

High-k Gate Stack Technology Beyond 0.5 nm EOT

**IUMRS-ICM 2010, Symp. K-31
@Qindao International Convention Center,
Qindao, China**

September 28, 2009

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Cool Earth by integrated circuits

1.By controlling the system by microprocessor (Integrated Circuits) more efficiently, energy consumption of the system will be significantly reduced.

Every human system : transportation system, manufacturing, Office

2.Power saving of Integrated Circuits in IT network (Server, Data Center, Router)

Power of Transistor = $CV^2/2$

C: Capacitance of Tr D D : Size

V: Supply Voltage

To reduce the power, D and V should be reduced!

Scaling: Every 3 years; D and V reduces with 0.7 times

k= 0.7 in 3 years

MOFET

$$V_{dd} \rightarrow 0.7$$

$$L_g \rightarrow 0.7$$

$$I_d \rightarrow 0.7$$

$$C_g \rightarrow 0.7$$

$$P \text{ (Power)/Clock} \rightarrow 0.7^3 = 0.34$$

$$\tau \text{ (Switching time)} \rightarrow 0.7$$

k= 0.7² =0.5 in 6 years

MOFET

$$V_{dd} \rightarrow 0.5$$

$$L_g \rightarrow 0.5$$

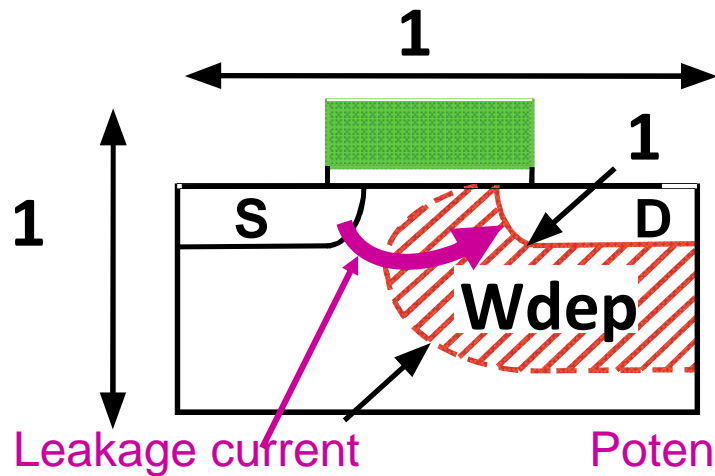
$$I_d \rightarrow 0.5$$

$$C_g \rightarrow 0.5$$

$$P \text{ (Power)/Clock} \rightarrow 0.5^3 = 0.125$$

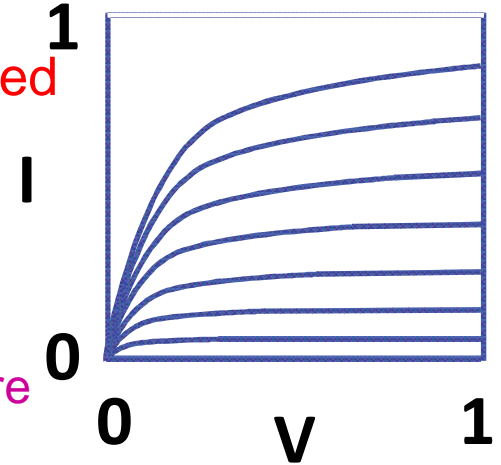
$$\tau \text{ (Switching time)} \rightarrow 0.5$$

Scaling Method: by R. Dennard in 1974



W_{dep} : Space Charge Region (or Depletion Region) Width

W_{dep} has to be suppressed
Otherwise, large leakage
between S and D



Potential in space charge region is high, and thus, electrons in source are attracted to the space charge region.

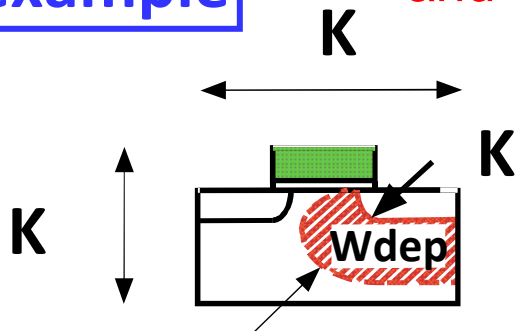
$K=0.7$
for
example



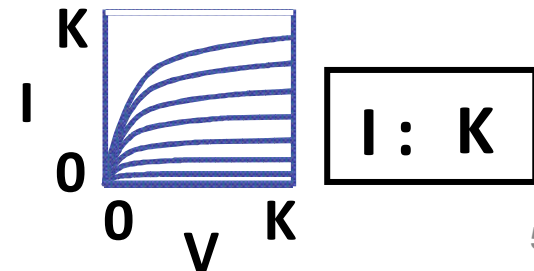
$X, Y, Z : K, \quad V : K, \quad N_a : 1/K$

By the scaling, W_{dep} is suppressed in proportion,
and thus, leakage can be suppressed.

