

ポストHfO<sub>2</sub>技術

希土類酸化膜

PVDデポ

# High-k Gate Dielectric Candidates

## Choice of high-k

k value less than 50 is desirable for suppression of short channel effects

Material	k	HfAl <sub>x</sub> O <sub>y</sub>	10-15
NO stack	5-6	HfSi <sub>x</sub> O <sub>y</sub> N <sub>z</sub>	10-15
Al <sub>2</sub> O <sub>3</sub>	8-9	ZrO <sub>2</sub> , HfO <sub>2</sub>	20-30
HfSi <sub>x</sub> O <sub>y</sub>	10-15	Lanthanide Oxides	15-30

# Other options?

Candidates

Exp Reported

● Gas or liquid at 1000 K

○ Radio active

Unstable at Si interface

①  $\text{Si} + \text{MO}_x \rightarrow \text{M} + \text{SiO}_2$   
 ②  $\text{Si} + \text{MO}_x \rightarrow \text{MSi}_x + \text{SiO}_2$   
 ③  $\text{Si} + \text{MO}_x \rightarrow \text{M} + \text{MSi}_x\text{O}_y$

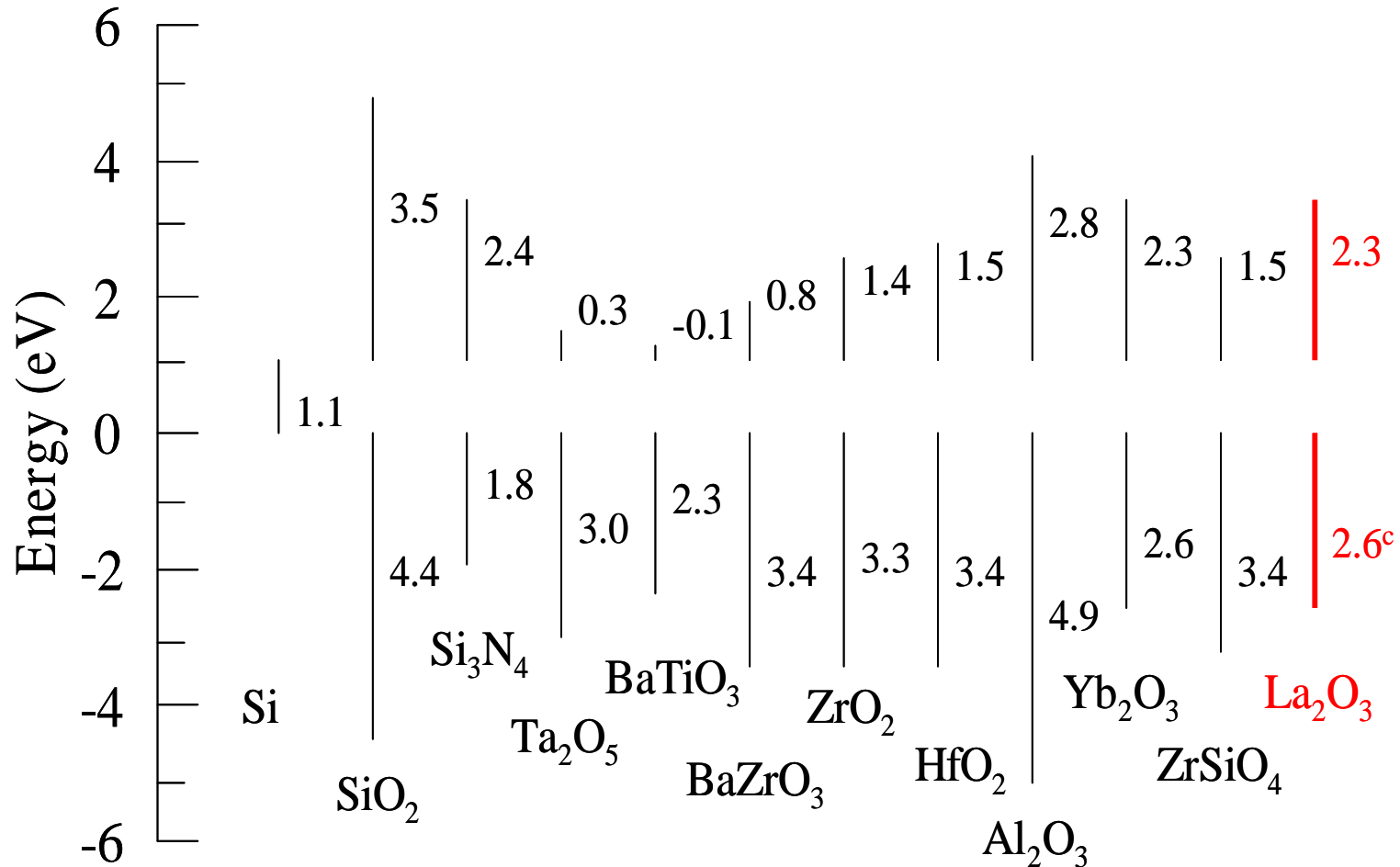
● H																			● He
● Li	● Be											● B	● C	● N	● O	● F	● Ne		
① Na	● Mg											● Al	● Si	● P	● S	● Cl	● Ar		
● K	● Ca	● Sc	② Ti	① V	① Cr	① Mn	① Fe	① Co	① Ni	① Cu	① Zn	① Ga	① Ge	● As	● Se	● Br	● Kr		
● Rh	● Sr	● Y	● Zr	① Nb	① Mo		① Tc	① Ru	① Rh	① Pd	● Ag	① Cd	① In	① Sn	① Sb	① Te	● I	● Xe	
● Cs	③ Ba	★	● Hf	① Ta	① W	① Re	① Os	① Ir	● Pt	● Au	● Hg	● Tl	① Pb	① Bi	○ Po	○ At	○ Rn		
○ Fr	○ Ra	★	○ Rf	○ Ha	○ Sg	○ Ns	○ Hs	○ Mt											

→

★	● La	● Ce	● Pr	● Nd	○ Pm	● Sm	● Eu	● Gd	● Tb	● Dy	● Ho	● Er	● Tm	● Yb	● Lu
★	○ Ac	○ Th	○ Pa	○ U	○ Np	○ Pu	○ Am	○ Cm	○ Bk	○ Cf	○ Es	○ Fm	○ Md	○ No	○ Lr

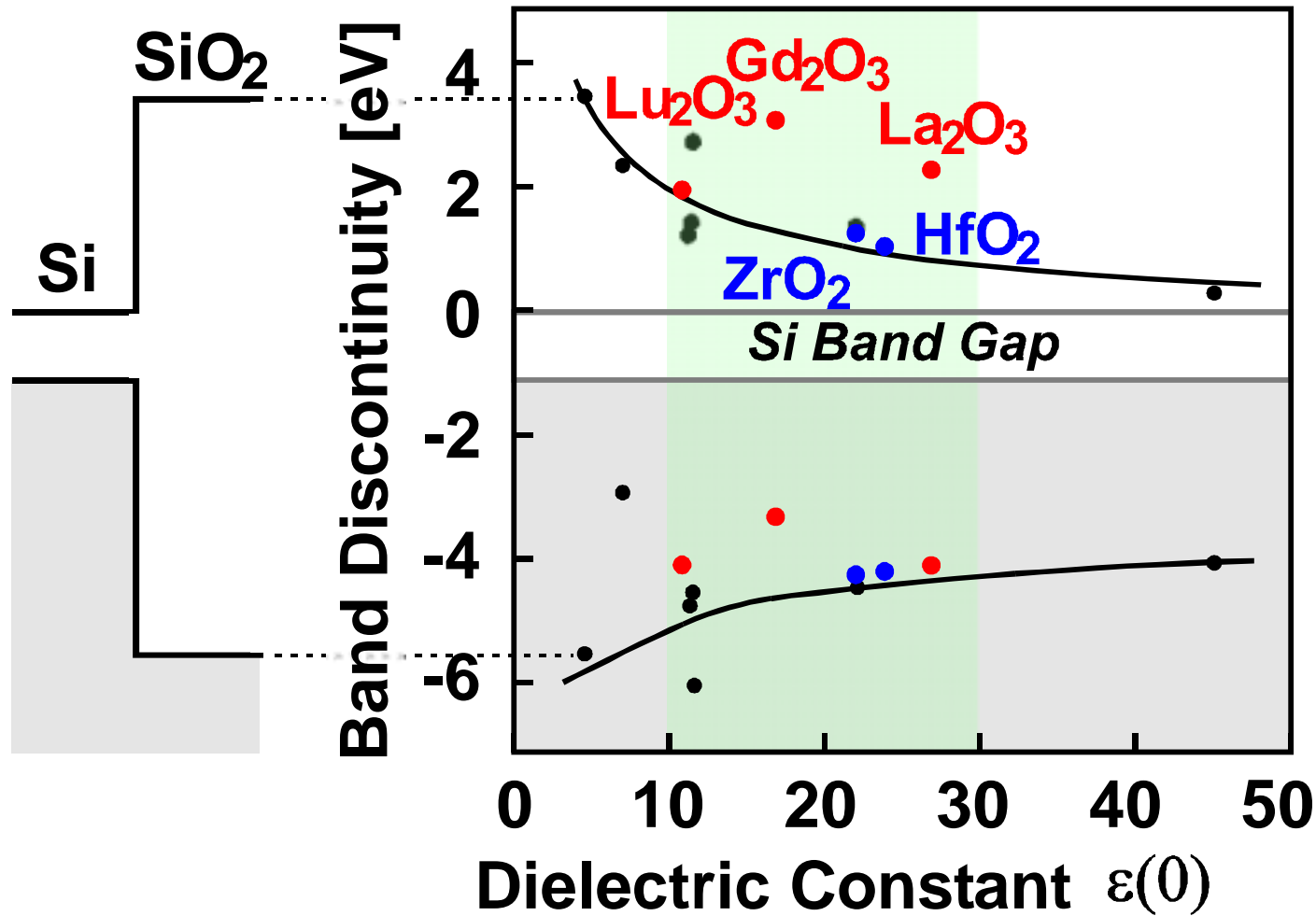
R. Hauser, IEDM Short Course, 1999

# Band offsets for High-k dielectrics on Si



\* <sup>c</sup> Estimates.

