Molecular Electronics and Spintronics Using Nano-carbon Molecules

2006.07.05 @ Regensburg Universitaet, Deutschland

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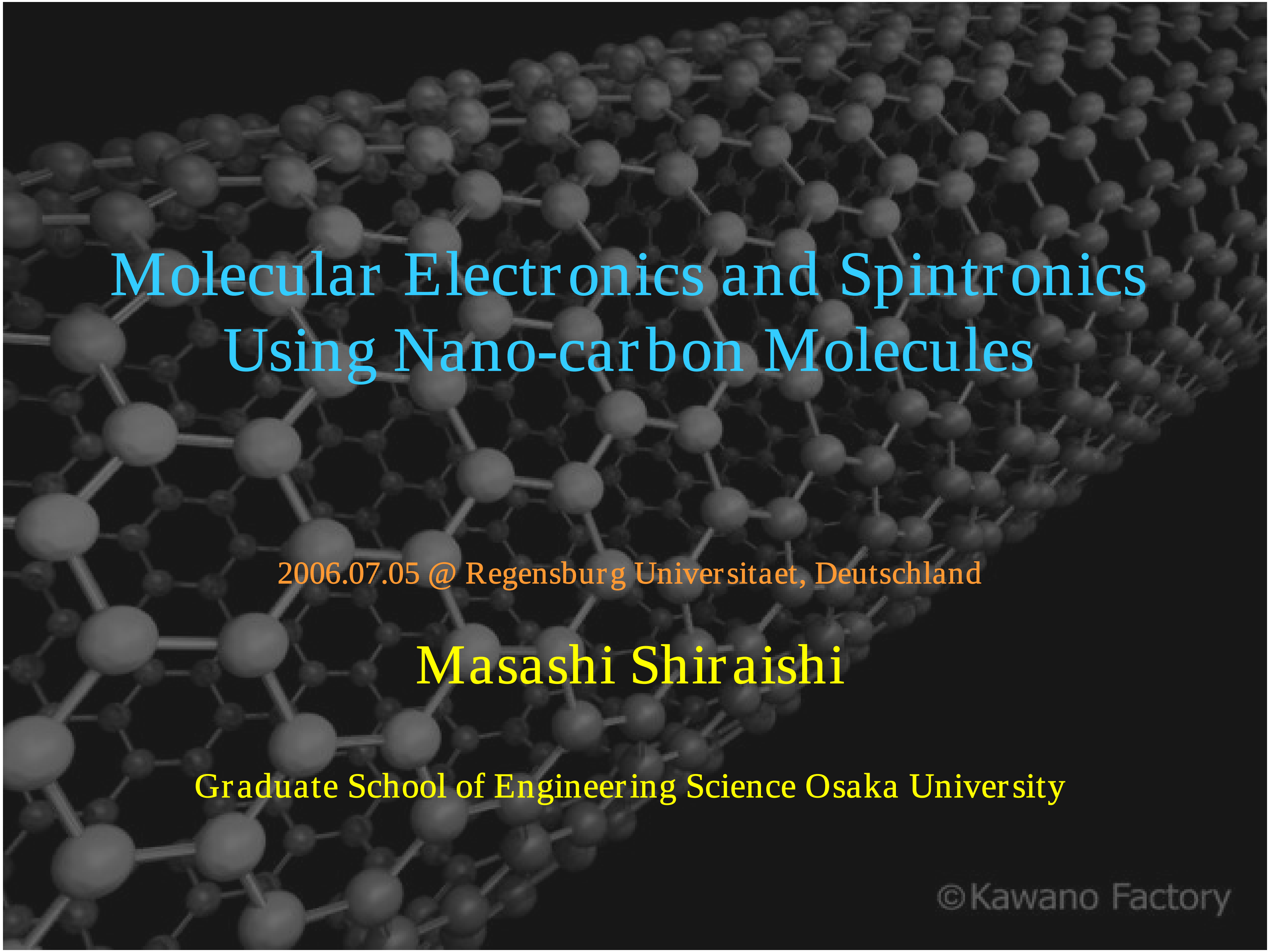
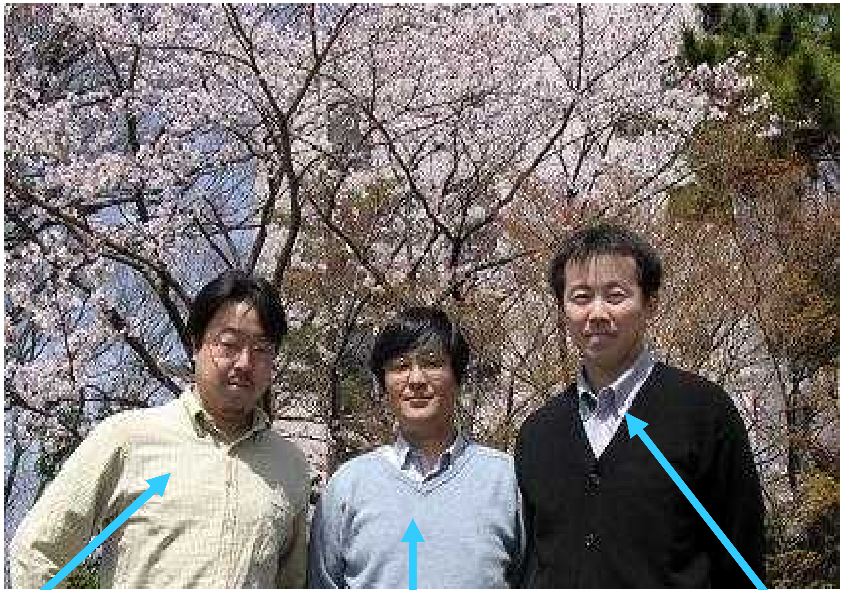


Co-workers related with the topics in my talk

Osaka Univ.



Dr. M. Mizuguchi
(Research Associate)

Dr. Y. Suzuki
(Professor)

Me

Tohoku Univ.
(SWNT- FET Pj.)

Prof. Iwasa
Dr. Takenobu

AIST
(SWNT production)

Dr. Kataura

Graduate School Students in Molecular Electronics & Spintronics
(OB) S. Nakamura (Shin-Nippon Steel Co.), K. Takebe (Nihon Ceramic Co.)
(M2) T. Fukao, S. Miwa, K. Matsuoka, A. Ogura
(M1) M. Ohishi, H. Kusai, H. Tomita
(B4) S. Tanabe, S. Danjoh

Research direction of our Osaka Univ. Group

Molecular Science Gp. (Shiraishi's Group)

Materials

Carbon Nanotubes
Fullerenes
Graphite
Organic Molecules (Rubrene, Alq_3, etc)

Research Field — **Molecular Spintronics**

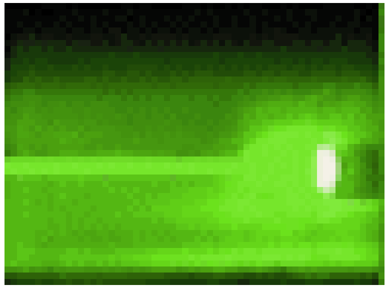
Research Field — **Molecular Electronics**

Magnetic Science Gp. (Suzuki's Group)

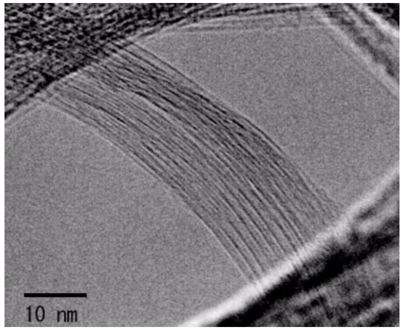
MgO Tunnel barriers for TMR (MR~400 %)
Magnetization reversal by spin injection for MRAMs

What are nano-carbon molecules?

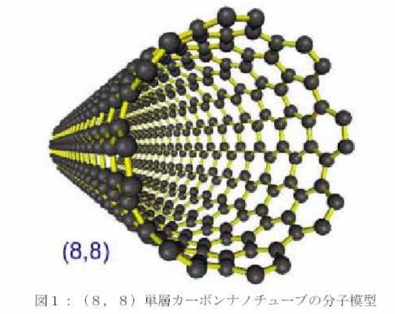
Single-walled Carbon Nanotube (SWNT)



Laser synthesis

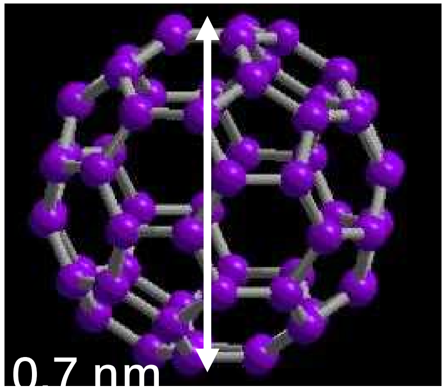


High purity



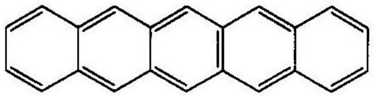
Semiconductive or metallic
(E_g ~ 1/d)

Fullerene(C_{60})

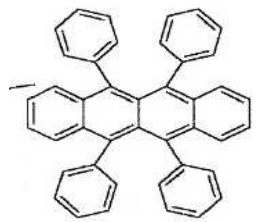


Semiconductive
(E_g=1.5-2.0 eV)

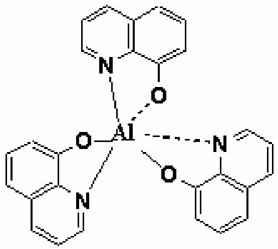
Other organic molecules



Pentacene



Rubrene



Alq3

PART I :

Molecular Electronics Using SWNTs

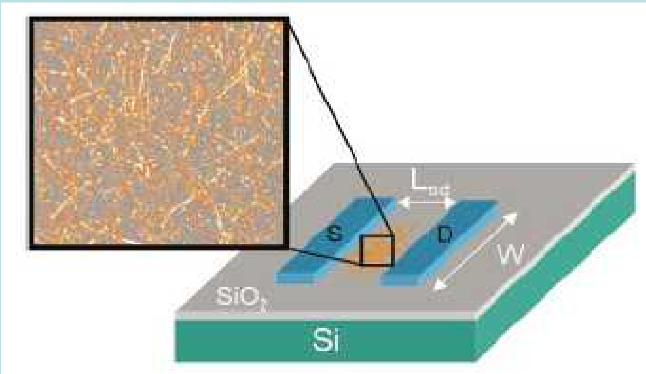
Single-walled Carbon Nanotubes (SWNTs) FETs

Realization of SWNT-FETs

Sin

Pioneering Work

E. Snow et al., APL 82, 2145 (2003).



Network SWNTs, but by CVD …

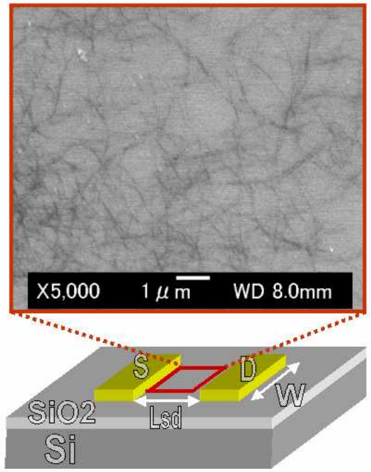
Serious disadvantage:

Heat application to substrates !

Not applicable for plastic substrates

Molecular aggregate FETs

Random-Network SWNT-FETs



M. Shiraishi et al. Chem. Phys. Lett. 394, 110 (2004).

Thermal Free Processes

Solution-process (easy and mass production)

⇒ Introduction of plastic substrates

Research Direction

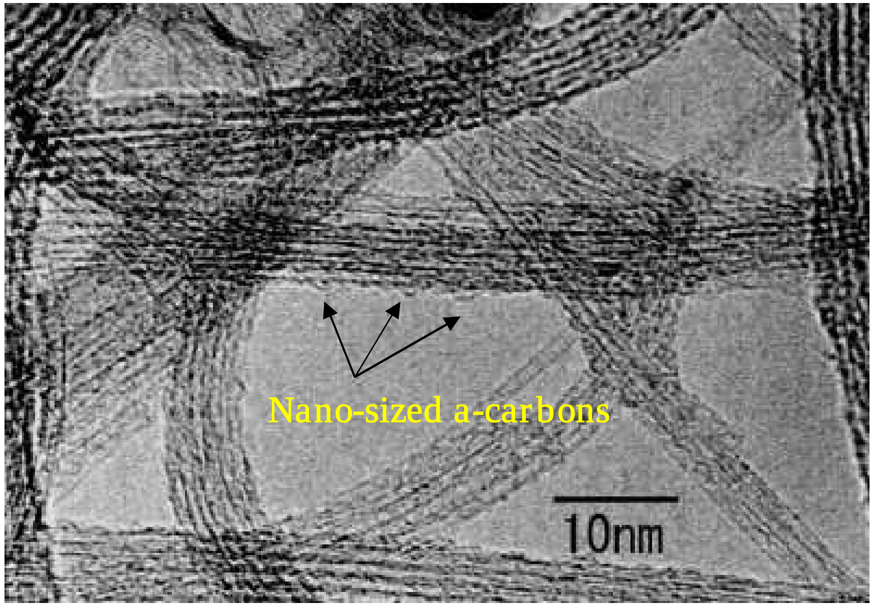
competition with OFETs

Latest achievement

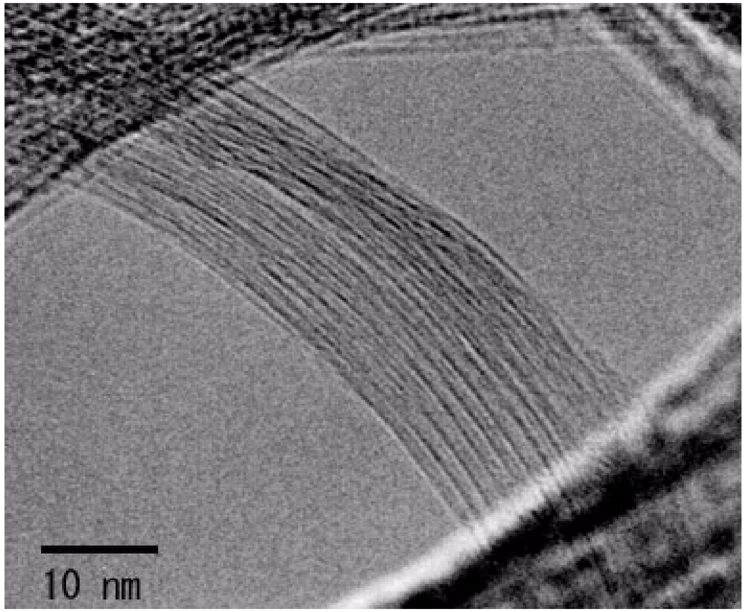
μ ~ 3.8 cm^2/Vs & on/off > 10^5 (simultaneously)

