



The Abdus Salam  
International Centre for Theoretical Physics



2157-18

**Workshop on Principles and Design of Strongly Correlated Electronic Systems**

*2 - 13 August 2010*

**Electric Field Induced Superconductivity with Electric Double Layer Transistors**

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# **Electric field induced superconductivity with electric double layer transistors (EDLT)**

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**Department of Applied Physics**  
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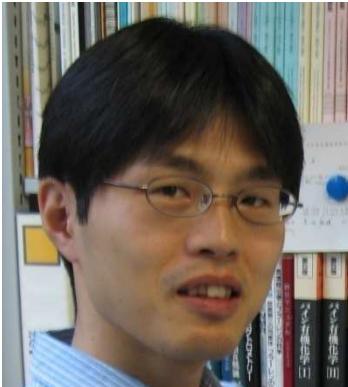
# OUTLINE

- Introduction :
  - Electric-field induced superconductivity
  - Electric double layer transistor (EDLT)
- Oxide semiconductors
  - ZnO and SrTiO<sub>3</sub>
- For further increase of carrier density
- Layered material ZrNCl
  - Bulk properties and E-induced SC
- Summary

# Acknowledgements (In-house collaboration at IMR, Tohoku)

## Development of EDLTs (IMR)

H. Shimotani



H. T. Yuan



J. T. Ye



Y. Kasahara



## Oxides (WPI-AIMR)

M. Kawasaki



K. Ueno



## Low-T physics (IMR)

T. Nojima



S. Nakamura

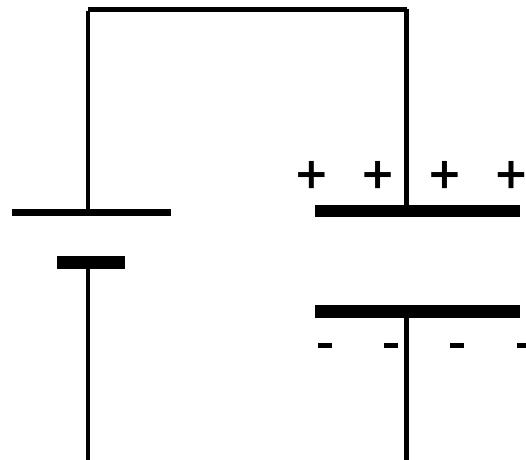


# History 1

## Measuring resistance of capacitor electrodes

**Capacitor**

**Charge accumulation device**



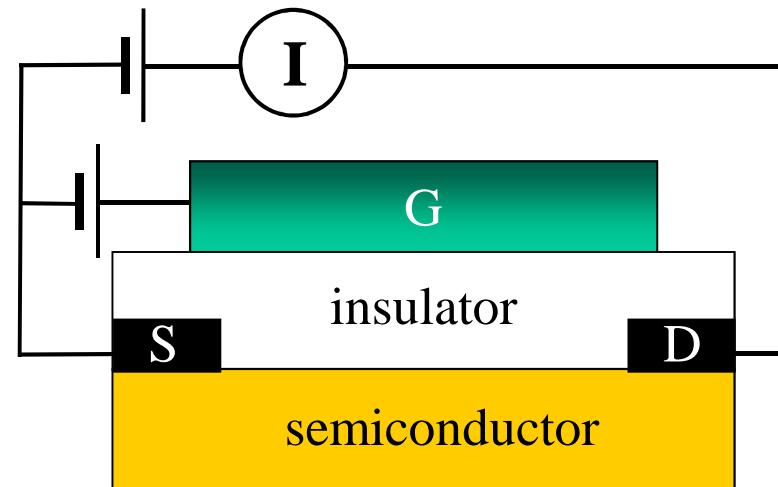
**Resistance measurement  
of capacitor electrodes (1906)**

**Electric field control of  
superconductor**

**R. E. Glover, III & M. D. Sherrill (1960)**

**Field Effect Transistor (FET)**

**Current switching device**



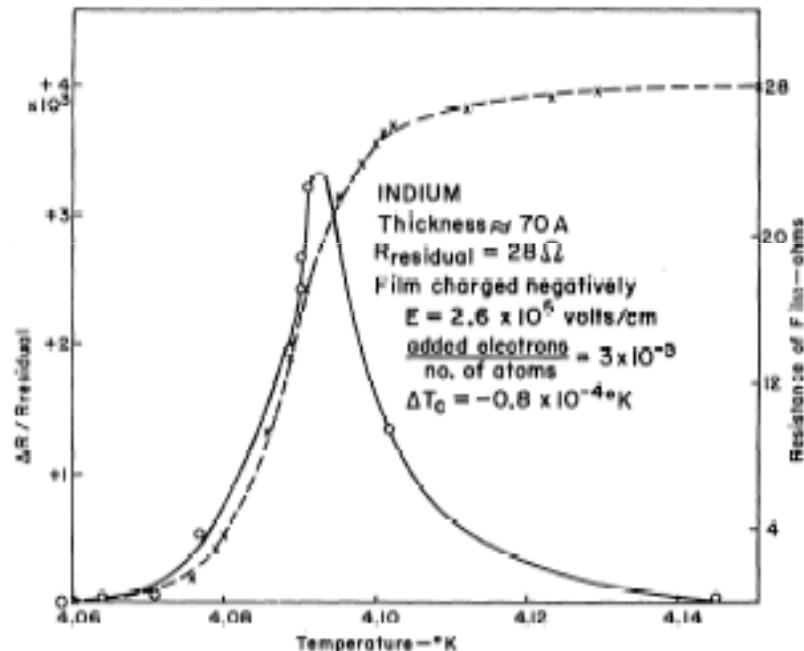
**Patent of MOS-FET (1930s)**

**Invention of Si-MOSFET  
D. Kahng & M. M. Atalla (1960)**

# History 2

## Electric Field Control of Tc in superconductors

R. E. Glover, III and M. D. Sherrill, Phys. Rev. Lett. 5, 248 (1960).



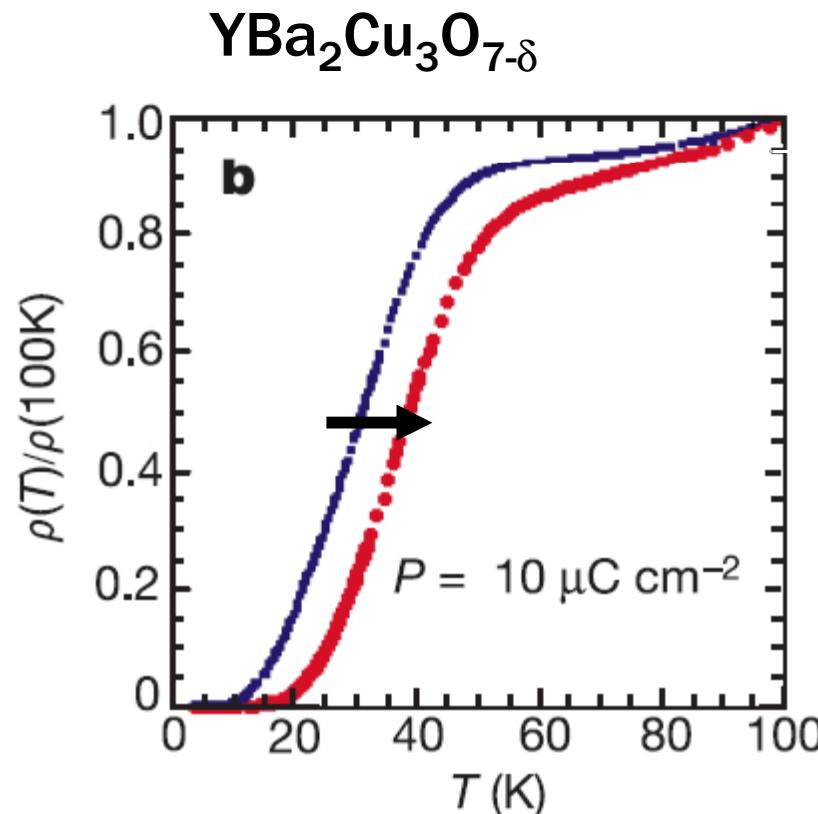
Indium  
 $T_c = 4.1 \text{ K}$ ,  $\Delta T_c = -0.8 \times 10^{-4} \text{ K}$

Challenge:  
Can you increase Tc  
from zero to finite?

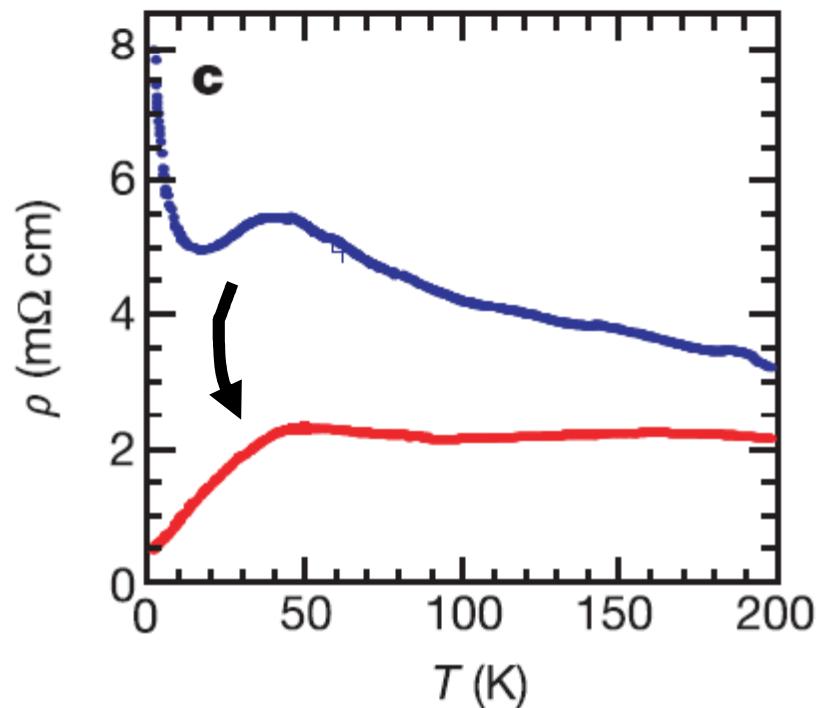
# History 3

## Field effects of High Tc cuprates

- { Chemical doping to insulators yields high Tc (1986)
- Field-effect in high Tc with chemical doping (1991)

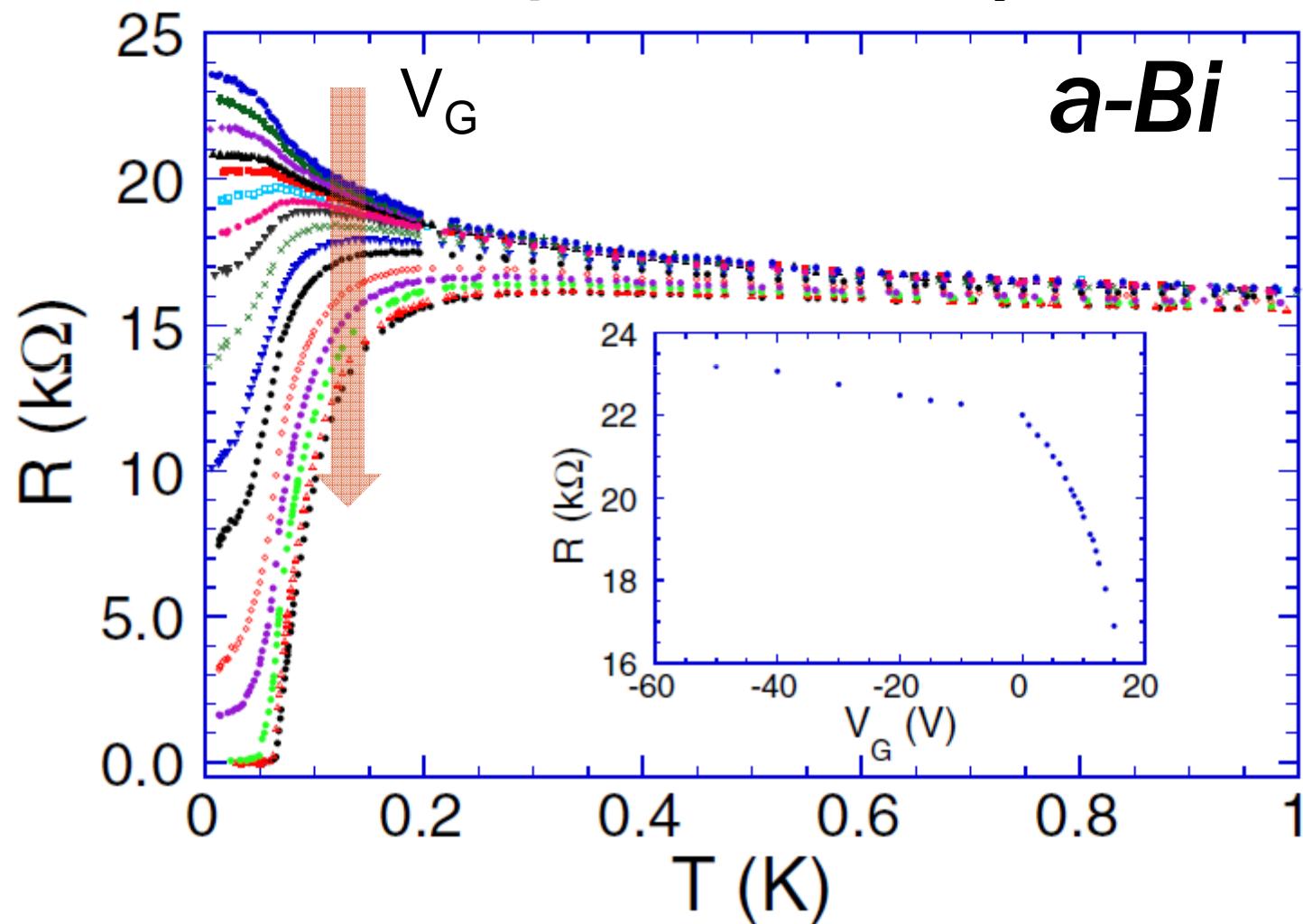


C. H. Ahn, J.-M. Triscone, and J. Mannhart  
Nature 423, 1015 (2003).



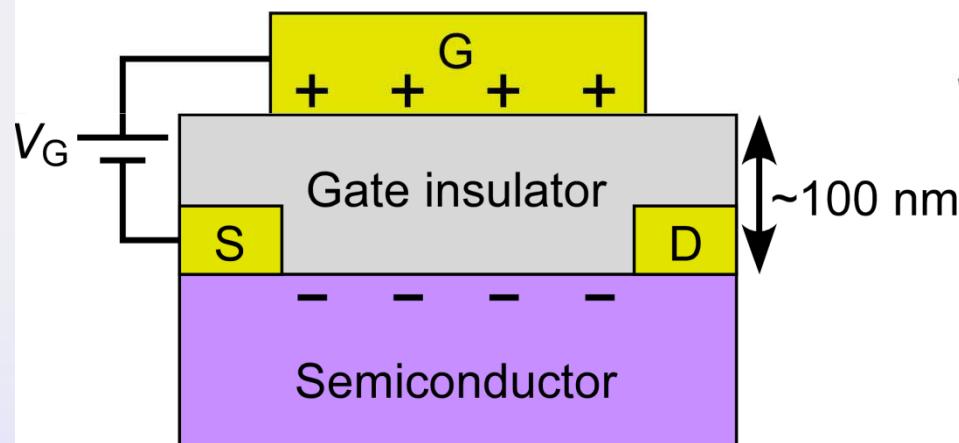
# History 3'

## Gate control of Localization-Superconductivity Transition



# Conventional FET

## Solid Gate



**Weak electric field**

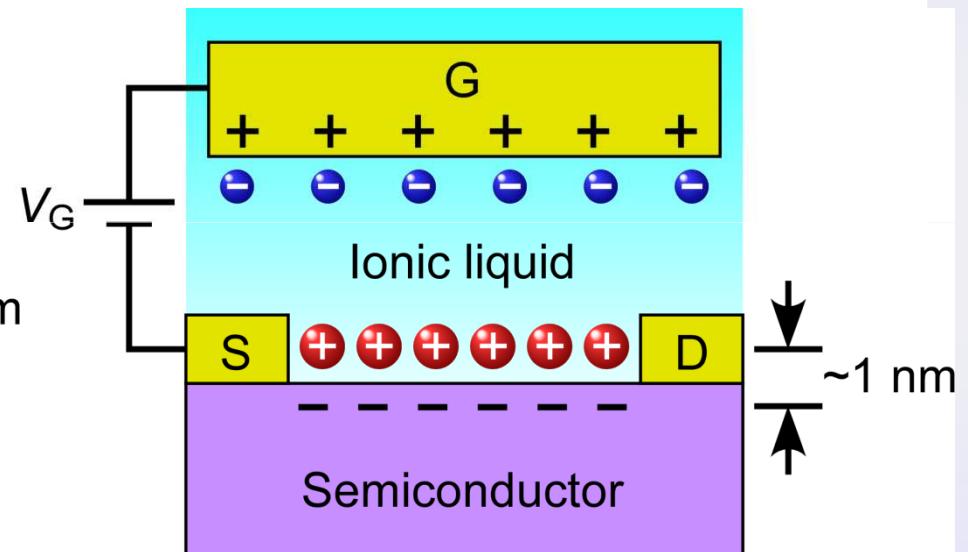
$\sim 1 \text{ MV/cm}$

$< 1 \times 10^{13} \text{ cm}^{-2}$

# Our approach

## Liquid gate

(electric double layer transistor)