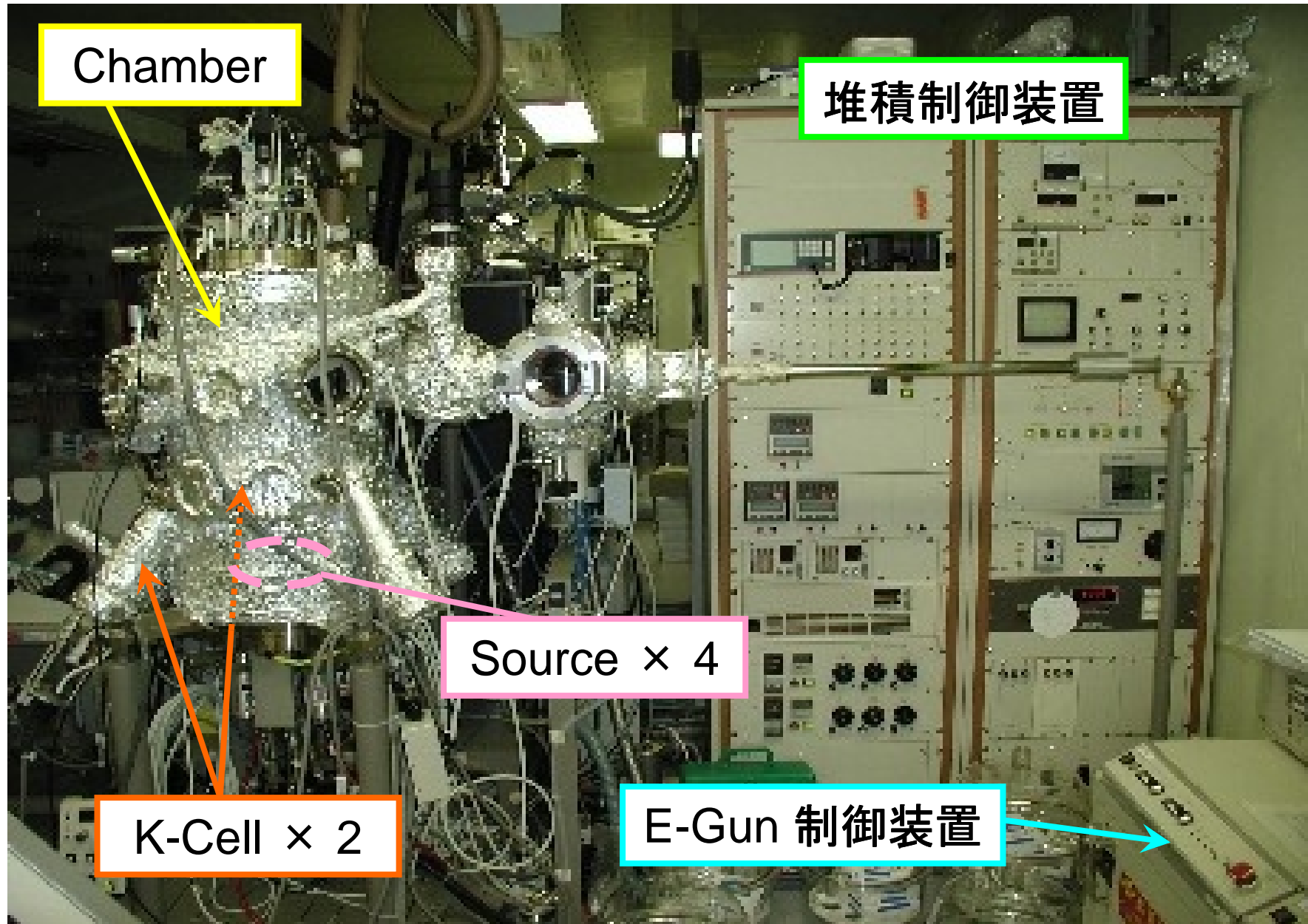
# Experimental data by XPS by Prof. T. Hattori



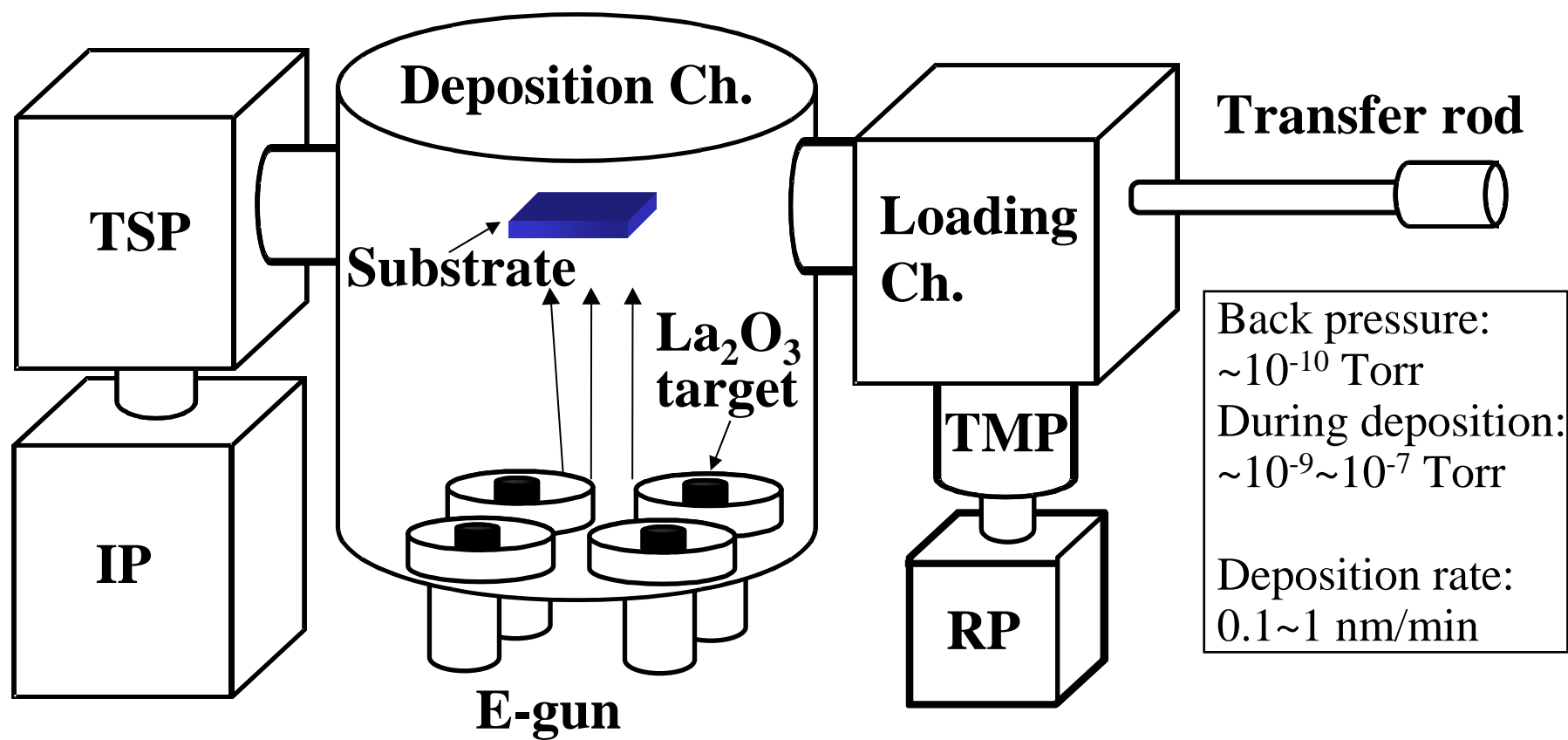
$\sqrt{\phi_B} * k$  : Figure of Merit of High-k