Features of SWNTs in this work

1. High quality SWNTs by a laser ablation method
2. High purity SWNTs by a NaOH treatment



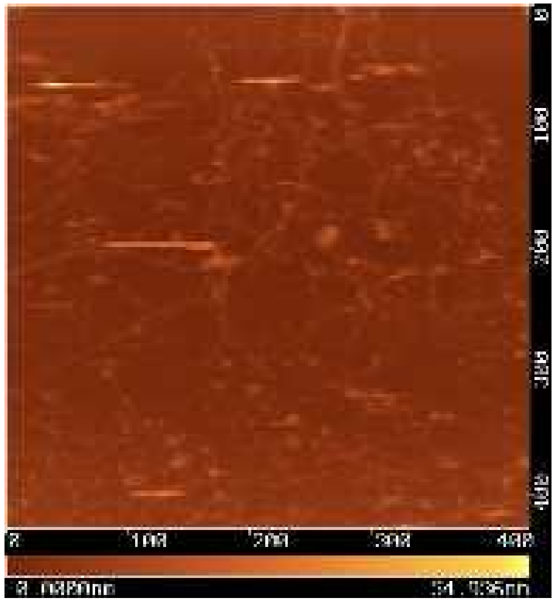
Before NaOH treatment



After NaOH treatment

M. Shiraishi et al., Chem. Phys. Lett. 358, 213 (2002)

Sample Preparation RN-SWNT-FETs (non-doped)



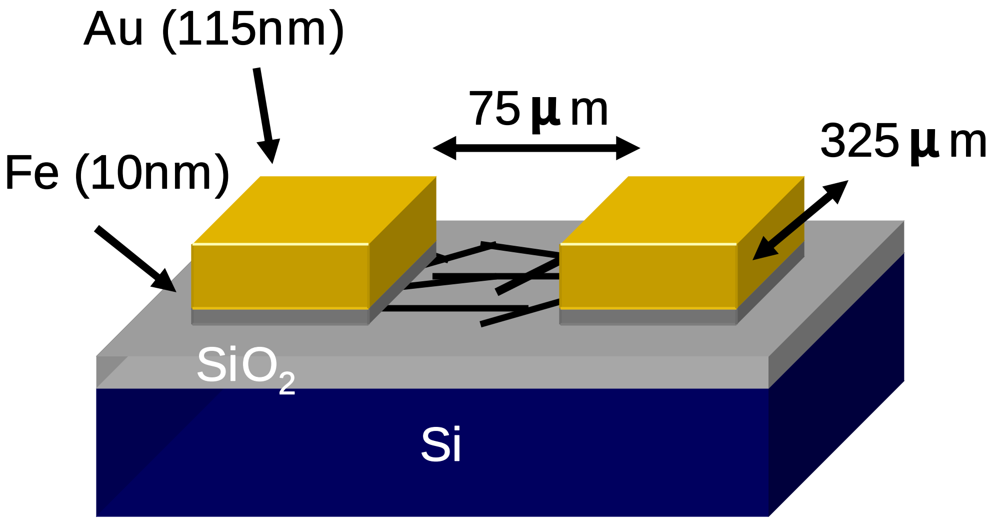
①Ultrasonic dispersion
9 hr in a DMF solution (1.5[mg]/DMF 50[ml])

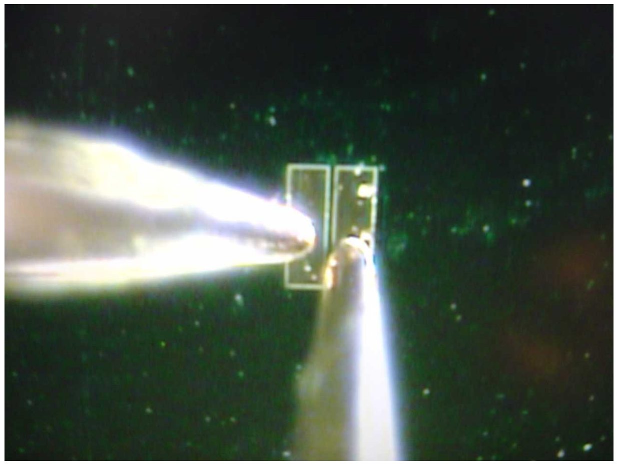
②Centrifugal separation
5000[rpm]/20[min]

③Dropping the solution on a back-gate FET substrate

④Evaporation of the DMF
Heat application at 353K for 10-20 min

A Typical Device Structure





Substrate

SiO_2 (200 nm)/Si

Electrode

Au(110 nm)/Fe(10 nm)

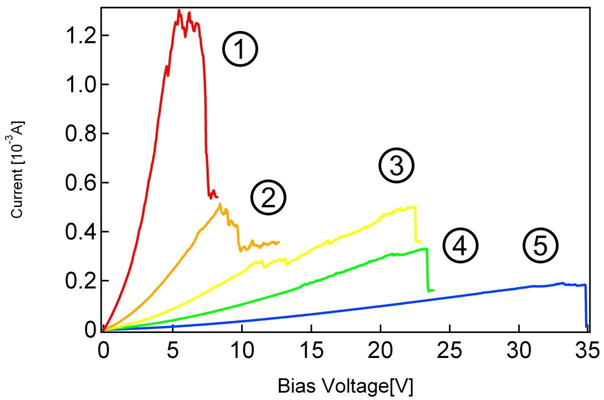
Gate length ; 50-325 µm

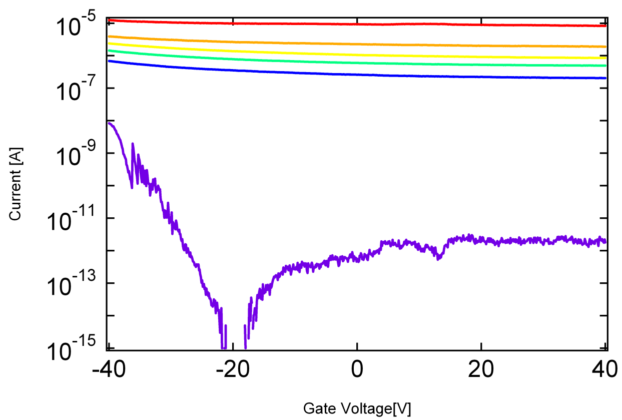
Gate width ; 10-75 µm

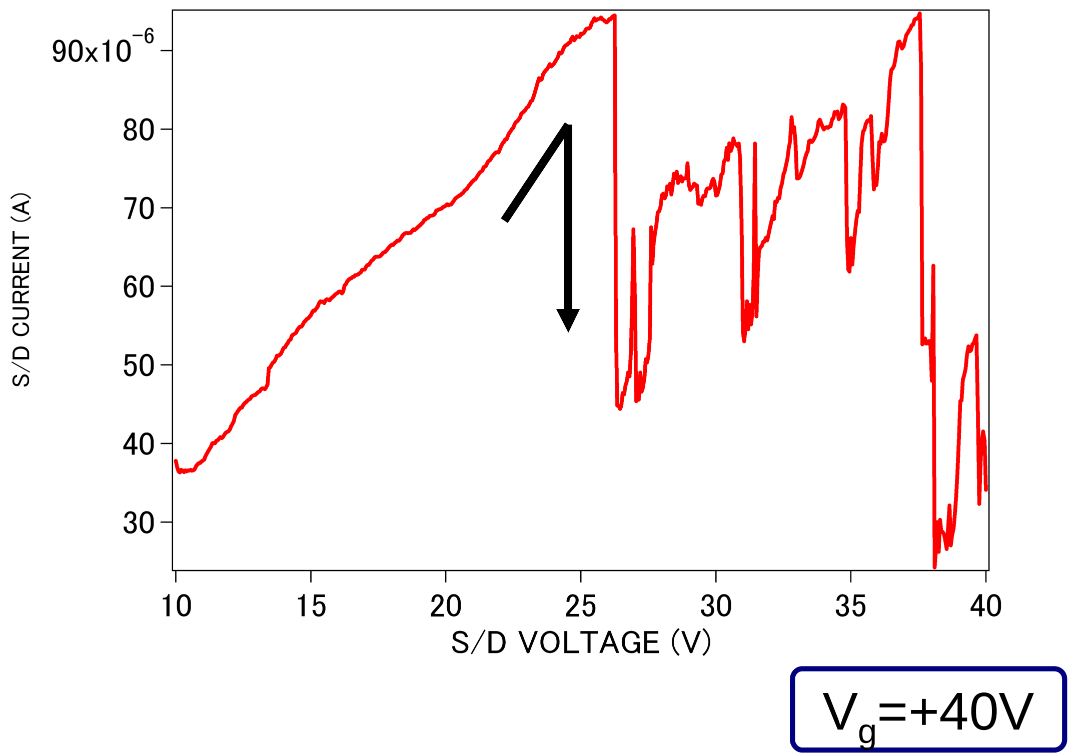
Improvement of Device Characteristics

Electrical breakdown

Removing metallic SWNTs to improve FET characteristics.

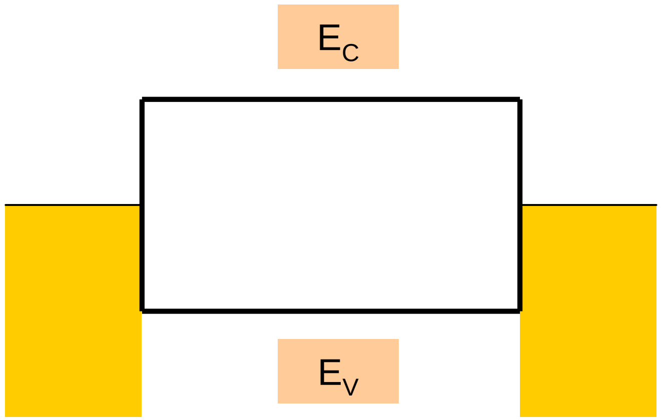


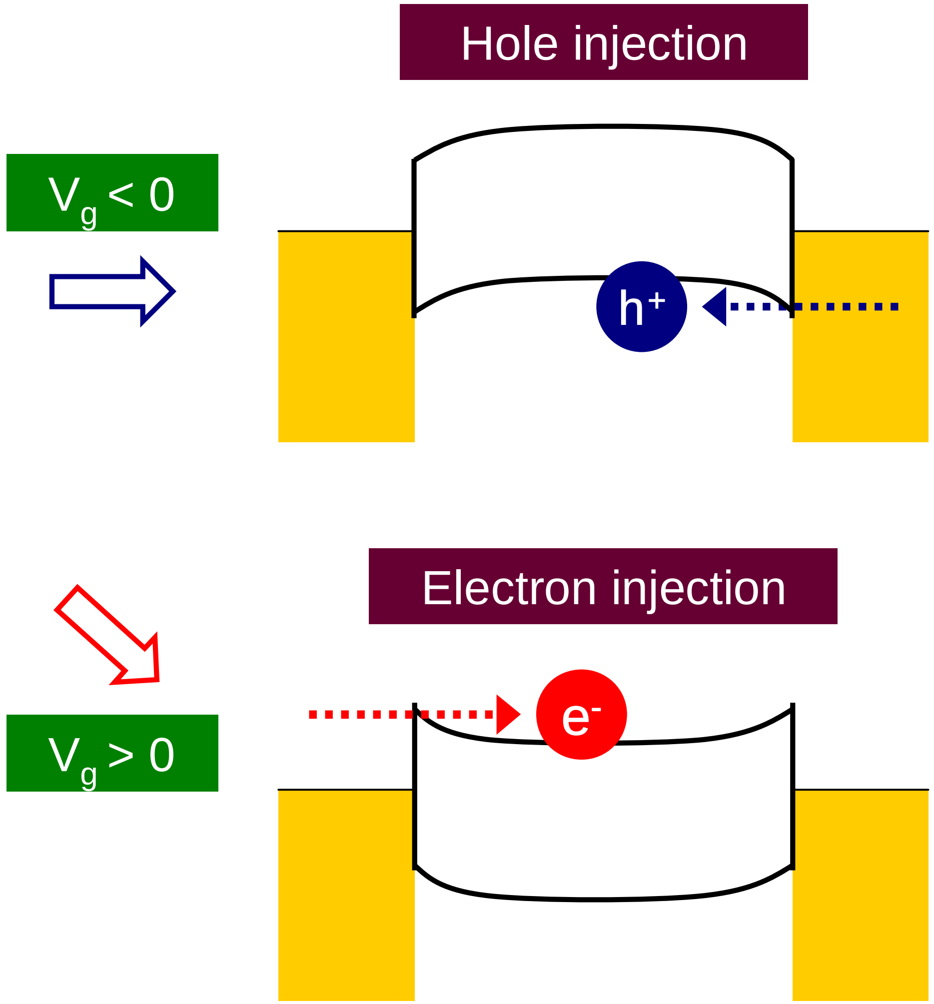




P. G. Collins et al., Science 292, 706 (2002).

Principle of Device Operation in Vacuum





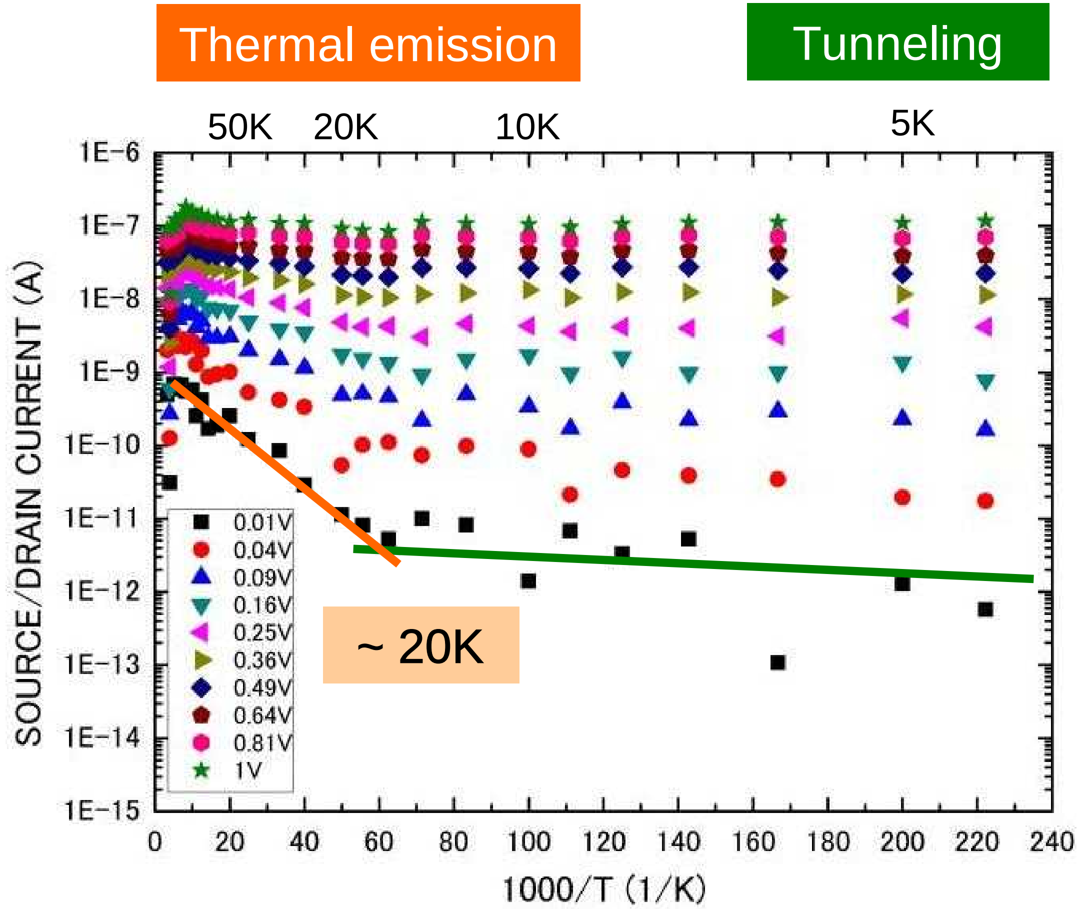
Carrier type is changed by V_g.

