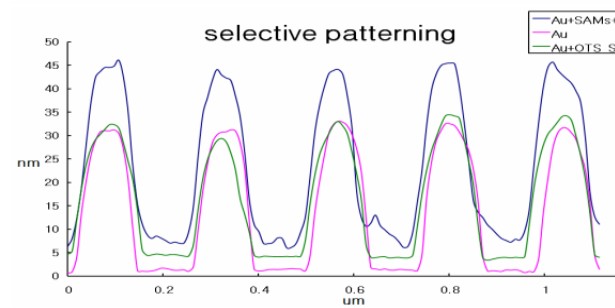
# Selective nano-patterning using Layer-by-Layer



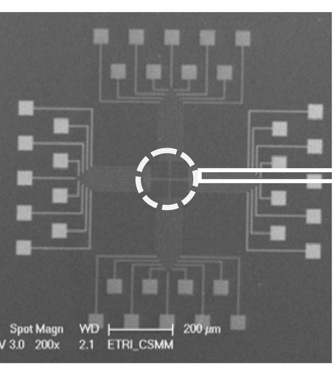

Au bare | Au + OTS | Au + SAMs + LBL

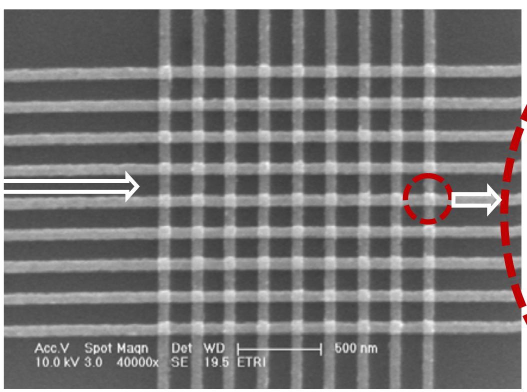