Insulating Films on Semiconductors Barcelona June 18-20, 2003

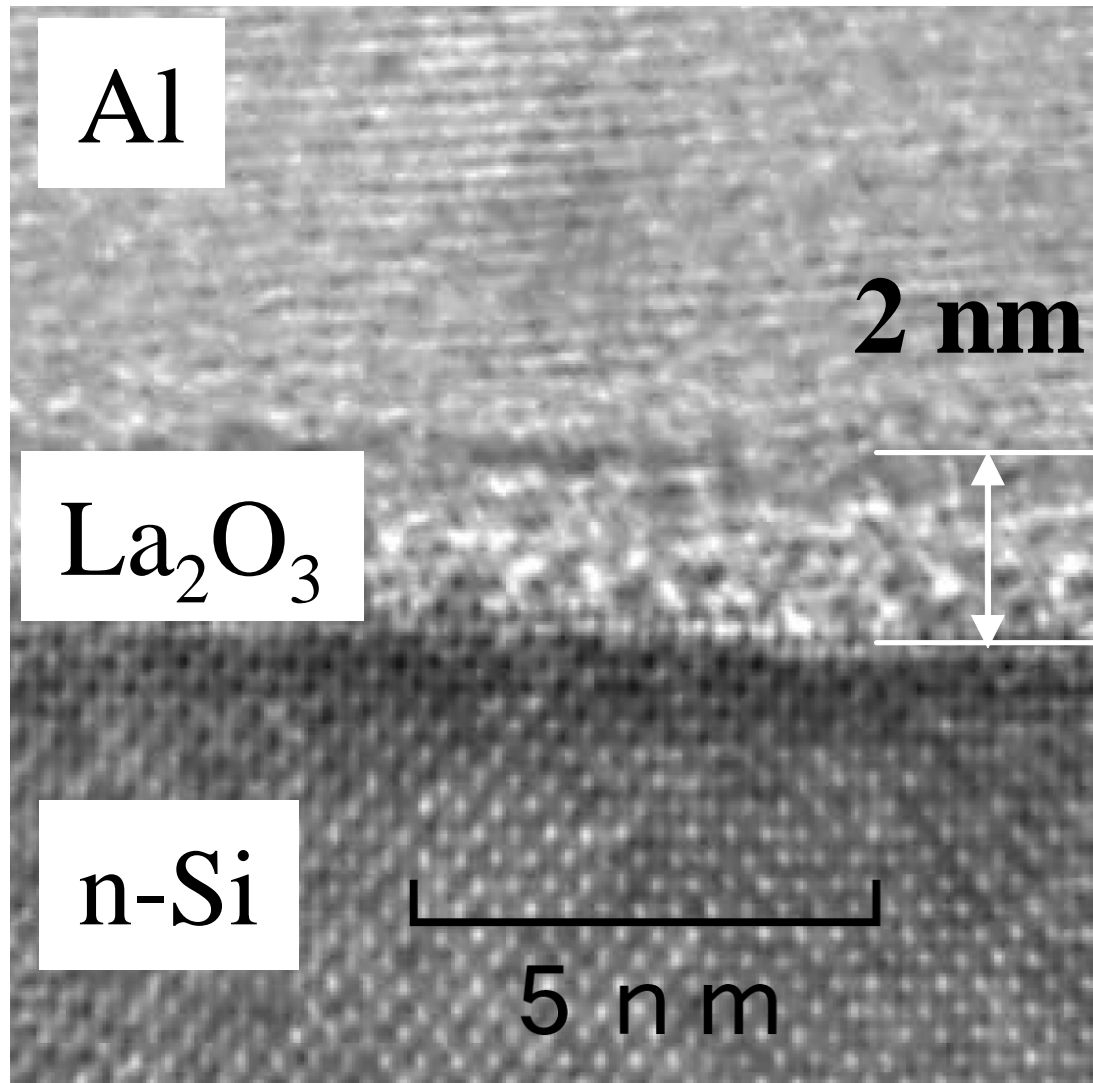
# MBE装置



# Our Molecular Beam Deposition System



Cross sectional TEM images for Al/La<sub>2</sub>O<sub>3</sub>/n-Si.  
400°C depo., 400°C RTA in N<sub>2</sub>.

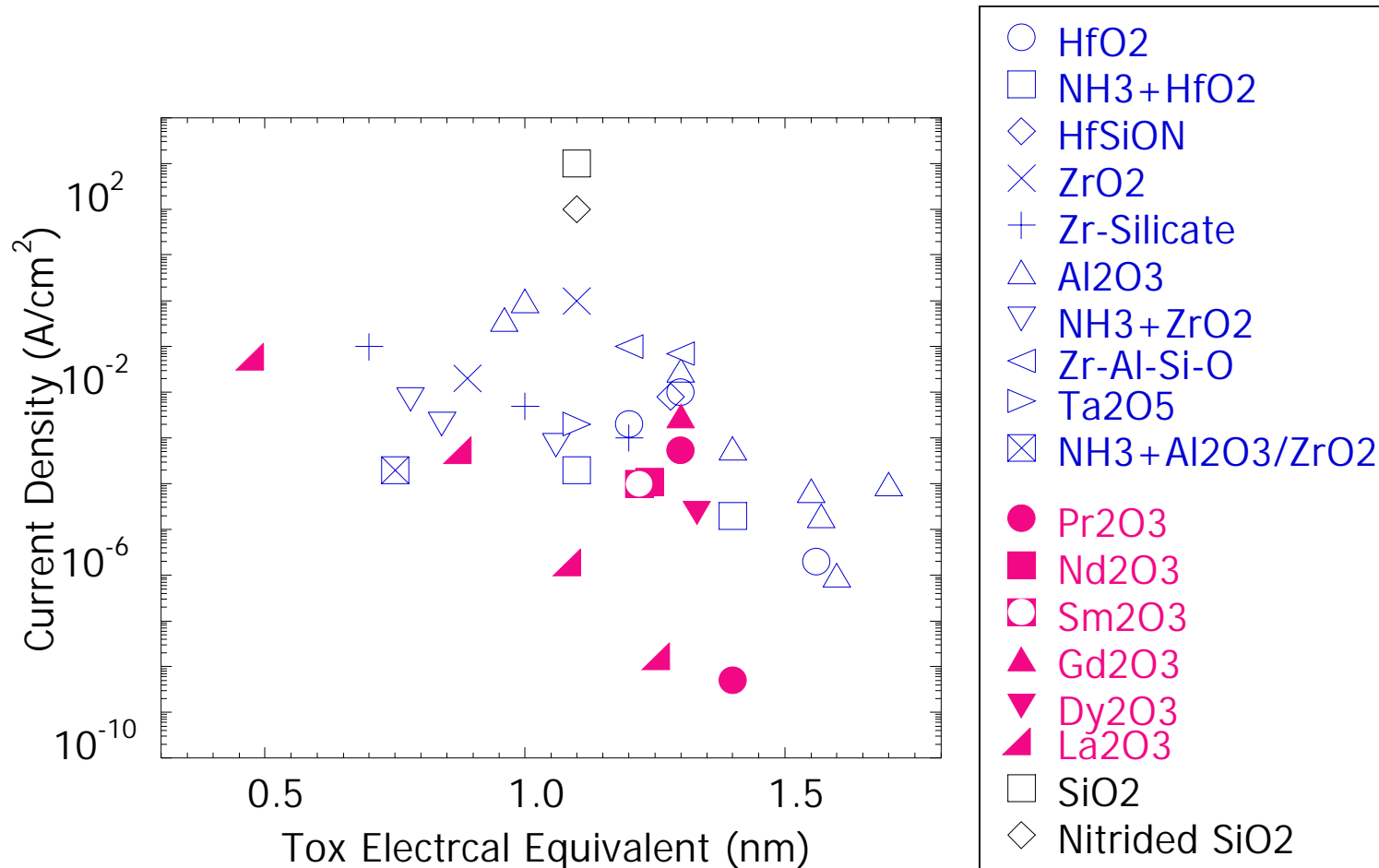


Physical thickness  
= 2 nm

EOT = 0.6 nm



# $T_{ox}$ Electrical Equivalent vs. Current Density



From IEDM 2000, IEDM 2001, SSDM 2001 and VLSI Symp. 2001(Advanced Program)

Annealing (5min)		EOT [nm]	Vfb [V]	$\Delta V_{fb}$ [V]	Relative Dielectric Constant	Leakage [A] @1V
without		1.760	0.806	0.123	17.0	1.06e-2
O <sub>2</sub>	200°C	1.762	0.823	0.165	15.6	3.09e-6
	300°C	1.617	0.870	0.257	16.9	9.51e-7
	400°C	3.103	0.391	-0.700	9.62	1.37e-5
N <sub>2</sub>	200°C	1.106	0.784	0.083	<b>27.0</b>	3.04e-7
	300°C	1.443	0.785	0.081	<b>26.1</b>	7.27e-6
	400°C	1.280	0.808	0.123	<b>23.3</b>	2.77e-6

$$V_{fb,fitted} = \Delta W_{func} + \Delta V_{fb,Calc} = W_{gate} - W_{silicon} + V_{fb,Calc}$$