→ Good scaled I-V characteristics



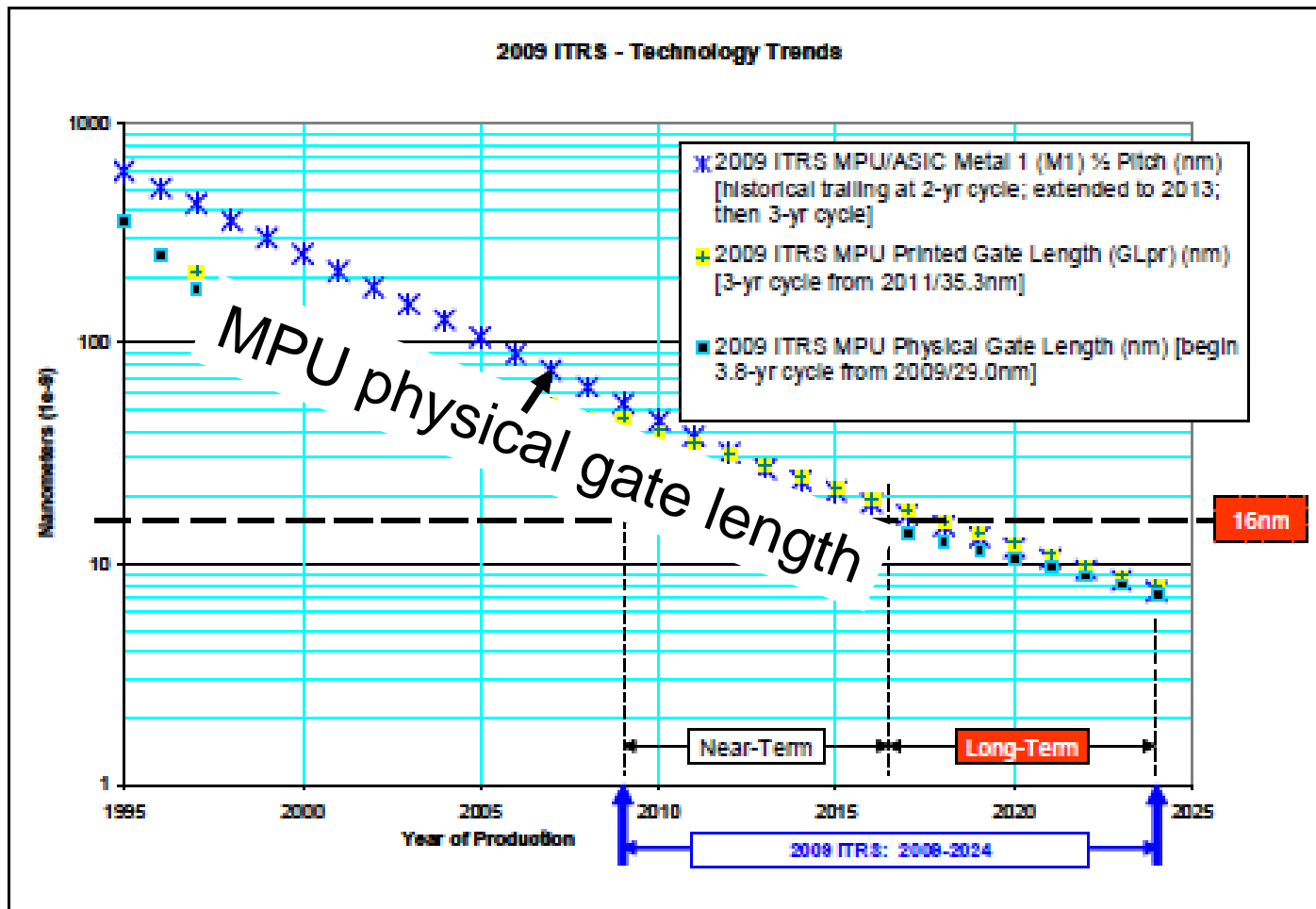
$W_{dep} \propto \sqrt{V/N_a}$
: K



ITRS expect Lg less than 10nm

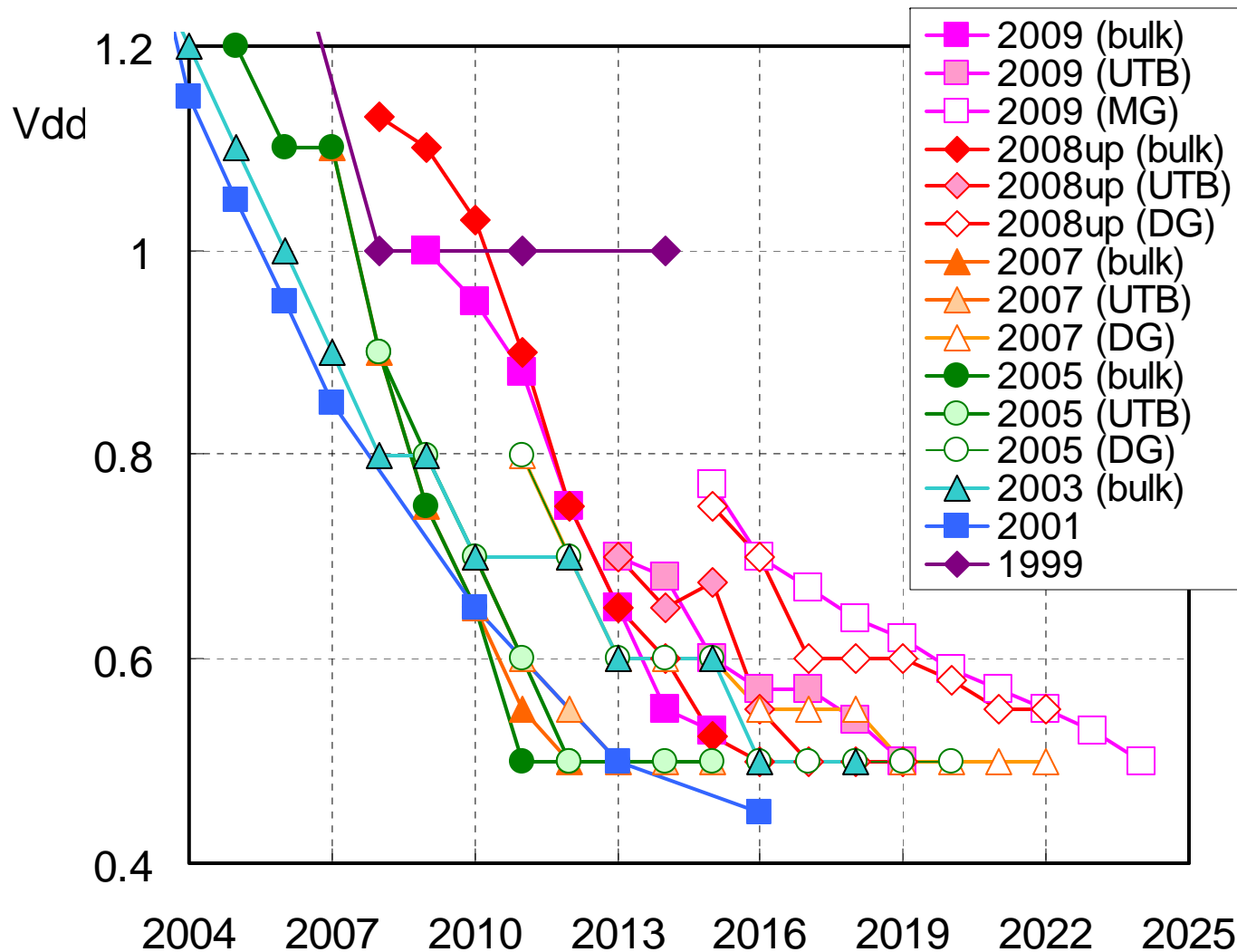
ITRS: International Technology Roadmap for Semiconductors

2009 ITRS Technology Trend: MPU gate length



However EOT stops at 0.5 nm in ITRS!

EOT (Equivalent oxide thickness of gate insulator)



How far can we go?

Past

0.7 times per 3 years In 40 years: 15 generations,
Size 1/200, Area 1/40,000

1973年



8 μm → 6 μm → 4 μm → 3 μm → 2 μm → 1.2 μm → 0.8 μm → 0.5 μm

→ 0.35 μm → 0.25 μm → 180nm → 130nm → 90nm → 65nm → 45nm

Now



Future

→ 32nm → 22nm → 16nm → 11.5 nm → 8nm → 5.5nm? → 4nm? → 2.9 nm?

- At least 5,6 generations, for 15 ~ 20 years
- Hopefully 8 generations, for 30 years

$k = 0.7$ and $\alpha = 1$

Single MOFET

$V_{dd} \rightarrow 0.7$

$L_g \rightarrow 0.7$

$I_d \rightarrow 0.7$

$C_g \rightarrow 0.7$

P (Power)/Clock

$\rightarrow 0.7^3 = 0.34$

τ (Switching time) $\rightarrow 0.7$

$k = 0.7^2 = 0.5$ and $\alpha = 1$

$V_{dd} \rightarrow 0.5$

$L_g \rightarrow 0.5$

$I_d \rightarrow 0.5$

$C_g \rightarrow 0.5$

P (Power)/Clock

$\rightarrow 0.5^3 = 0.125$

τ (Switching time) $\rightarrow 0.5$

Chip

N (# of Tr) $\rightarrow 1/0.7^2 = 2$

f (Clock) $\rightarrow 1/0.7 = 1.4$

P (Power) $\rightarrow 1$

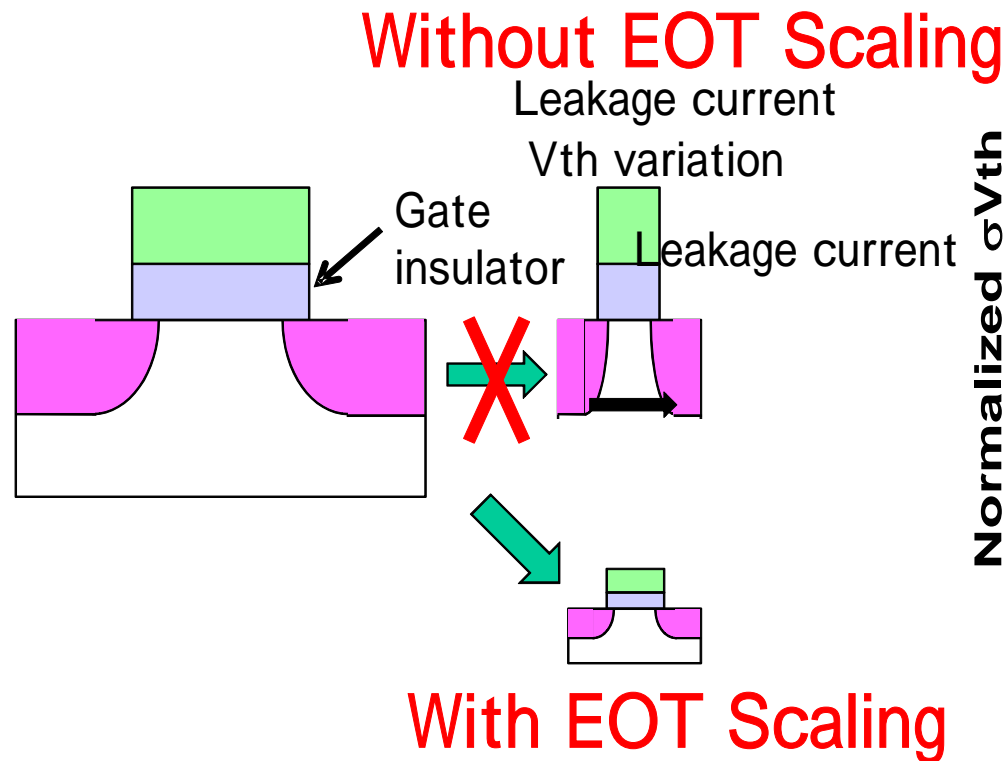
N (# of Tr) $\rightarrow 1/0.5^2 = 4$

f (Clock) $\rightarrow 1/0.5 = 2$

P (Power) $\rightarrow 1$

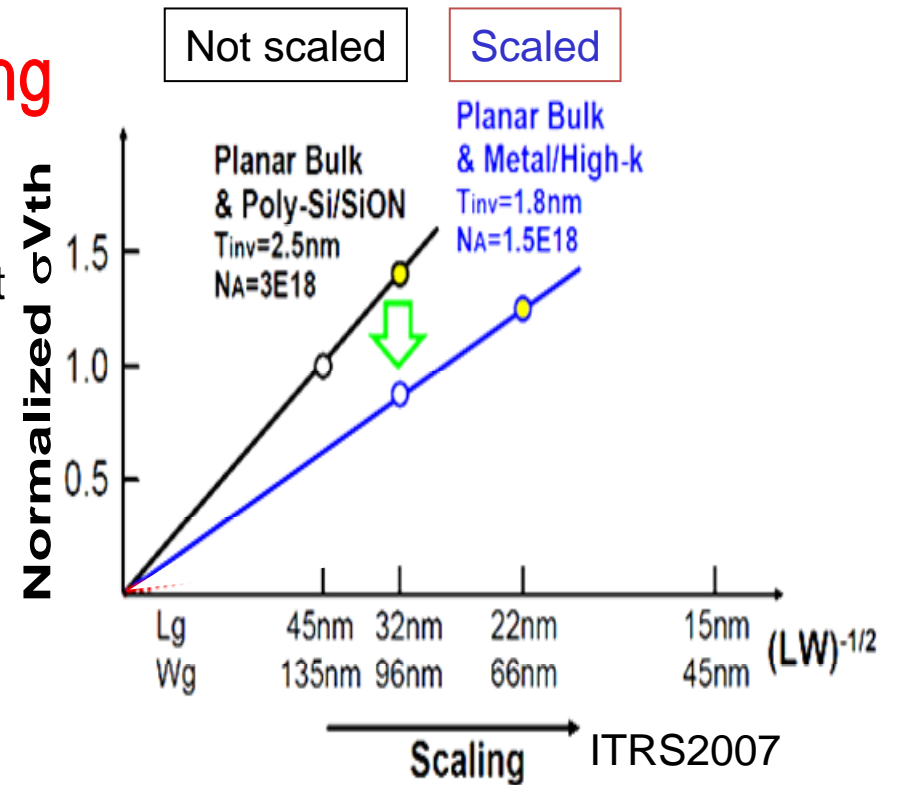
Without EOT scaling

→ Huge Off leakage and V_{th} variation



V_{th} variation

Gate insulator



Thus, EOT scaling beyond
0.5 nm is very important!