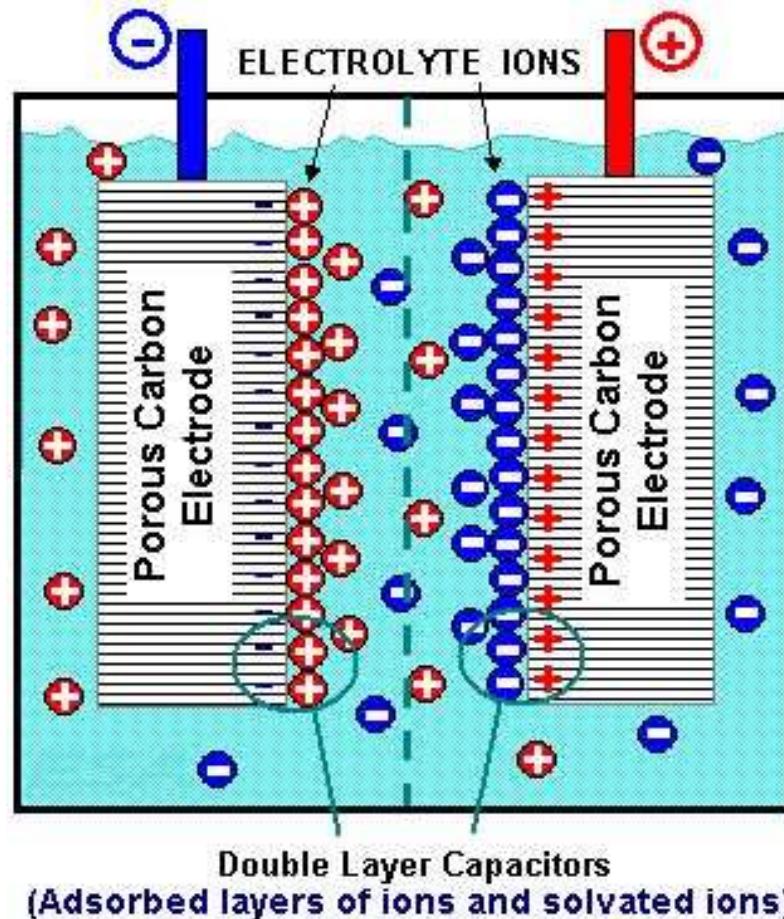
**Strong electric field**

$> 10 \text{ MV/cm}$

$> 5 \times 10^{14} \text{ cm}^{-2}$

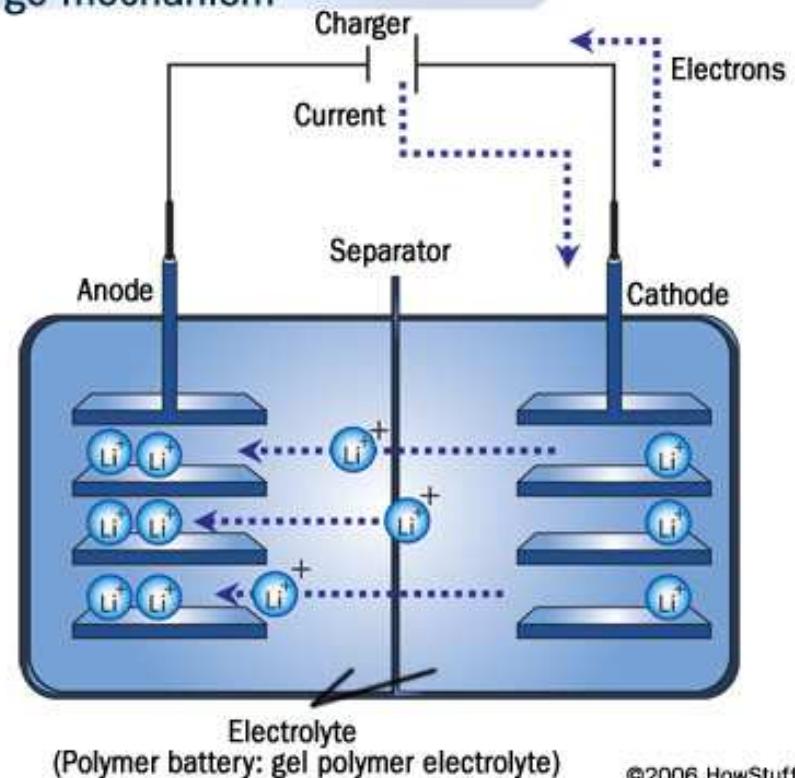
# Charge accumulation devices

Electric Double Layer Capacitor



Lithium Ion Secondary Battery

Lithium-ion rechargeable battery  
Charge mechanism

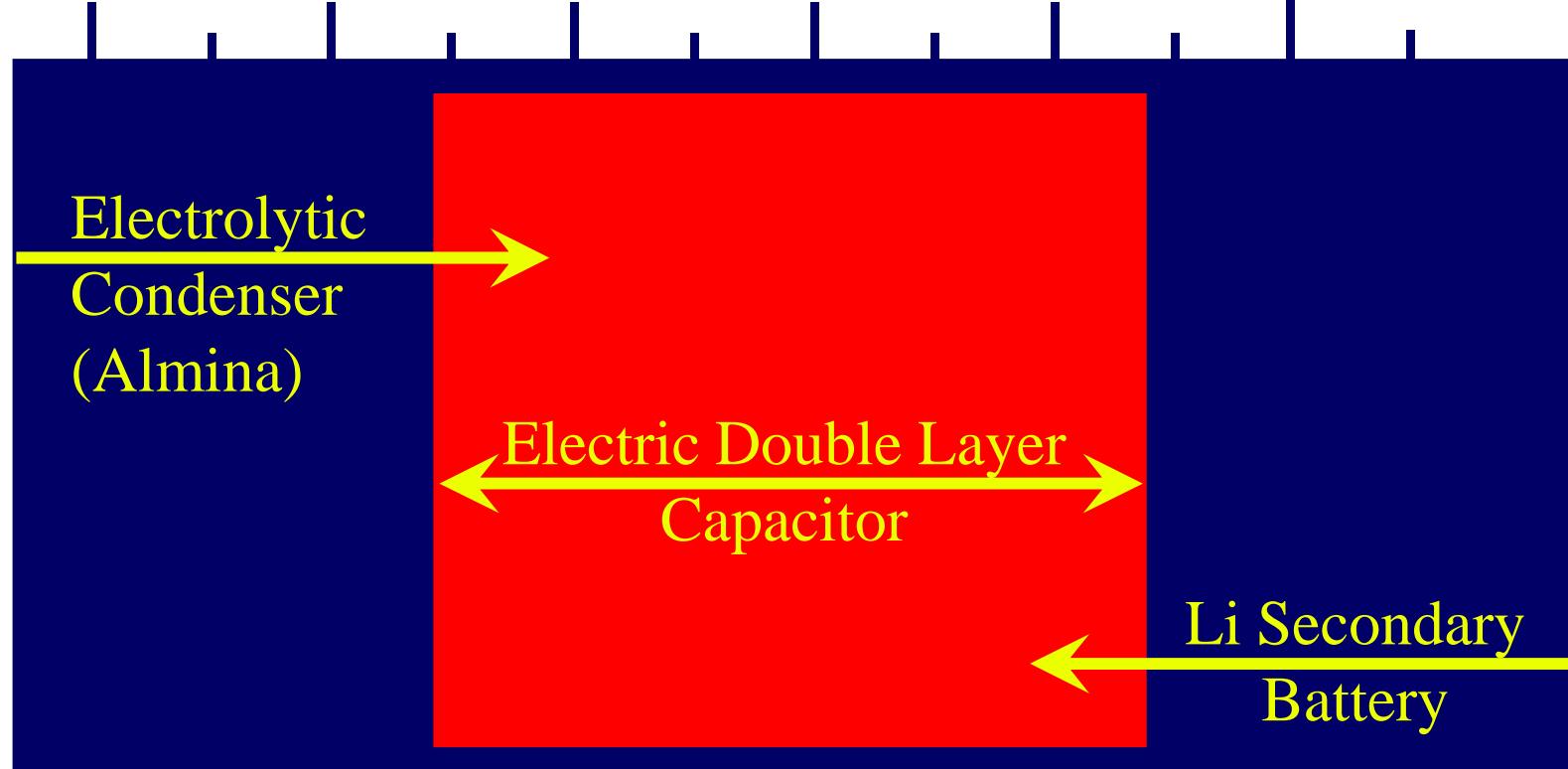


©2006 HowStuffWork

# Charge Accumulation Devices

Capacitance (F)

$1\mu$        $100\mu$        $10000\mu$       1      100      10000



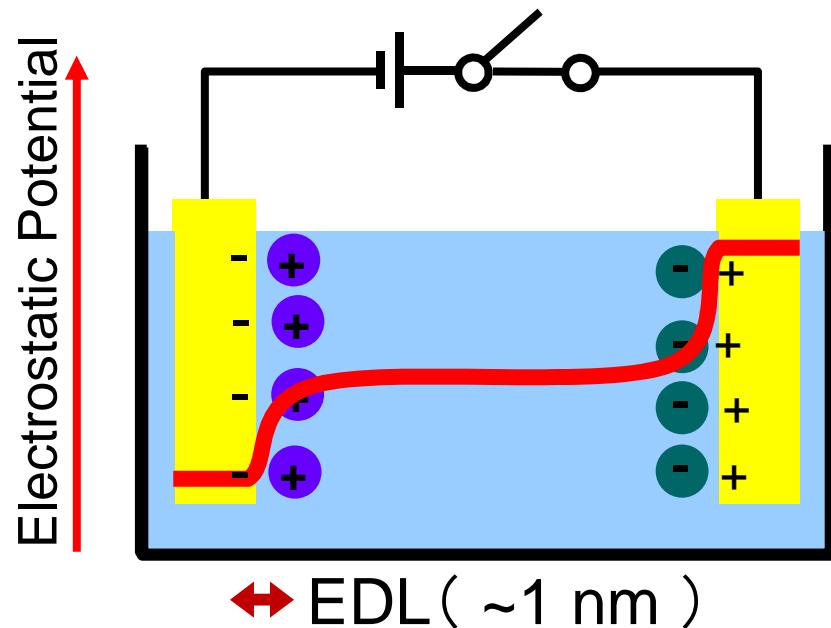
electrostatic

chemical

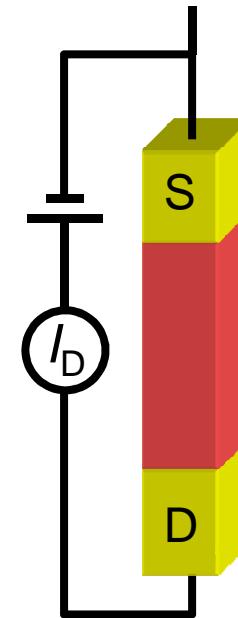
Electric Double Layer Transistor

# Electric Double Layer (EDL)

Electric Double Layer Capacitor (EDLC)



Replace one of the electrodes by



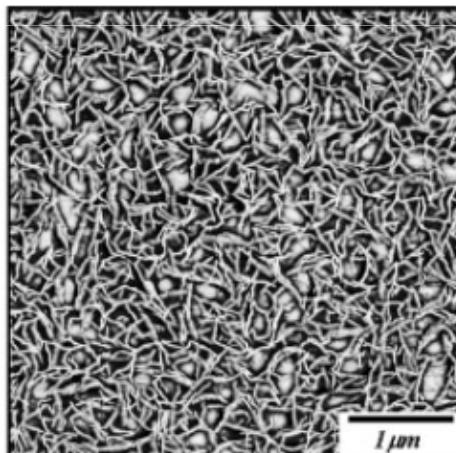
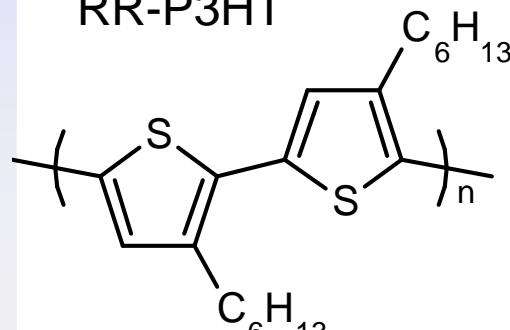
EDLC on market (Japan Chemicon Inc.)



EDL-transistor (EDLT)  
{ large capacitance  
large charge density }

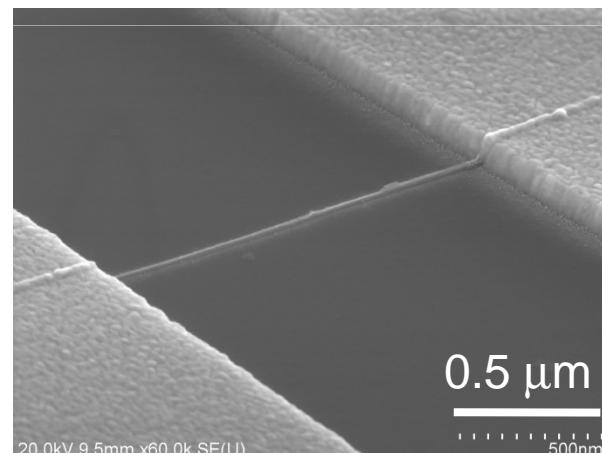
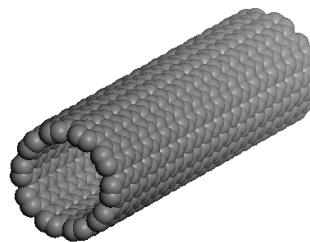
# Application of EDLTs to organic transistors with low voltage operation

polythiophene  
RR-P3HT



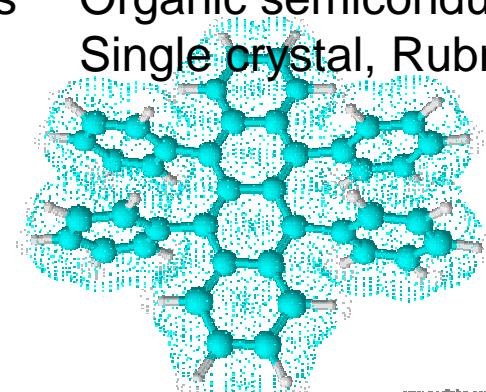
H. Shimotani *et al.*,  
*APL* (2005)

Single walled carbon nanotubes  
SWNT



H. Shimotani *et al.*,  
*APL* (2006)

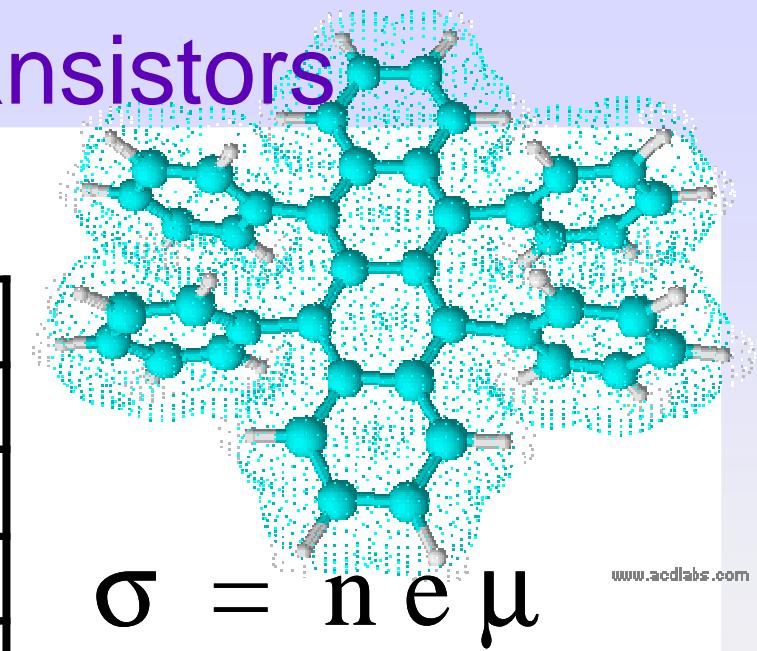
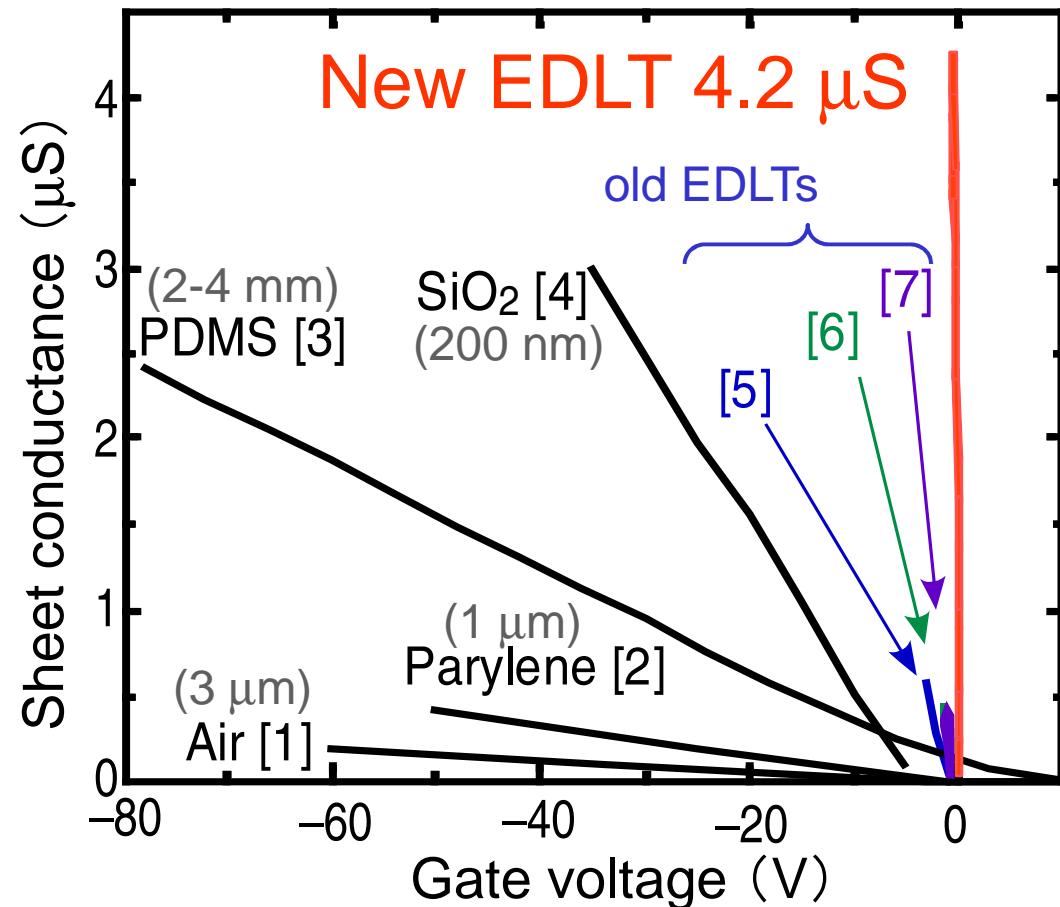
Organic semiconductor  
Single crystal, Rubrene



H. Shimotani *et al.*,  
*APL* (2006), *JJAP* (2007)

# Rubrene single crystal transistors

## : solid gate vs. liquid gate



- [1] Menard *et al.*, Adv. Mat. (2004)
- [2] Podzorov *et al.*, APL (2003)
- [3] Sundar *et al.*, Science (2004)
- [4] Stassen *et al.*, APL (2004)
- [5] Panzer *et al.*, APL (2006)
- [6] Takeya *et al.*, APL (2006)
- [7] Shimotani *et al.*, APL (2006)

● Low voltage operation and highest conductance

H. Shimotani *et al.* JJAP 46 3613 (2007)

# EDLT for sensor applications (since 1980s)



## Application of EDLTs to high density charge accumulation and electric-field induced superconductivity

|                         |  |
|-------------------------|--|
| Polymer                 | H. Shimotani <i>et al.</i> , <i>APL</i> 86, 022104 (2005)          |
| Nanotube                | H. Shimotani <i>et al.</i> , <i>APL</i> 88, 073104 (2006)          |
| Rubrene Xtal            | H. Shimotani <i>et al.</i> , <i>APL</i> 89, 203501 (2006)          |
| Rubrene Xtal            | H. Shimotani <i>et al.</i> , <i>JJAP</i> 46, 3613 (2007)           |
| ZnO Xtal                | H. Shimotani <i>et al.</i> , <i>APL</i> 91, 082106 (2007)          |
| NiO Xtal                | H. Shimotani <i>et al.</i> , <i>APL</i> 92, 242107 (2008)          |
| SrTiO <sub>3</sub> Xtal | K. Ueno <i>et al.</i> , <i>Nat. Mater.</i> 7, 855 (2008)           |
| Ionic Liquid            | H. T. Yuan <i>et al.</i> , <i>Adv. Funct. Mater.</i> ONLINE (2009) |