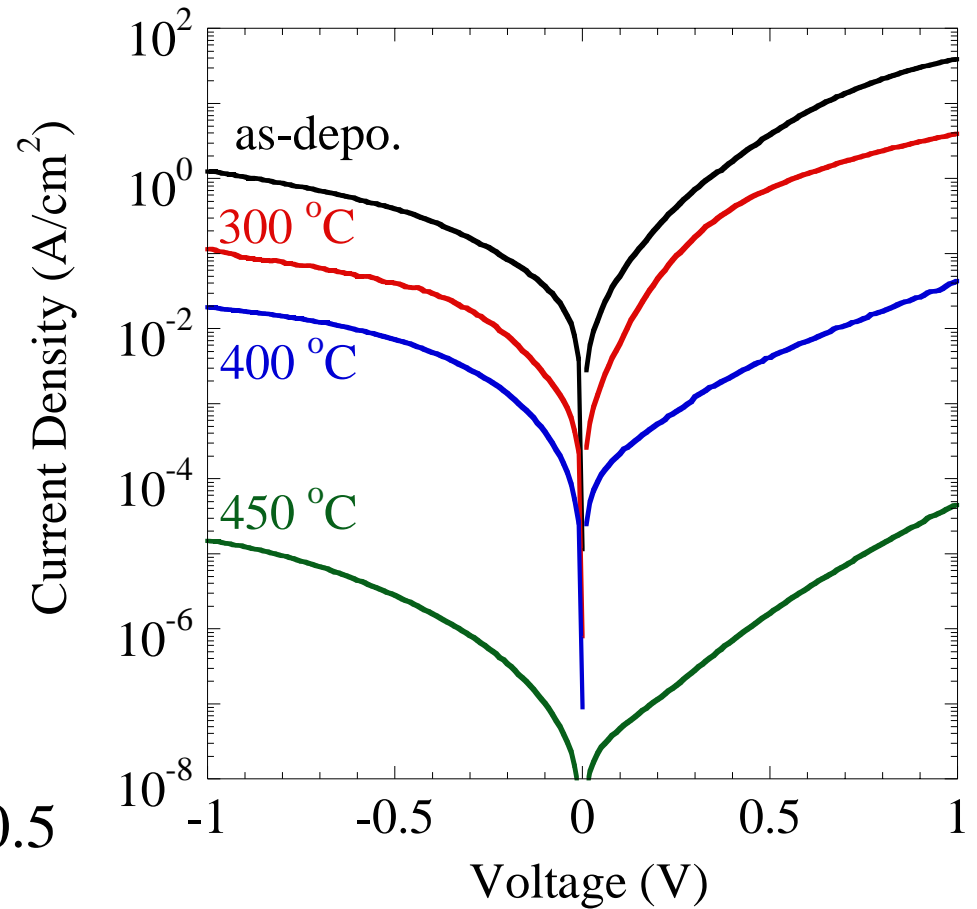
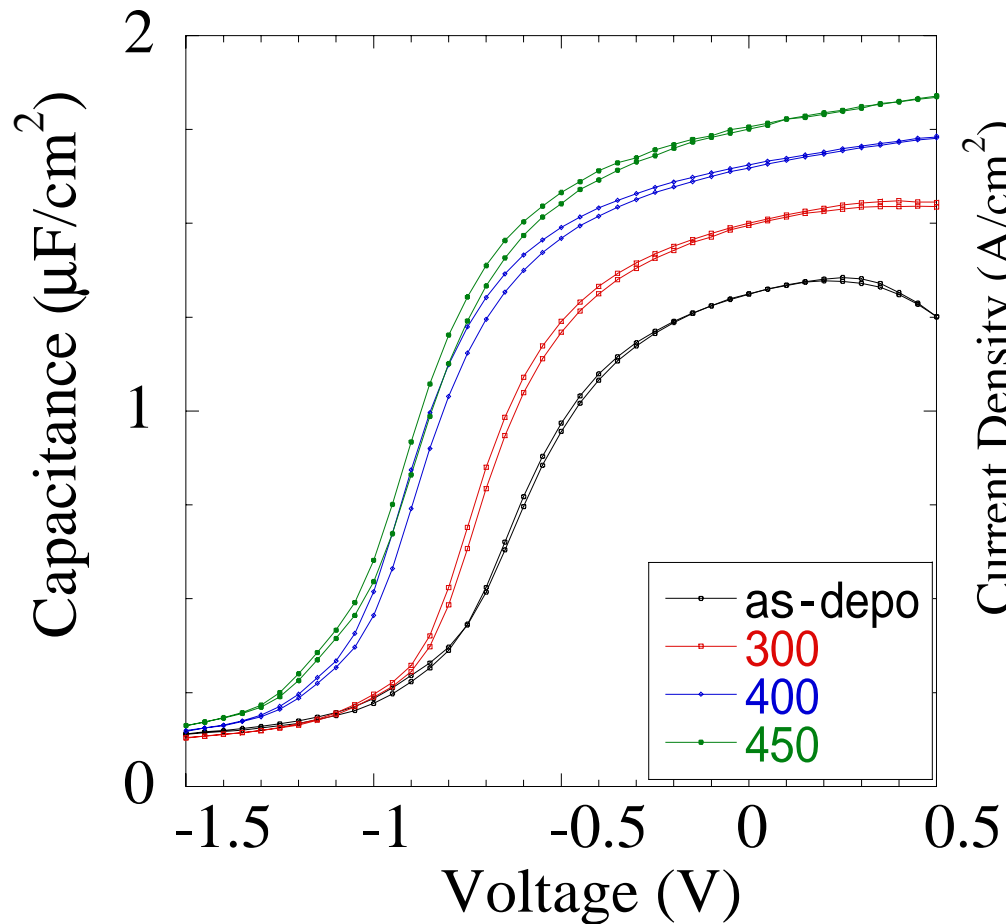
# Preliminary results

Densification: good

Vfb shift: problem

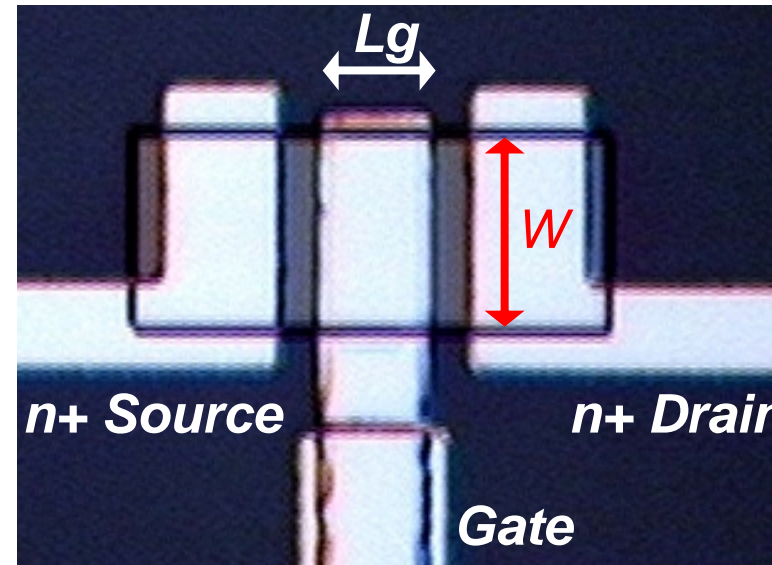
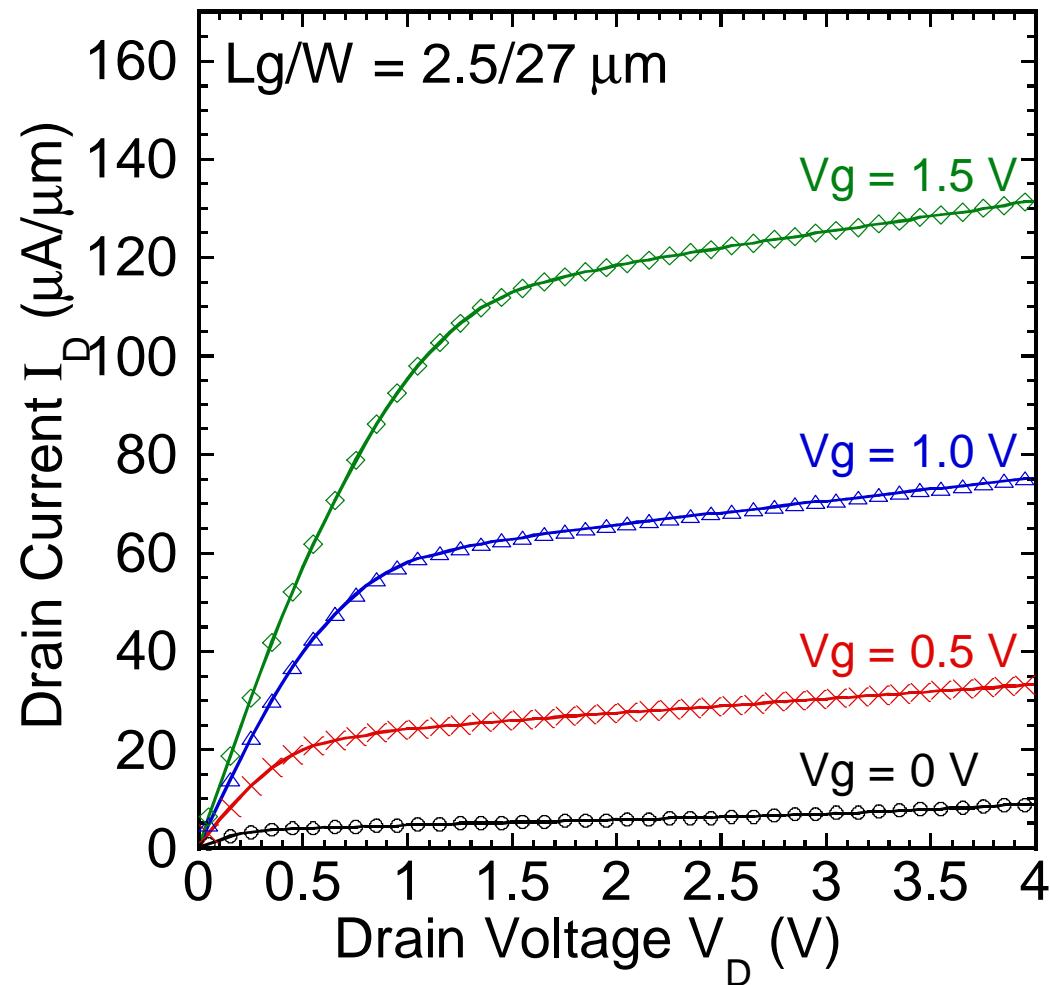
Dry N2 annealing