Choice of High-k

| Candidates | | Gas or liquid at 1000 K | | | | | | | | | | Radio active | | | | |
|--------------------------|---------|-------------------------|-------------------------------------|----|----|----|----|----|----|----|----|--------------|----|----|----|-----------------|
| Unstable at Si interface | | | | | | | | | | | | | | | | |
| H | | Si + MO _x | M + SiO ₂ | | | | | | | | | | | | | He |
| Li | Be | Si + MO _x | MSi _x + SiO ₂ | | | | | | | | | | | | | B C N O F Ne |
| Na | Mg | Si + MO _x | M + MSi _x O _y | | | | | | | | | | | | | Al Si P S Cl Ar |
| K | Ca Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rh | Sr Y Zr | Nb | Mo | Tc | Ru | Rb | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| Cs | Ba | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | 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 |

HfO₂ based dielectrics are selected as the first generation materials, because of their merit in

- 1) band-offset,
- 2) dielectric constant
- 3) thermal stability

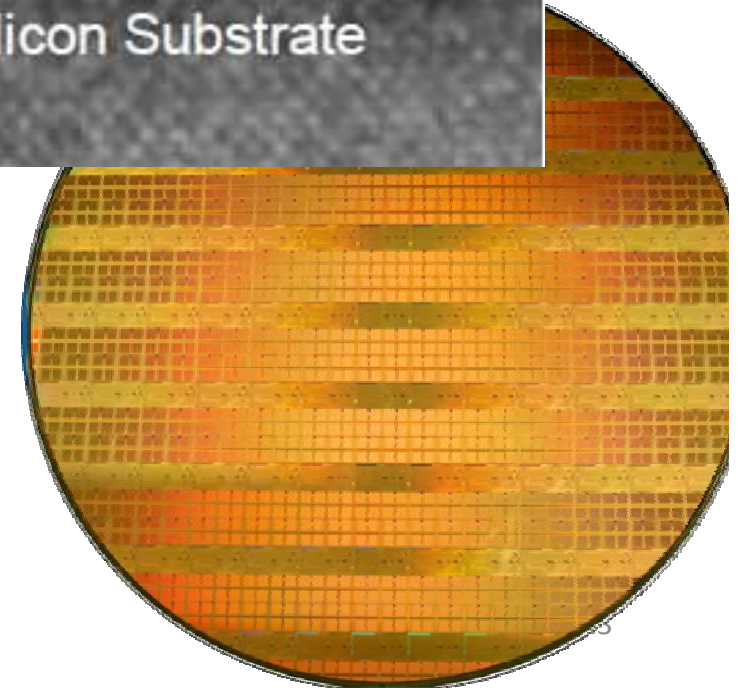
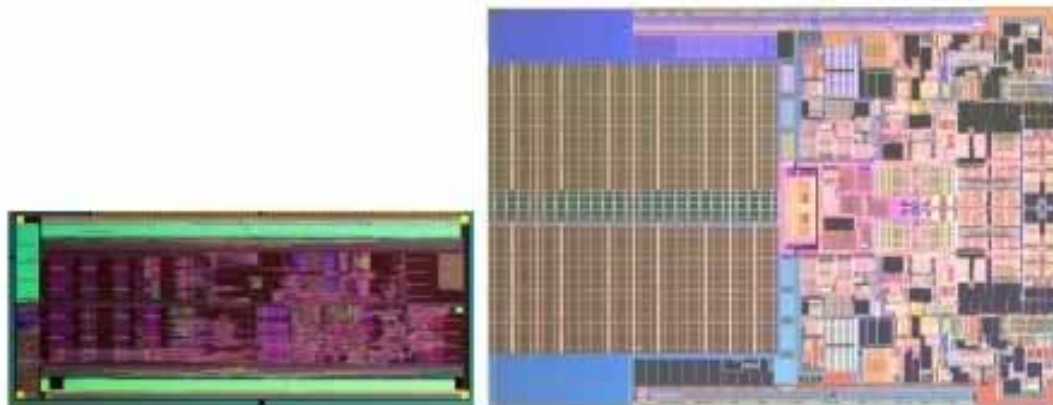
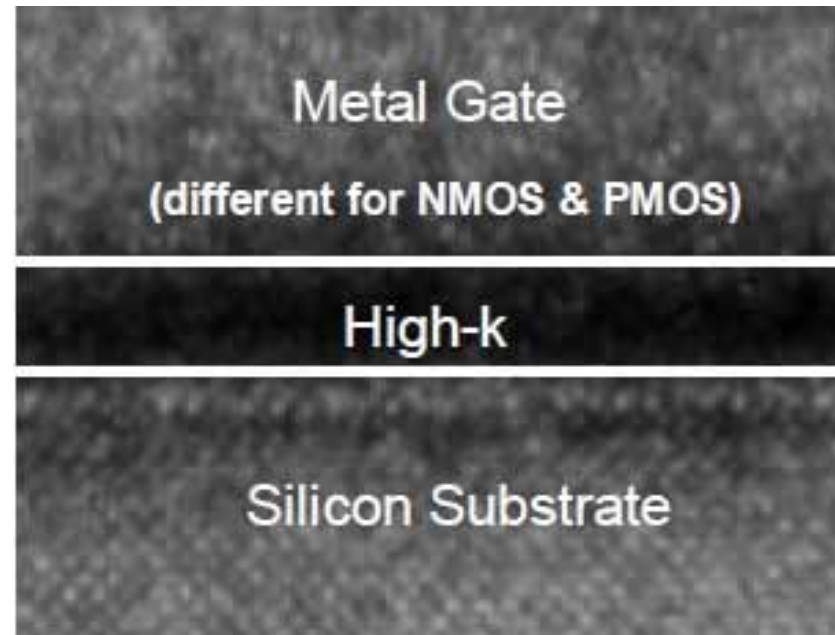
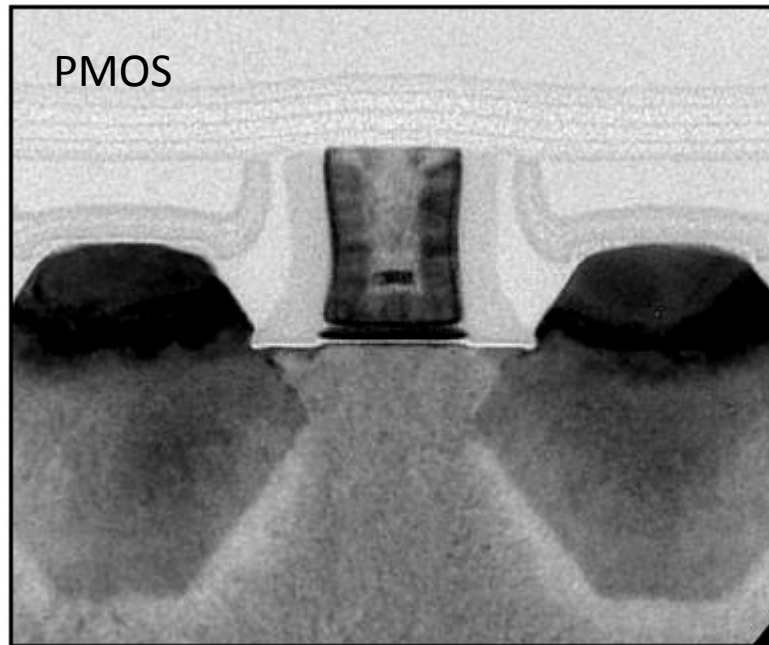
La₂O₃ based dielectrics are thought to be the next generation materials, which may not need a thicker interfacial layer