# OUTLINE

## ■ Introduction :

Electric-field induced superconductivity

Electric double layer transistor (EDLT)

## ■ Oxide semiconductors

$\text{ZnO}$  and  $\text{SrTiO}_3$

## ■ For further increase of carrier density

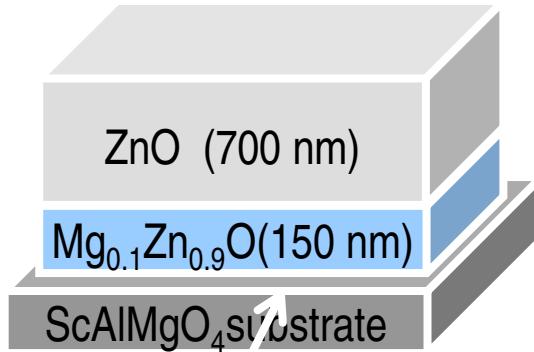
## ■ Layered material $\text{ZrNCl}$

Bulk properties and E-induced SC

## ■ Summary

# Device fabrication

- ZnO single crystalline thin film

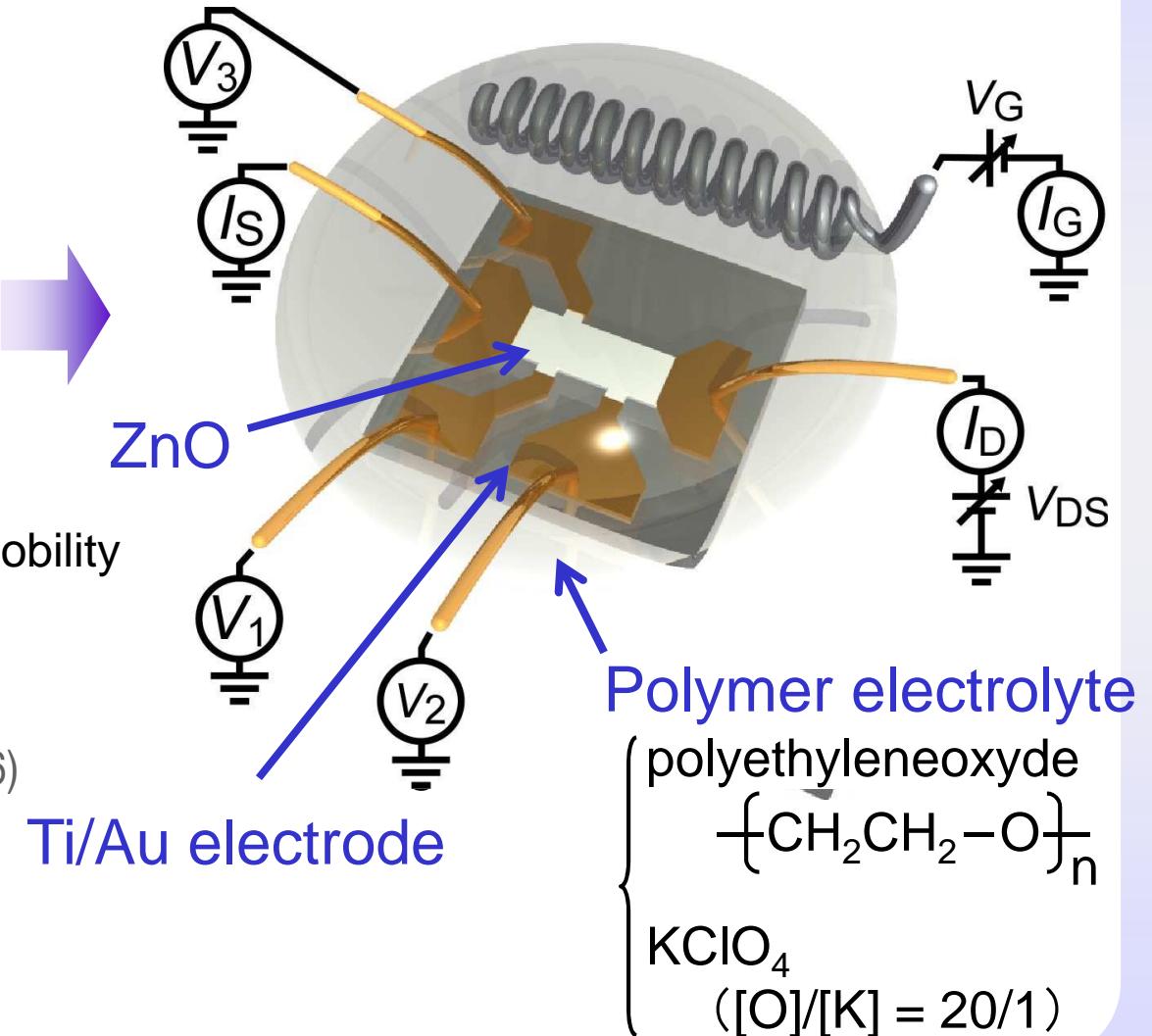


Low carrier density and high mobility

$$\begin{cases} \mu = 100 \text{ cm}^2 \text{V}^{-1} \text{s}^{-1} \\ n = 7.7 \times 10^{15} \text{ cm}^{-3} \end{cases}$$

Tsukazaki et al., APL 88, 152106 (2006)

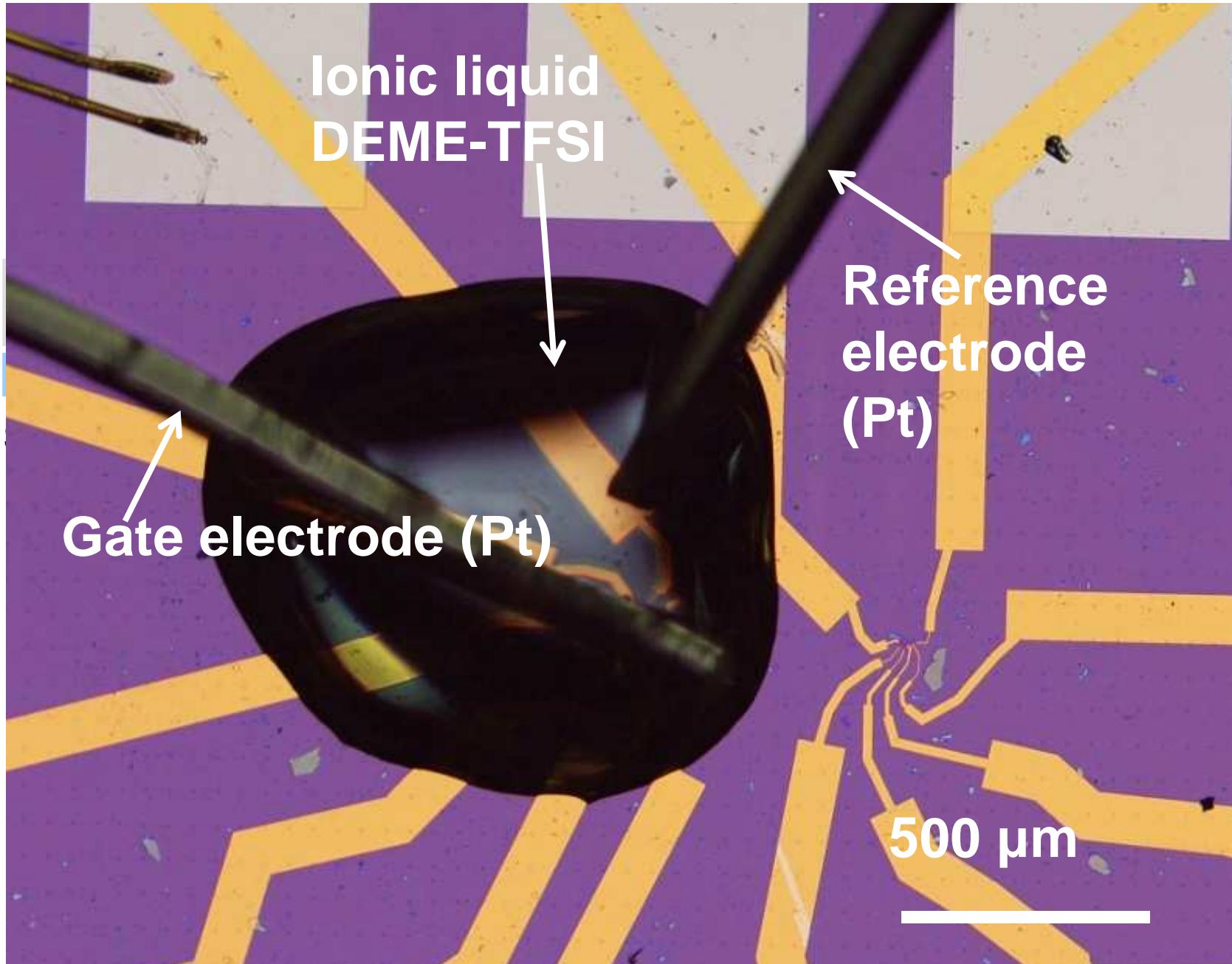
- EDL-FET



# Device fabrication

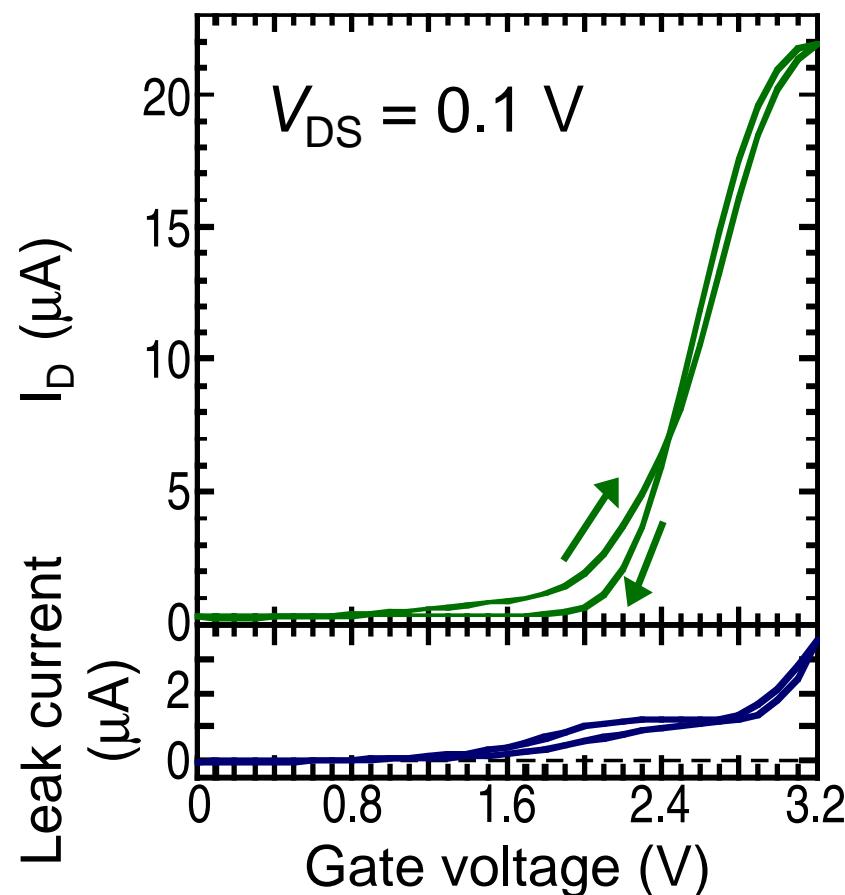


# Device fabrication

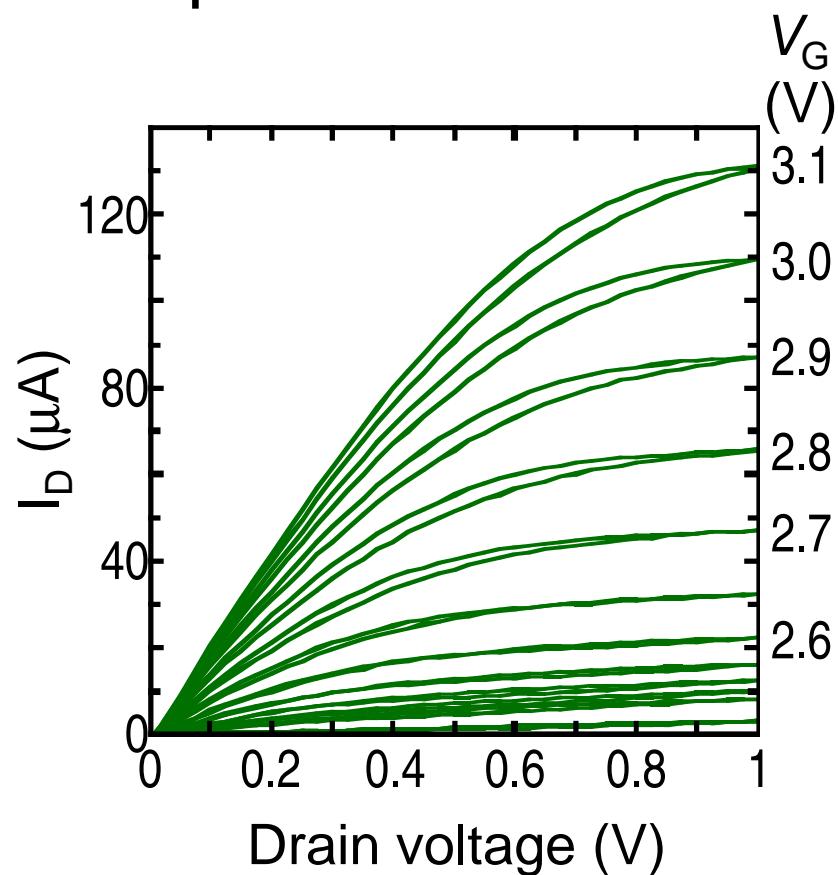


# Characteristics of ZnO-EDLT

■ Transfer curve

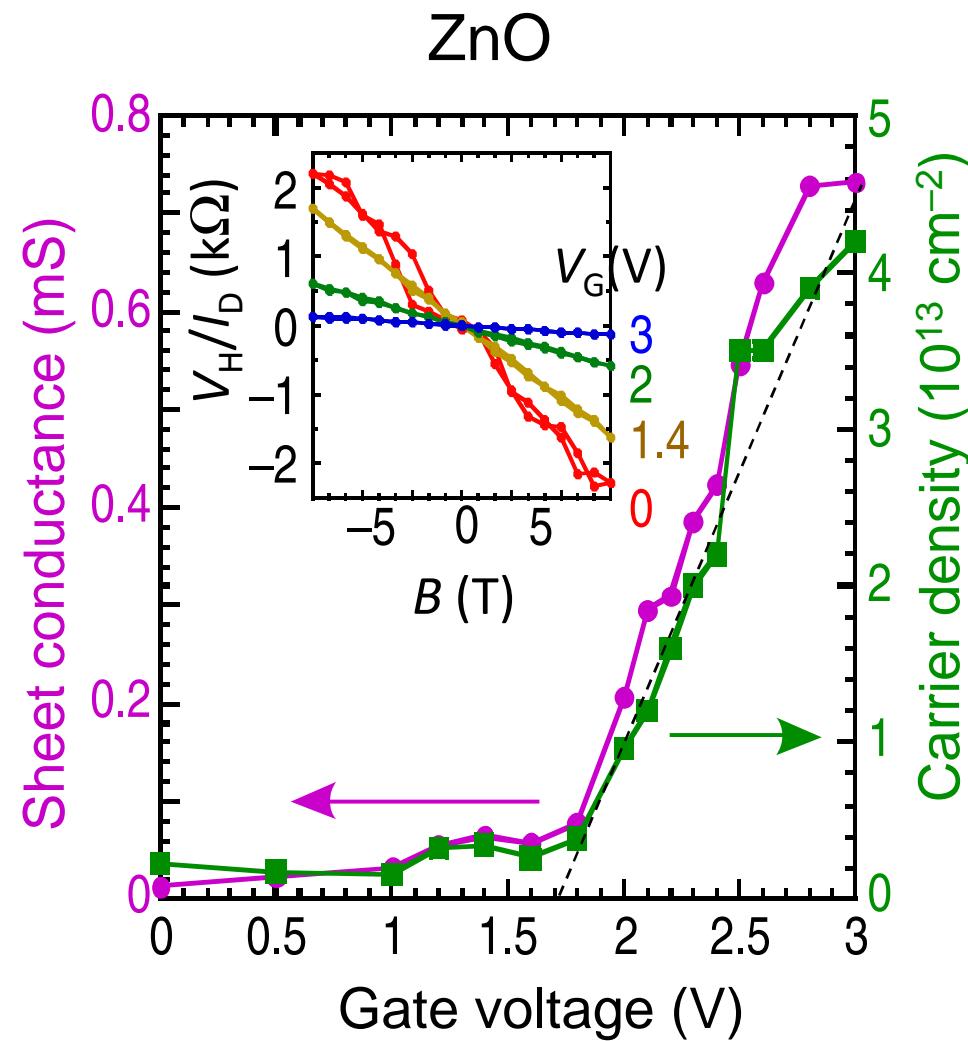


■ Output curve



n-type operation

# Direct measurement of carrier density (Hall effect)

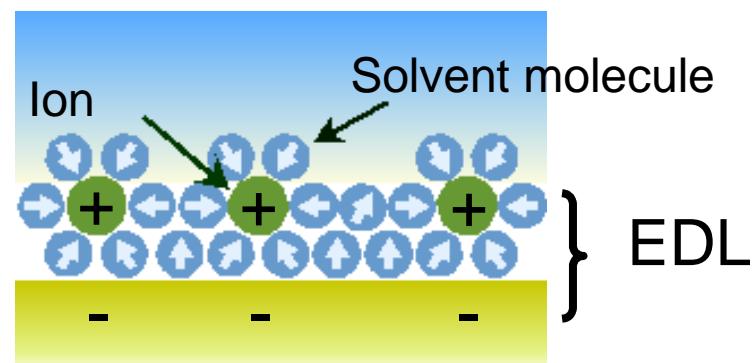


$$ne = Q = CV$$

$C \sim 7.8 \mu\text{F}/\text{cm}^2$   
(cf.  $15 \mu\text{F}/\text{cm}^2$  on Au)