Being solved by PM anneal

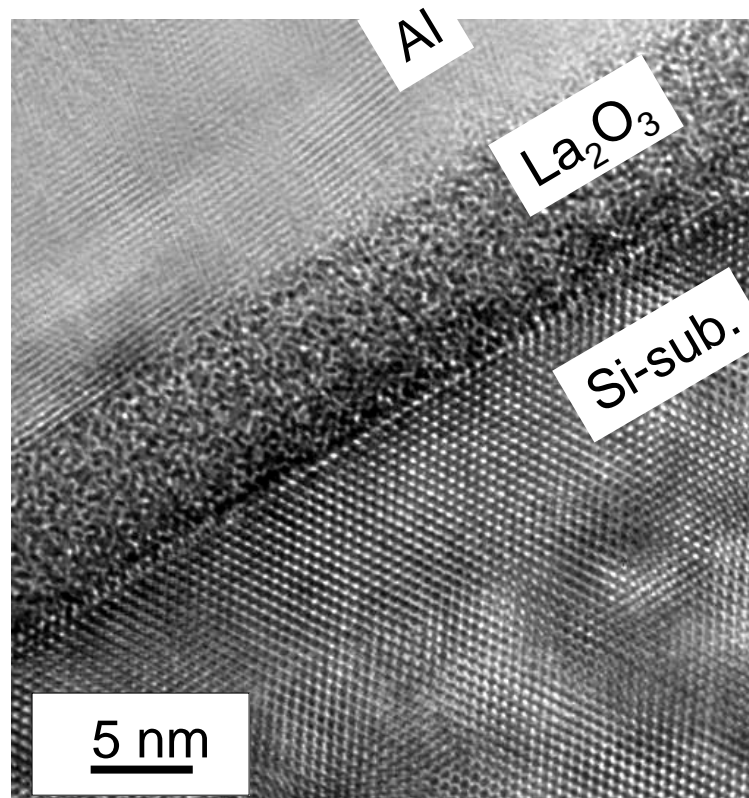


# $I_D - V_D$ Characteristics ( $L_g = 2.5 \mu\text{m}$ )

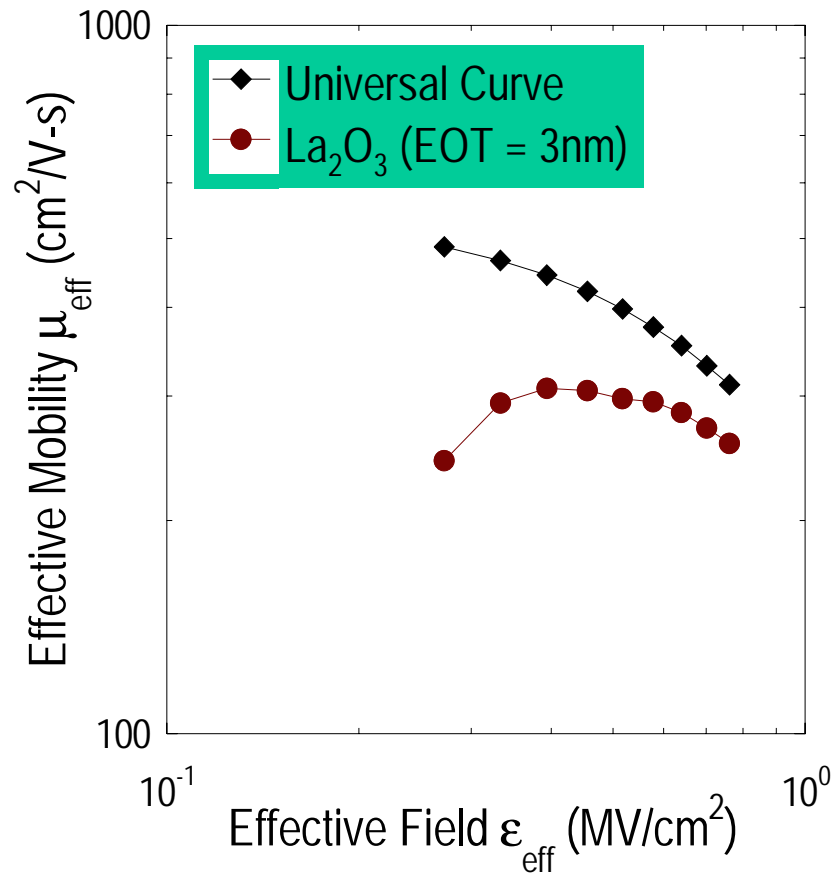
*Chemical Oxide, Deposition Temp. = 250°C,  
 $L_g = 2.5 \mu\text{m}$ ,  $W = 27 \mu\text{m}$ ,  $EOT = 3.0 \text{ nm}$*



Deposition Temp. = 250°C, T<sub>phy</sub> = 10 nm, Annealed  
in O<sub>2</sub> 400°C 5min

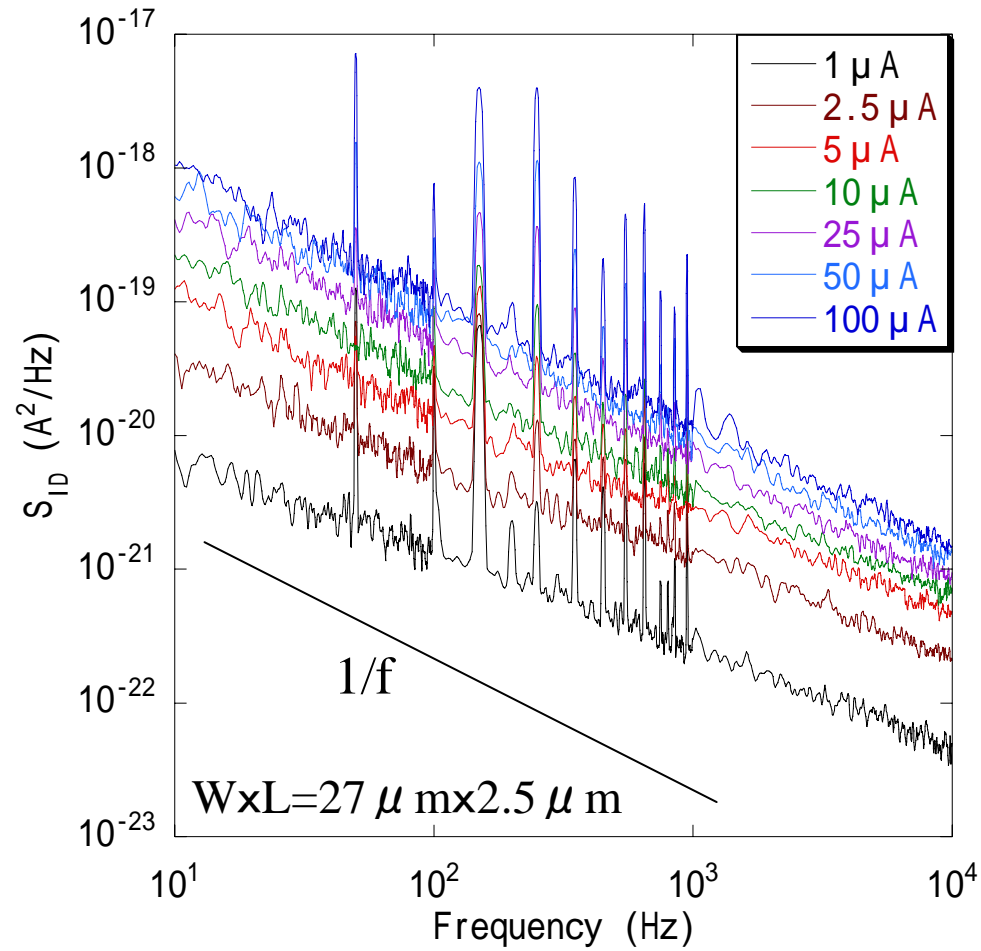


## Electrical Characteristics – Mobility $\mu_{\text{eff}}$



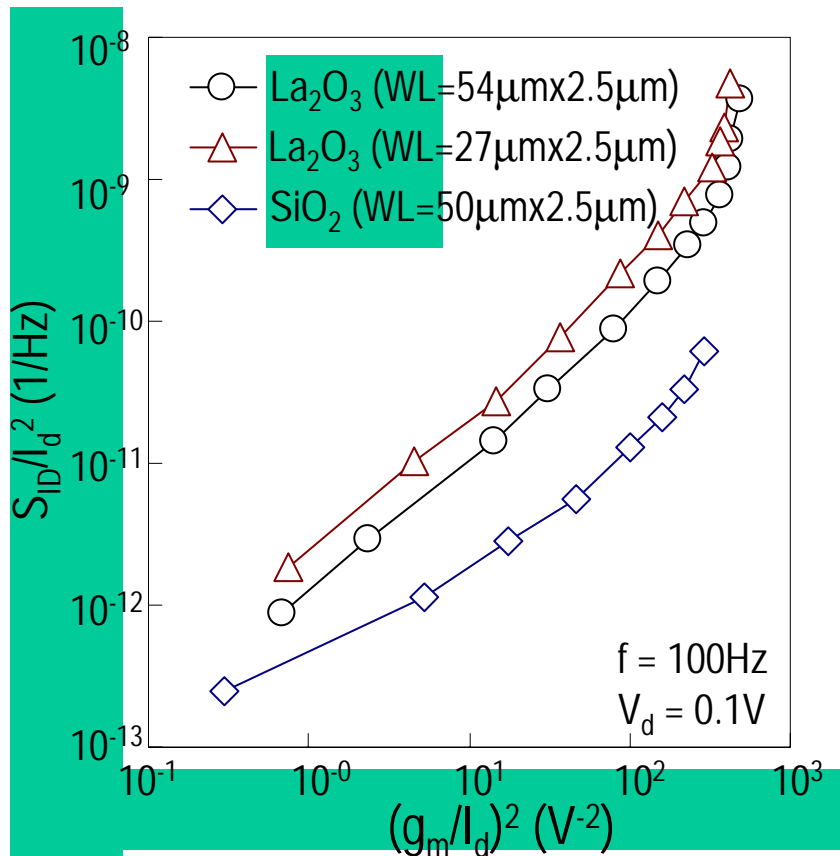
High effective mobility of nearly the same to the universal curve was obtained with EOT = 3nm La<sub>2</sub>O<sub>3</sub> gate dielectrics.