R. Hauser, IEDM Short Course, 1999

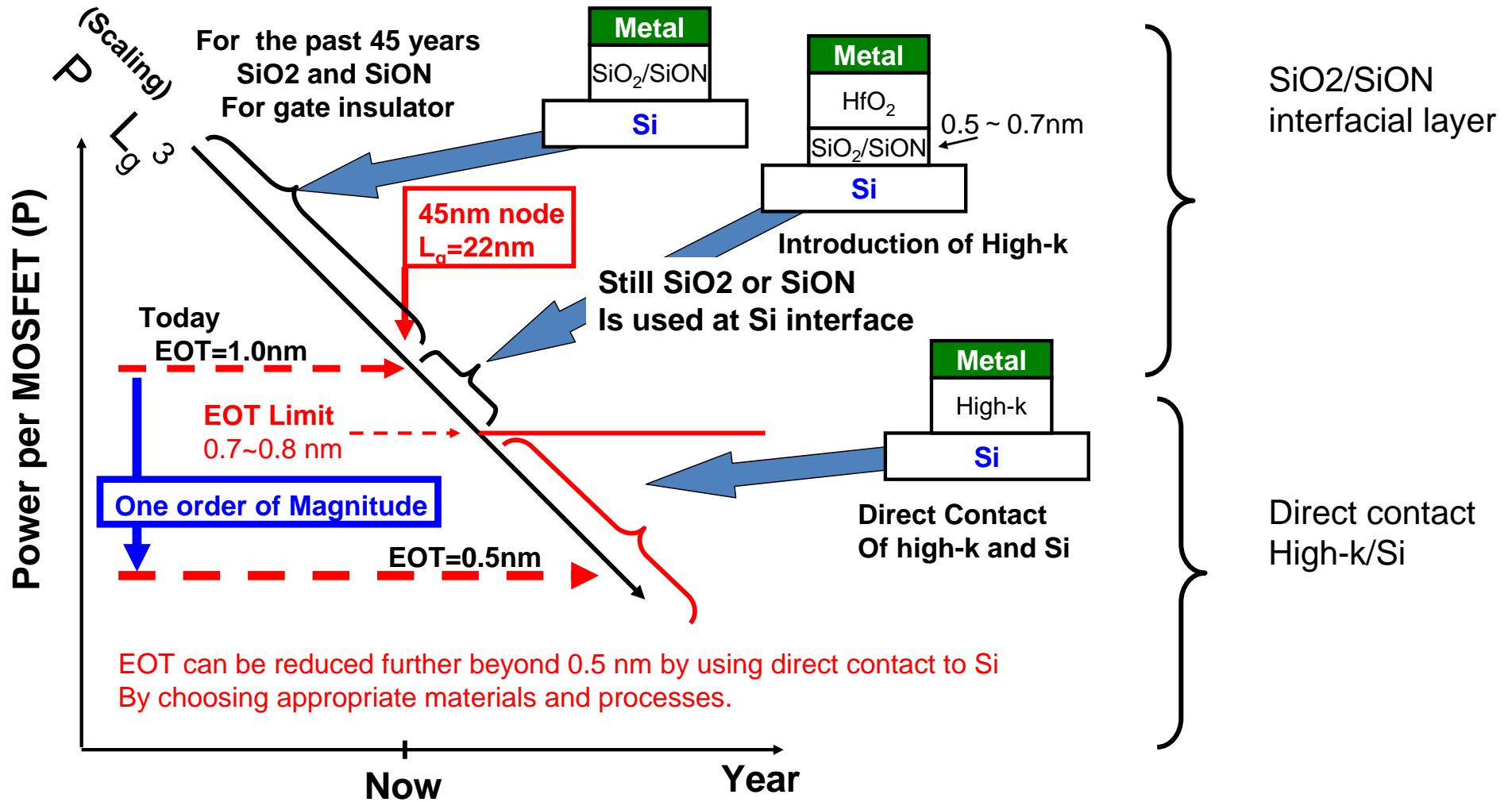
Hubbard and Schlom, J Mater Res 11 2757 (1996) ¹²