$(\epsilon = 10 \epsilon_0$  for PEO solvent)

thickness of EDL  $\sim 1 \text{ nm}$

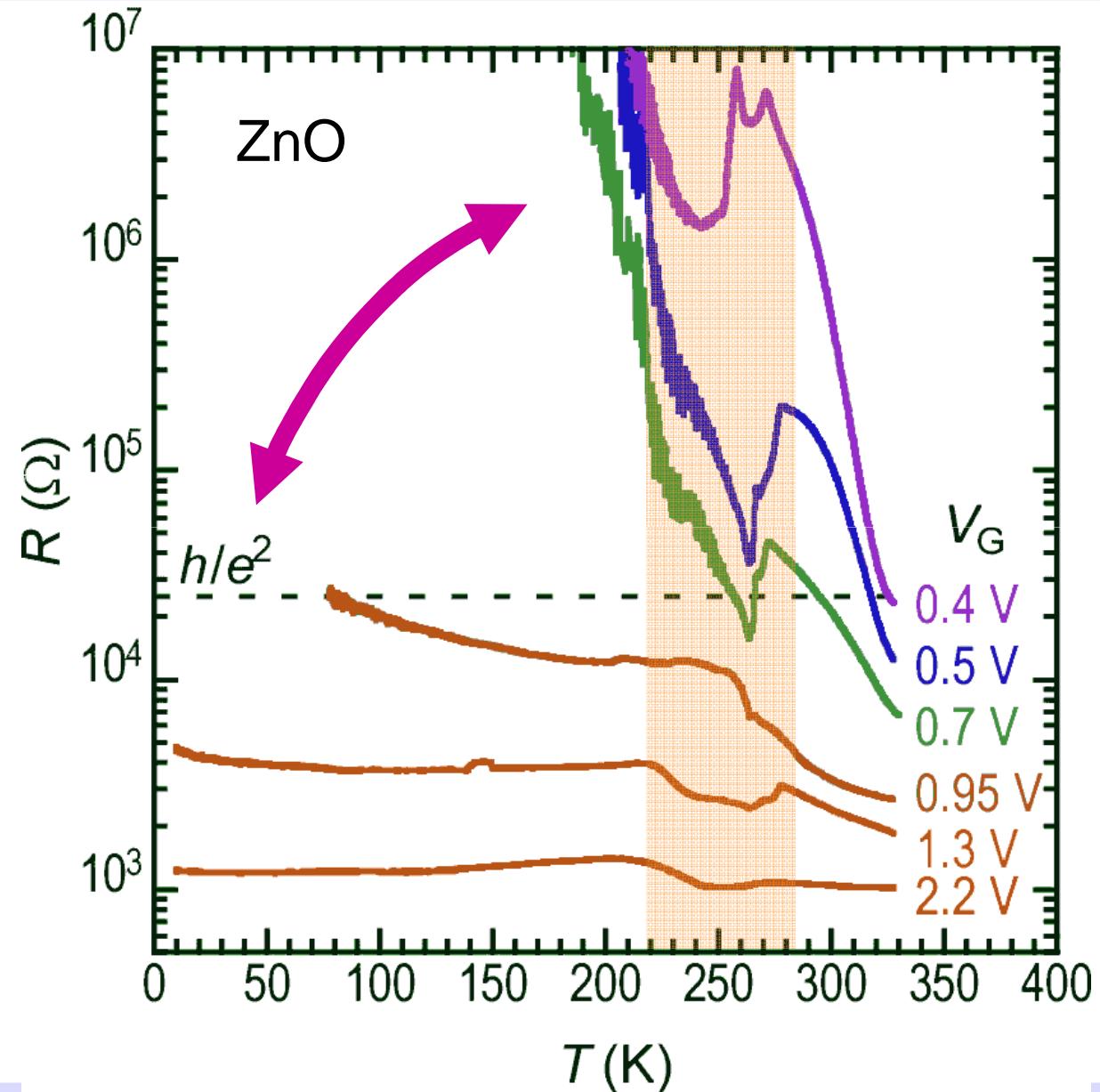


H. Shimotani et al. APL 91, 082106 (2007)

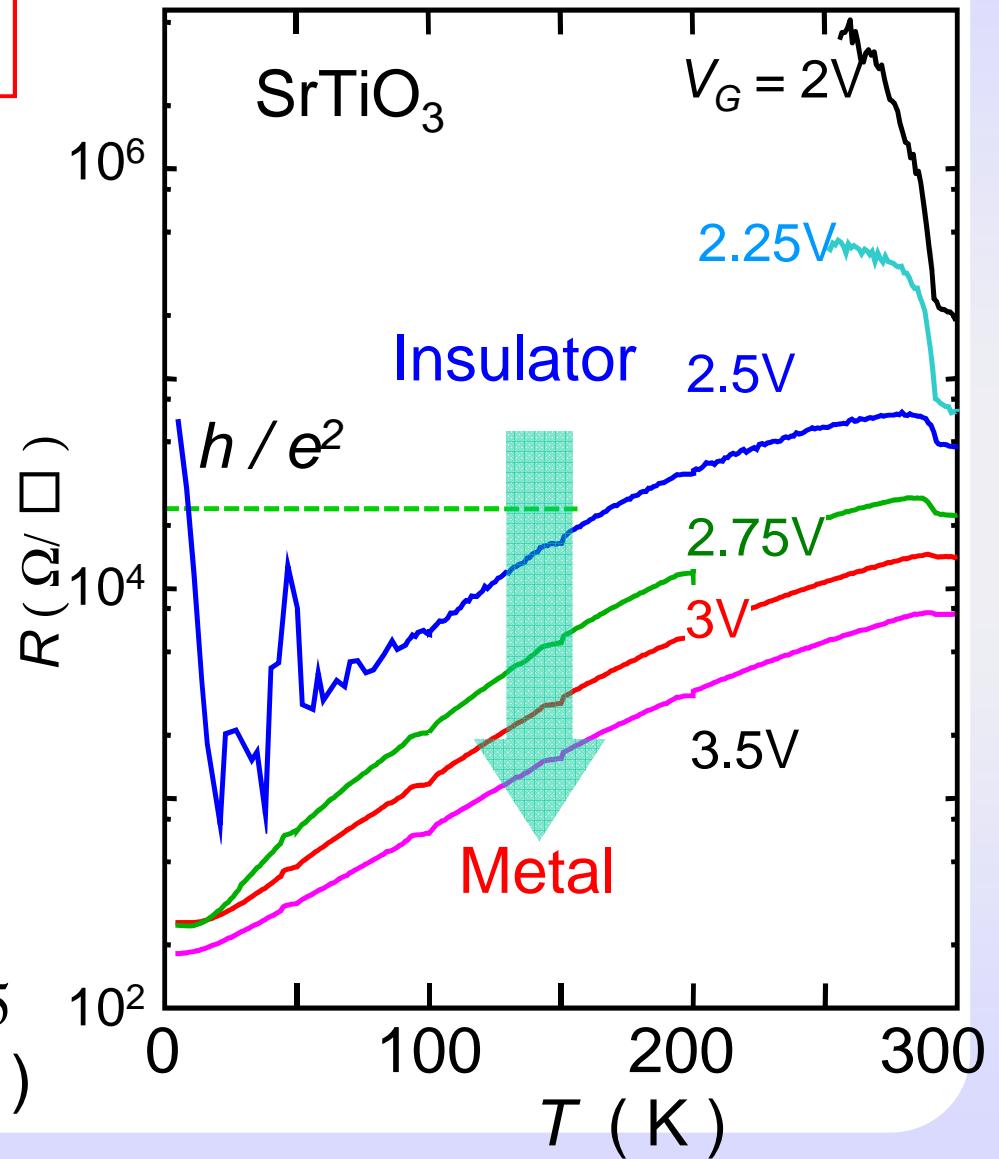
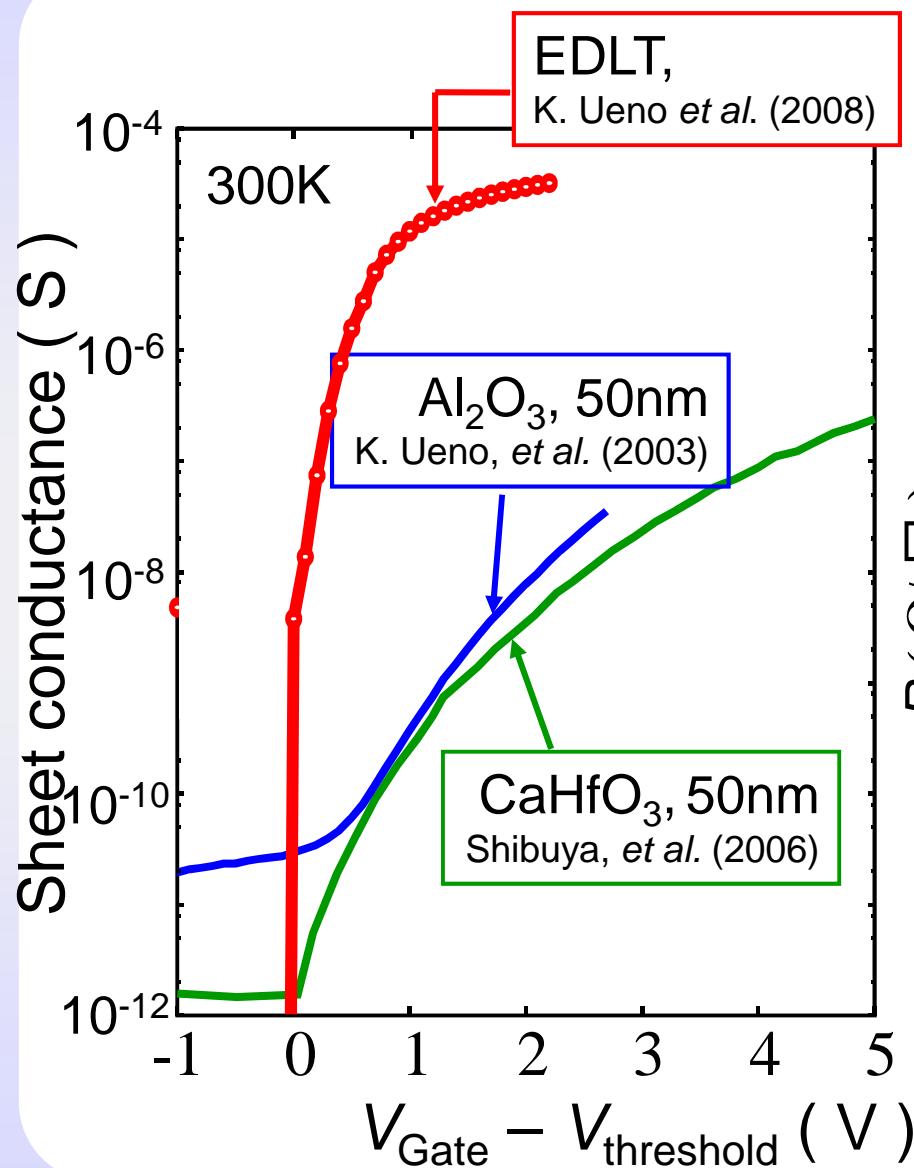
Electric Double Layer Transistor

# Gate-induced Insulator-metal transition in ZnO

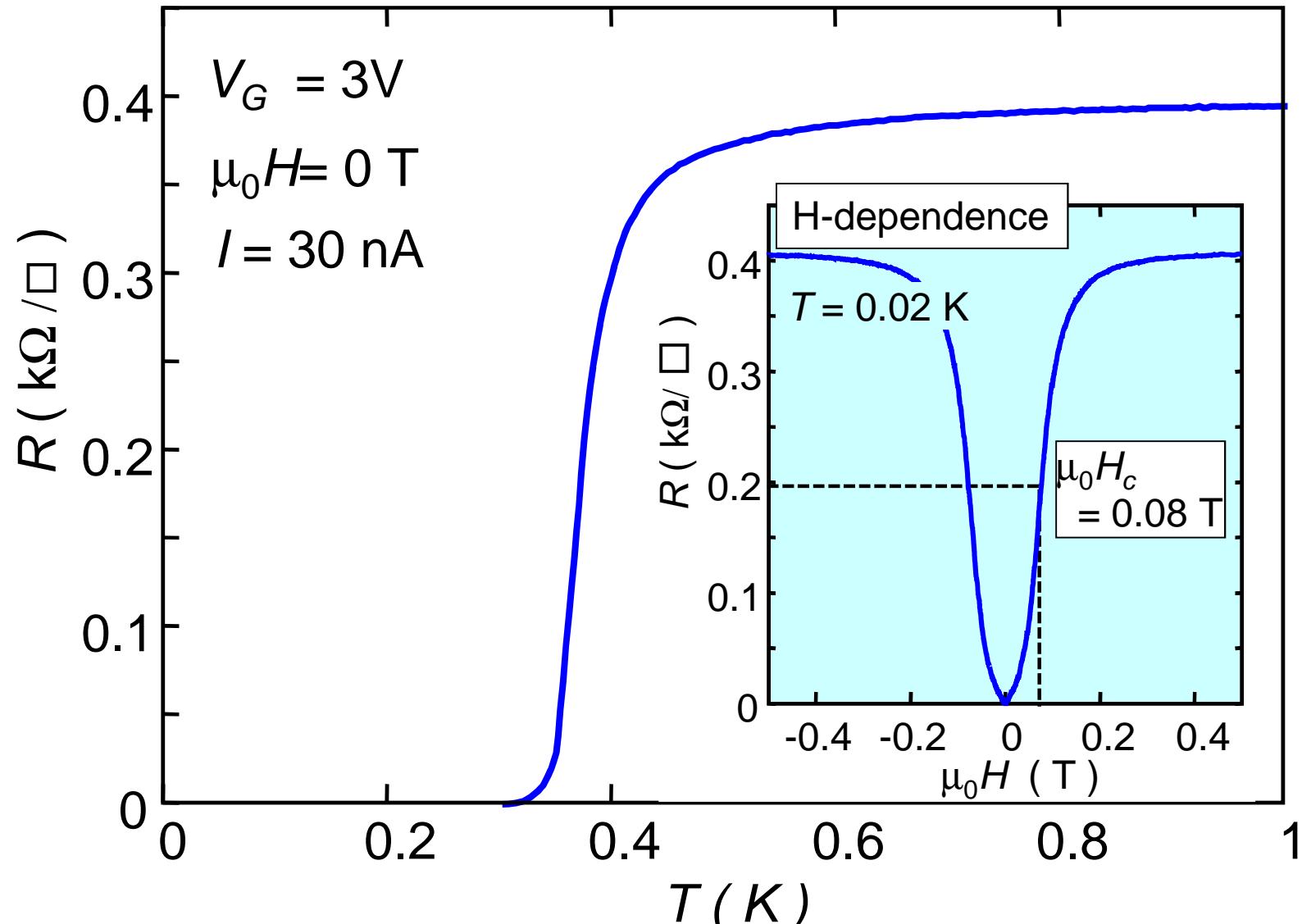
H. Shimotani et al.  
Appl. Phys. Lett.  
91, 082106 (2007)



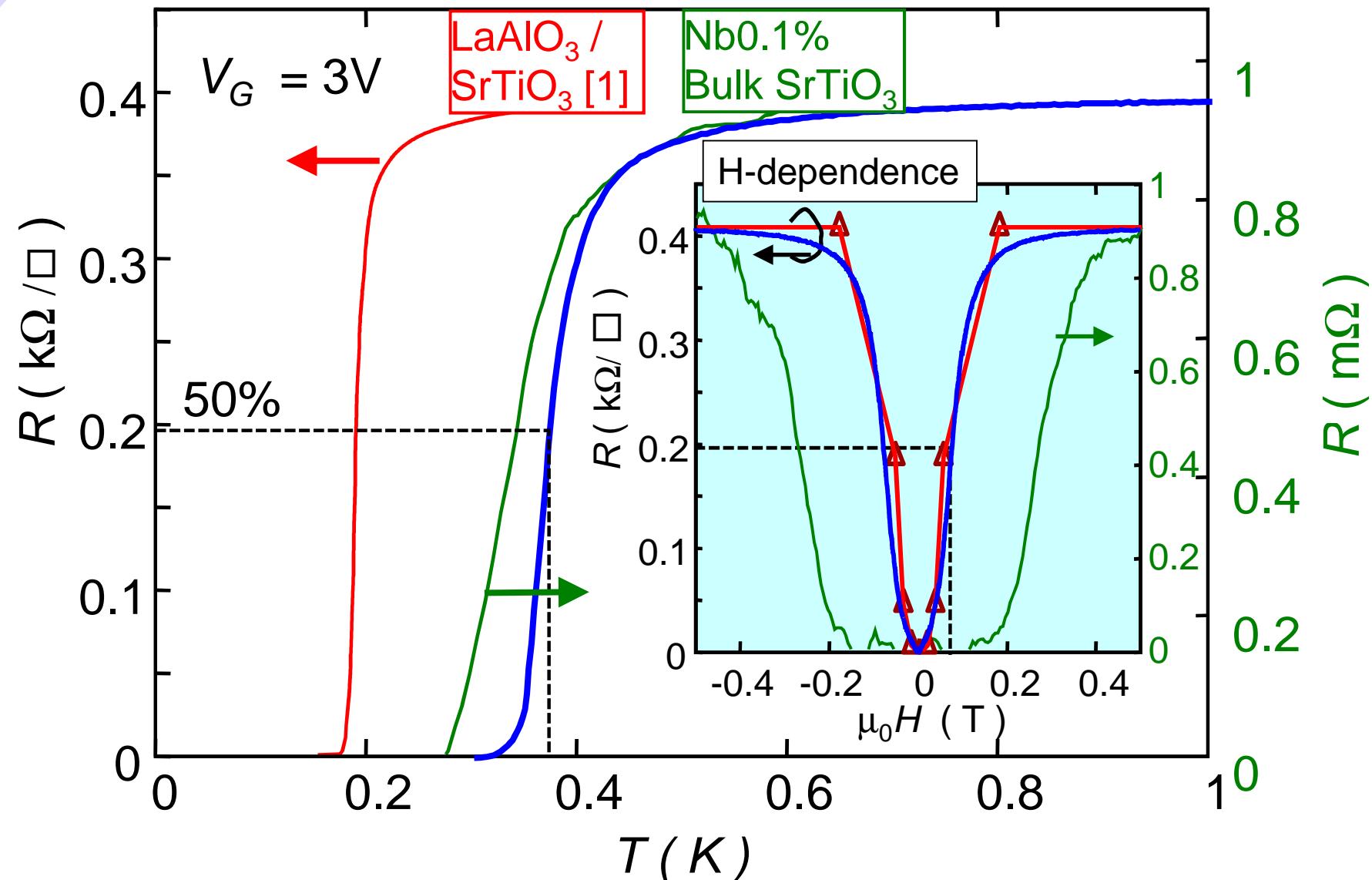
# $\text{SrTiO}_3$ / PEO( $\text{KClO}_4$ )-EDLT



# Electric field-induced superconductivity in SrTiO<sub>3</sub>



## Comparison with other systems



# OUTLINE

- Introduction :
  - Electric-field induced superconductivity
  - Electric double layer transistor (EDLT)
- Oxide semiconductors
  - ZnO and SrTiO<sub>3</sub>
- For further increase of carrier density
- Layered material ZrNCl
  - Bulk properties and E-induced SC
- Summary