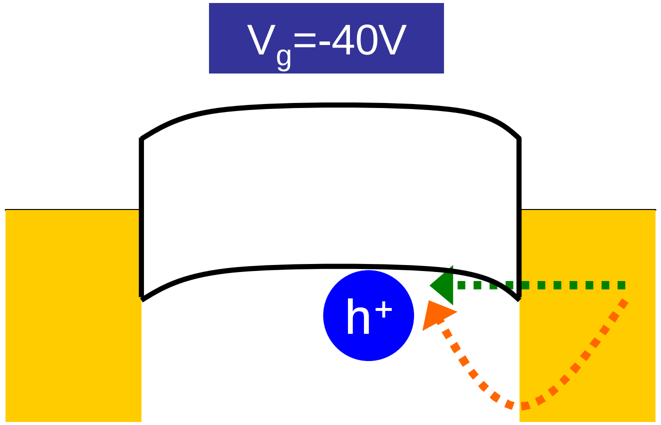
Ambipolar characteristics

(p-type & n-type)

Activation Energy & Schottky Barrier Height

Arrhenius plot



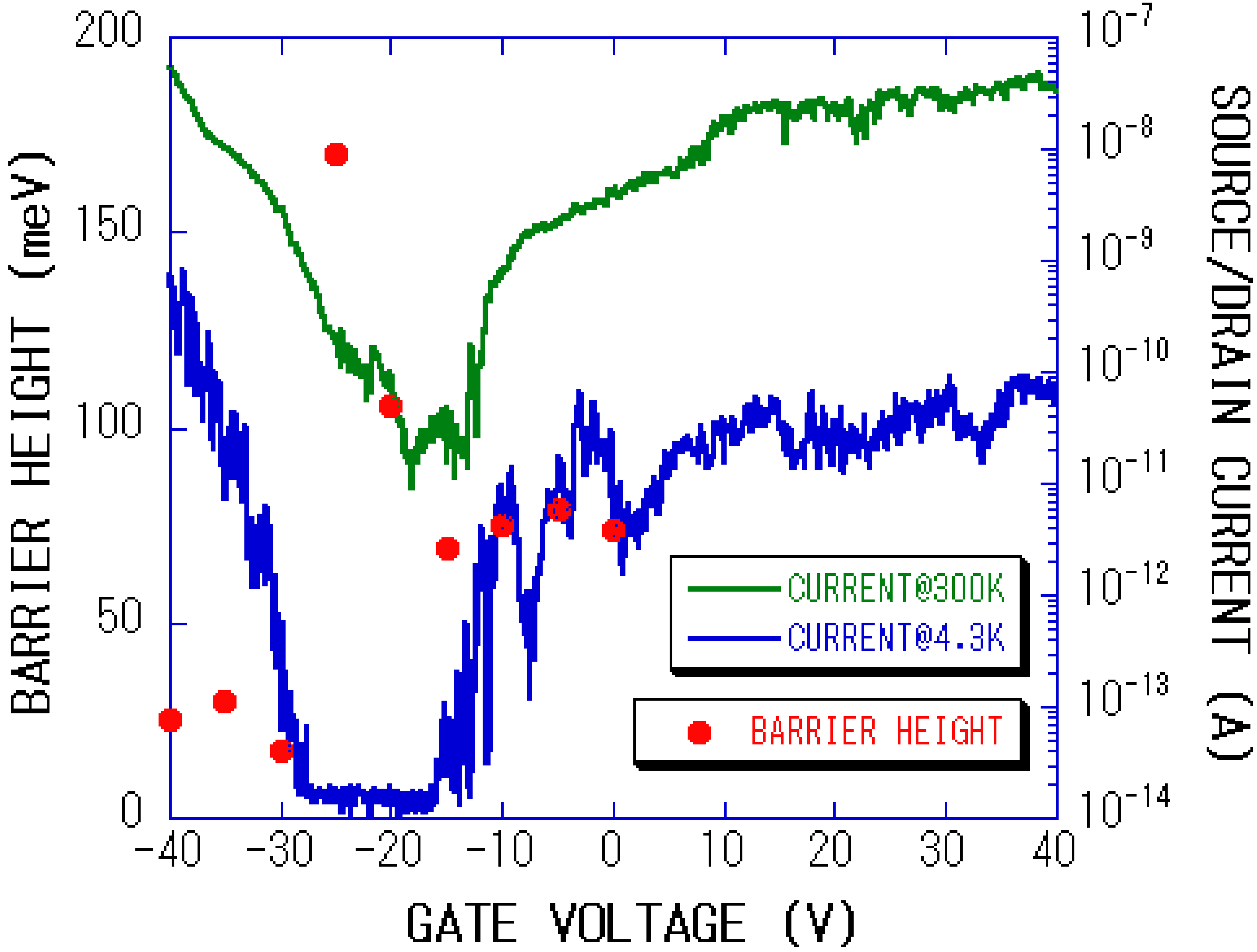


E_a (activation energy)

$$I_{ds} \sim A_0 \cdot \exp\left[\frac{-E_a}{kT}\right]$$

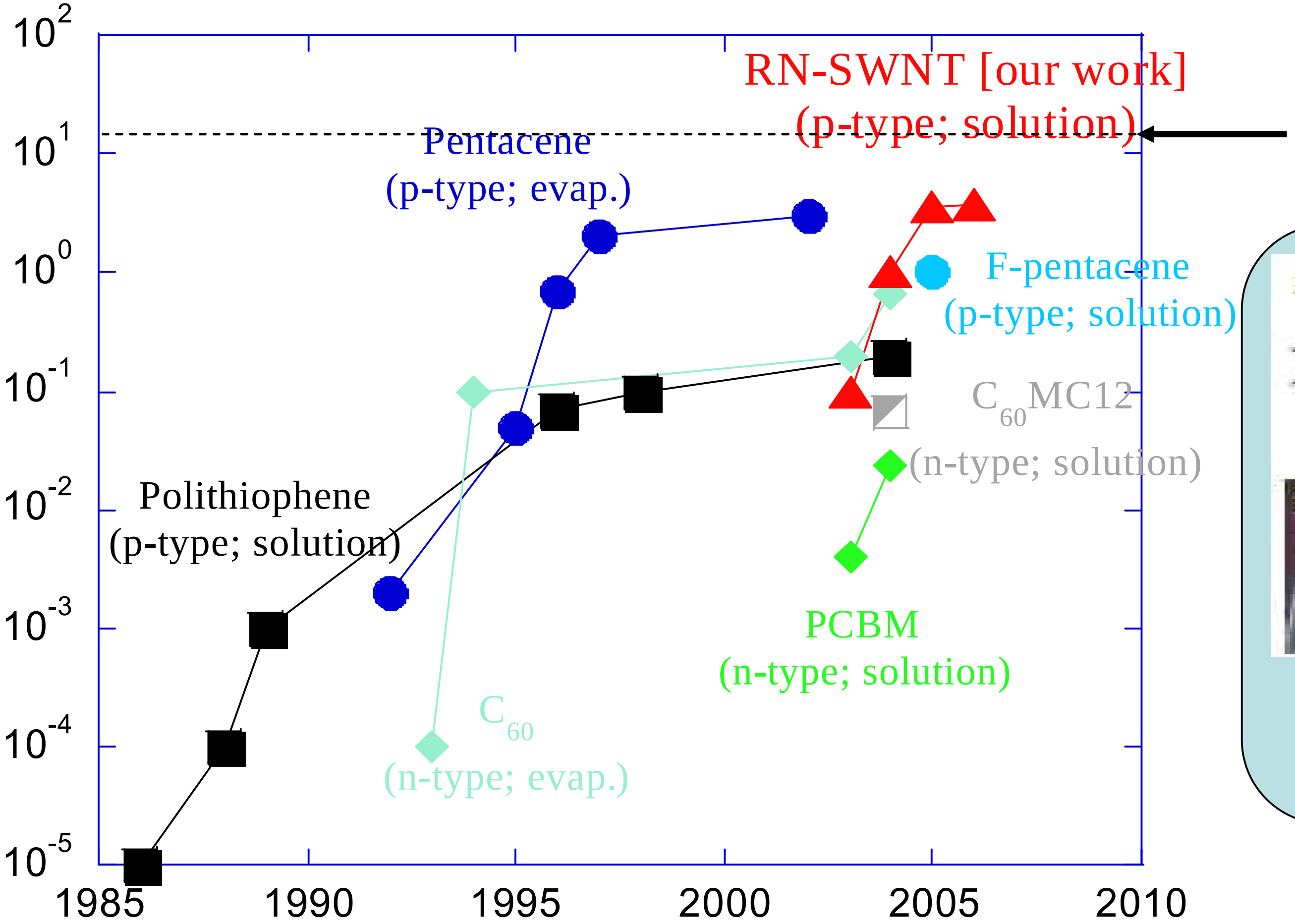
⇨ Schottky barrier height

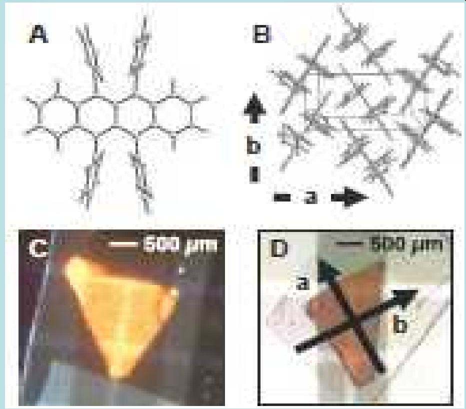
FET Characteristics of non-doped RN-SWNT-FETs



Recent Progress in Field Effect Mobility of OFETs

Solution-processed RN-SWNT-FET: m = 3.8 cm^2/Vs, on/off > 10^5 (simultaneously !!)





Sunder, Podzorov et al., Science 303, 1644 (2004).

Mobility estimation

Calculation of μ (mobility)

$$\mu = \frac{(dI_{ds} / dV_g)}{\varepsilon V_{ds} W / L_{ox} L_{ds}}$$

I_{ds} : Source-drain current
V_g : Gate voltage
ε : SiO_2 Dielectric constant
V_{ds} : Source-drain voltage
L_{ox} : Width of SiO_2
L_{ds} : Gate length
W : Gate width

Parallel-plain model

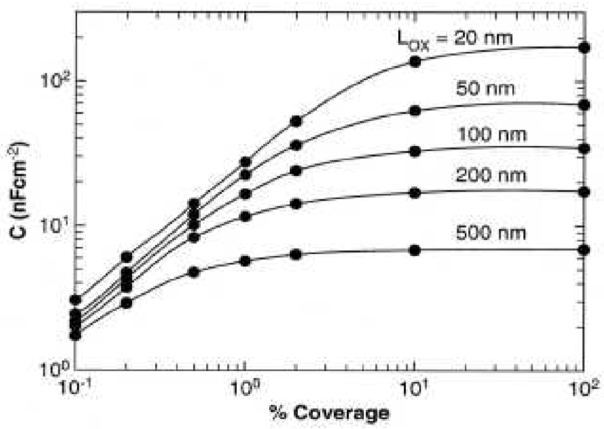


FIG. 3. Calculated values of the gate capacitance (circles) vs the % coverage of SWNTs for various gate oxide (SiO_2) thicknesses ranging from 20 to 500 nm. The solid lines are guides for the eye.

E.S. Snow et al., APL 86 (2005) 33105.

Capacitance is underestimated !!

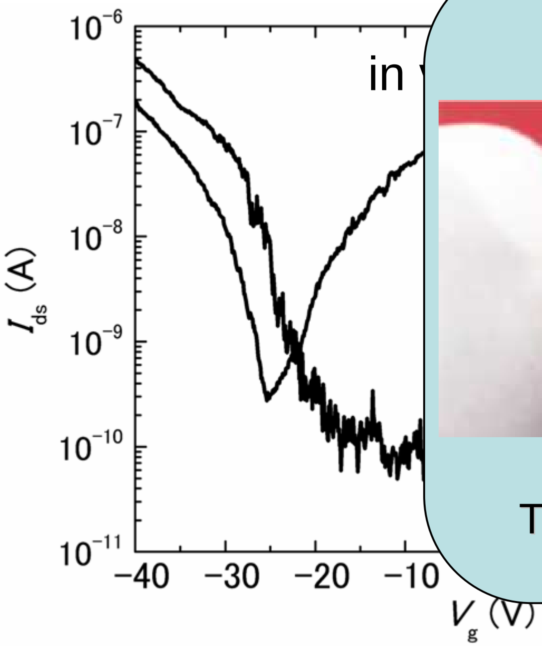
Much room for obtaining larger mobility !!