High-k gate insulator MOSFETs for Intel: EOT=1nm

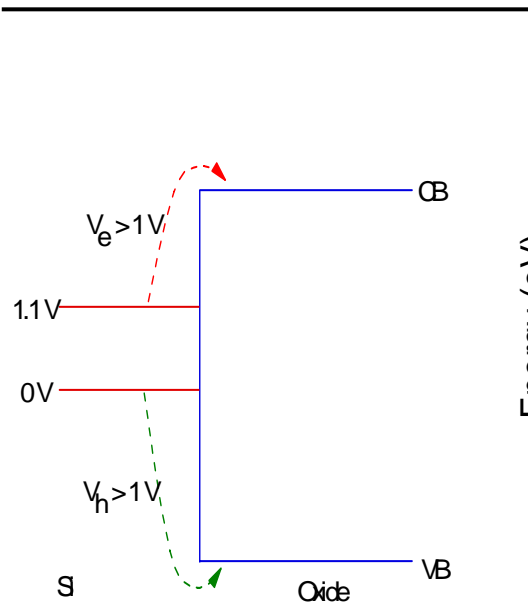
EOT: Equivalent Oxide Thickness



Direct contact technology of high-k to Si



Band Offsets



Dielectric constant₆

SiO₂; 4

Si₃N₄: ~ 7

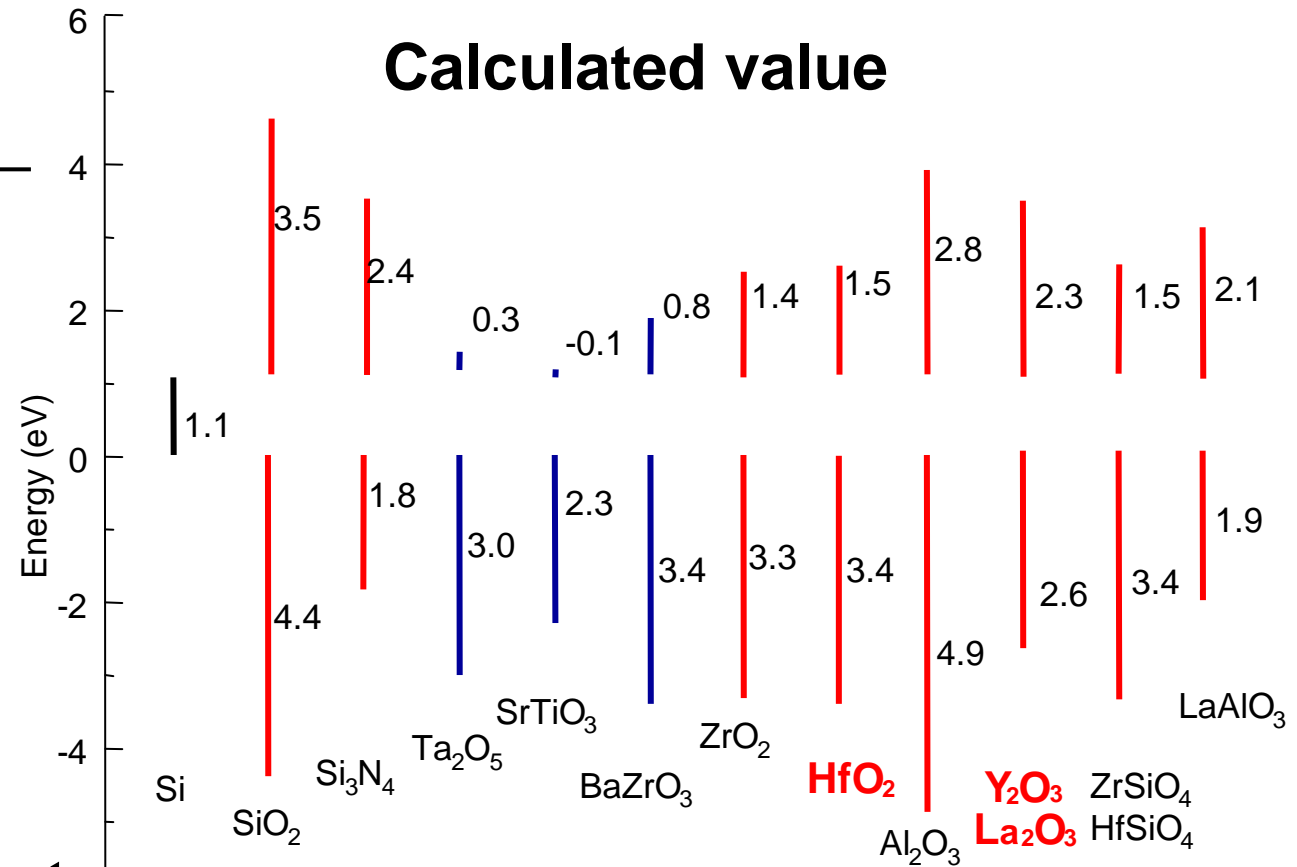
Al₂O₃: ~ 9

Y₂O₃; ~10

Gd₂O₃: ~10

HfO₂; ~23

La₂O₃: ~27



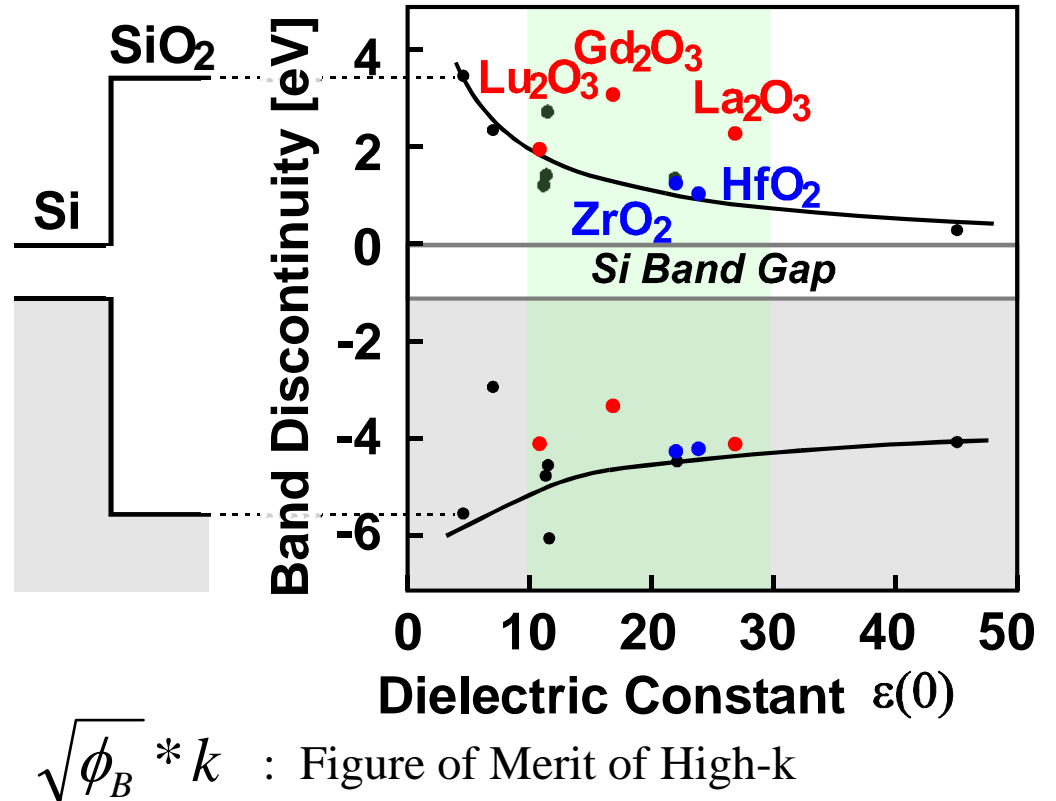
J Robertson, J Vac Sci Technol B 18 1785 (2000)

HfO₂ was chosen for the 1st generation

La₂O₃ is more difficult material to treat

Dielectric constant value vs. Band offset (Measured)

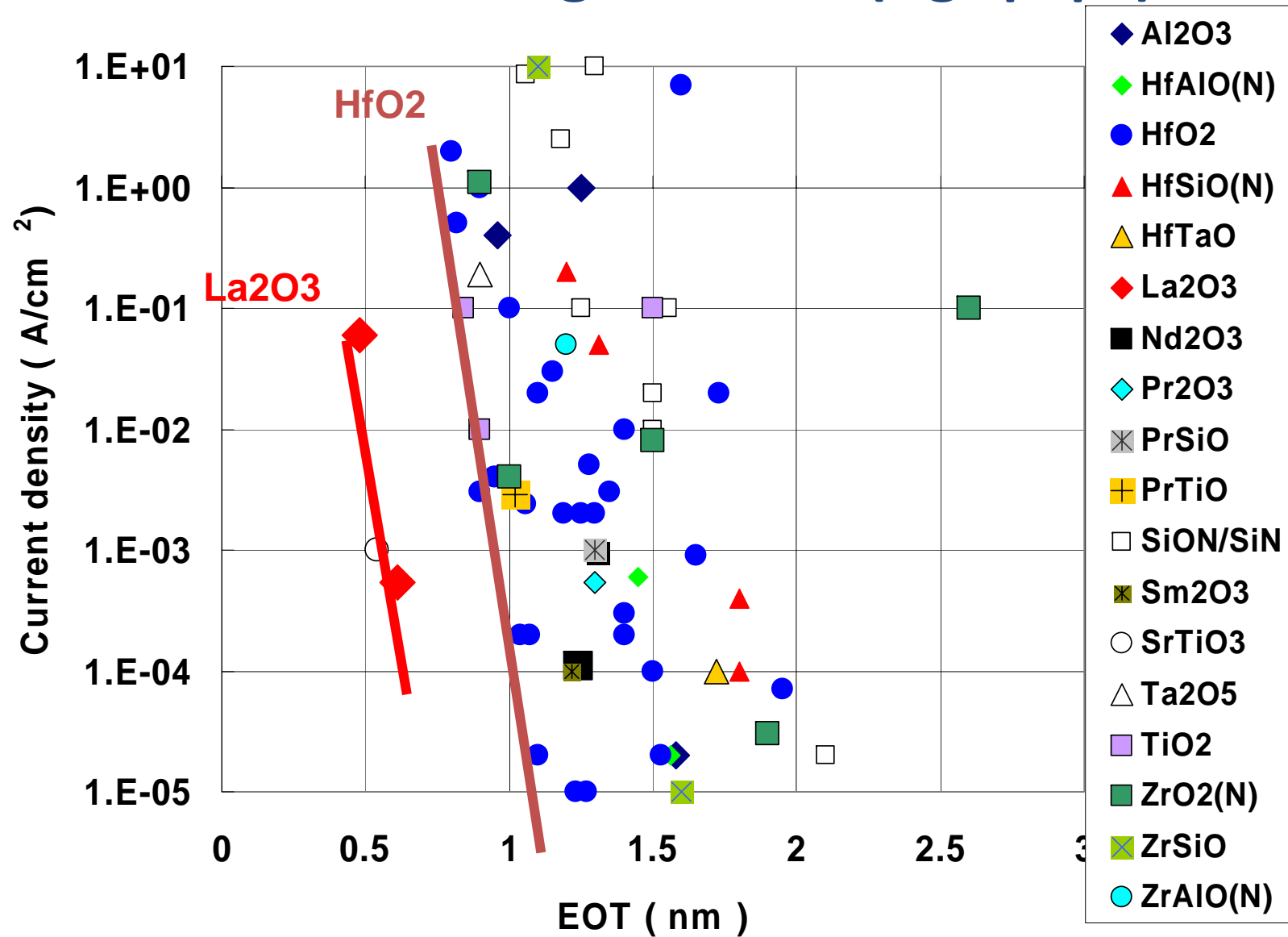
| | | | |
|--|----------|--|---------|
| SiO ₂ | 3.9 | NdAlO ₃ | 22.5 |
| Al _x Si _y O _z | | PrAlO ₃ | 25 |
| (Ba,Sr)TiO ₃ | 200-300 | Si ₃ N ₄ | 7 |
| BeAl ₂ O ₄ | 8.3-9.43 | SmAlO ₃ | 19 |
| CeO ₂ | 16.6-26 | SrTiO ₃ | 150-250 |
| CeHfO ₄ | 10-20 | Ta ₂ O ₅ | 25-24 |
| CoTiO ₃ /Si ₃ N ₄ | | Ta ₂ O ₅ -TiO ₂ | |
| EuAlO ₃ | 22.5 | TiO ₂ | 86-95 |
| HfO ₂ | 26-30 | TiO ₂ /Si ₃ N ₄ | |
| Hf silicate | 11 | Y ₂ O ₃ | 8-11.6 |
| La ₂ O ₃ | 20.8 | Y _x Si _y O _z | |
| LaScO ₃ | 30 | ZrO ₂ | 22.2-28 |
| La ₂ SiO ₅ | | Zr-Al-O | |
| MgAl ₂ O ₄ | | Zr silicate | |
| | | (Zr,Sn)TiO ₄ | 40-60 |



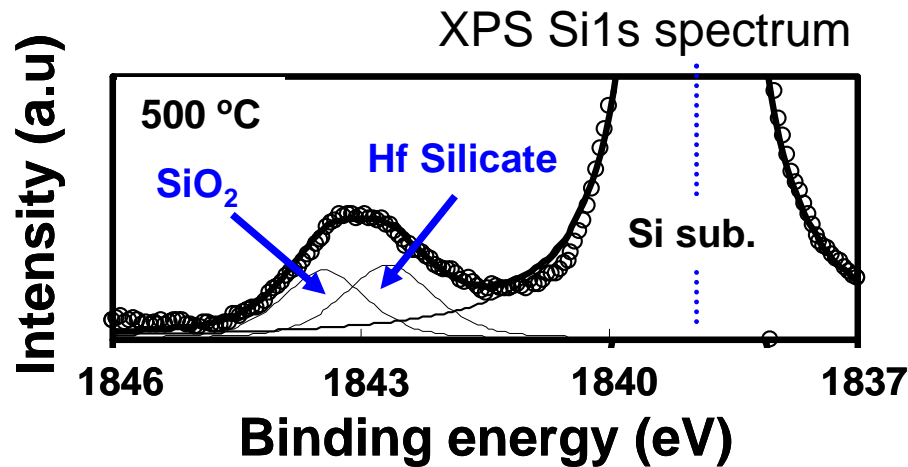
C.A. Billmann et al., MRS Spring Symp., 1999,
 R.D.Shannon, J. Appl. Phys., 73, 348, 1993
 S. De Gebdt, IEDM Short Course, 2004

T. Hattori, INFOS , 2003

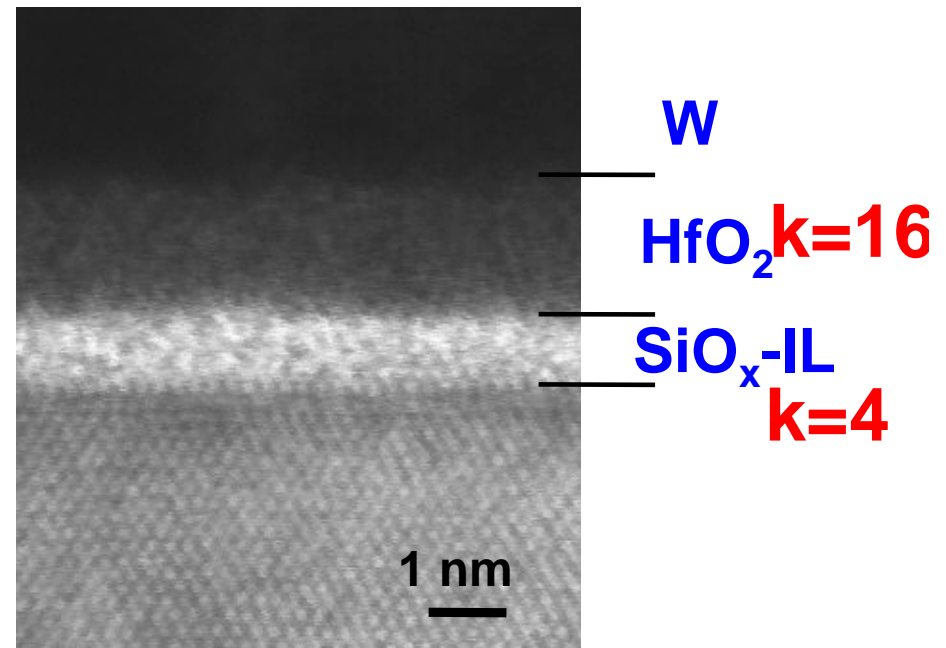
Gate Leakage vs EOT, ($V_g = |1|V$)