# Go beyond SrTiO<sub>3</sub>

## Uniqueness of SrTiO<sub>3</sub>

1. Nb:SrTiO<sub>3</sub>, SrTiO<sub>3-δ</sub>

The lowest carrier density superconductor

2. Established know-how to make atomically-flat surfaces (Kawasaki, 1994)

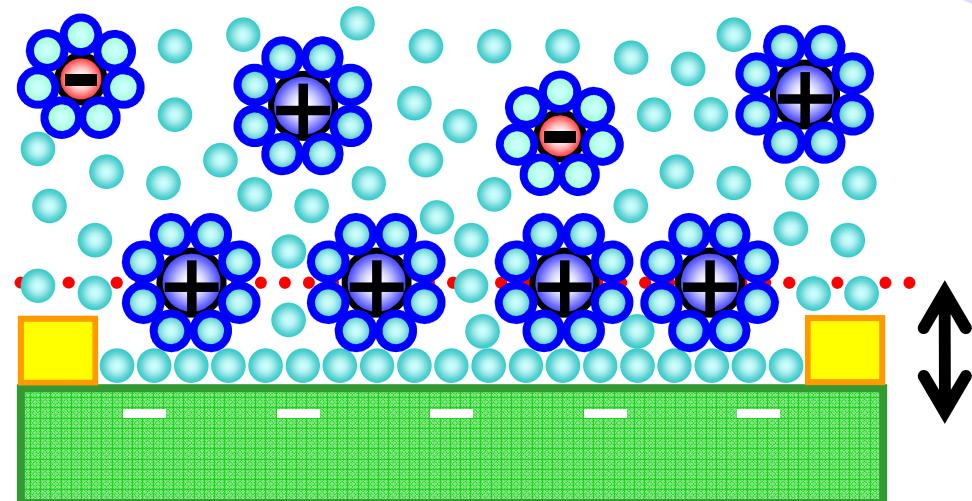
3. SrTiO<sub>3</sub>-FET with solid gate was already fabricated (Ueno, Takagi, Kawasaki, Tokura, 2003)

4. SrTiO<sub>3</sub> is a quantum paraelectric.

# Ionic Liquids

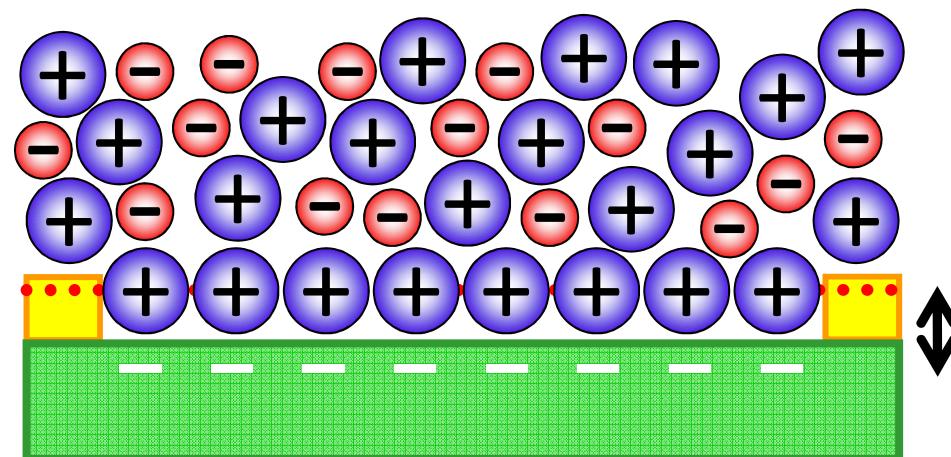
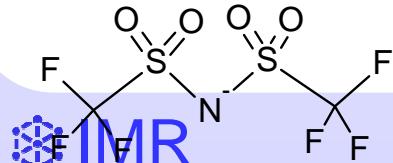
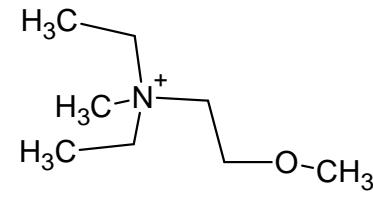
## Polymer Electrolyte

Solvent + Salt



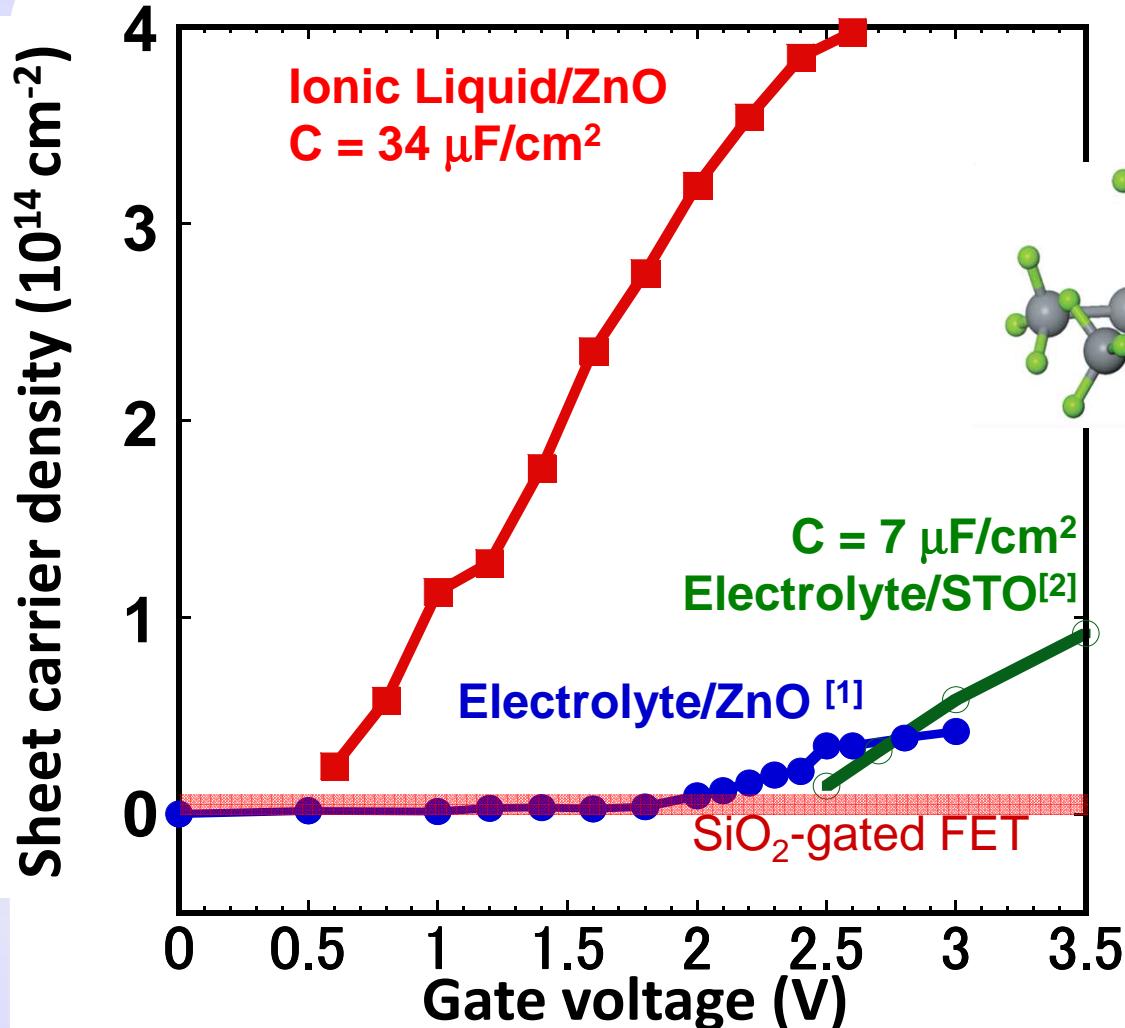
## Ionic Liquid

Melt at RT

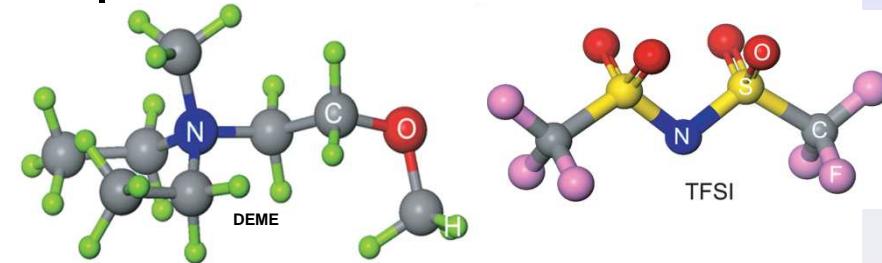


**d ~ size of cation molecule  
smaller than electrolyte**

# Ionic liquid vs. Electrolyte for ZnO



**Ionic liquid:** *DEME-TFSI*

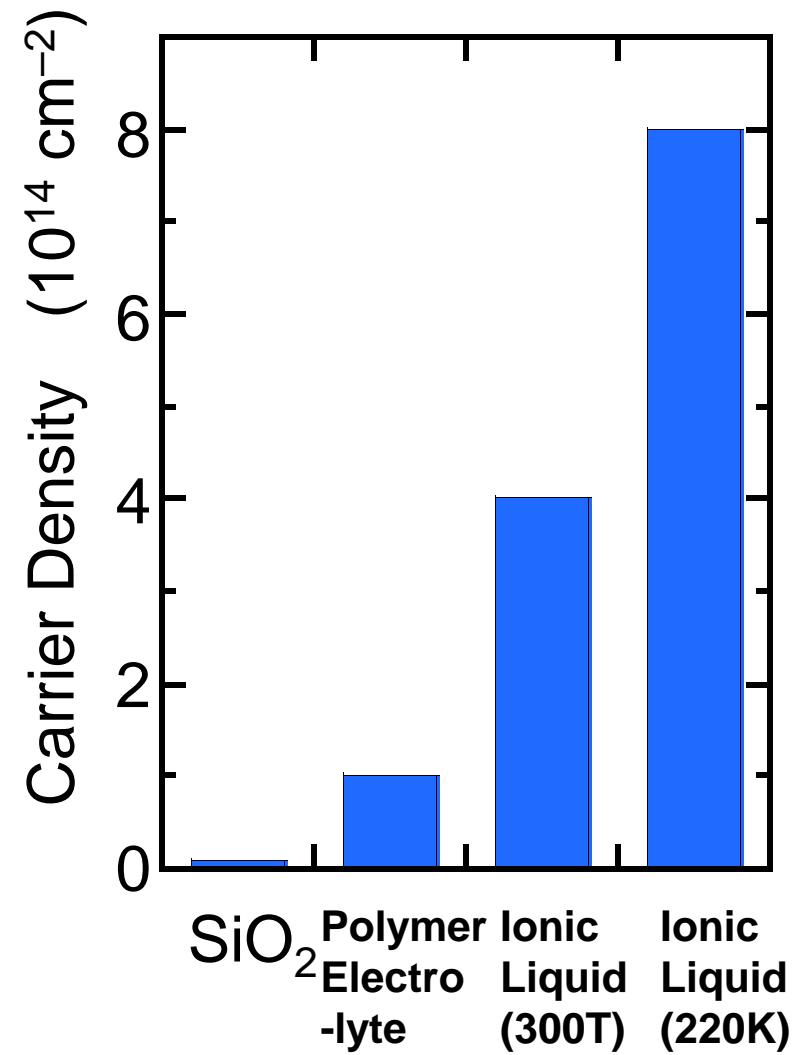
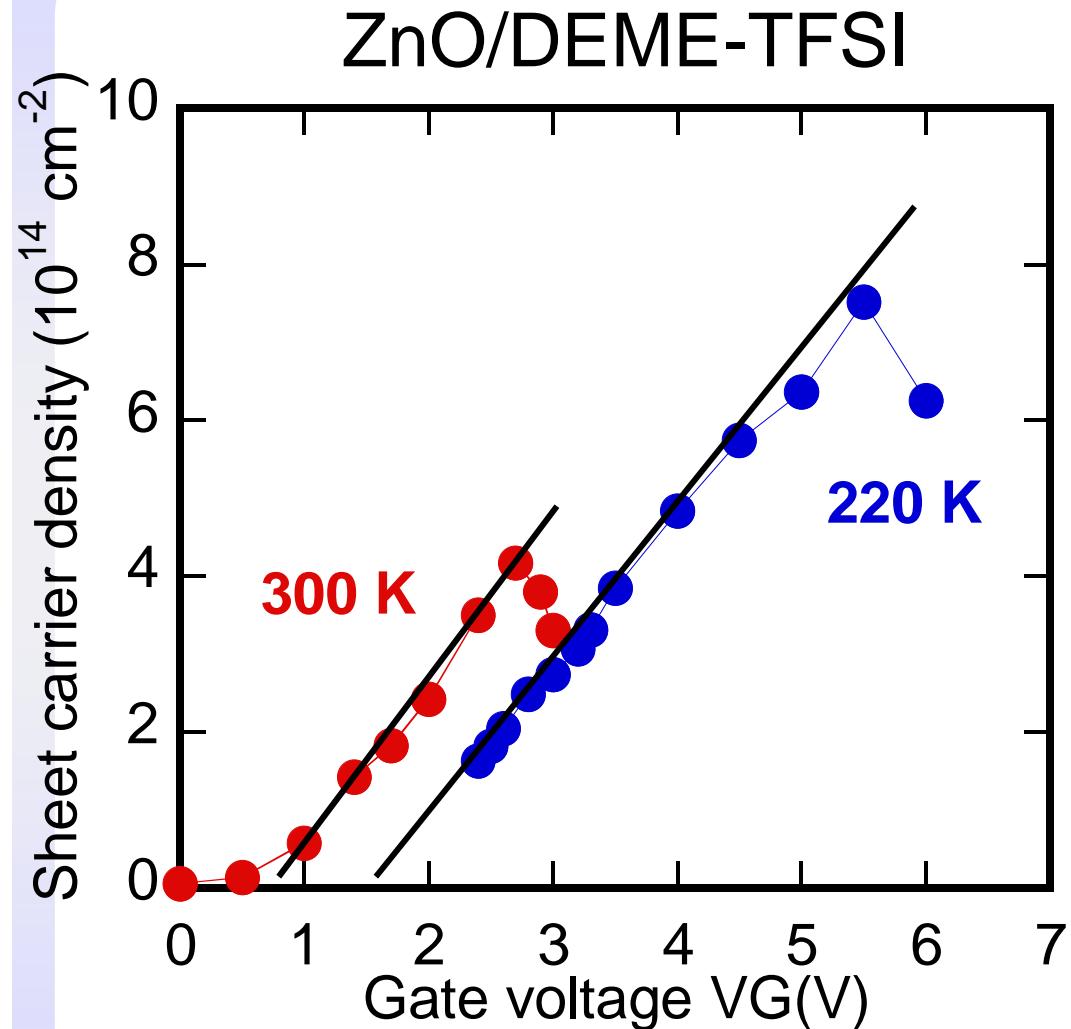


H. T. Yuan *et al.*, *Adv. Funct. Mater.* 19, 1046 (2009)

[1] H. Shimotani *et.al.*, *APL.* **91**, 082106 (2007)

[2] K. Ueno *et al.*, *Nat. Mater.* **7**, 855 (2008)

# Enhanced Electrostatic Charging at Low T



$4 \times 10^{14} \text{ cm}^{-2} \geq n_{2D}$  required for superconductivity  
in cuprates, fullerides, organics, ...

# OUTLINE

- Introduction :

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  - Electric double layer transistor (EDLT)

- Oxide semiconductors

  - ZnO and SrTiO<sub>3</sub>

- For further increase of carrier density

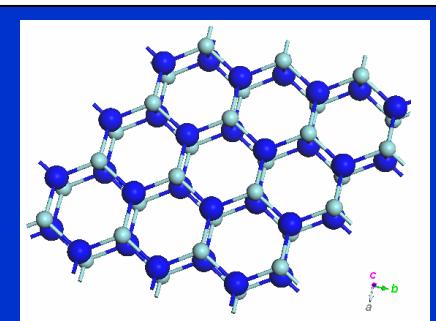
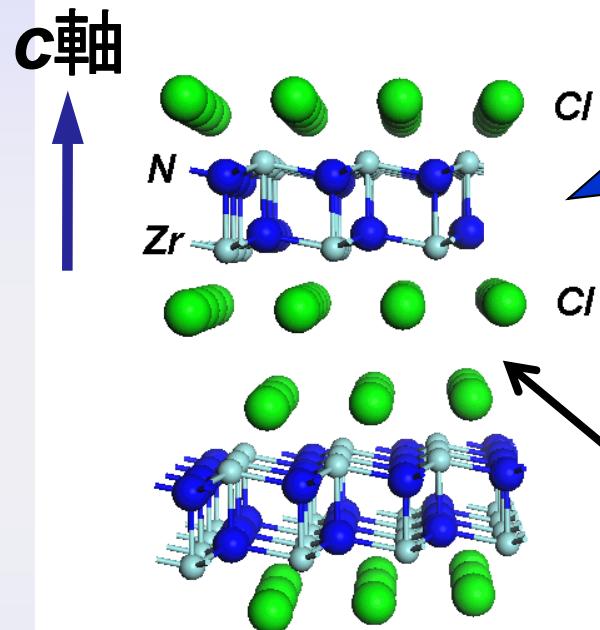
- Layered material ZrNCl