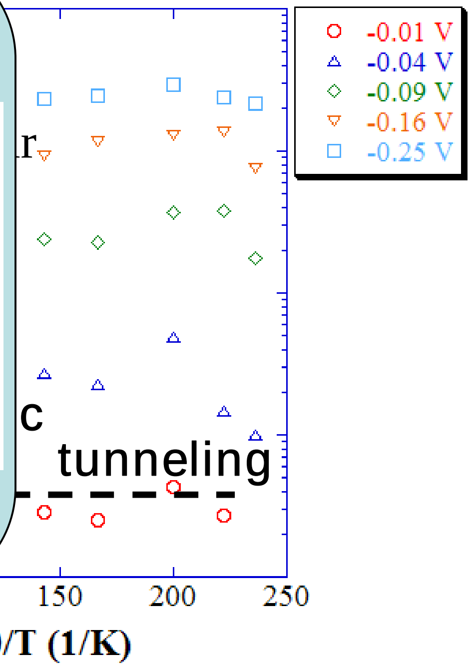
Features of Network SWNT-FETs and next...

i) Ambipolar behaviors
ii) Schottky FETs

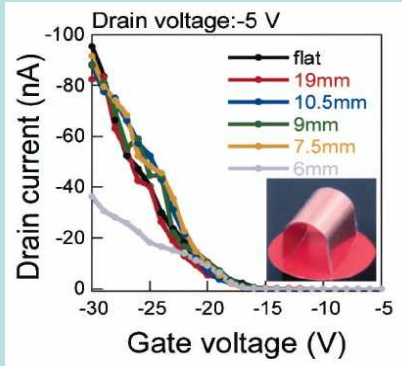
(F$_B$ (hole) ~ 170 meV [E$_g$=600 meV])

→ **Similar with individual SWNT-FETs**





Transparent & flexible SWNT-FETs



T. Takenobu et al., APL 88, 33511 (2006).

T. Fukao, M. S. et al., JJAP in press.

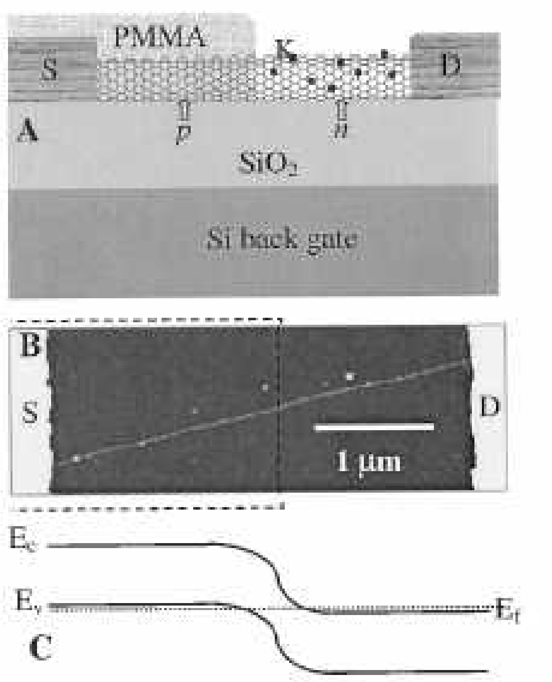
→ Next milestone: Stable polarity control

Previous Studies on Polarity Control

Modulated Chemical Doping of Individual Carbon Nanotubes

Chongwu Zhou, Jing Kong, Erhan Yenilmez, Hongjie Dai*

Science 290, 1552 (2000).

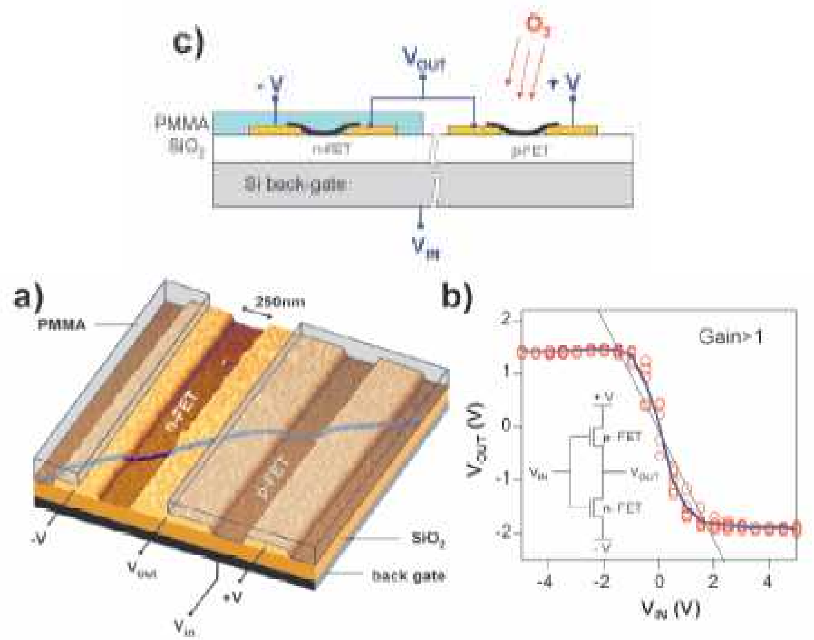


Carbon Nanotube Inter- and Intramolecular Logic Gates

V. Derycke, R. Martel, J. Appenzeller, and Ph. Avouris*

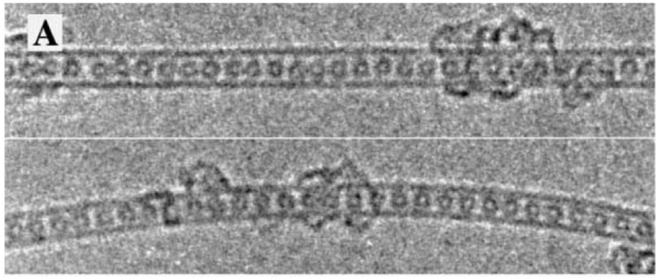
IBM Research Division, T. J. Watson Research Center, Yorktown Heights, New York 10598

Nano Lett. 1, 453 (2000).



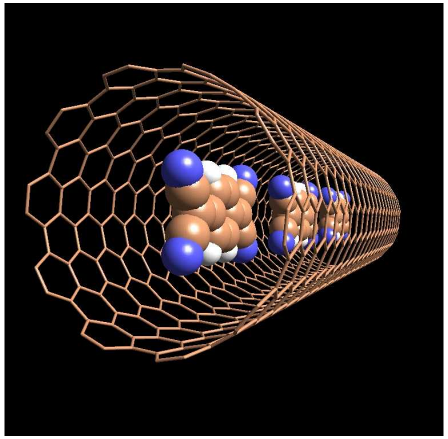
Unstable polarity control !!

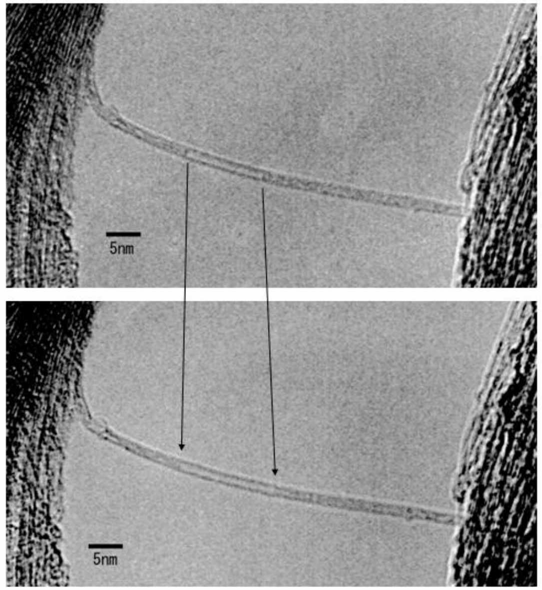
Polarity Control of SWNTs by Molecular Encapsulation

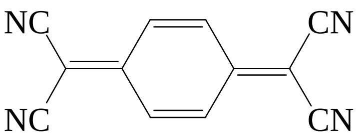


Encapsulation

C_{60}@SWNTs

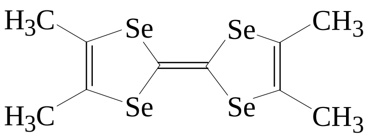






TCNQ

p dopant



TMTSF

n dopant

Stable p- and n-type control !!

T. Takenobu et al. Nature Mat. 2, 683 (2003).
M. Shiraishi et al. Phys. Rev. B 71, 125419 (2005).

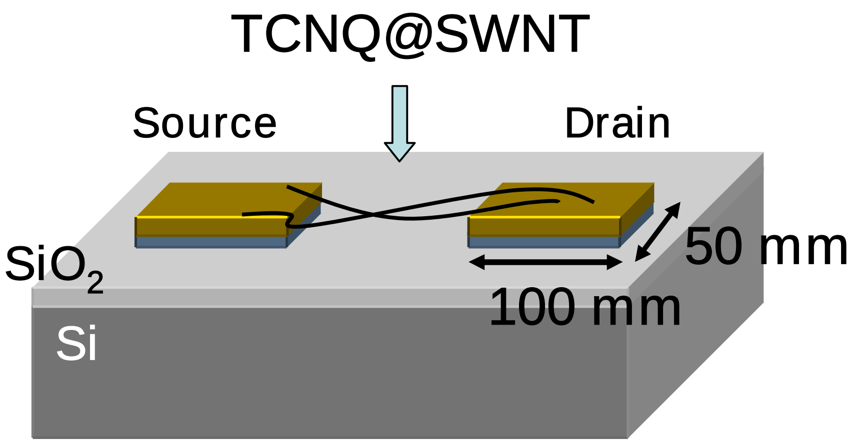
No device operation

Operation & Characterization of TCNQ@SWNT-FETs

Sample Preparation of TCNQ@SWNT-FETs

SWNTs : Laser synthesized and well purified (d=1.4 nm, E_g~0.6 eV)
TCNQ encapsulation : conventional sublimation

1. Ultrasonication : 10 hours in a DMF solution
2. Centrifugation (Kokusan H-201FR) : 10000 [rpm] / 15 [min]
3. Extraction of a well-debundled TCNQ@SWNTs-solution
4. Dispersion of the solution onto Si substrates

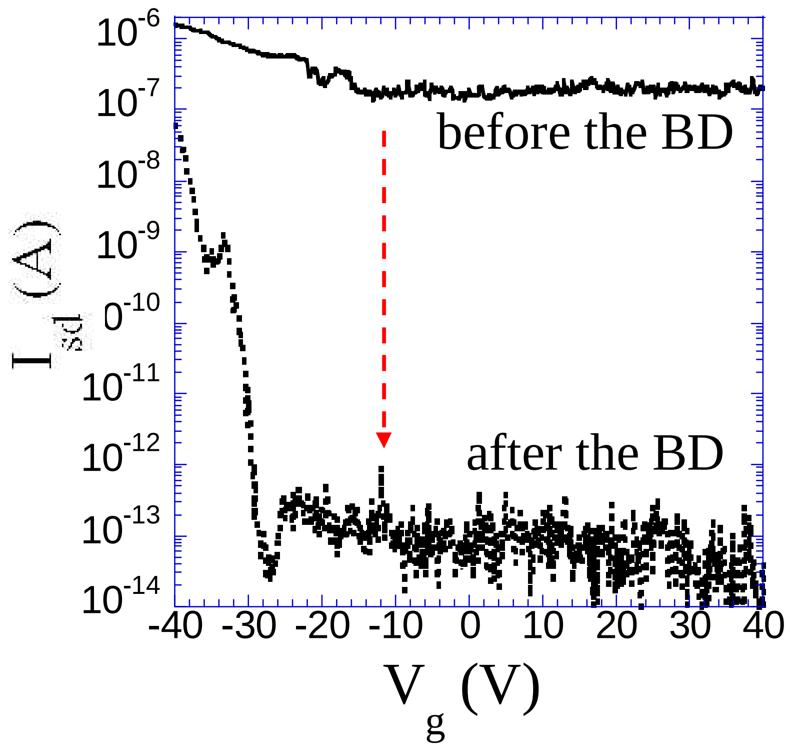


Electrode Au(70 nm) / Ti(10 nm)
Gap Width = 2 mm
SiO_2 thickness = 200 nm

Electrical breakdown : removing metallic SWNTs
improving device characteristics

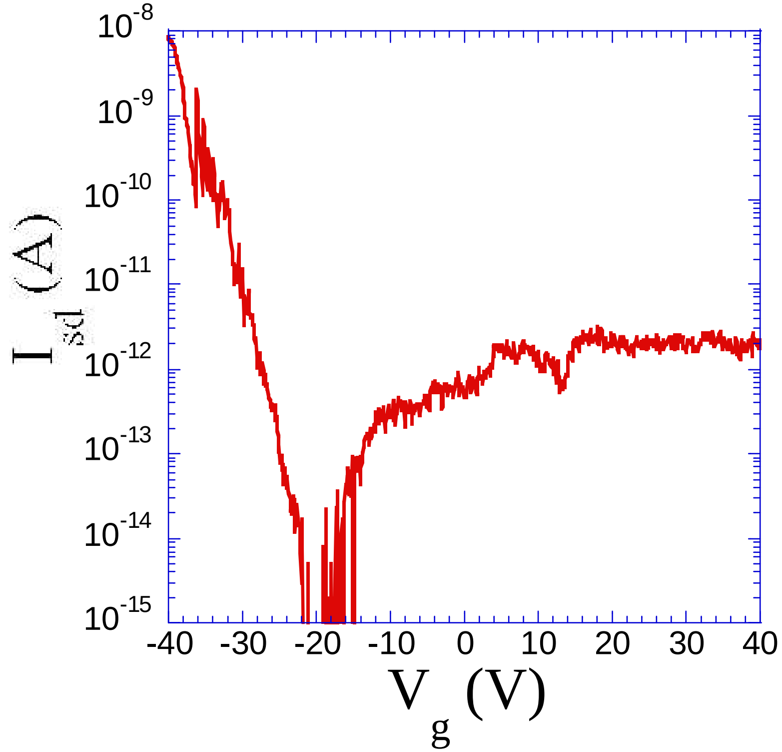
Device Characteristics of TCNQ@SWNT-FETs (I)