# Flicker noise at $V_{ds}=100\text{mV}$



## Results and Discussion (6)

### LF Noise – Comparison with SiO<sub>2</sub>



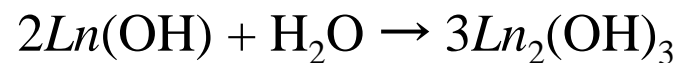
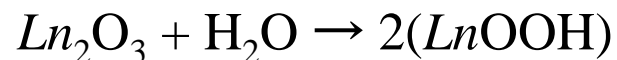
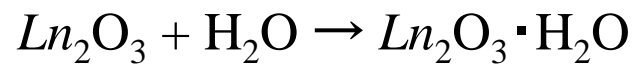
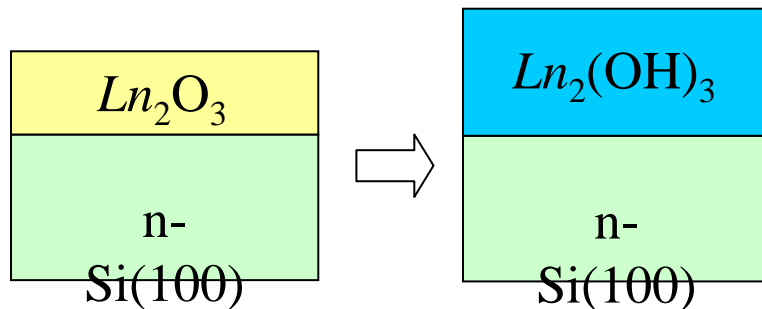
The normalized noise spectrum of n-type MISFET's with La<sub>2</sub>O<sub>3</sub> gate dielectrics is about one order in magnitude higher than that of SiO<sub>2</sub> obtained from thermal oxidation.



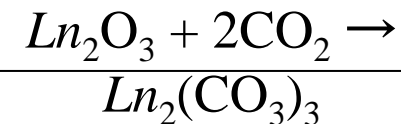
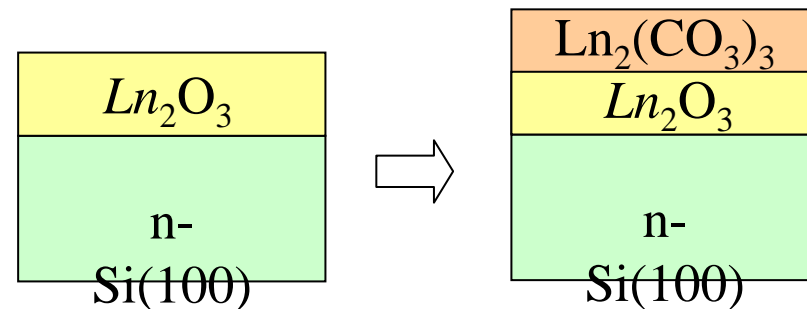
# Absorption of moisture and CO<sub>2</sub>

The oxides become hydroxide and carbonate in H<sub>2</sub>O and CO<sub>2</sub> ambient.

hydroxide



carbonate



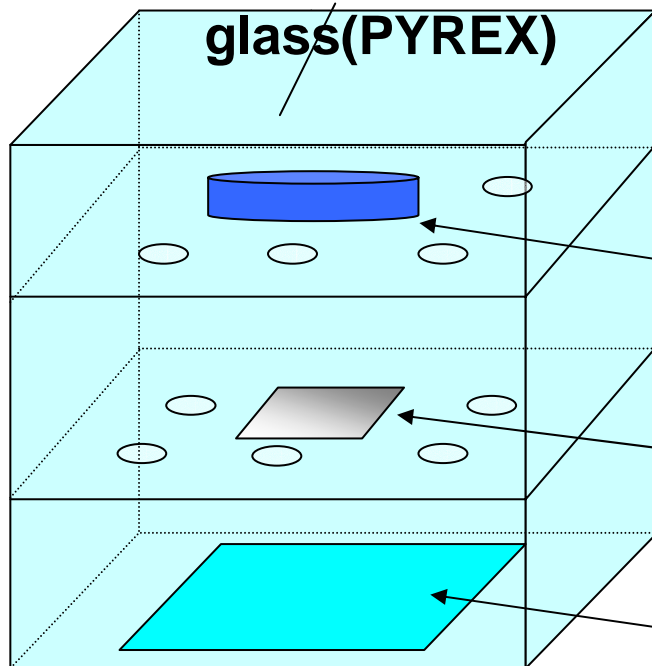
※  $Ln$ : Lanthanide

# Experimental apparatus

Temperature: ~20°C  
Humidity: 80%  
Humidification time:  
0 ~120

hrs

acryl(PMMA)  
or  
glass(PYREX)



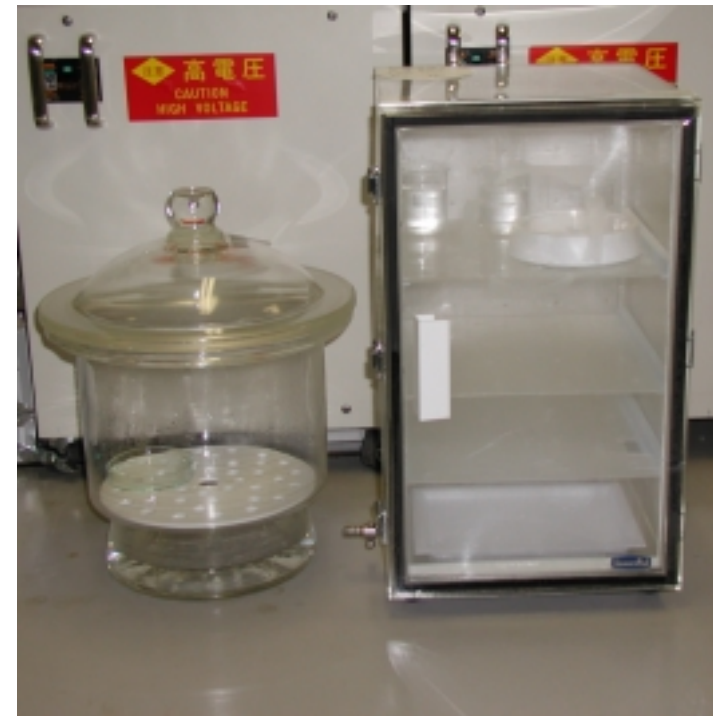
Thermometer  
Hygrometer

Samples

Ultra pure  
water

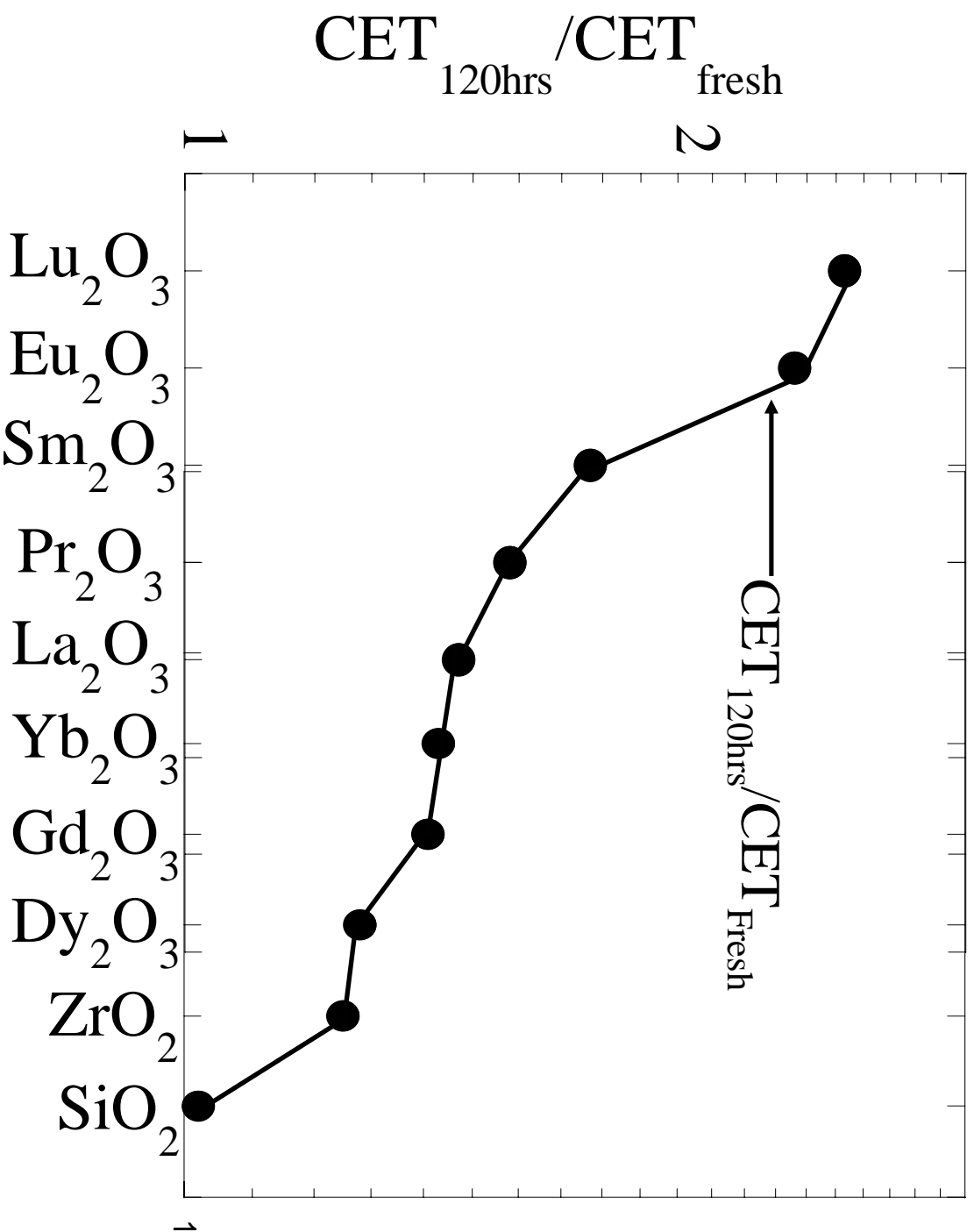
glass  
(PYREX)

acryl  
(PMMA)