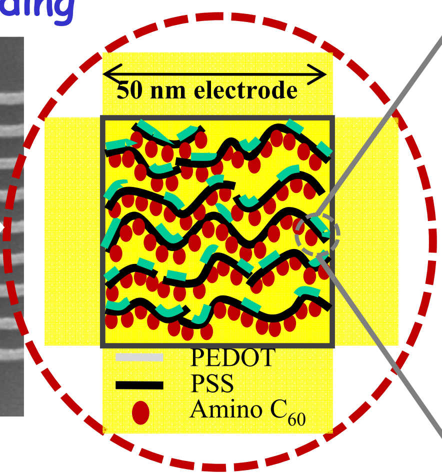



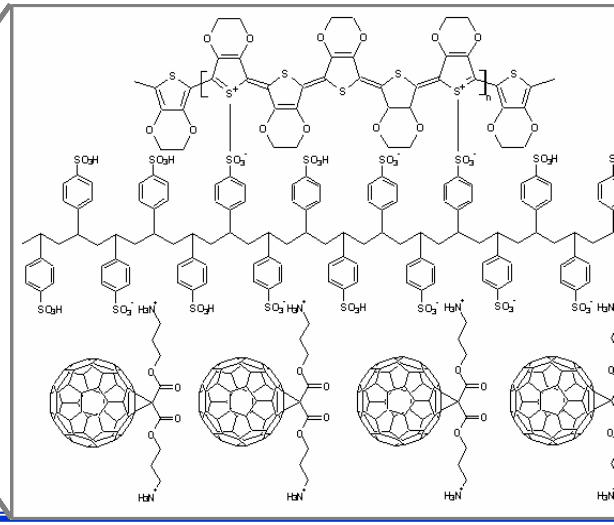




tent : Korea 2008-0072940, US pat. Pending



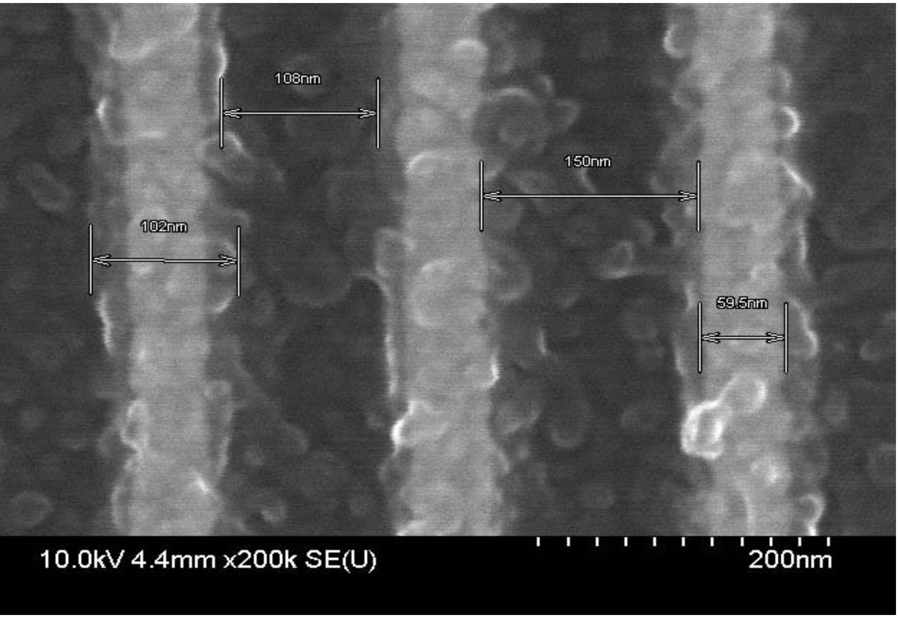



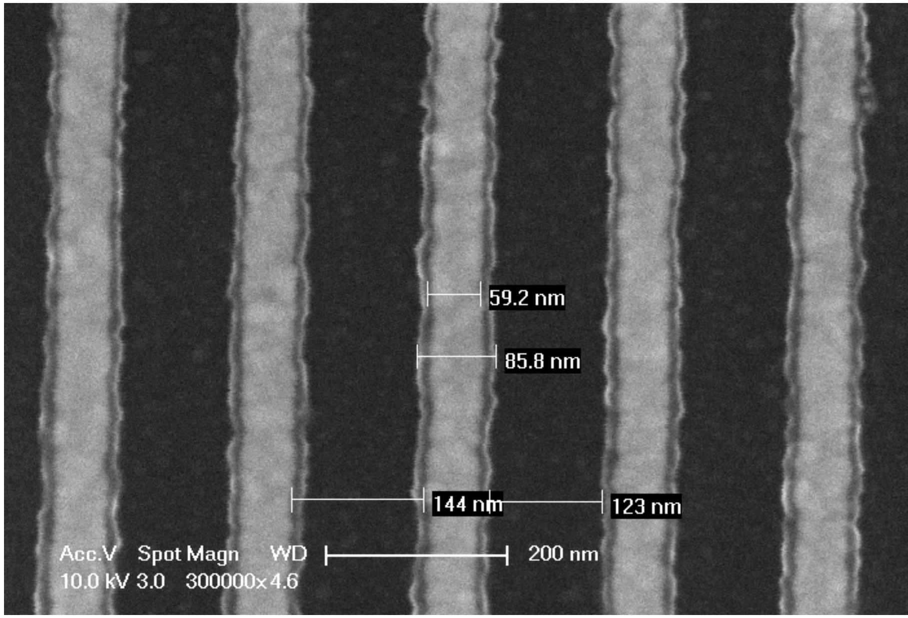