Network TCNQ@SWNT-FETs



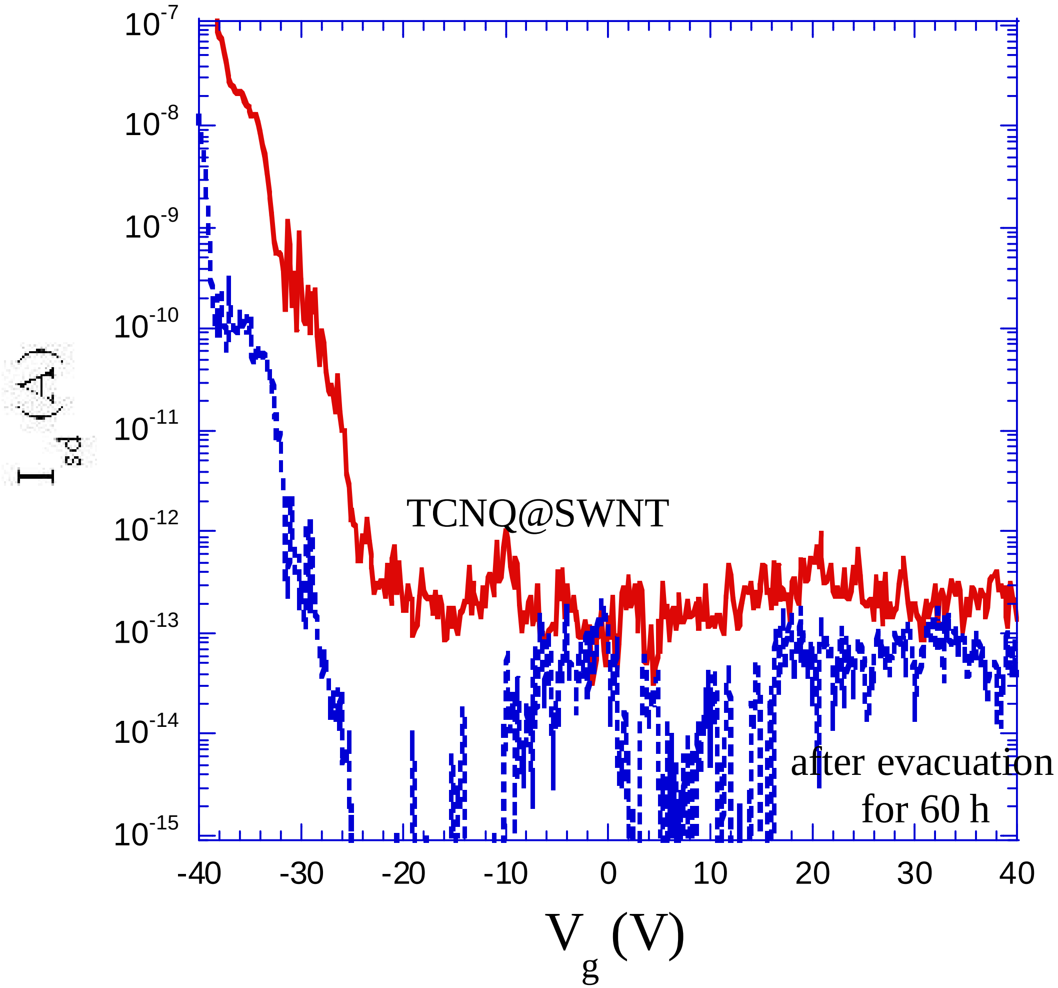
p-type behavior in evacuation

pristine network SWNT-FETs



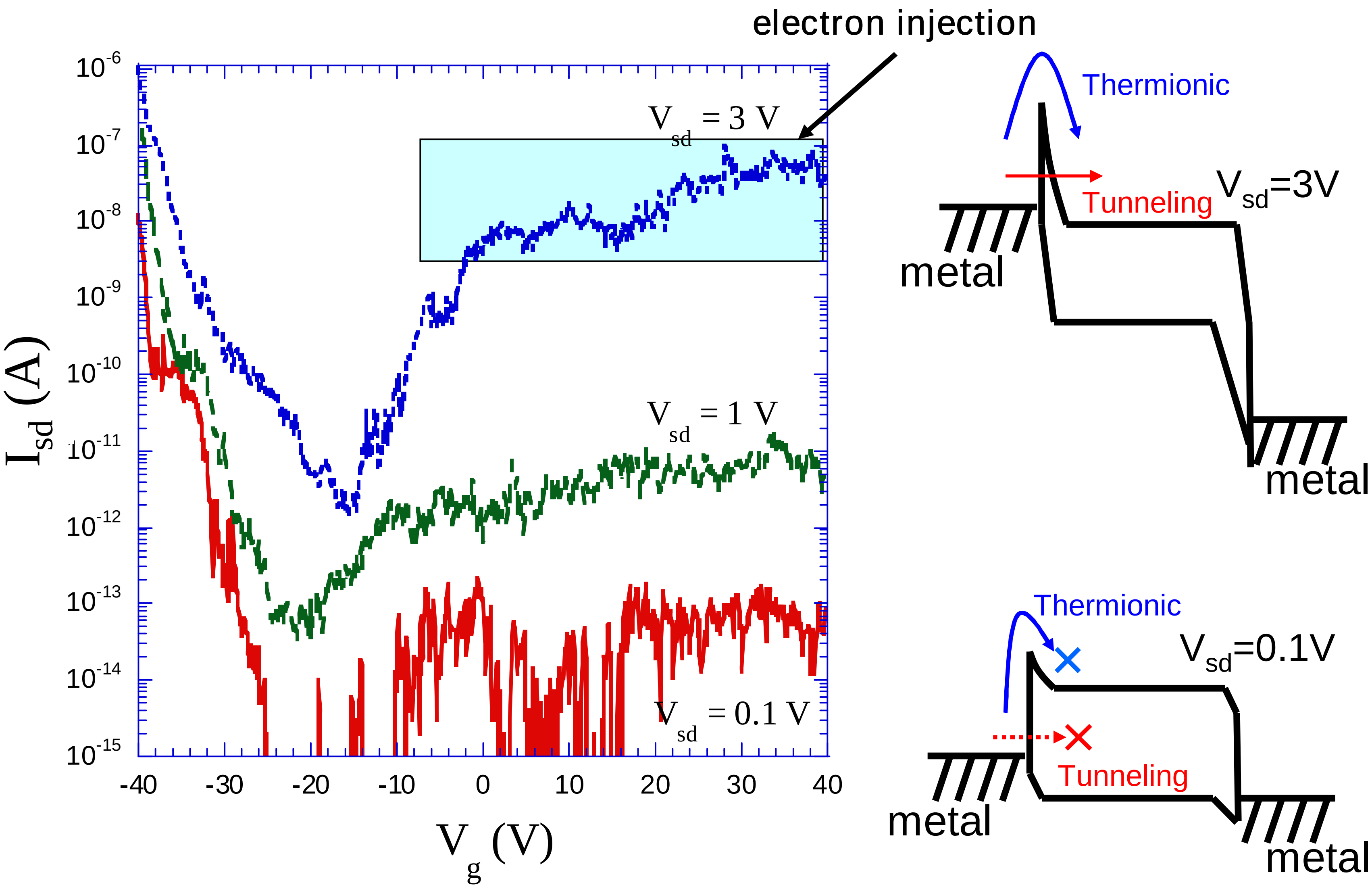
ambipolar behavior in evacuation

Device Characteristics of TCNQ@SWNT-FETs (II)



Even after 60 h of evacuation, the p-type behavior is maintained.

Carrier Injection Control



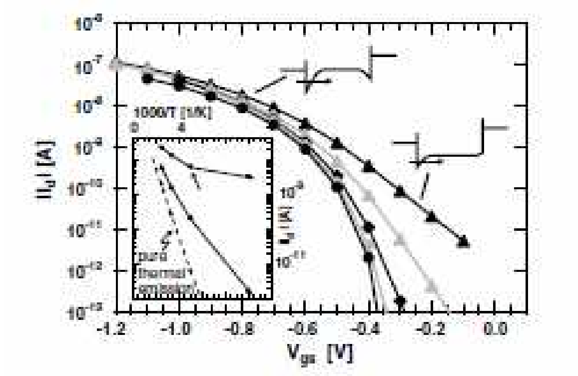
Schottky barrier modulation (doping, bias voltage application,...)

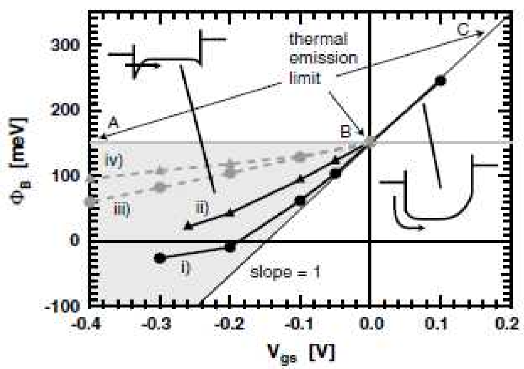
Estimation of the Schottky Barrier Height (I)

VOLUME 92, NUMBER 4 PHYSICAL REVIEW LETTERS week ending 30 JANUARY 2004

Tunneling Versus Thermionic Emission in One-Dimensional Semiconductors

J. Appenzeller,[1] M. Radosavljević,[1] J. Knoch,[2] and Ph. Avouris[1]
[1]*IBM T.J. Watson Research Center, Yorktown Heights, New York 10598, USA*
[2]*Institut für Schichten und Grenzflächen, Forschungszentrum Jülich, D-52425 Jülich, Germany*
(Received 27 June 2003; published 28 January 2004)



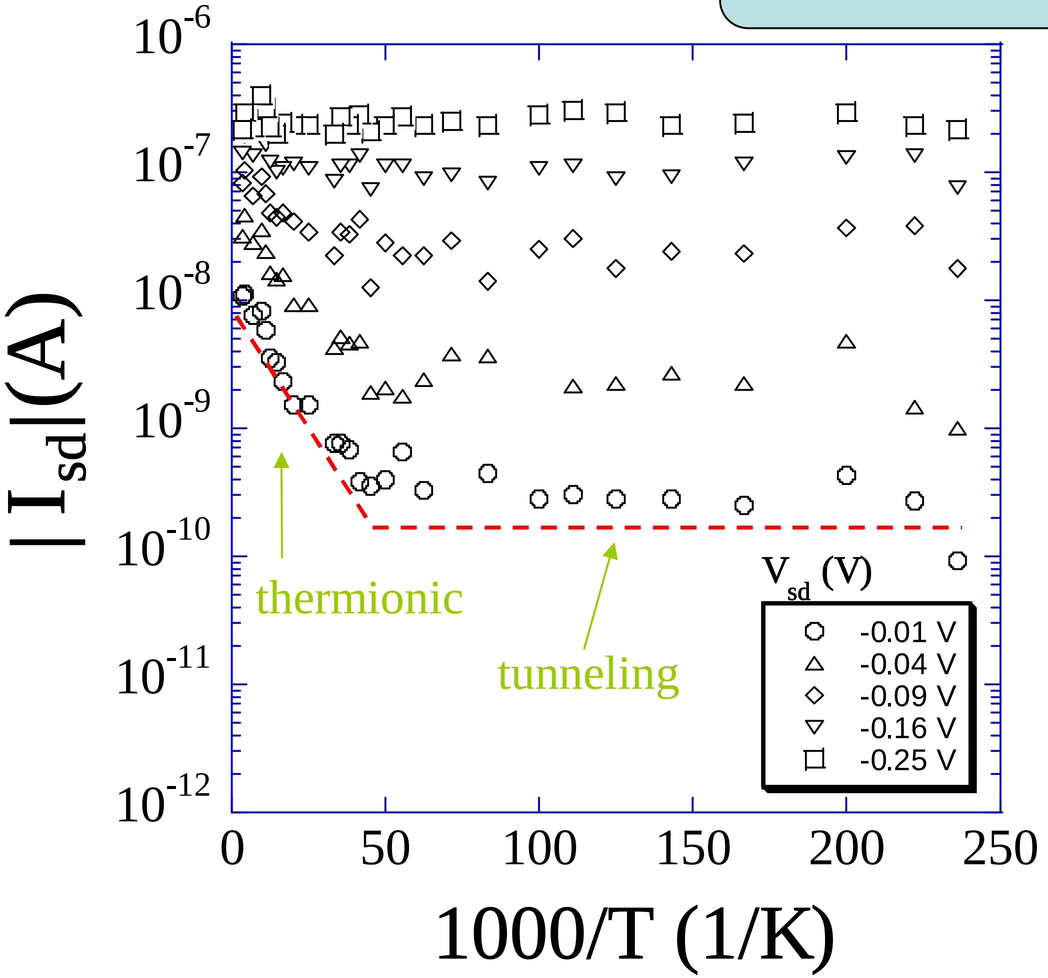


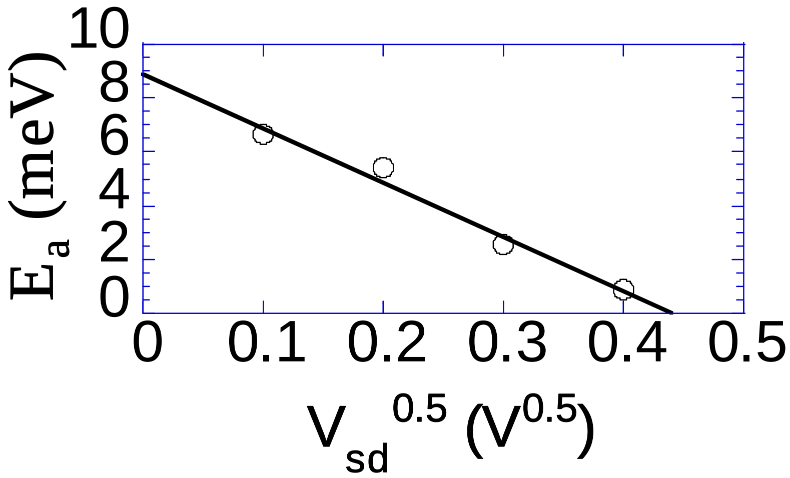
A suitable combination of V_g and V_{sd} is needed !!

	$V_g > V_{th}$	$V_g < V_{th}$
$V_{sd} > 0$ V	electron injection	×
$V_{sd} < 0$ V	×	hole injection

Estimation of the Schottky Barrier Height (II)

V_g = -40 V





Important features

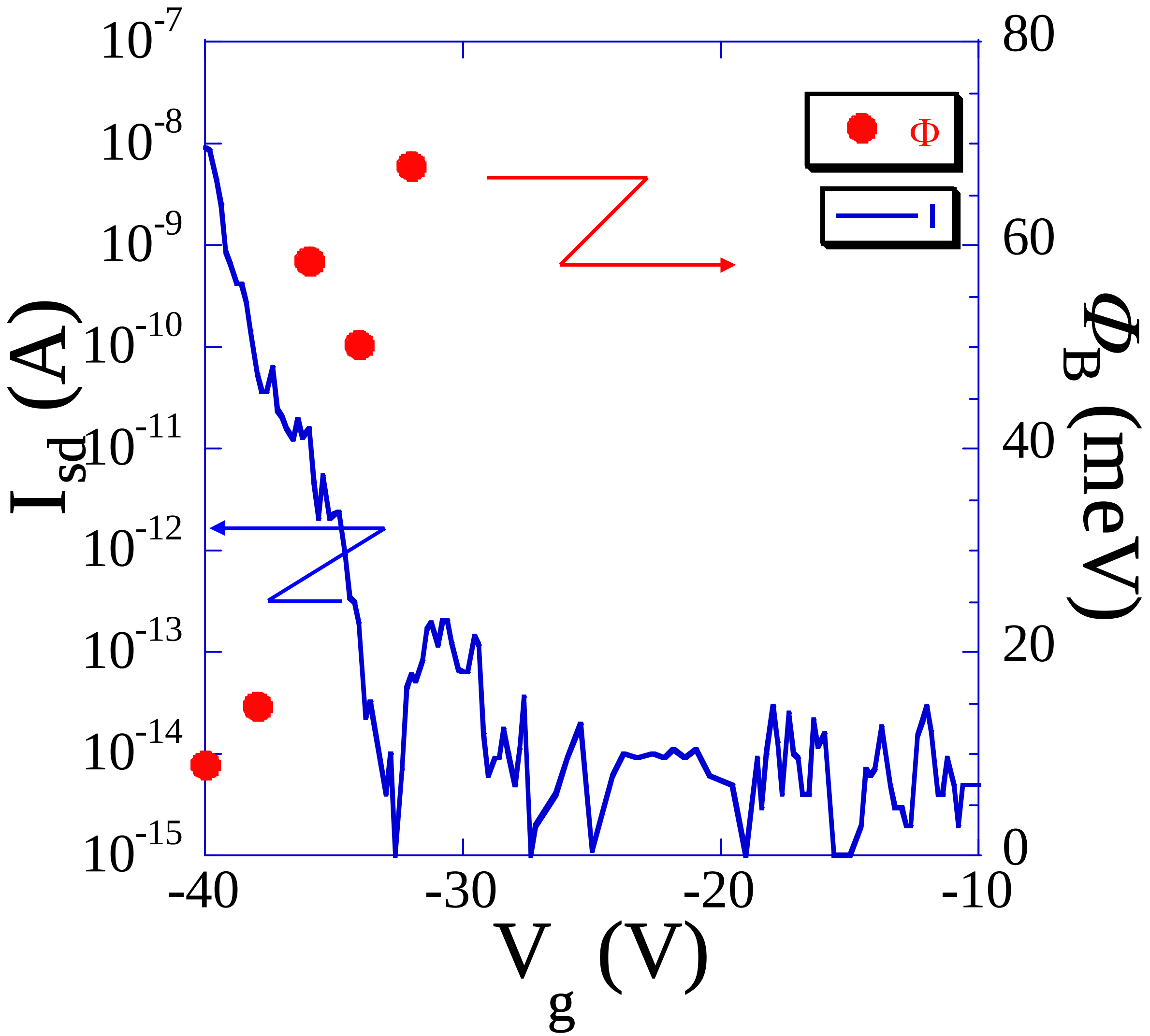
i) Combination of thermionic & tunneling current.

ii) Effective E_a (Φ_B) can be obtained by extrapolation.

iii) E_a (Φ_B) for V_g = -40 V was 8.6 meV.