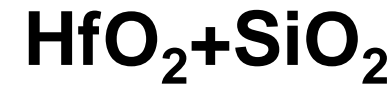
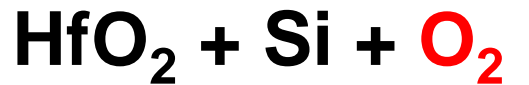
SiO_x-IL growth at HfO₂/Si Interface



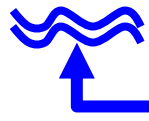
TEM image 500 °C 30min



Phase separator



H. Shimizu, JJAP, 44, pp. 6131



Oxygen supplied from W gate electrode

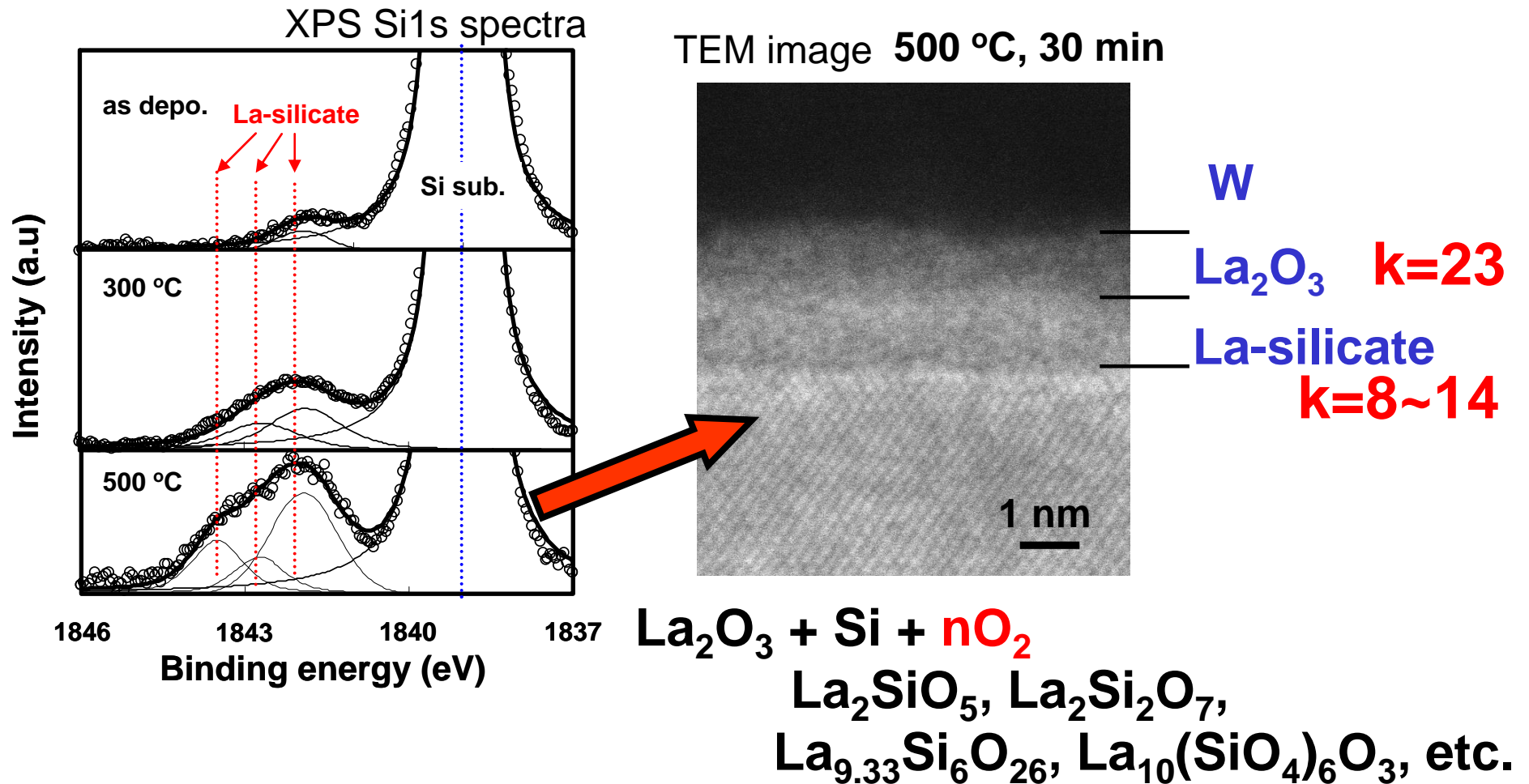
D.J.Lichtenwalner, Tans. ECS 11, 319

SiO_x-IL is formed after annealing

Oxygen control is required for optimizing the reaction

La-Silicate Reaction at $\text{La}_2\text{O}_3/\text{Si}$

Direct contact high-k/Si is possible

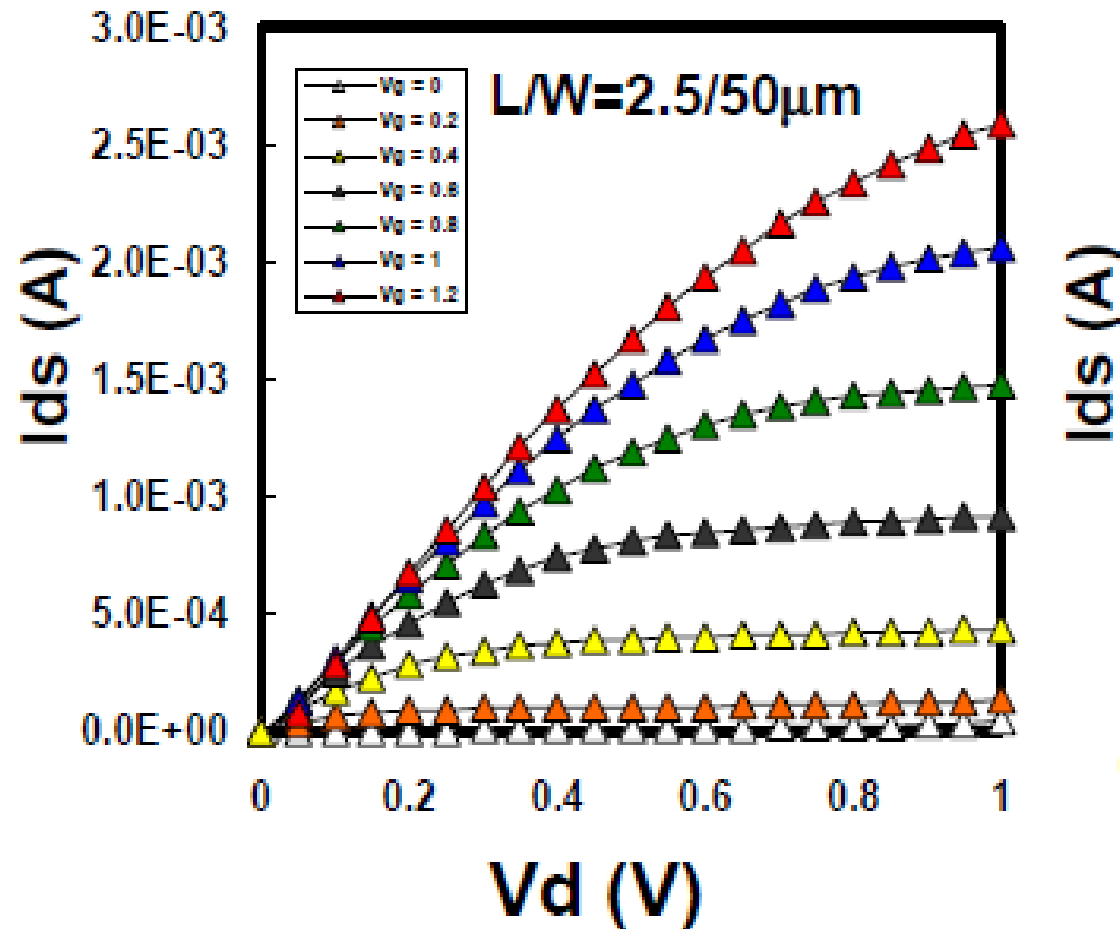


La_2O_3 can achieve direct contact of high-k/Si