  - Bulk properties and E-induced SC

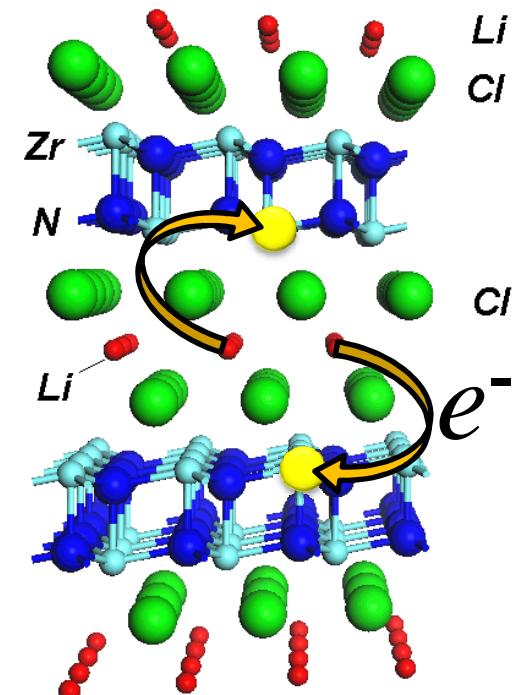
- Summary

# Electron doped $\beta$ -ZrNCl (Yamanaka et al. (1996, 1998))

$\beta$ -ZrNCl



$\text{Li}_x\text{ZrNCl}$



$4d^0$

Intercalation of Alkali metals

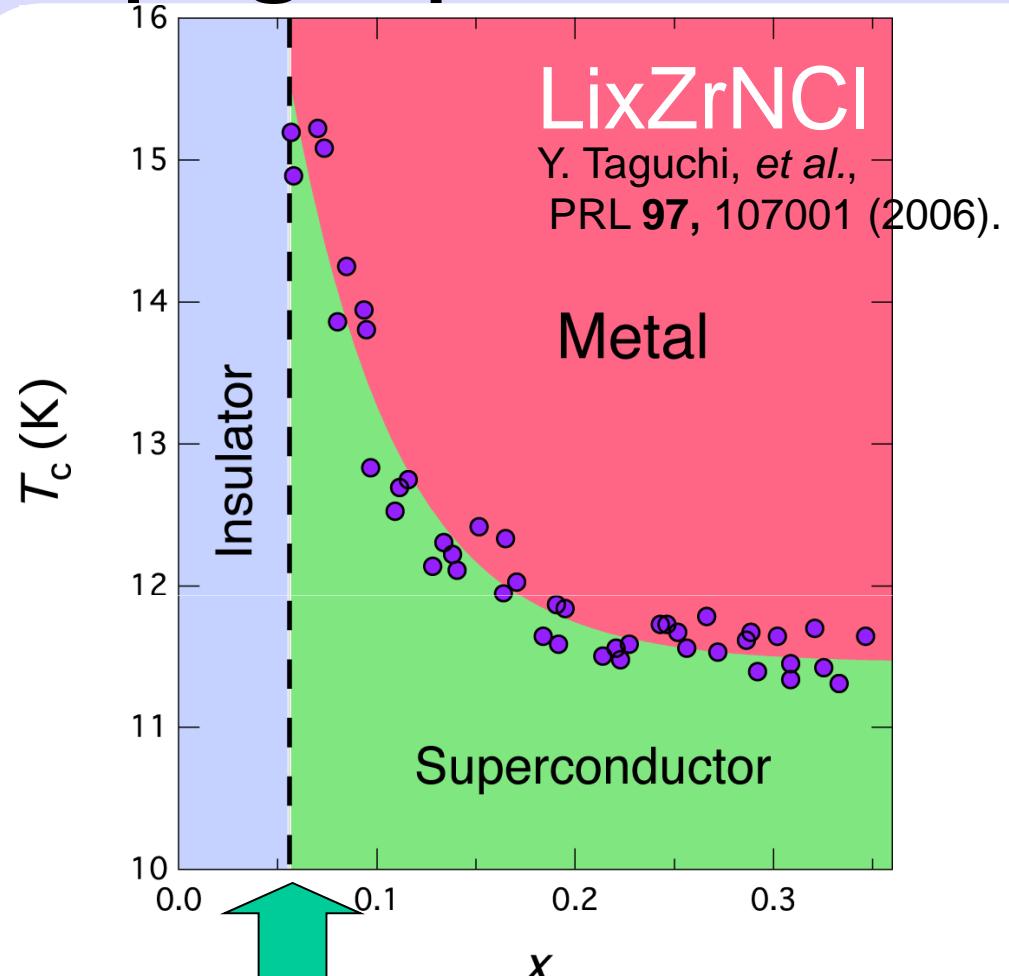
Electron doping in Zr-N layer

$4d^x$

Band Insulator

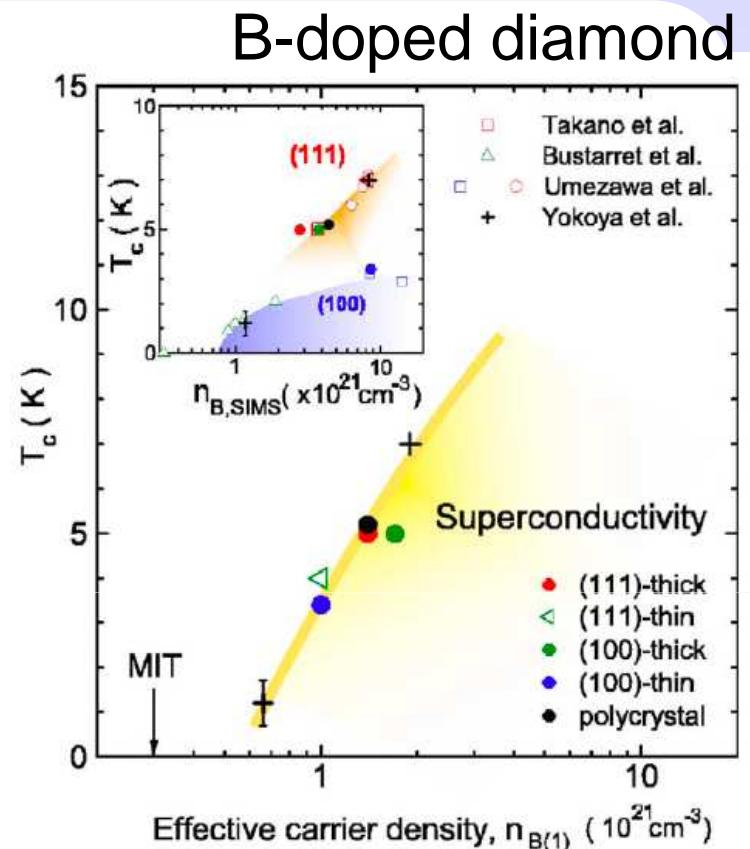
Superconductor  
Zr; 15K, Hf; 25K

# Doping dependence of T<sub>c</sub>



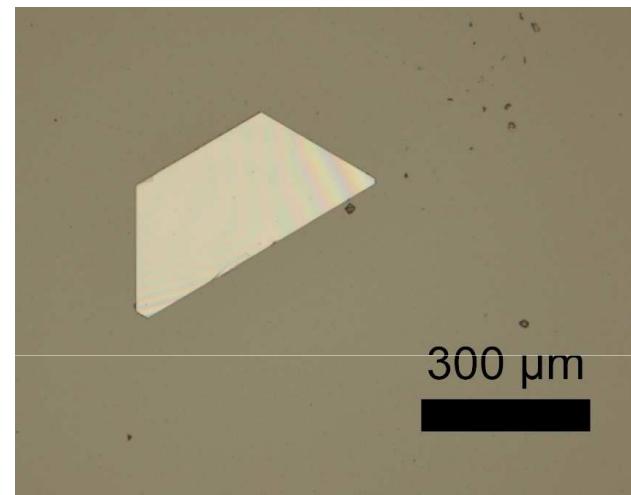
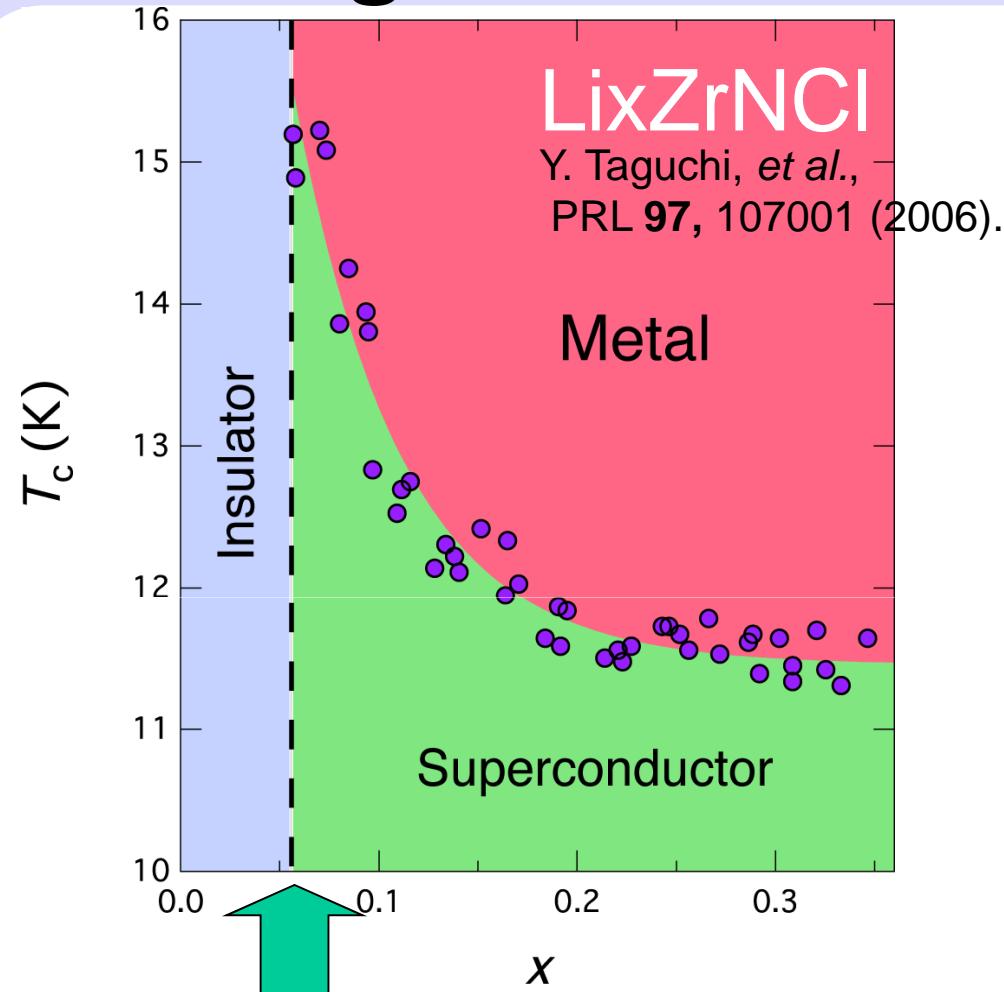
$\text{Li}_x\text{ZrNCl}$   
Y. Taguchi, et al.,  
PRL 97, 107001 (2006).

1.  $0.8 \times 10^{14} \text{ cm}^{-2}/\text{layer}$  reachable with IL



K. Mukuda et al., PRB 75, 033301 (2007)

# Advantage of ZrNCl for EDLT



1.  $0.8 \times 10^{14} \text{ cm}^{-2}/\text{layer}$  reachable with IL
2. Cleavable; atomically flat surface available

# Characteristic features of superconductivity in $\text{Li}_x\text{ZrNCl}$ : Small $\gamma$

## ■ Small density of states

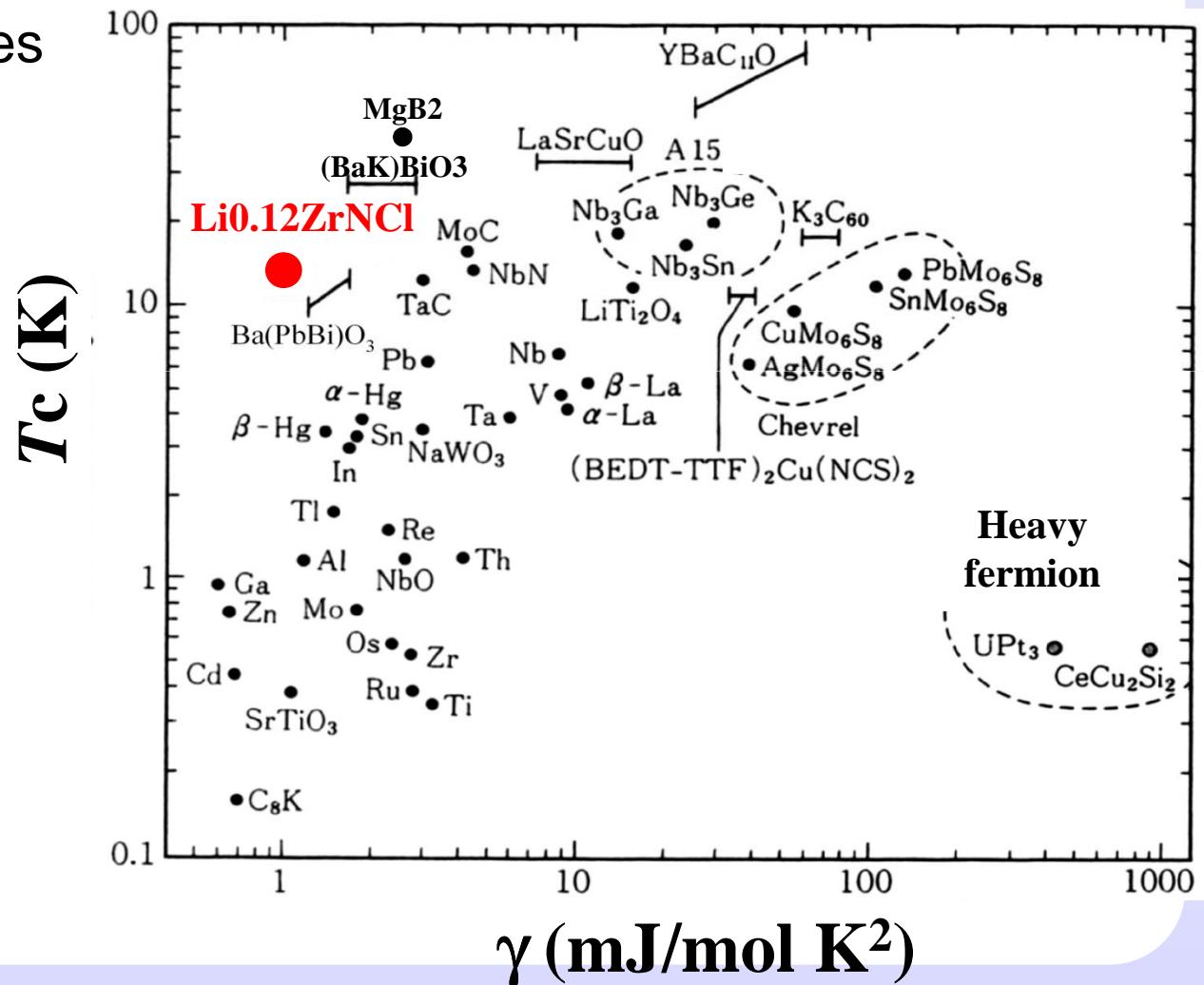
$$\gamma_n = 1.1 \text{ mJ/mol K}^2$$

$$\gamma_n = \frac{2}{3} \pi^2 k_B^2 (1 + \lambda) N(0)$$

## ■ Very weak electron-phonon coupling

- Raman scattering
- Isotope effect

Y. Taguchi, et al., PRL 94, 217002 (2005).



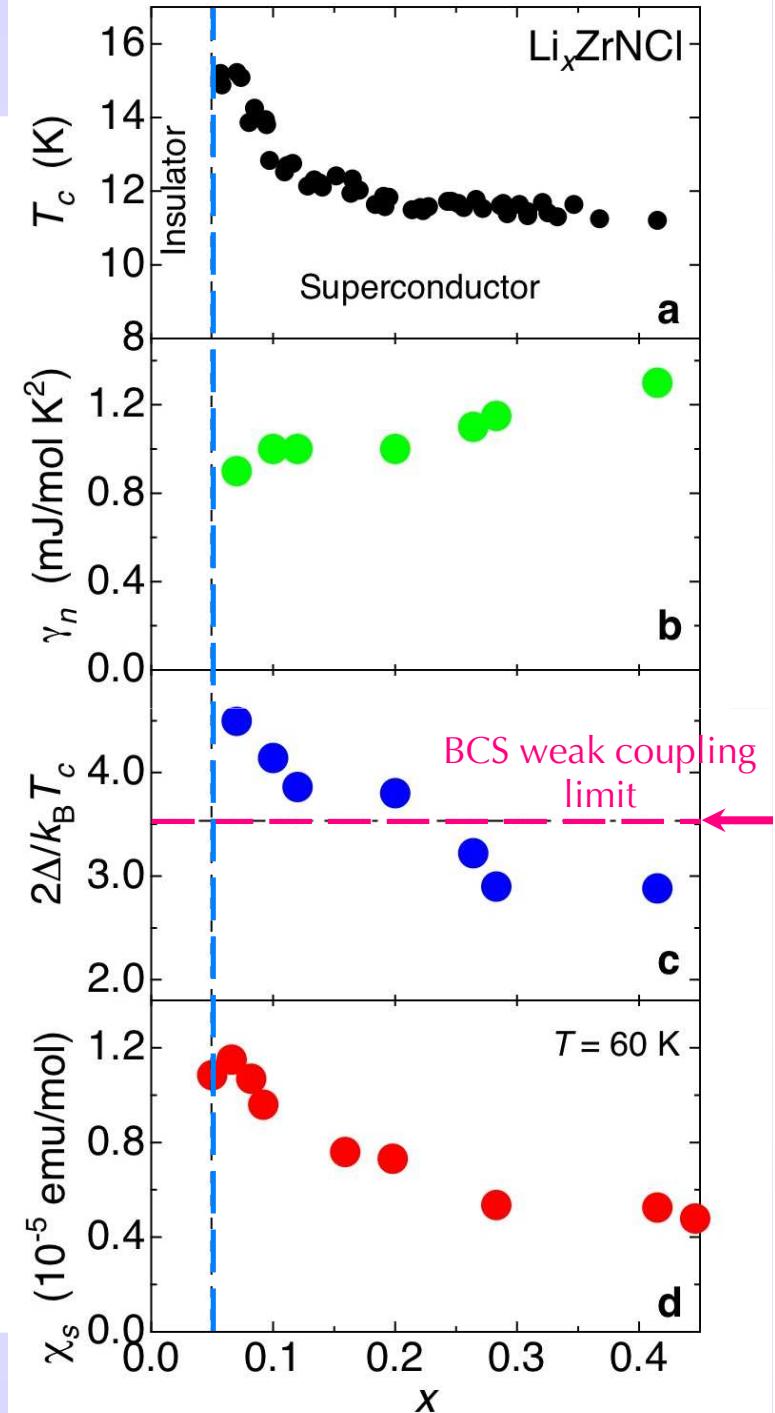
## Specific heat & magnetic susceptibility in Li doped ZrNCl

With reducing  $x$ ,

- $T_c$  **INCREASES**
- $\gamma_n$  : **Density of states DECREASES**
- $2\Delta/k_B T_c$  : **Pairing interaction INCREASES**  
Enhancement of  $T_c$  is due to pairing interaction not due to DOS.
- Spin susceptibility **INCREASES**