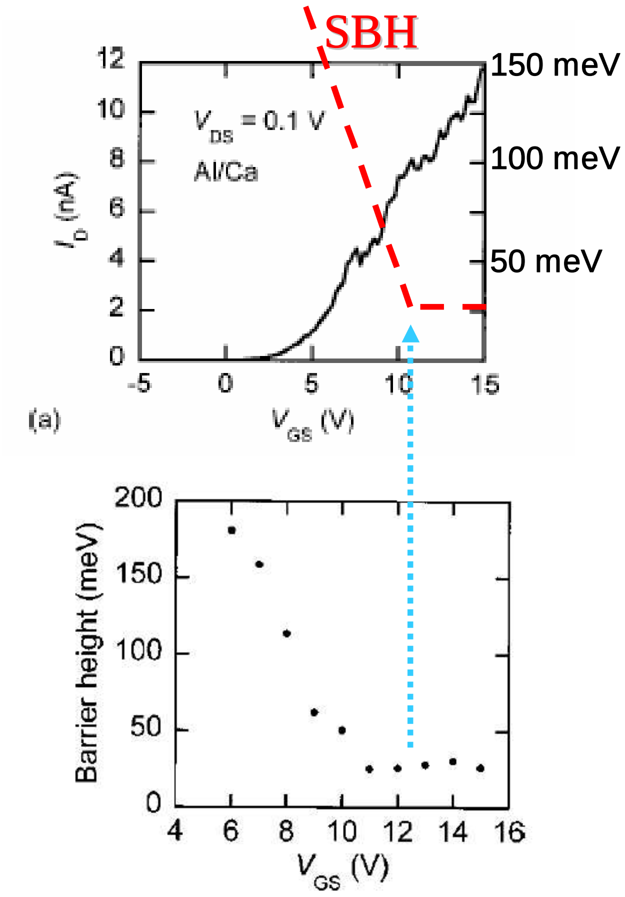
A Schottky FET !! (no obvious contribution from inter-tube hopping !!)

Estimation of the Schottky Barrier Height (IV)



Φ_B ~ 70 meV (for hole)

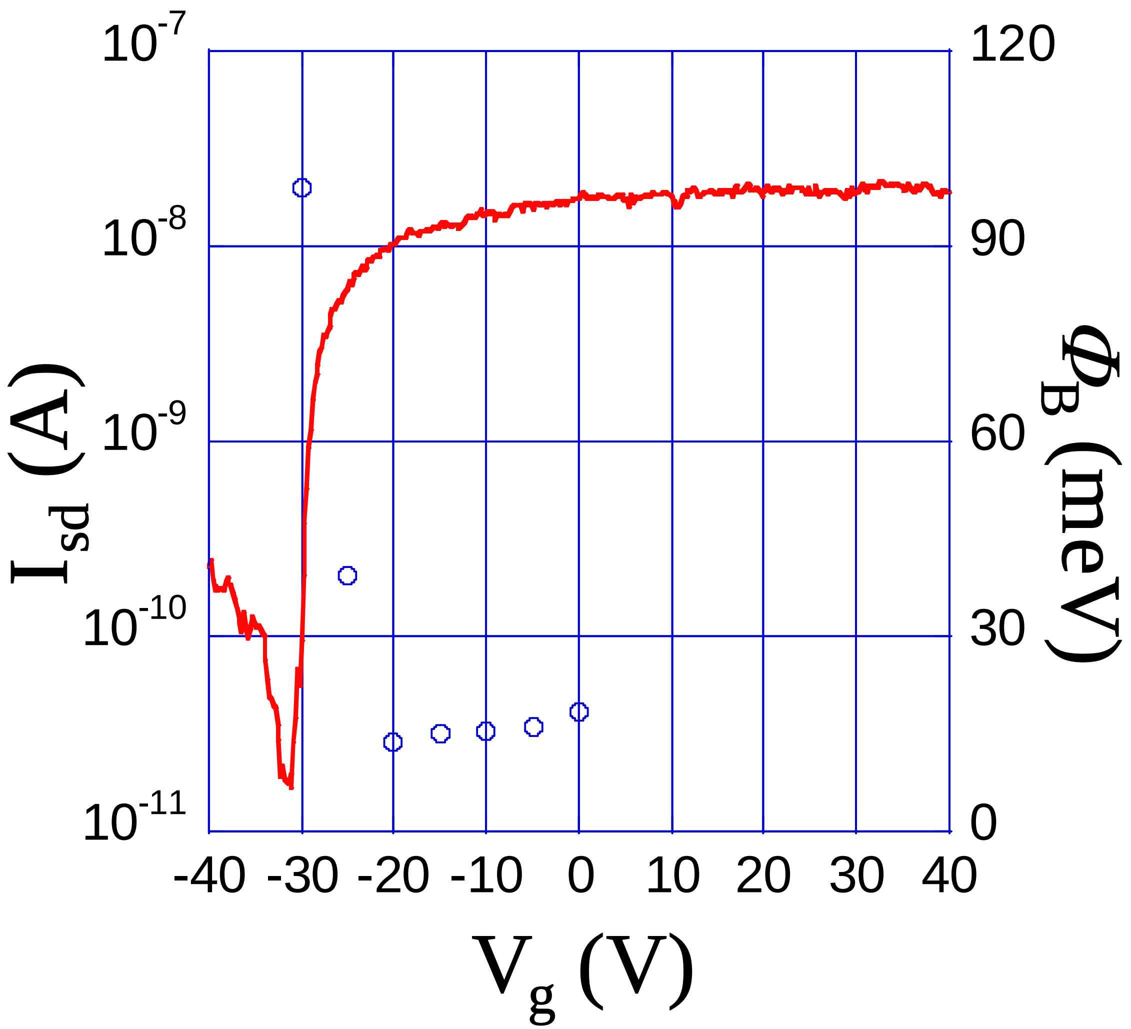
Similar Vg dep. in n-type FETs



SWNT-FET with Ca electrodes

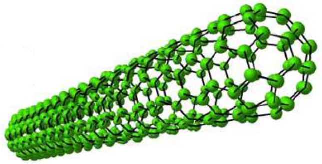
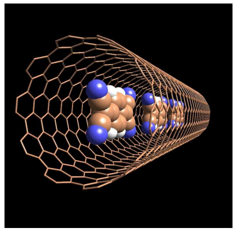
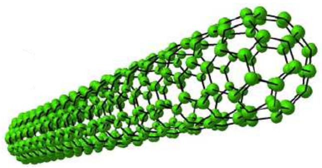
Y. Nosho et al., APL86 (2005) 73105.

Comparison with PEI-doped SWNT-FETs (n-type)



$\Phi_B \sim 100$ meV (for electron)

Shift of the Schottky Barrier Height in network SWNT-FETs

Types of network SWNT-FETs	The Schottky barrier height
Pristine SWNT-FETs 	170 meV for hole T. Fukao, M.S. et al., JJAP in press.
TCNQ@SWNT-FETs 	70 meV for hole S. Nakamura, M.S. et al., APL in press.
PEI -adsorbed SWNT-FETs  + $H_2N(CH_2CH_2N)_x$-$(CH_2CH_2NH)_y$ with branch CH_2-CH_2-NH_2	100 meV for electron S. Nakamura, M.S. et al., APL in press.

The SB can be modulated by doping in network SWNT-FETs.

Summary & References of PART I

1. Fabrication of solution-processed network SWNT-FETs.
2. The Schottky barrier governs device properties.
3. The barrier height : 170 meV (for hole)
4. The barrier height can be modulated by doping.
   TCNQ@SWNT-FET : 70 meV (for hole)
   PEI-SWNT-FET : 100 meV (for electron)

~ Network SWNT-FETs ~

M. Shiraishi et al., Chem. Phys. Lett. 394 (2005), 110.
M. Shiraishi et al., Appl. Phys. Lett.87 (2005), 93107.
S. Nakamura, M.S. et al., Appl. Phys. Lett. in press.
T. Fukao, M.S. et al., JJAP, in press.
M. Ohishi, M.S. et al., APL submitted.
T. Takenobu et al., Adv. Mat. 17 (2005), 2430.
T. Takenobu et al., APL88 (2006), 33511.

~ Doping by molecular encapsulation ~

T. Takenobu et al., Nature Mat. 2 (2003), 687.
M. Shiraishi et al., Phys. Rev. B 71 (2005), 125419.

PART II :

Molecular Spintronics Using C_{60}, SWNT and More...

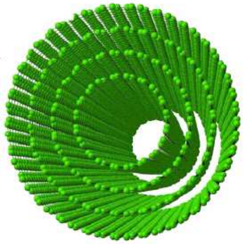
Background of this work

Molecular spintronics as a novel research field

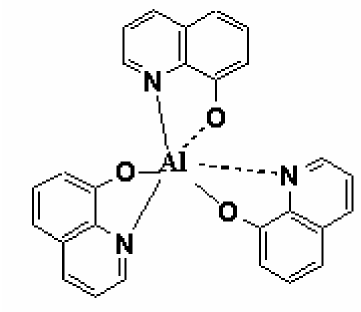
Small spin-orbit interaction ⇒long spin coherent length

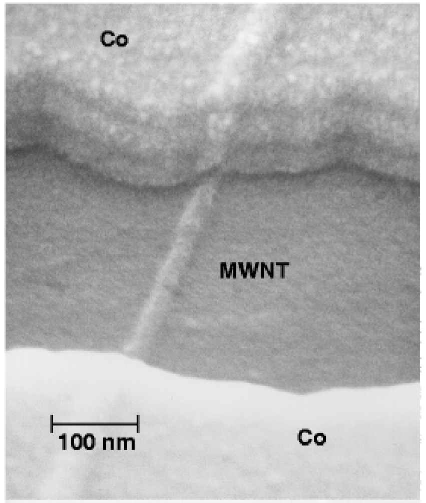
Novel molecular spin-devices???

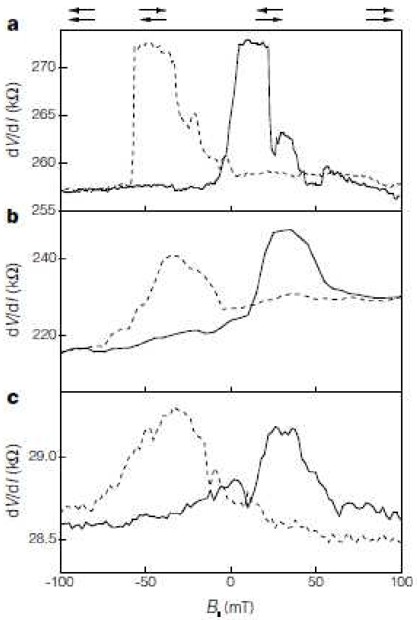
MWNT



Alq_3

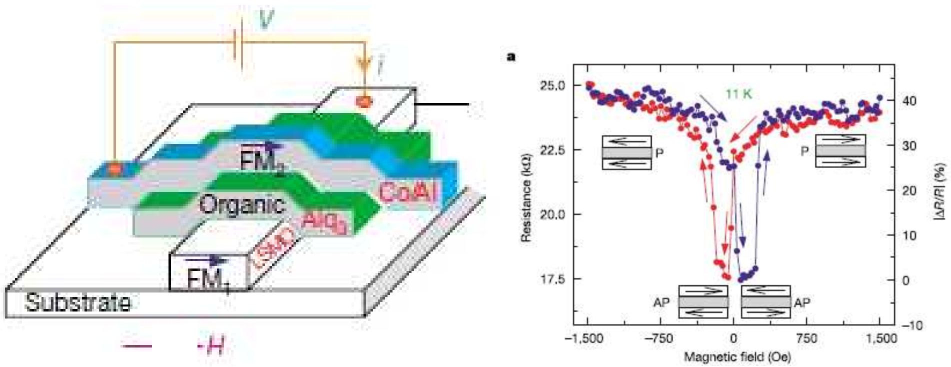






9 % GMR (4 K)

K. Tsukagoshi et al., Nature 1999.

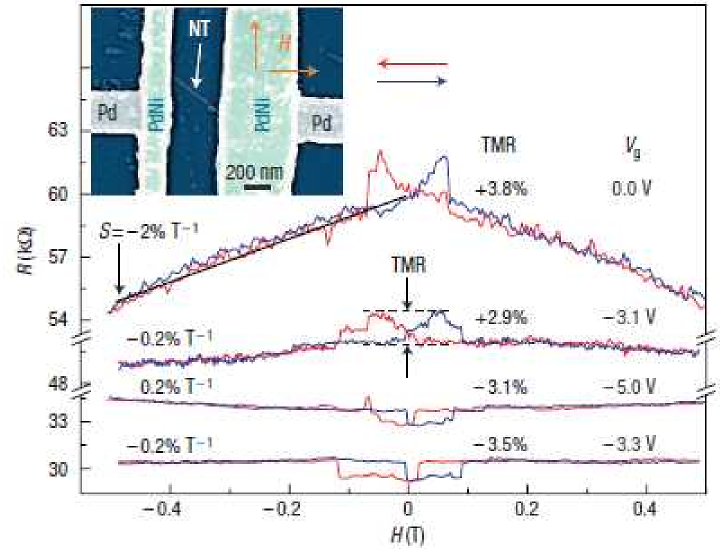


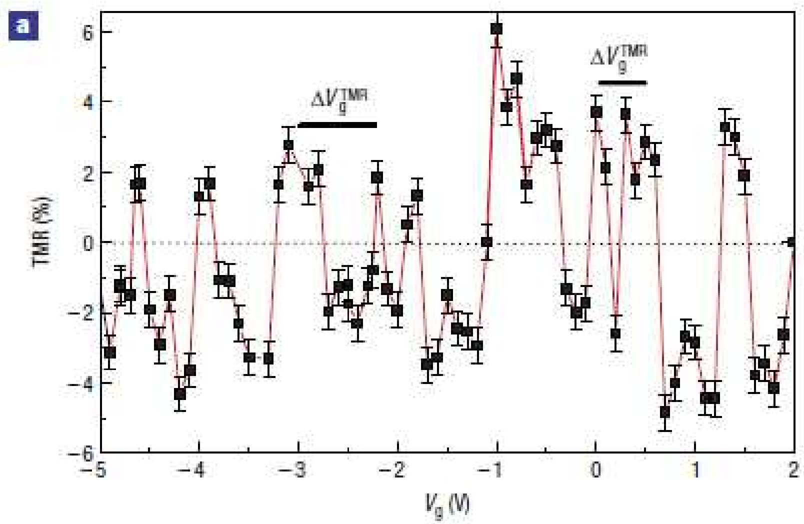
40 % GMR (11 K)

Z. H. Xiong et al., Nature 2004.

Reliable (?) studies

Probably only one reliable report on spin-dependent transport via molecules





TMR can be changed by applying a gate voltage.