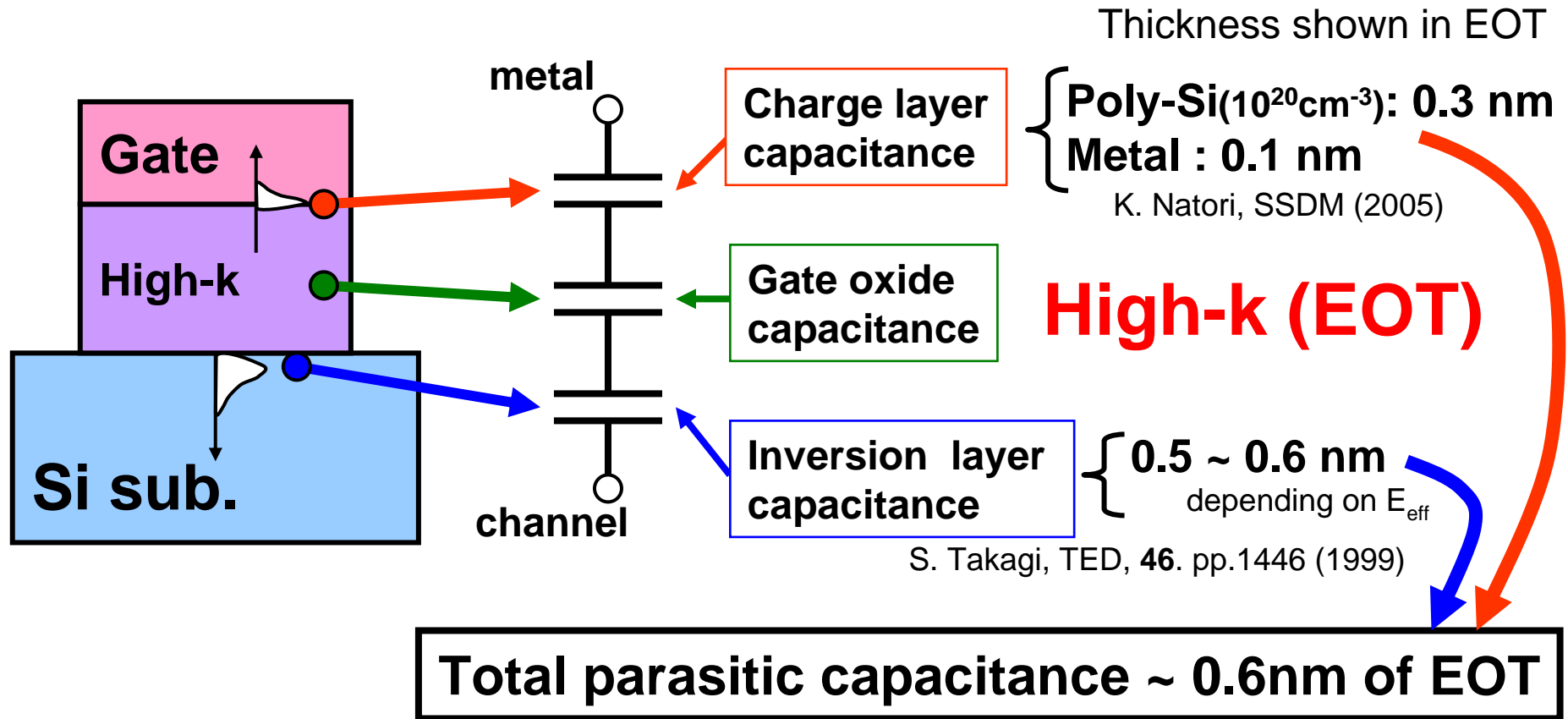
EOT = 0.48 nm

Our results

Transistor with La₂O₃ gate insulator

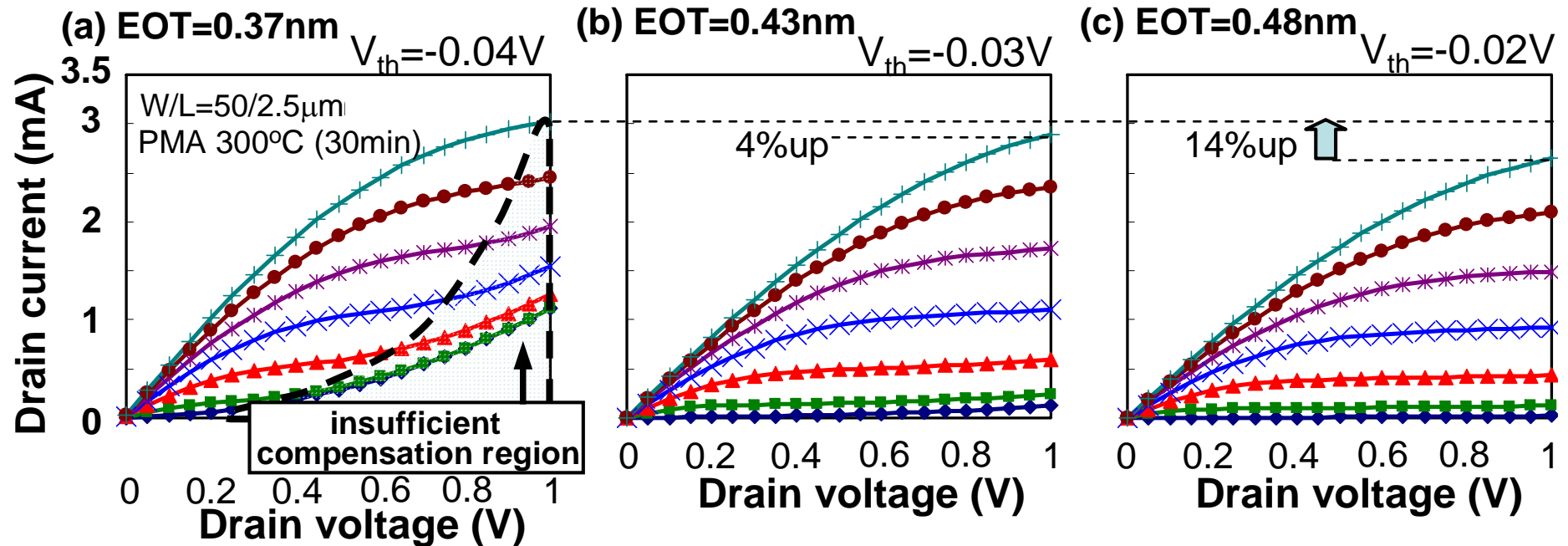


Quantum Effect in Gate Stack

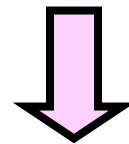


- A question if the performance improvement can be obtained with $EOT < 0.5\text{nm}$
- Is $EOT < 0.5\text{nm}$ achievable?

EOT < 0.5nm with Gain in Drive Current



14% of I_d increase is observed even at saturation region

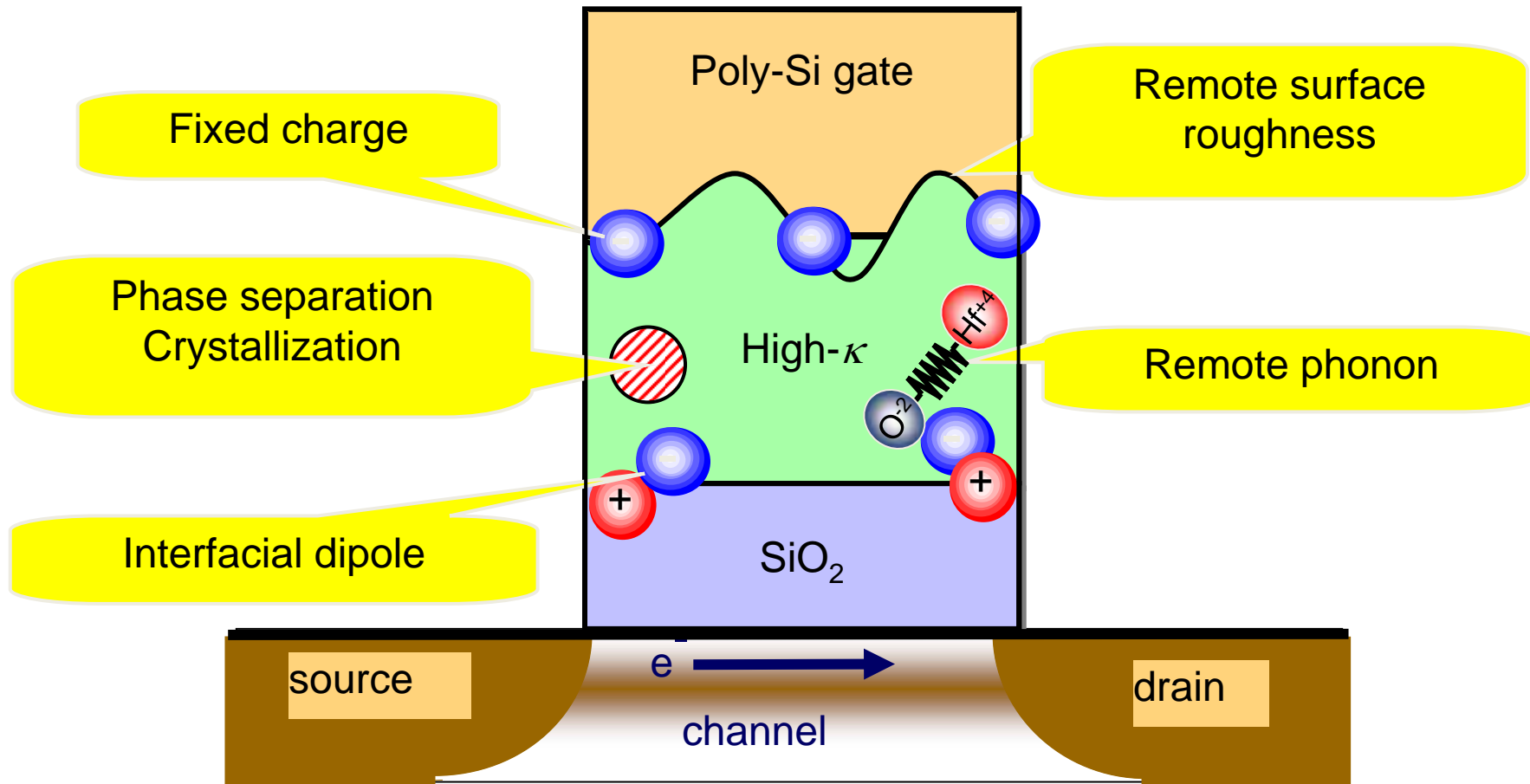


EOT below 0.4nm is still useful for scaling

Mobility concerns

Mobility degradation causes for High-k MOSFETs (HfO_2 , Al_2O_3 based oxide)