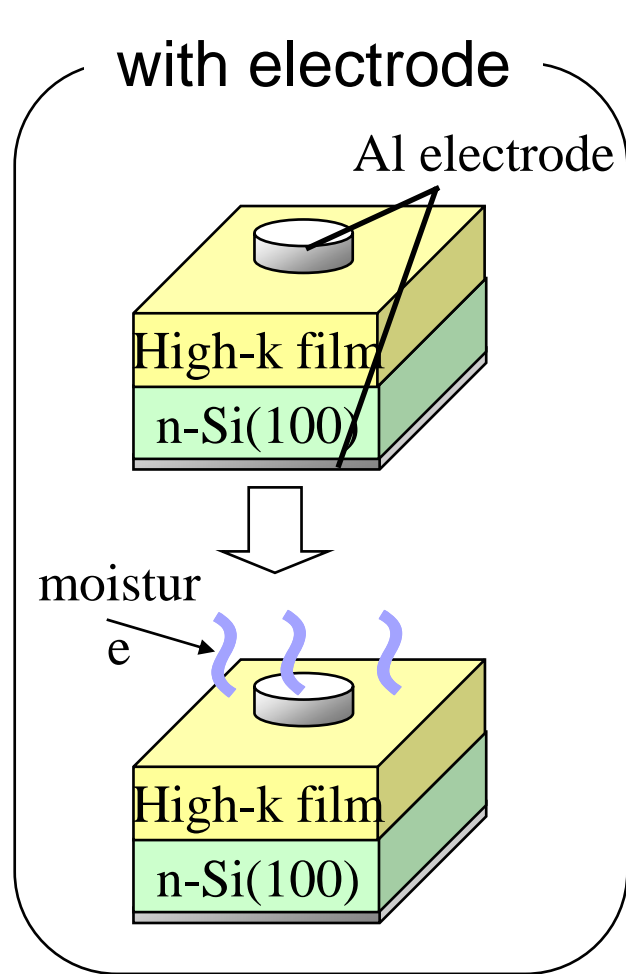


\*PMMA :  
 $\text{CH}_2\text{C}(\text{CH}_3)\text{COOCH}_3$

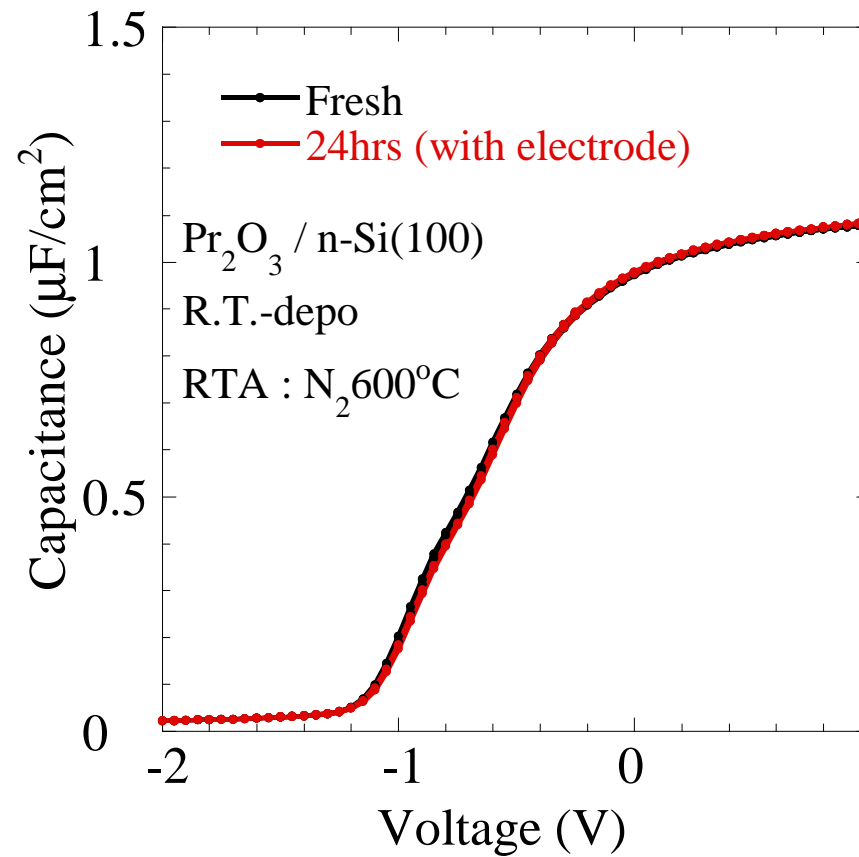
# Change of CET for all studied



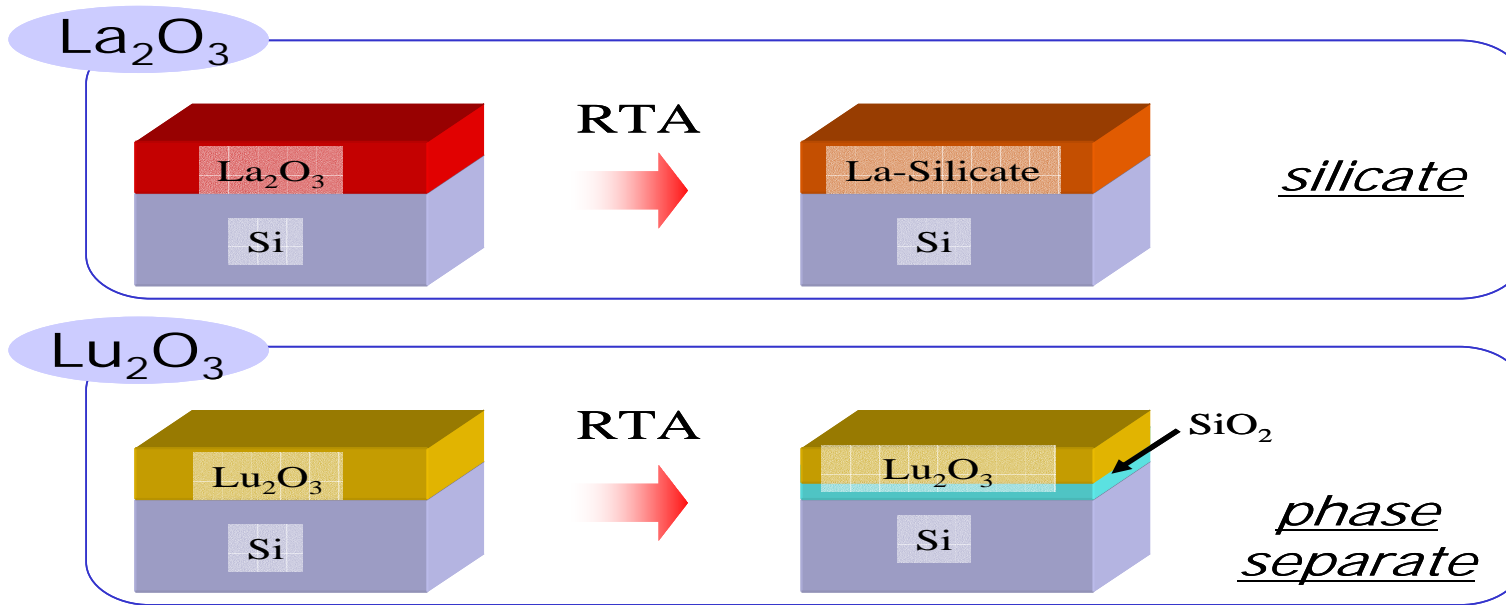
# Absorption test in case of acryl apparatus after the Al electrode formation for $\text{Pr}_2\text{O}_3$ .



C-V

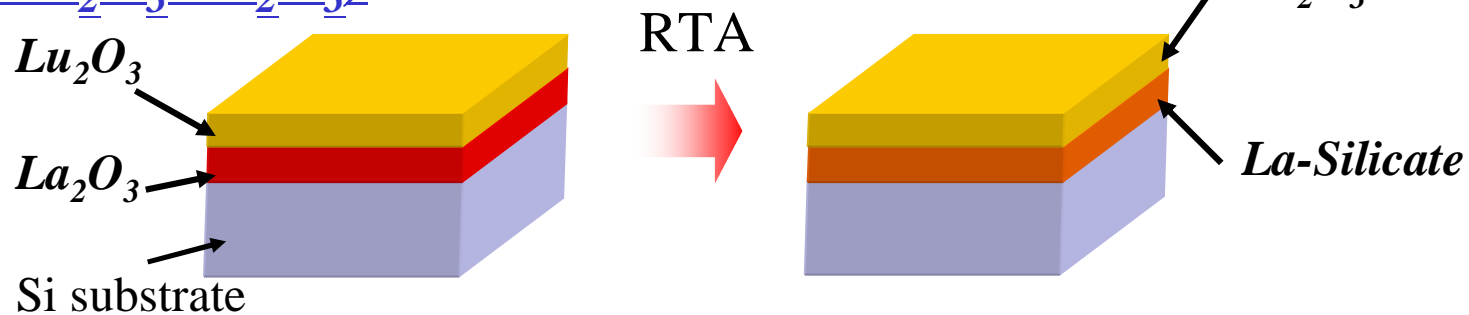


# 研究目的



Ref. S.Ohmi, et al., *J. Electrochem. Soc.*, 150, F134(2003)  
H.Nohira et al., *J. Appl. Surf. Sci.*, 216(2003)