S. Sahoo et al., Nature Phys. 1, 99 (2005).

Problem : No characterization of a magnetization process (No correspondence)
No characterization of background physics

Current Problems and Our Strategy

Current situation

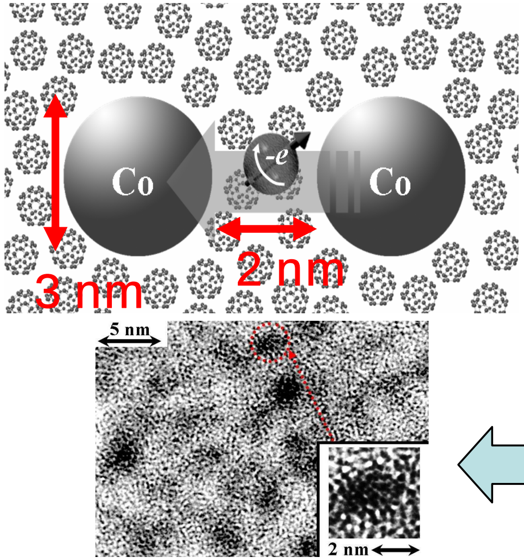
1. Excessive large contact resistance
2. "ill-defined" interface between metal and molecules

impedes reliable measurements.

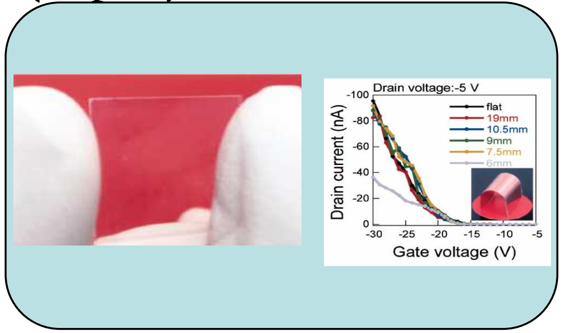
1. No apparent progress !!
2. Less reliability and reproducibility !!

Our strategy

C_{60}-Co nano-composite



(Flexible and Transparent) (doped) SWNT-FETs

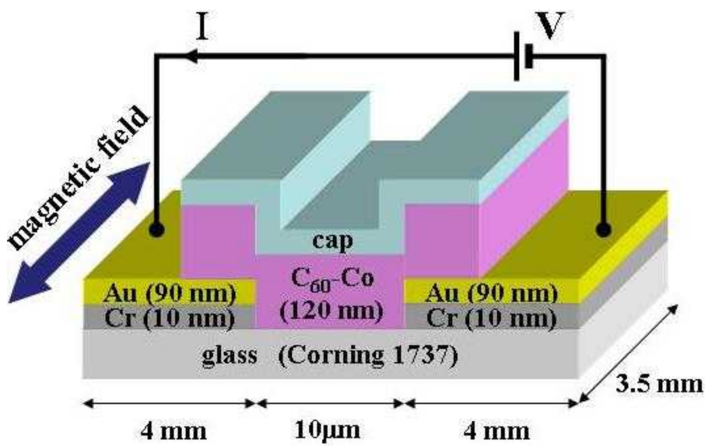


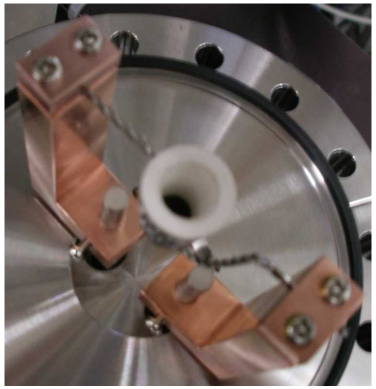
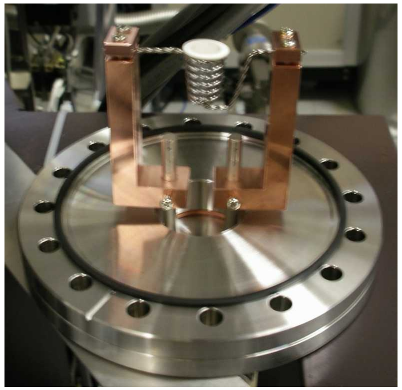
Characterization of an interface between Metal/Molecules (Schottky barrier modulation…)

Spin current detection in SWNTs

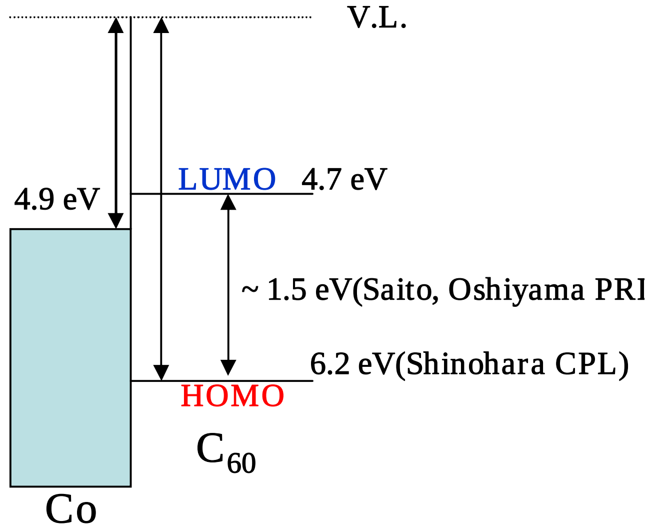
C_{60}-Co nano-composite

1. Photo-lithography
2. Evaporation of Cr, Au
3. Lift-off
4. Evaporation of C_{60}-Co (10^{-6}~10^{-7} Torr)
5. Capping layer formation(C_{60}+SiO)
7. ZEP-520A coating
8. Annealing at 180 ℃ for 30 min. in vac.
9. Magnetoresistance measurements



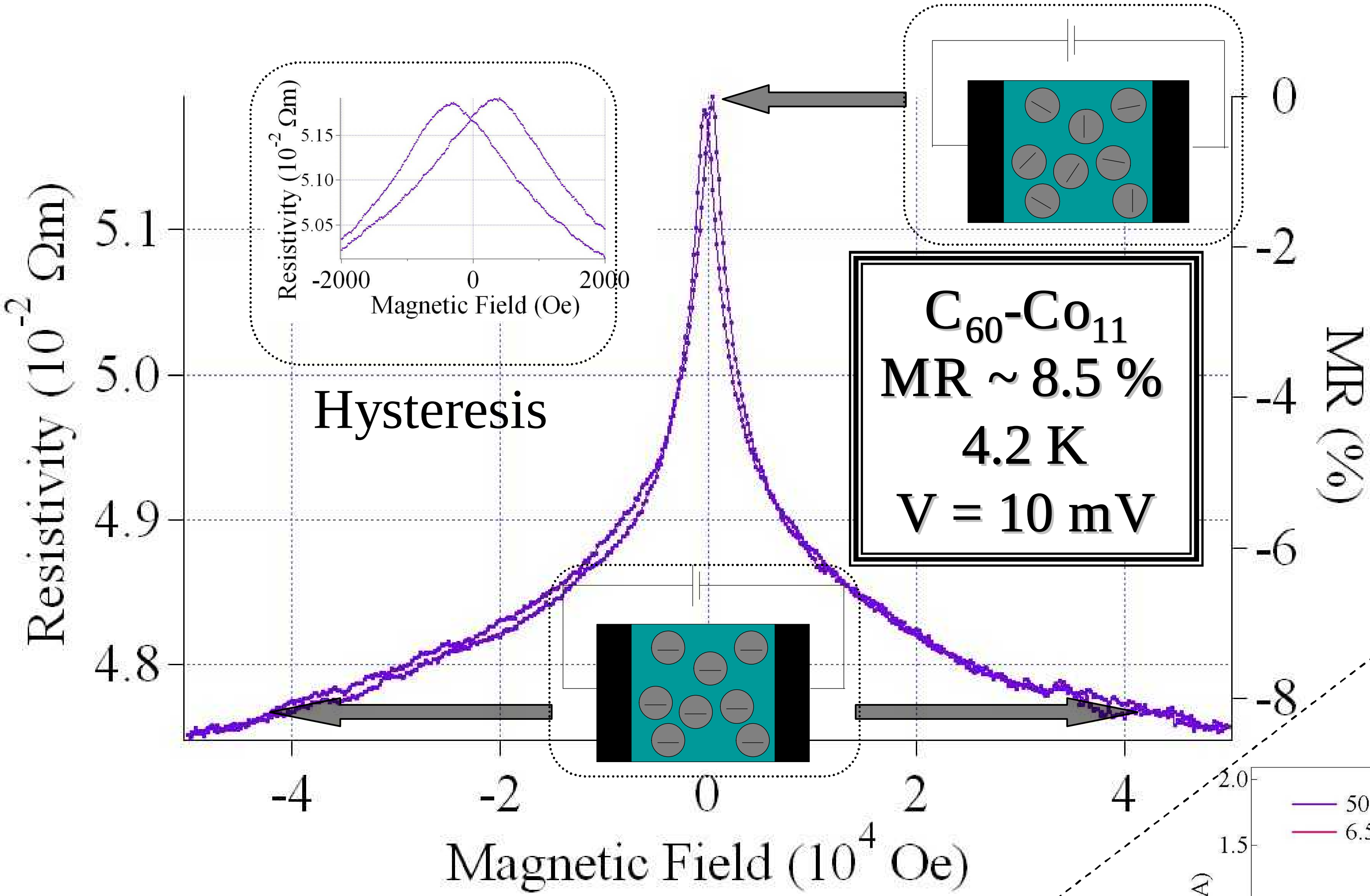



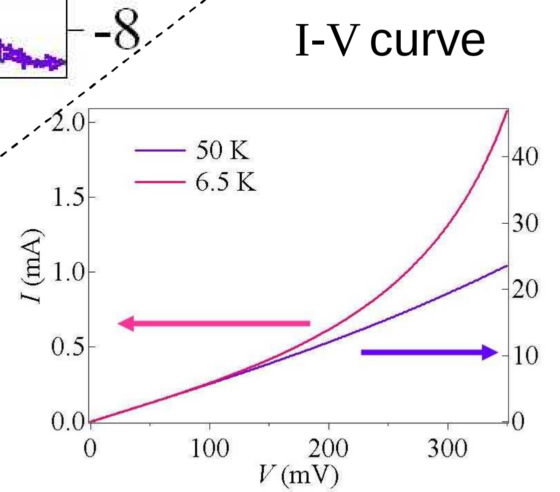

C_{60} Evaporation Chamber C_{60}



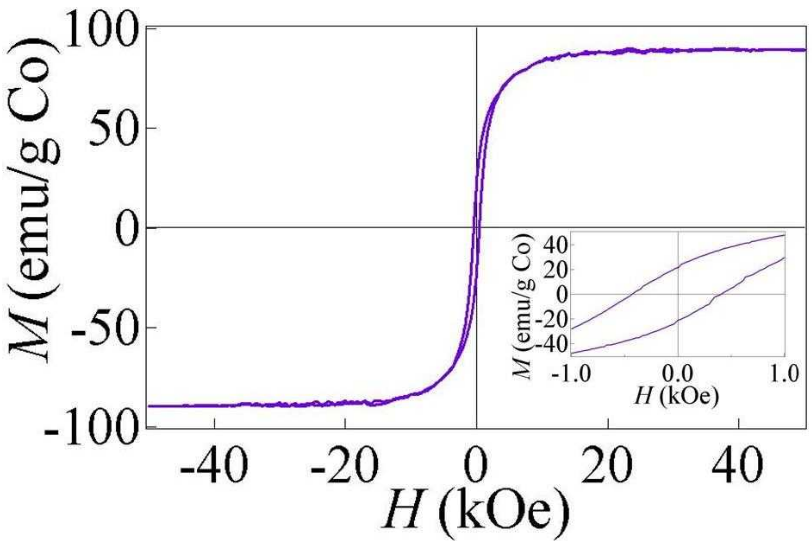
Small band-gap between W.F.(Co) and LUMO

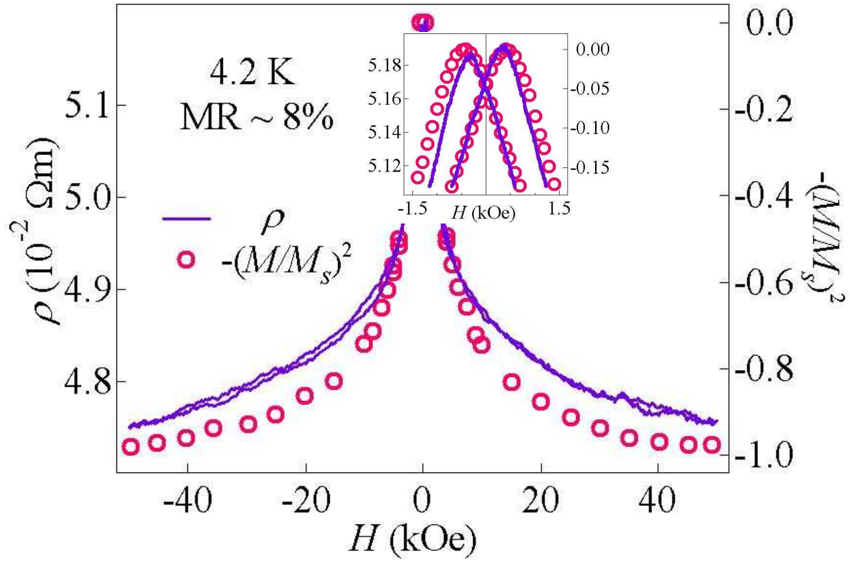
Magnetoresistance (MR) at 4.2 K





M-H curve measurements by SQUID





Good Accordance with the hysteresis

⇓

Magnetization of the Co
induces the observed MR effect.

Julliere model

P : Polarization of Co (=0.34)

(MR ratio) = $P^2/1-P^2$

~ 13 (%)

⇒ More than half of the limit.