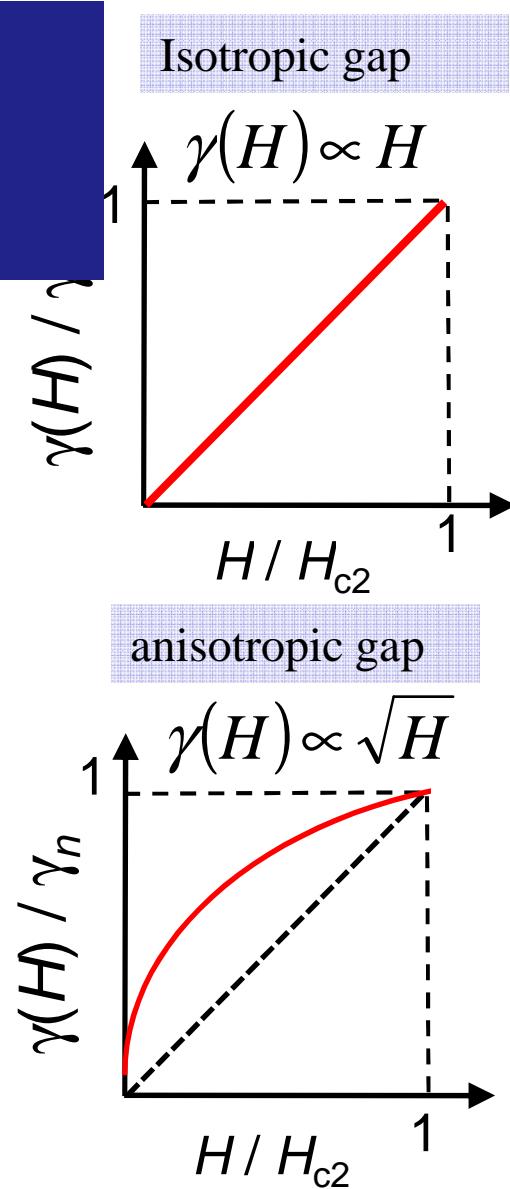
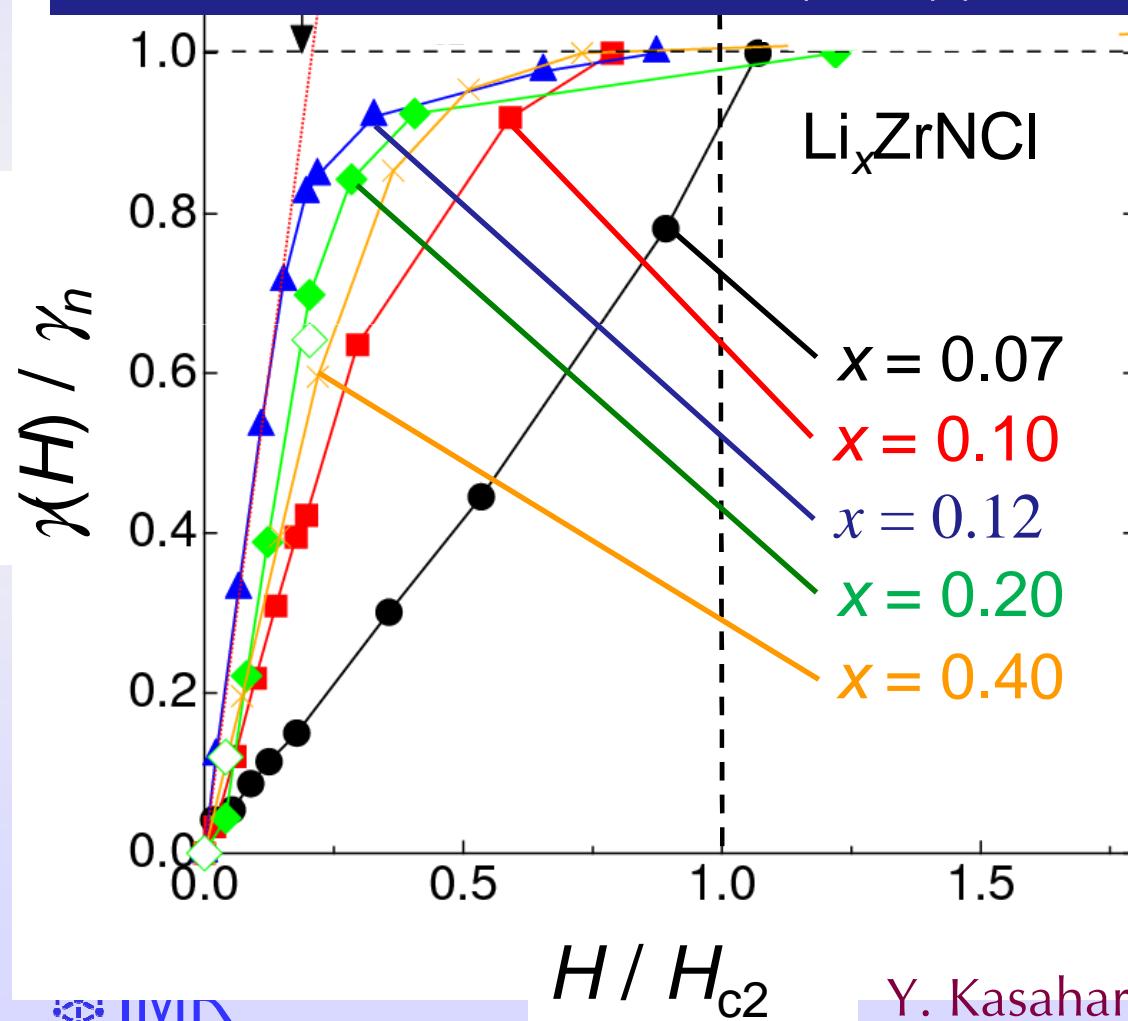
Magnetic fluctuations is enhanced toward the band insulator as  $x$  is reduced.

Y. Kasahara et al., PRL103, 077004 (2009)

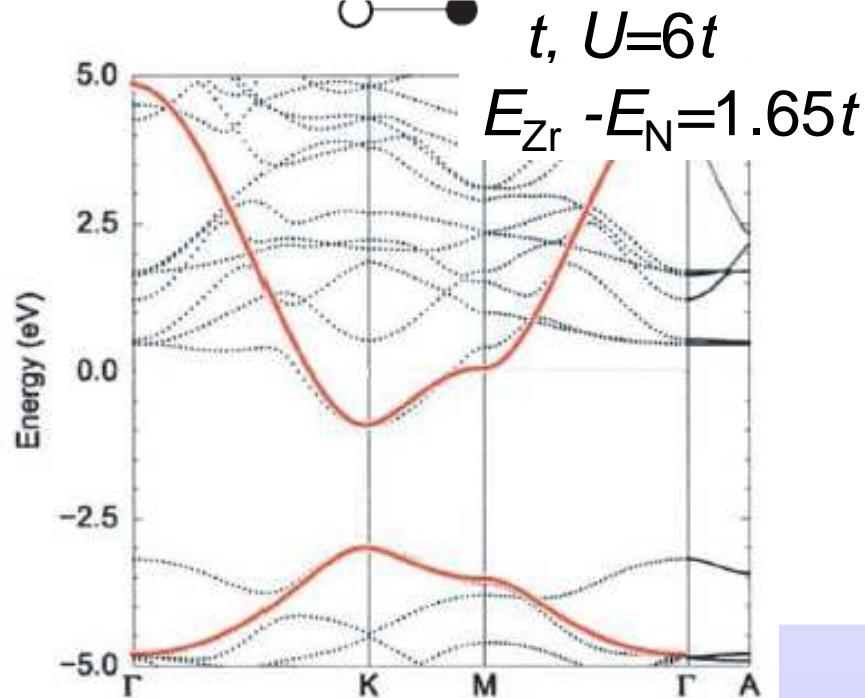
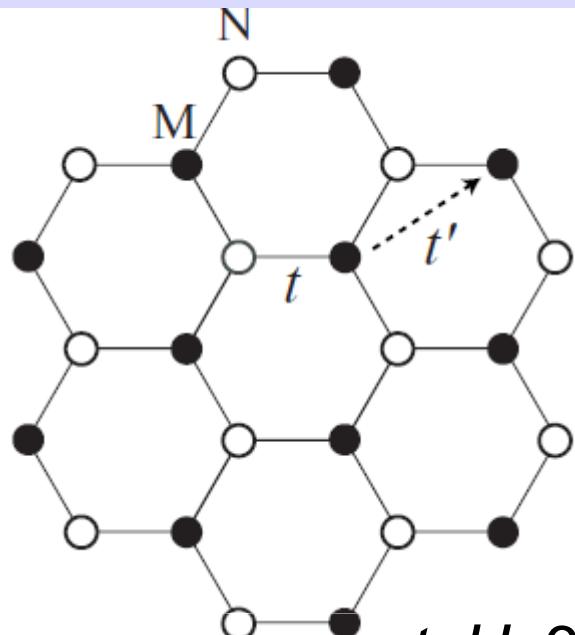


# Possible anisotropic superconducting gap

Crossover from isotropic gap (light doping) to anisotropic gap (high doping)  
in agreement with  $\mu$ SR  
(Hiraishi et al., PRB81.014525 (2010).)

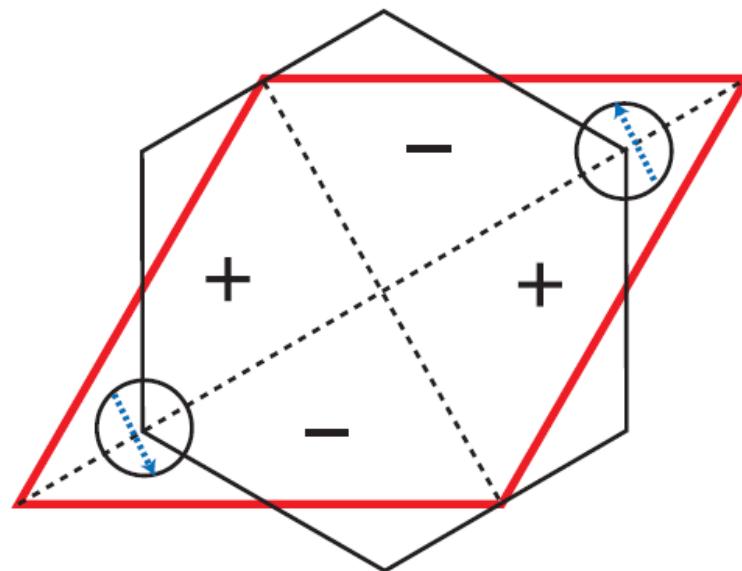


# Fluctuation exchange (FLEX) approximation theory on A-B honeycomb lattice with U



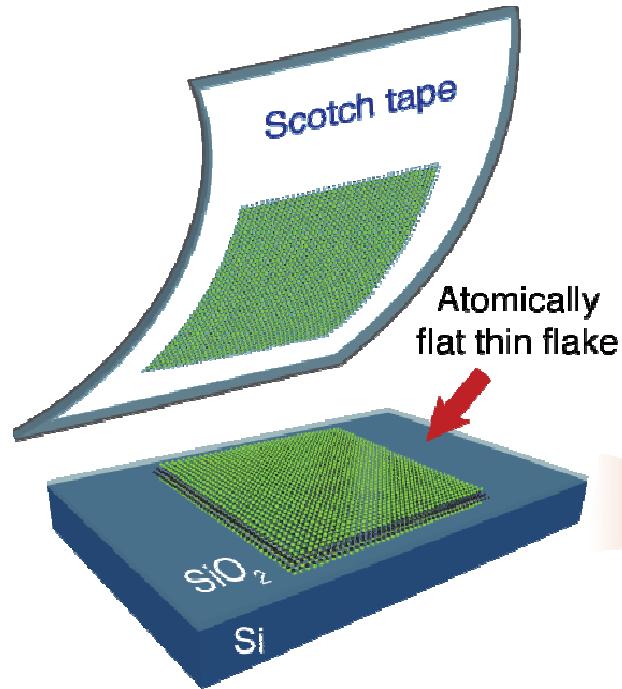
K. Kuroki,  
*Sci. Technol. Adv. Mater.* **9**, 044202 (2008).  
*Phys. Rev. B* **81**, 104502 (2010)

Antiferromagnetic fluctuation  
develops causing  $d + id'$  paring,  
even in doped BAND insulator

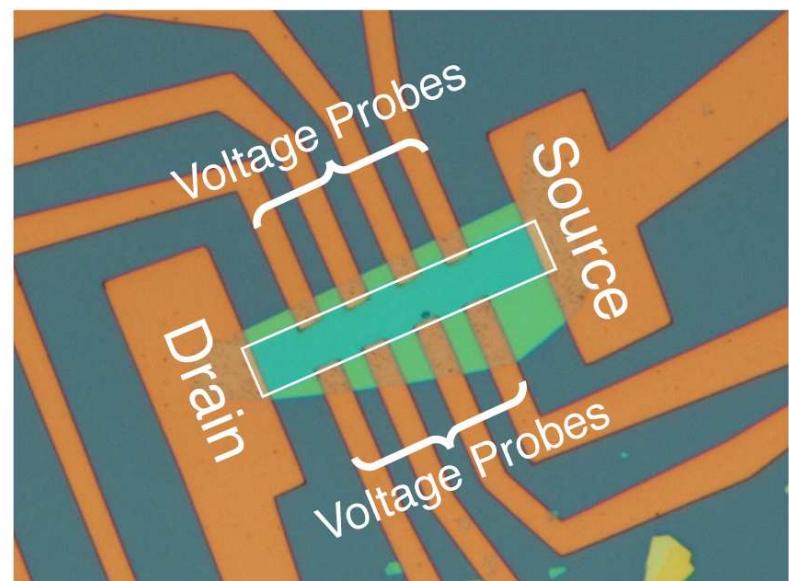
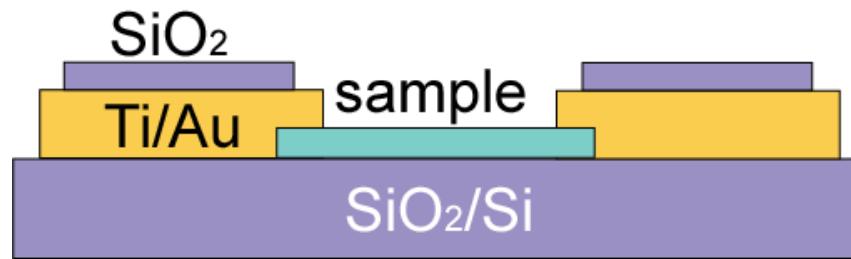