ll be submitted to XXXX. 2009

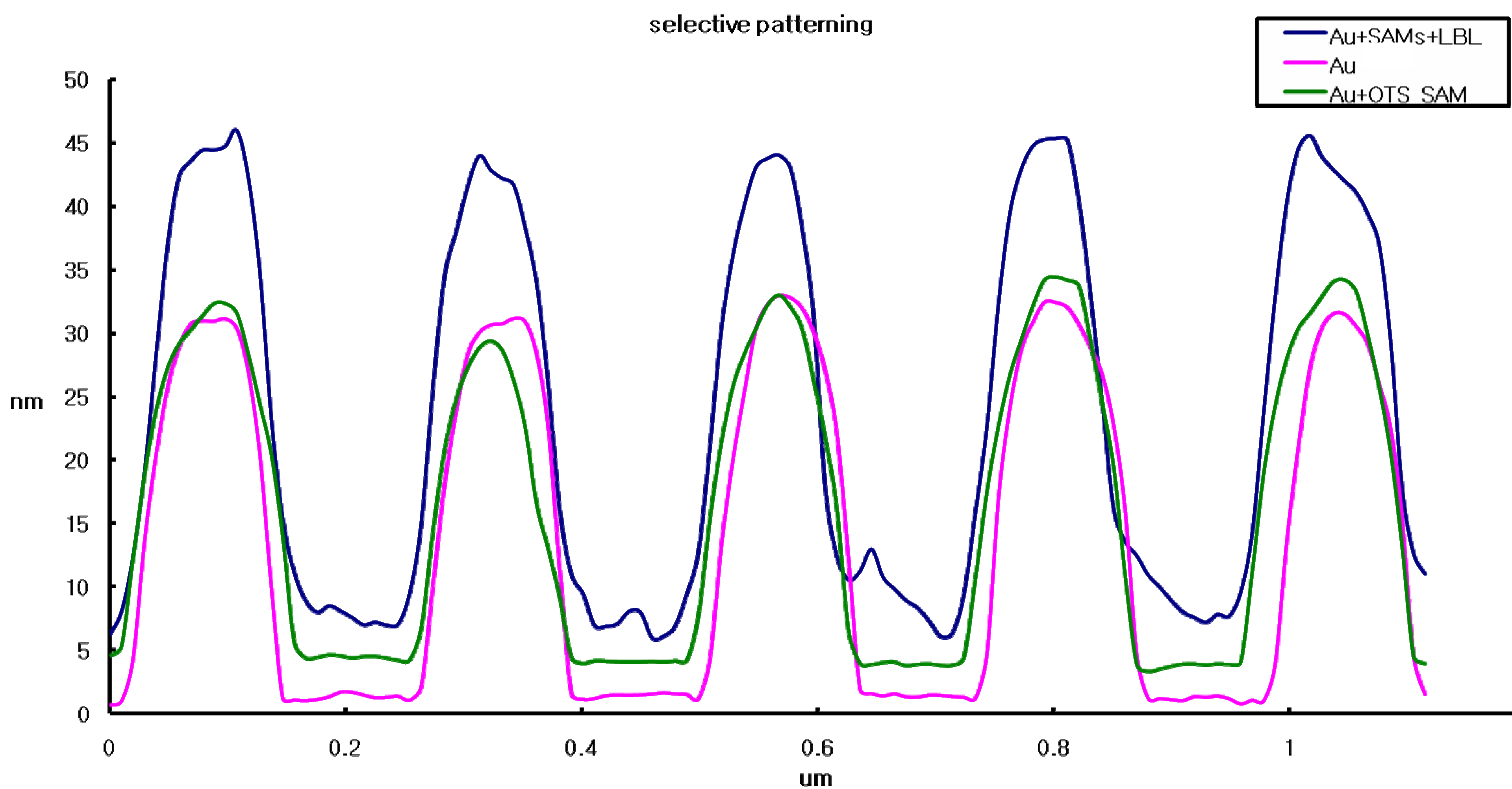
# Selective Patterning of LBL Nanolines

## SEM Analysis



# Selective Patterning of LBL Nanolines




Will be submitted soon

Thank you very much for your attention