Structural characterizations

Fig. 1

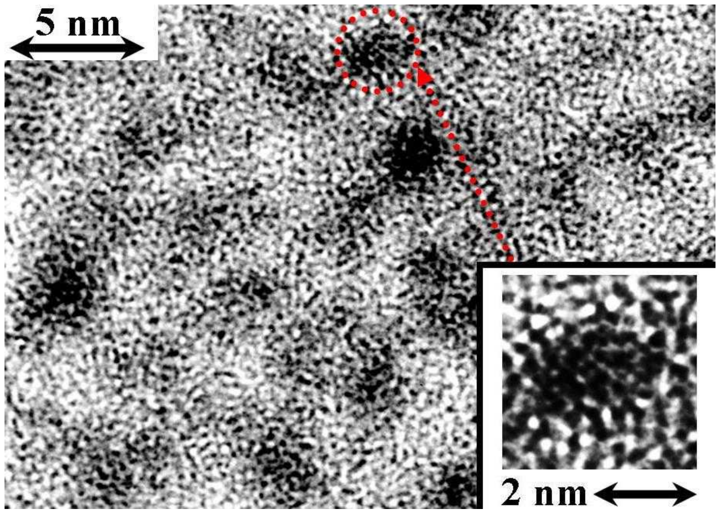
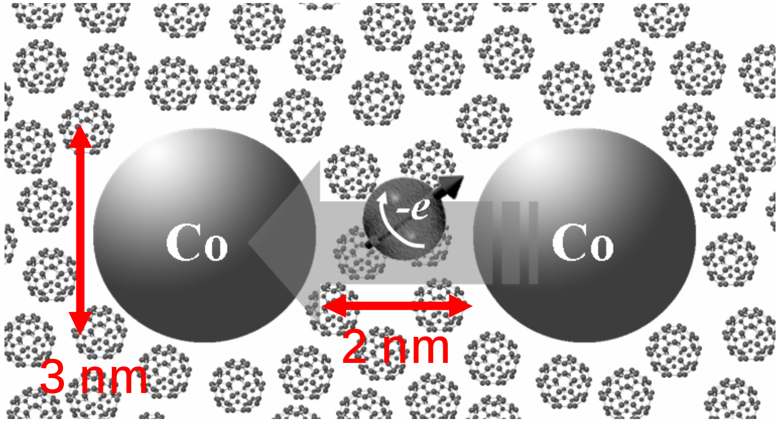
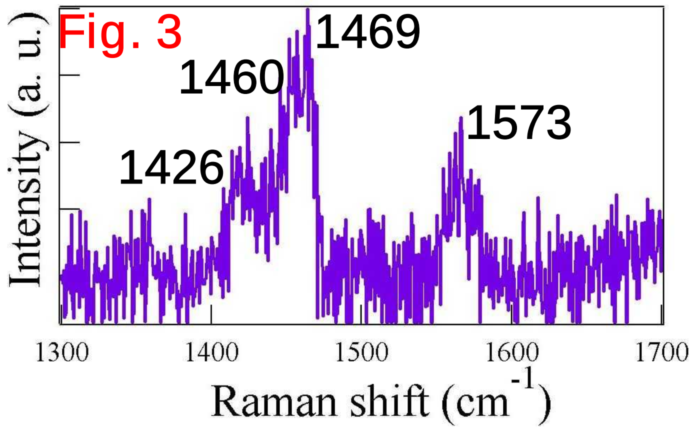


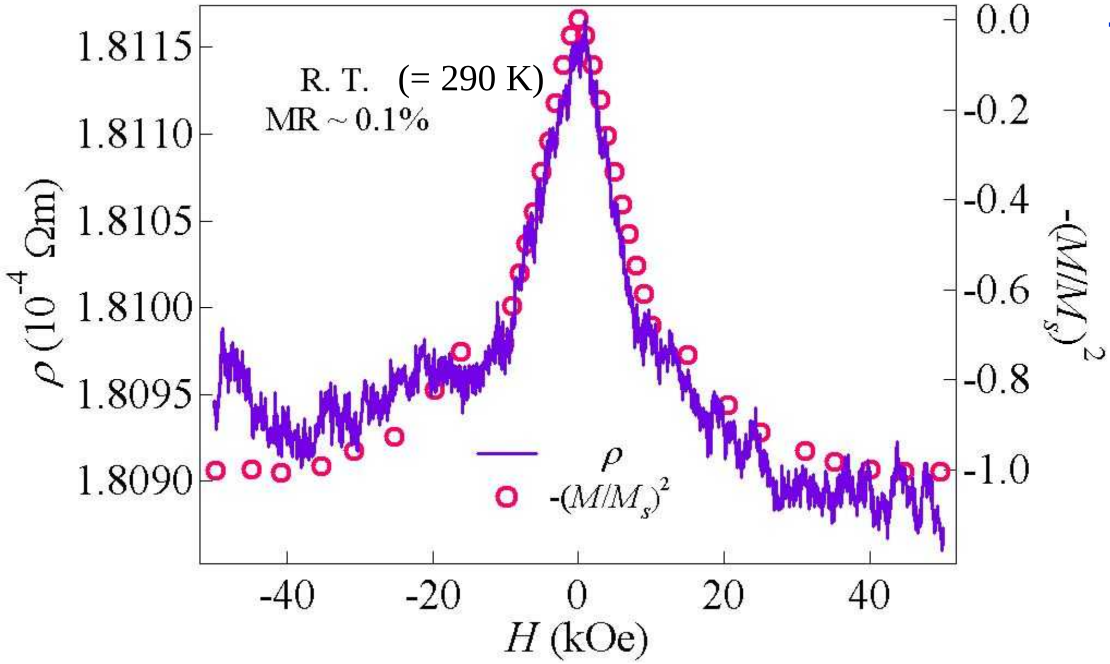
Fig. 2



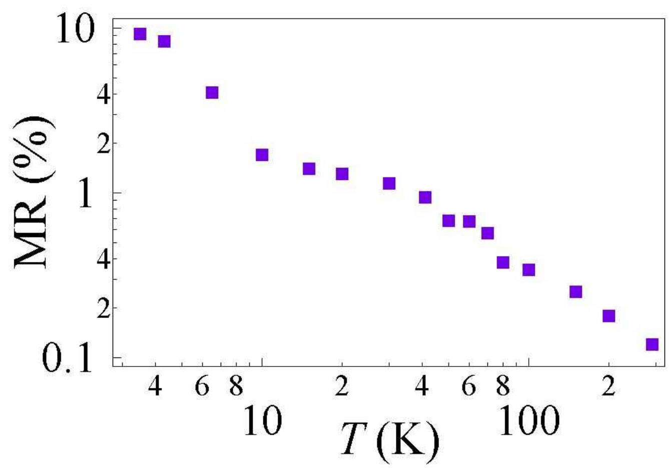
1. The Co size：2-3 nm (Fig.1,XRD：2 nm)
2. Distance ~ 1.5-2.2 nm (XRDより)
3. No percolation of the Co (Fig.1)
4. Spin dependent transport via C_{60} (Fig.2)
5. No obvious damage to C_{60} (Fig. 3)



A MR effect at room temperature

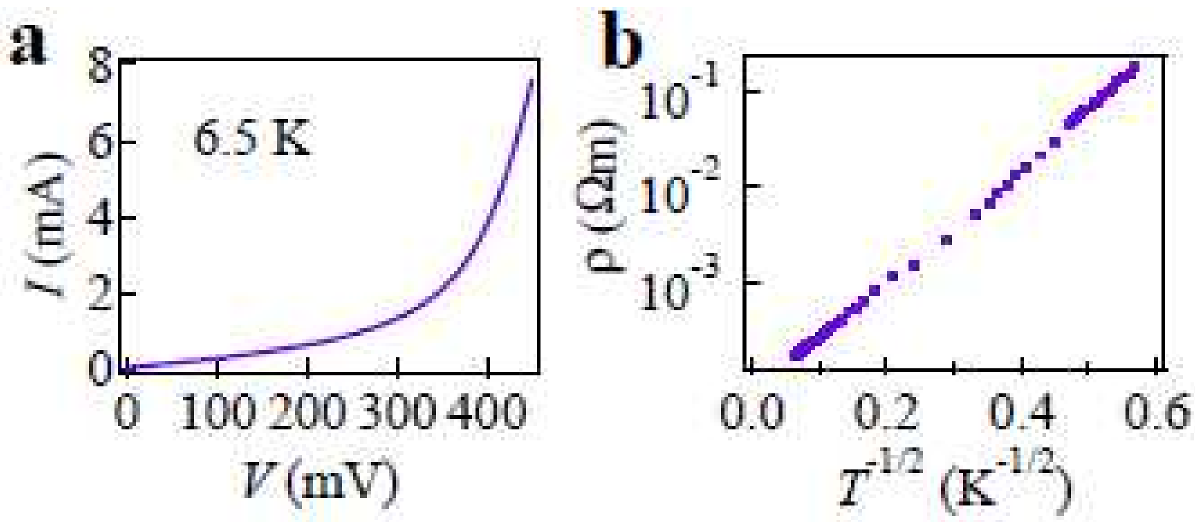


Temperature-dep. of the MR ratio



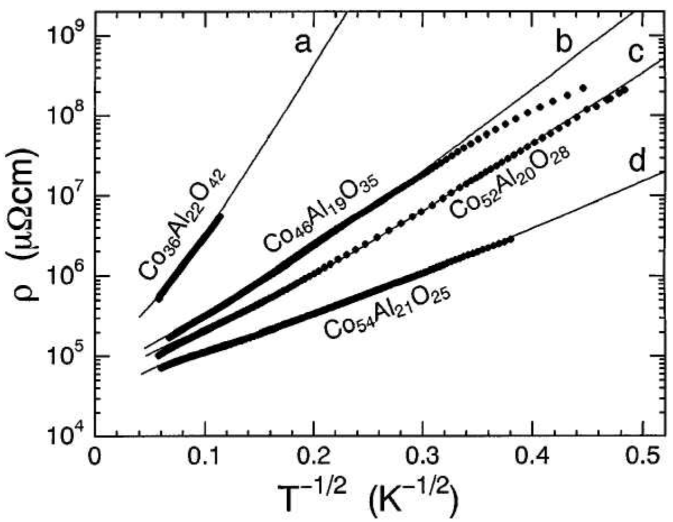
The first observation of a MR effect
in molecular spin devices !!

Electrical properties of nano-composites



$T^{-1/2}$ dep (Hopping transport) ⇒ Coulomb interaction between conducting electrons

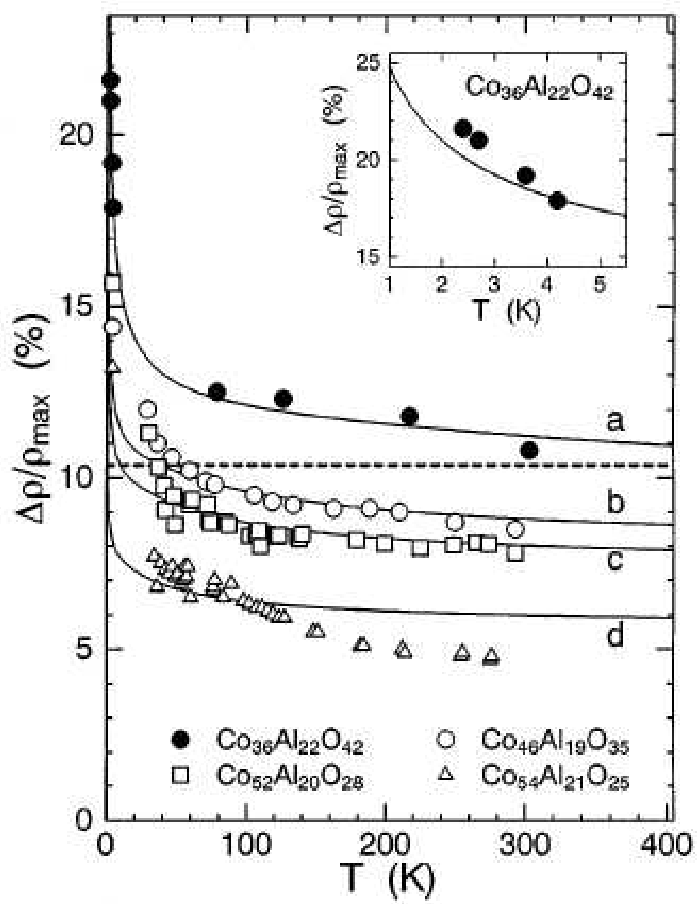
Similar behavior



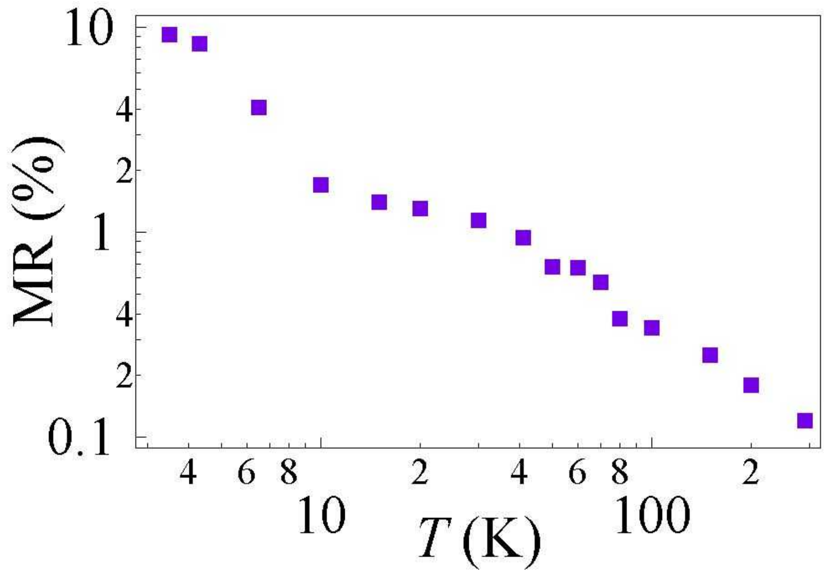
Co-Al-O granular film
S. Mitani et al., PRL 1998.

An unique feature

Co-Al-O



C_{60}-CO



Difference in temperature dependence of MR ratio : Open question ?

Our Message

1. The first reliable spin dependent transport via C_{60}.
2. The first MR effect at RT in molecular spin devices.

S. Miwa, M. Shiraishi, M. Mizuguchi, T. Shinjo and Y. Suzuki
“Spin-dependent Transport via C_{60} Molecules”
Jpn. J. Appl. Phys. (Express Letters), in press.

Summary and References in PART II

C_{60}-Co nano-composite

1. Success in a reliable MR effect by using a novel C_{60}-Co system.
2. The observed MR ratio : 8 % at 4 K、0.1 % at 290 K.
3. The first reliable spin dependent transport via C_{60}.
4. The first MR effect at RT in molecular spin devices.

S. Miwa, M.S. et al., JJAP (Express Letter) in press.

Berlin !! Berlin !!

Wir Fahren Nach Berlin !!

Stuttgart…., Stuttgart,…

Wir Muessen Nach Stuttgart Fahren…