## Stack(Lu<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub>)

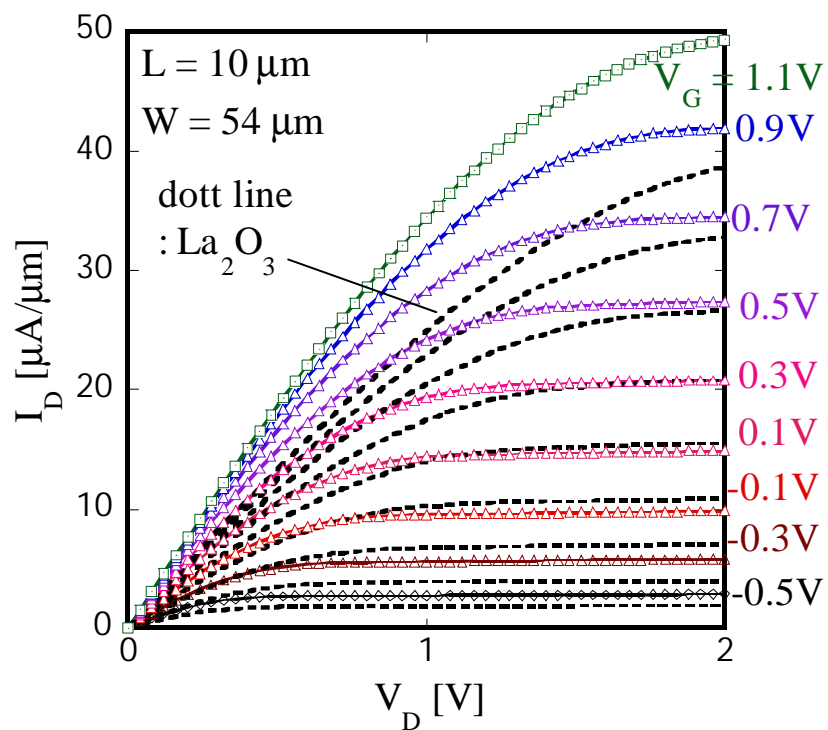


La<sub>2</sub>O<sub>3</sub>で界面層成長と微結晶化を抑える  
Lu<sub>2</sub>O<sub>3</sub>で膜全体silicateを抑え、耐湿性を向上 } 誘電率を保ちつつリーク電流を抑制

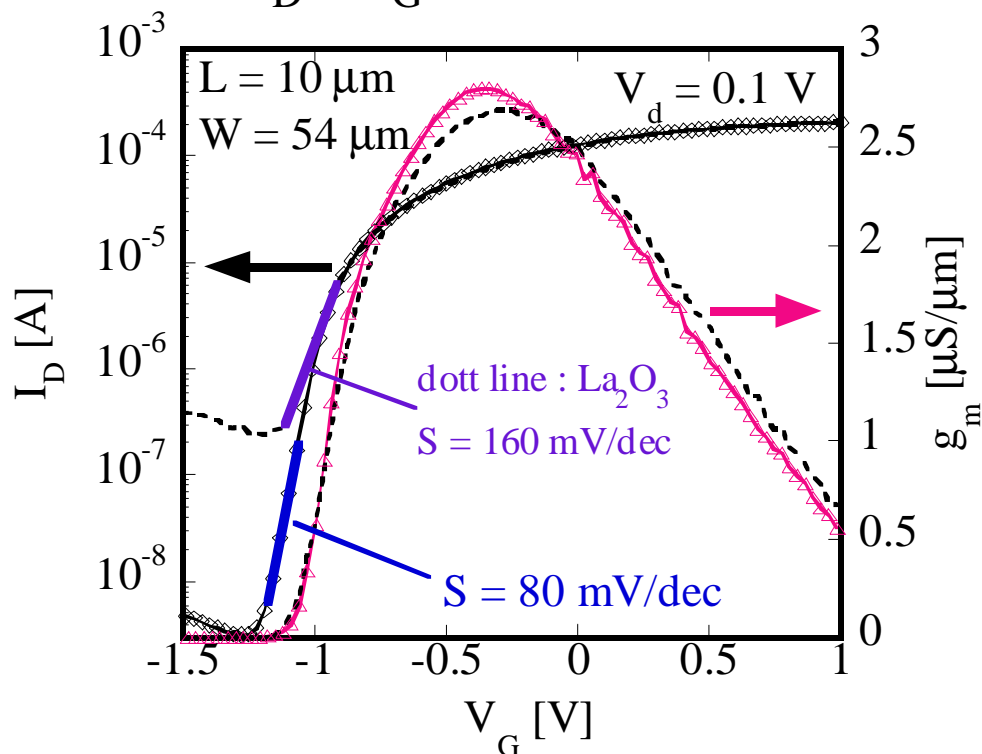
# 積層構造(Lu<sub>2</sub>O<sub>3</sub>/La<sub>2</sub>O<sub>3</sub>/n-Tr)の作製

nMIS 250°C堆積, annealed at 400°C, Al電極を使用

## I<sub>D</sub>-V<sub>D</sub> Characteristics

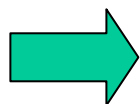


## I<sub>D</sub> - V<sub>G</sub> Characteristics



O<sub>2</sub>300→O<sub>2</sub>400でより改善がみられ、  
同条件のLa<sub>2</sub>O<sub>3</sub>と比較して、良好な特性が得られた

$\mu_{\text{eff}} = 163 [\text{cm}^2\text{V}^{-1}\text{s}^{-1}]$   
(EOT = 2.05 nm)



Lu<sub>2</sub>O<sub>3</sub>の耐湿性により、電気特性が改善した

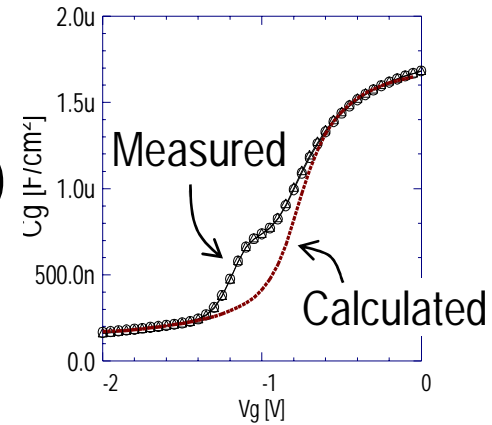
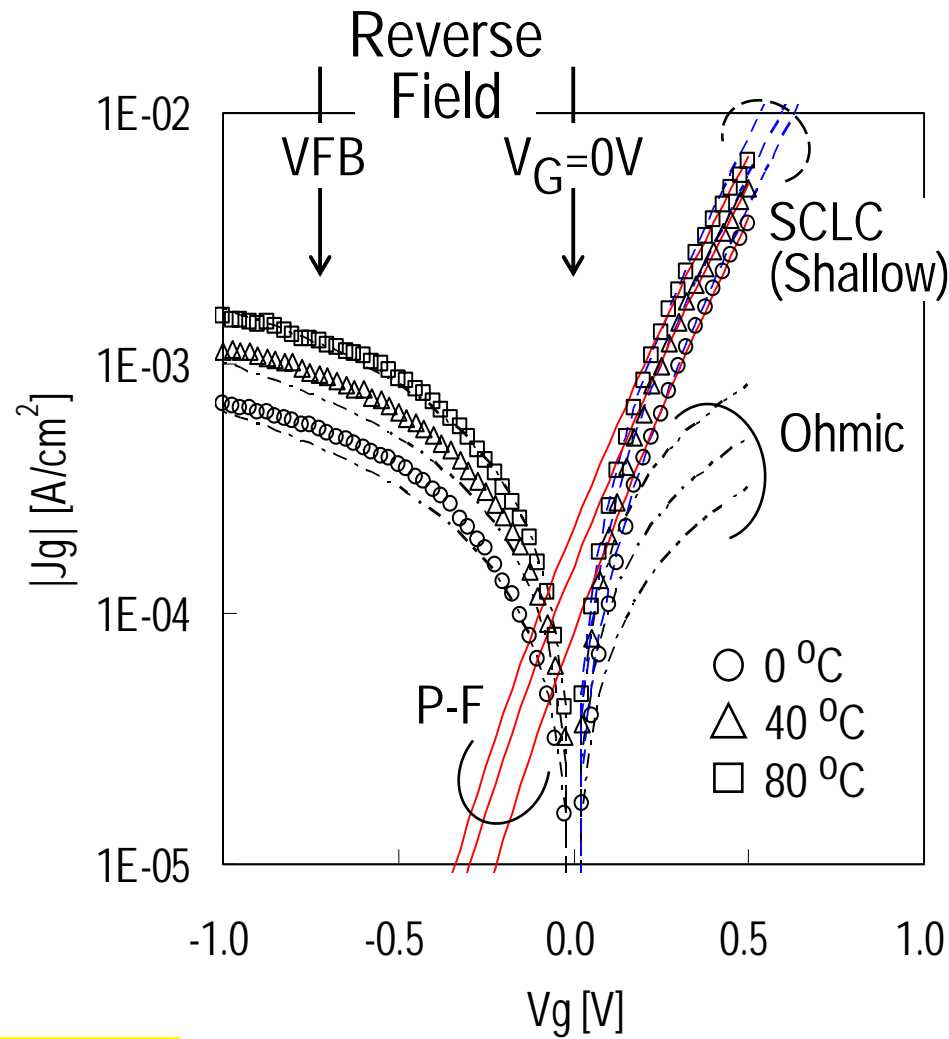
# Conduction Modes and Expressions

	Mode	Expression	
Bulk-Free	Schottky*	(1) $\ln(J) \propto E^{1/2}$	$\ln(J/T^2) \propto -1/T$
	DT**	(2) $\ln(J) \propto E$	$J \propto T^2$ ( <i>weak</i> )
	F-N	(3) $\ln(J/E^2) \propto 1/E$	
	Ohmic	(4) $J \propto E$	$\ln(J) \propto -1/T$
Bulk-Limited	Poole	(5) $\ln(J) \propto E$	$\ln(J) \propto -1/T$
	P-F	(6) $\ln(J/E) \propto E^{1/2}$	
	SCLC***	(7) $\ln(J/E) \propto E$	
		(8) $J \propto E^2$	

\*Thermionic Current, \*\*Direct Tunneling Current,

\*\*\*Space-Charge-Limited Current : single trap level for shallow (7) and deep (8) distribution

# Al Electrode Case – Leakage Current



Q.EOT 1.54 nm  
O.TOX 4.7nm  
RDC 11.9



# 超高真空アニール後の $\text{La}_2\text{O}_3$ 薄膜中のトラップ準位