# Device fabrication for ZrNCl

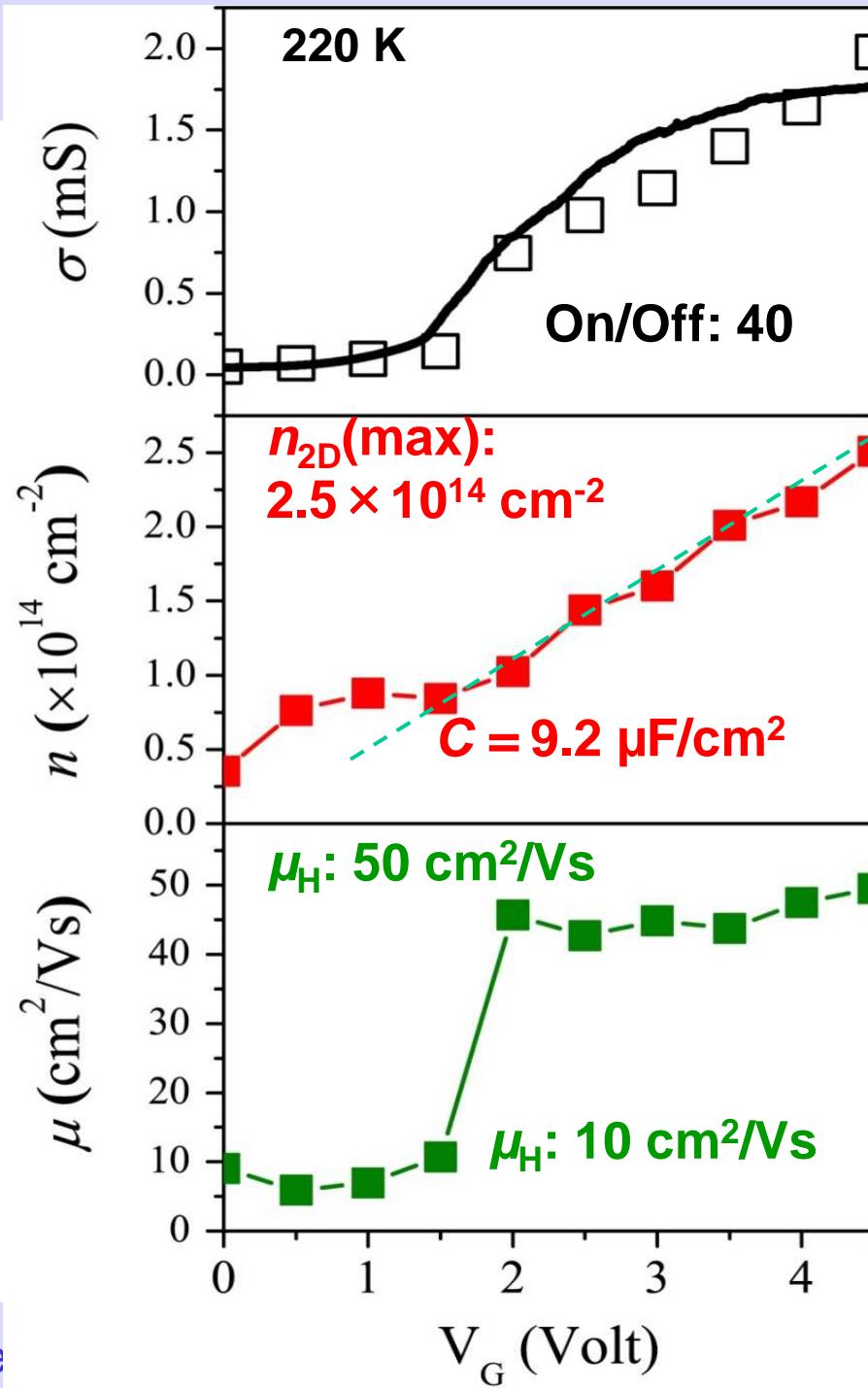
## 1. Exfoliating single crystals



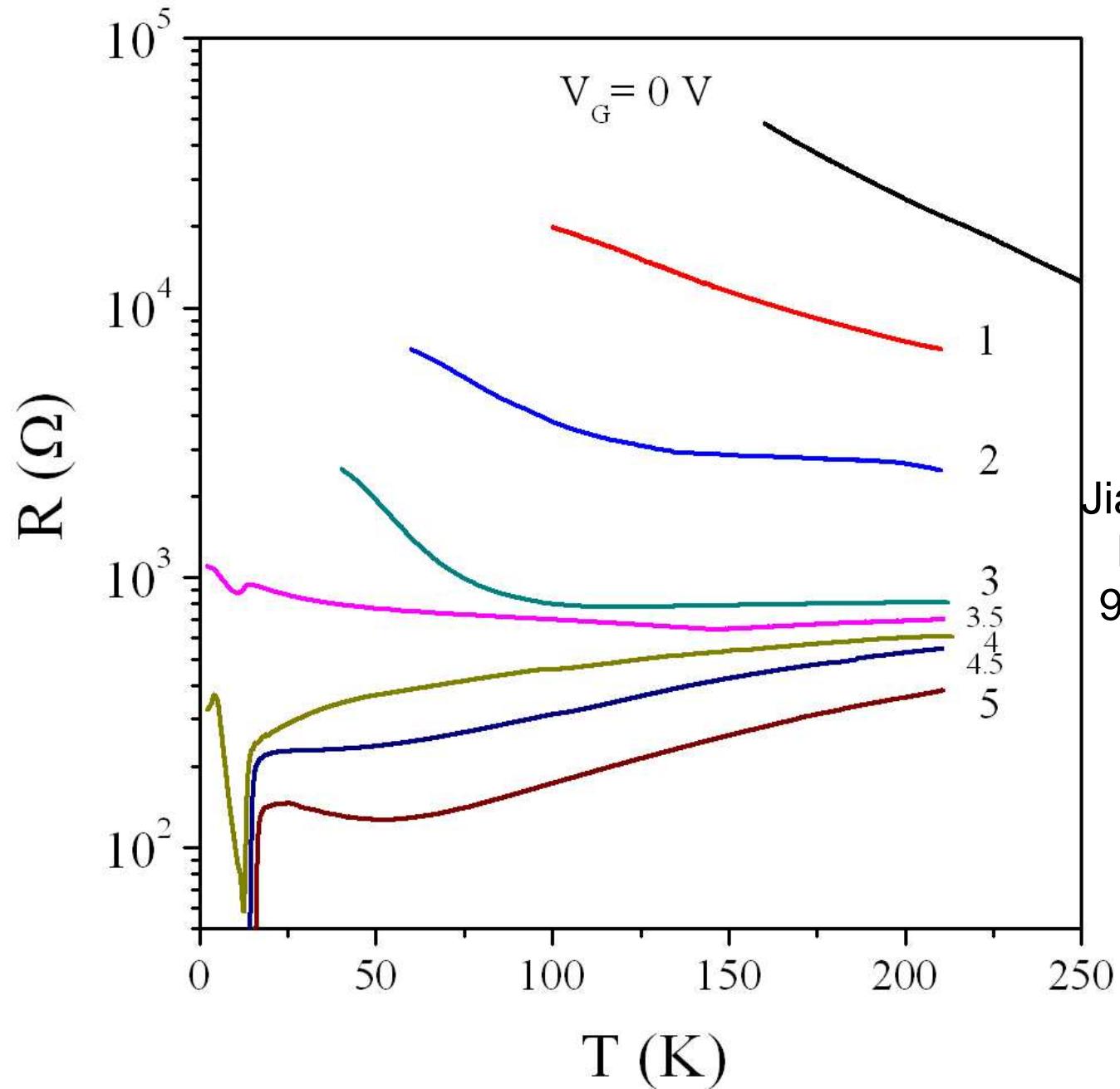
## 2. Electrodes by EB lithography



## FET Characteristics

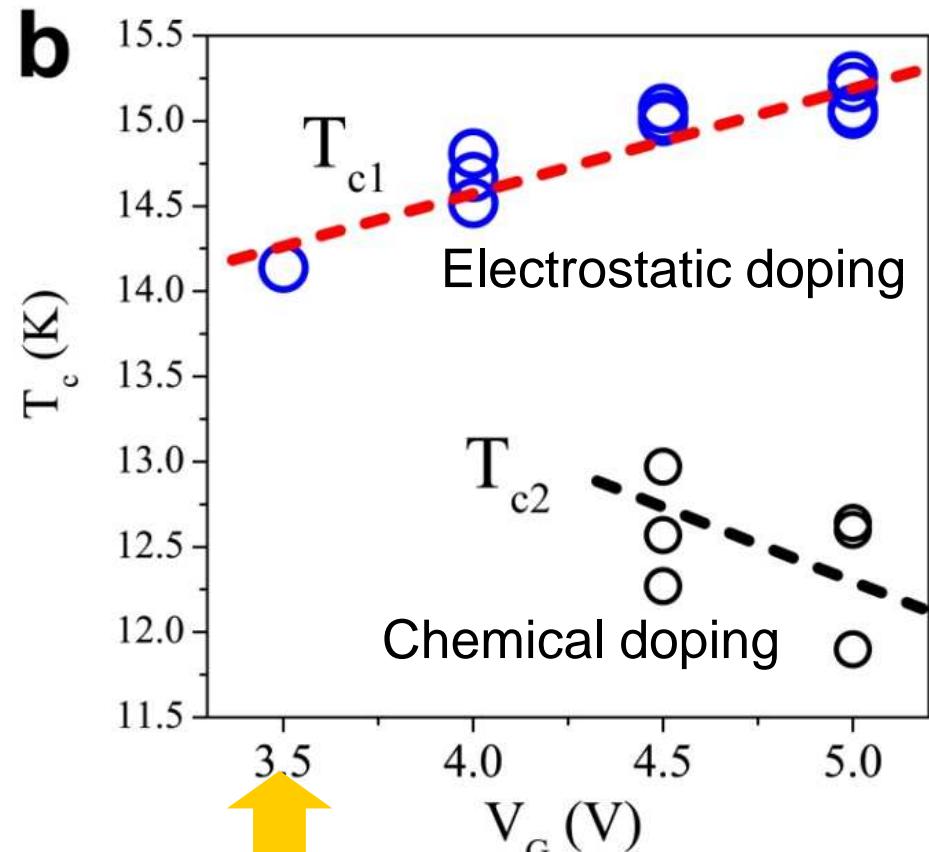
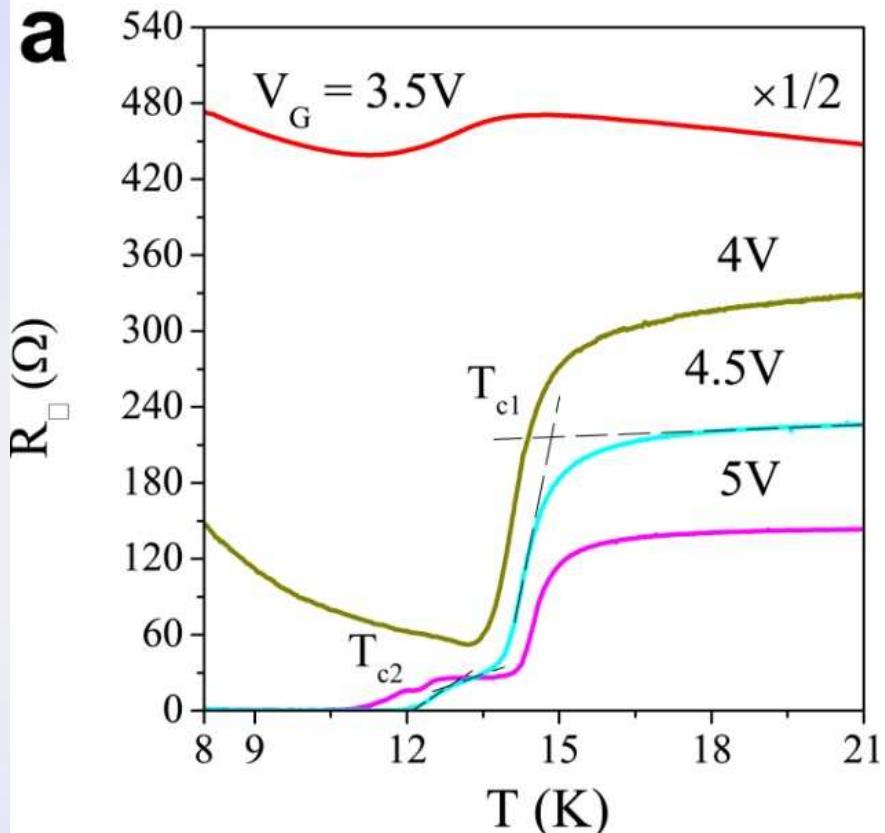


## Gate-induced superconductivity in ZrNCl ( $T_c \sim 15K$ )

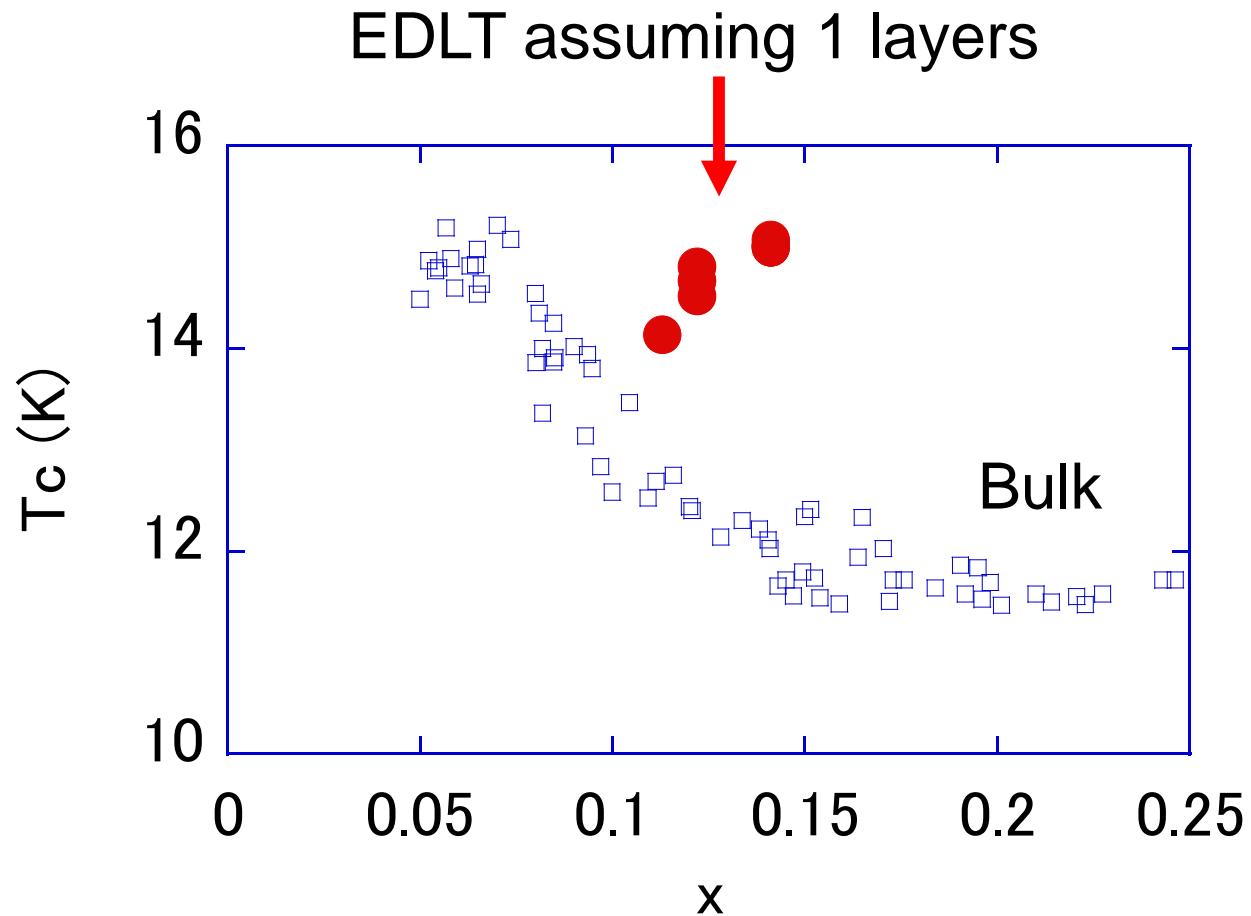


Jianting Ye et al.  
Nat. Mater.  
9, 125 (2010)

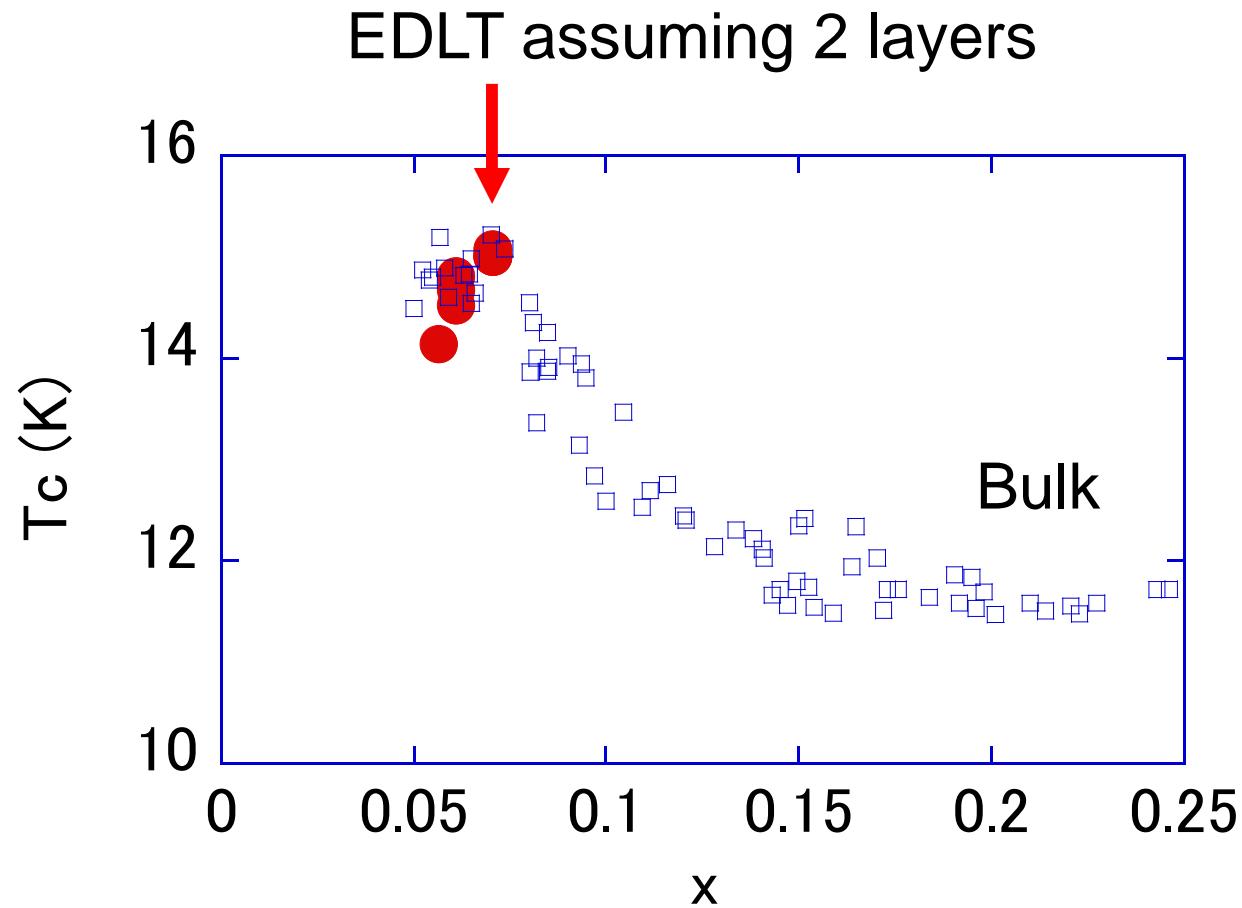
# $V_G$ dependence



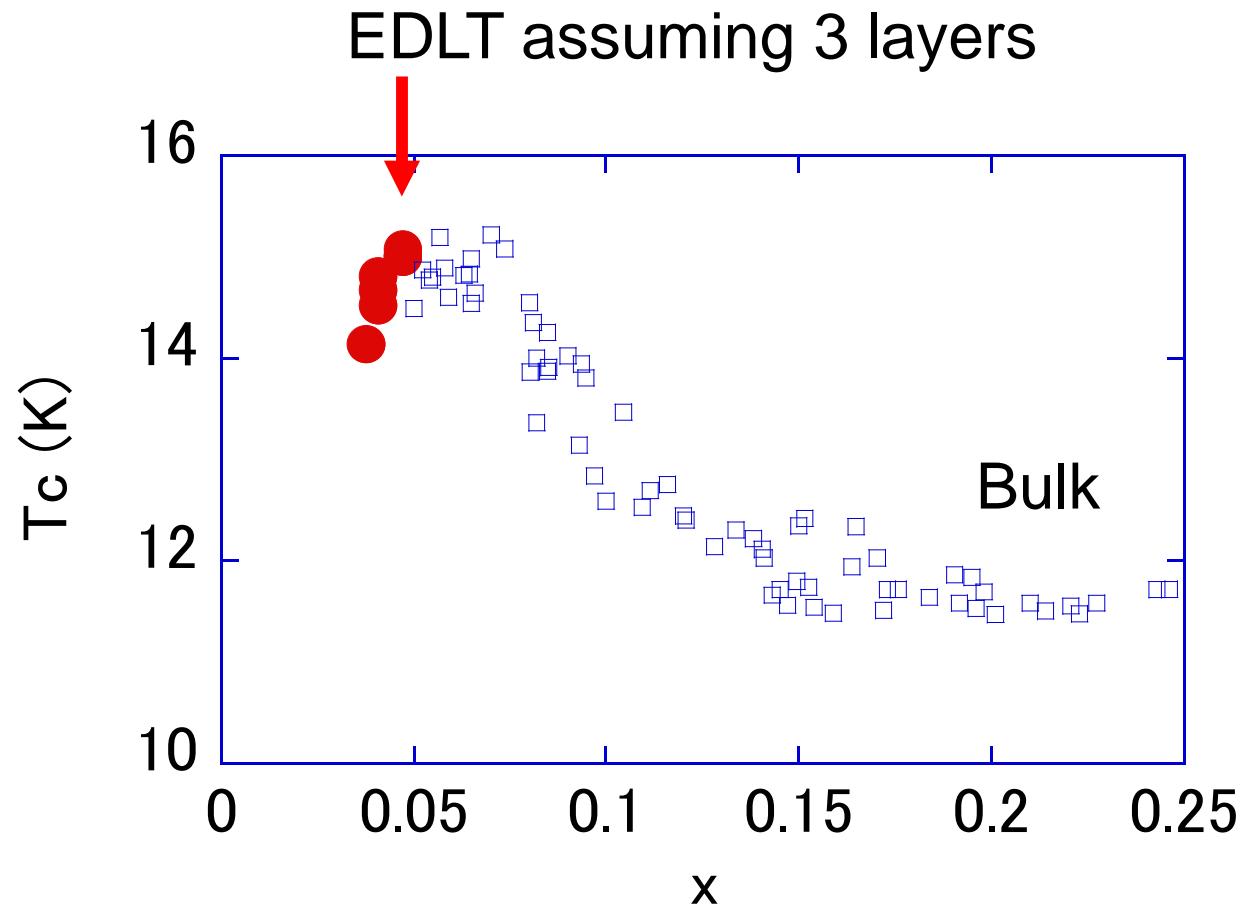
# $T_c$ - $x$ phase diagram for ZrNCI EDLT



# $T_c$ -x phase diagram for ZrNCI EDLT



# $T_c$ -x phase diagram for ZrNCl EDLT



Potentially unified phase diagram  
EDLT is covering the low x region?

# Summary

## EDLT + E-field induced superconductivity

- New tunable 2D systems
- Challenge: Increase T<sub>c</sub>  
Discover new superconductors
- New states at interfaces, which are inaccessible by conventional chemistry

### Solid/liquid interfaces