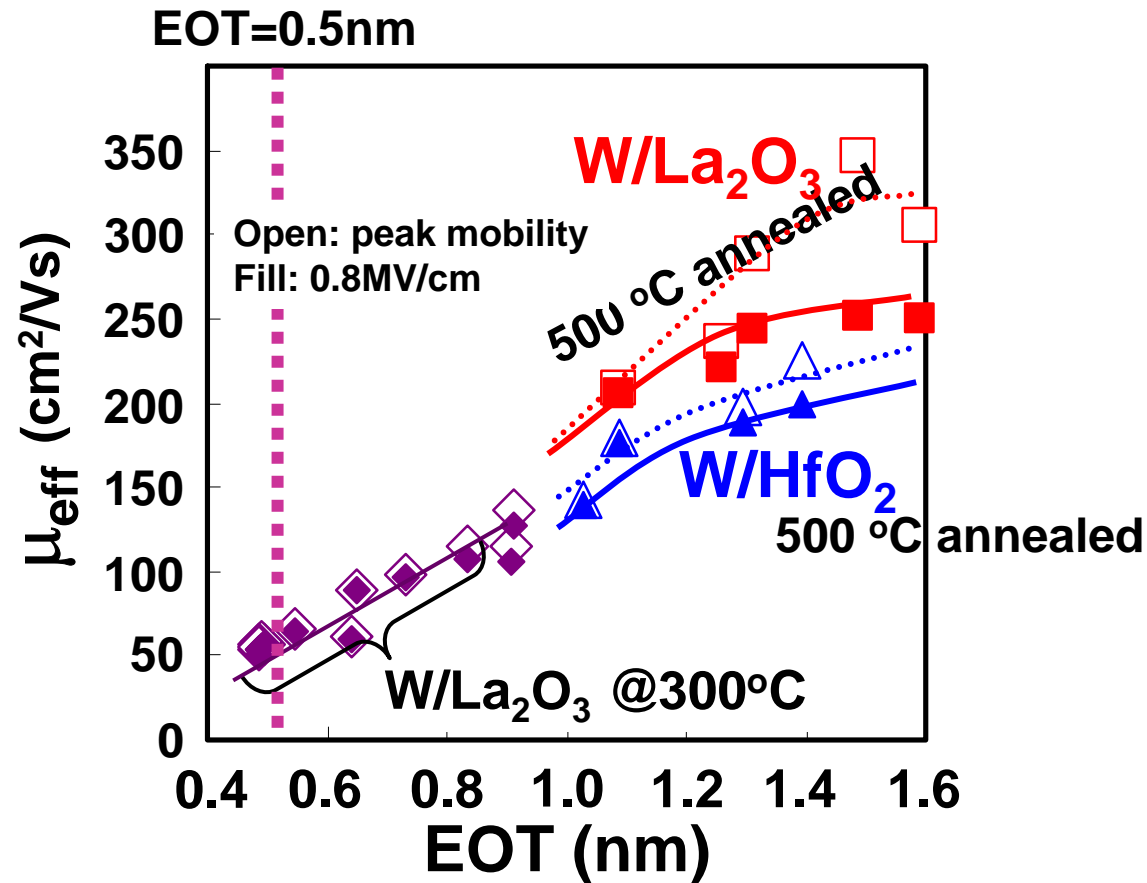
Remote scattering is dominant



S. Saito et al., IEDM 2003,

S. Saito et al., ECS Symp. on ULSI Process Integration

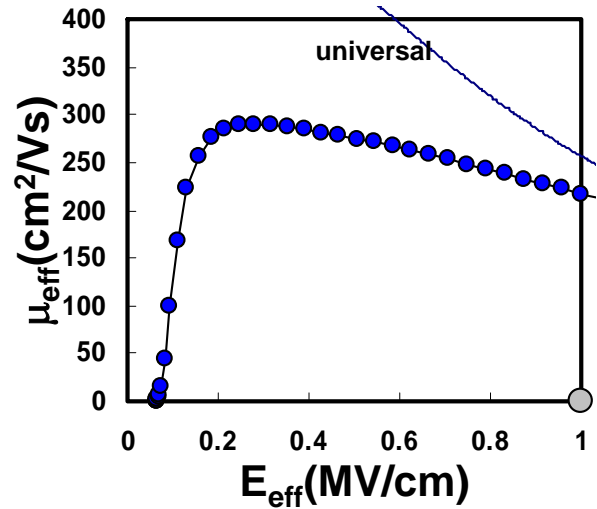
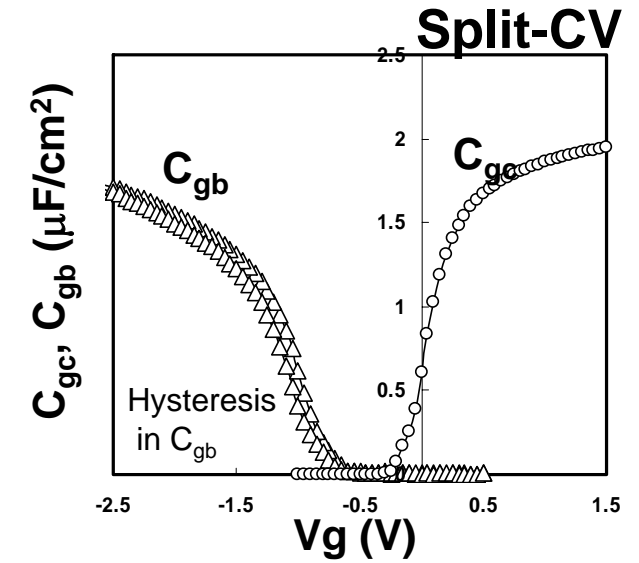
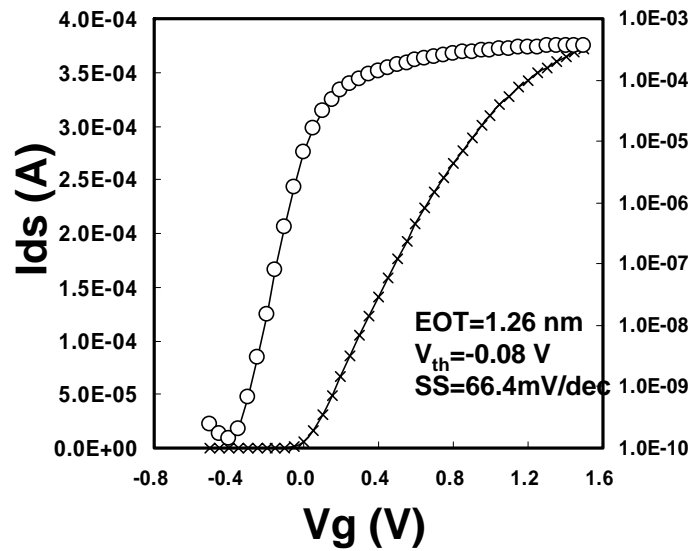
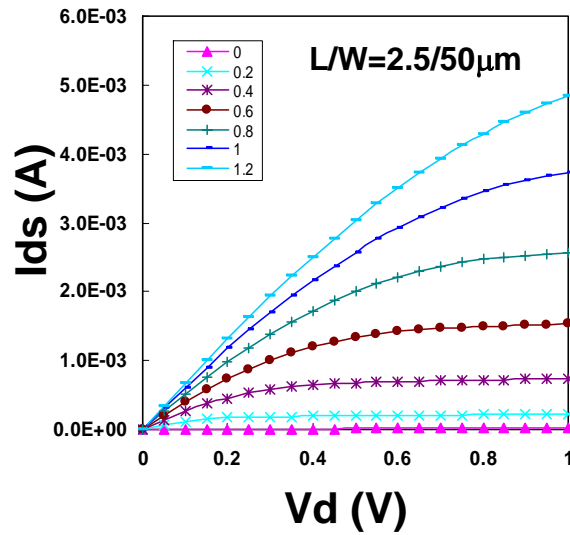
μ_{eff} of W/La₂O₃ and W/HfO₂ nFET on EOT



- W/La₂O₃ exhibits higher μ_{eff} than W/HfO₂
- μ_{eff} start degrades below EOT=1.4nm

Electrical characteristics of W/La₂O₃ nFET annealed at 500 °C

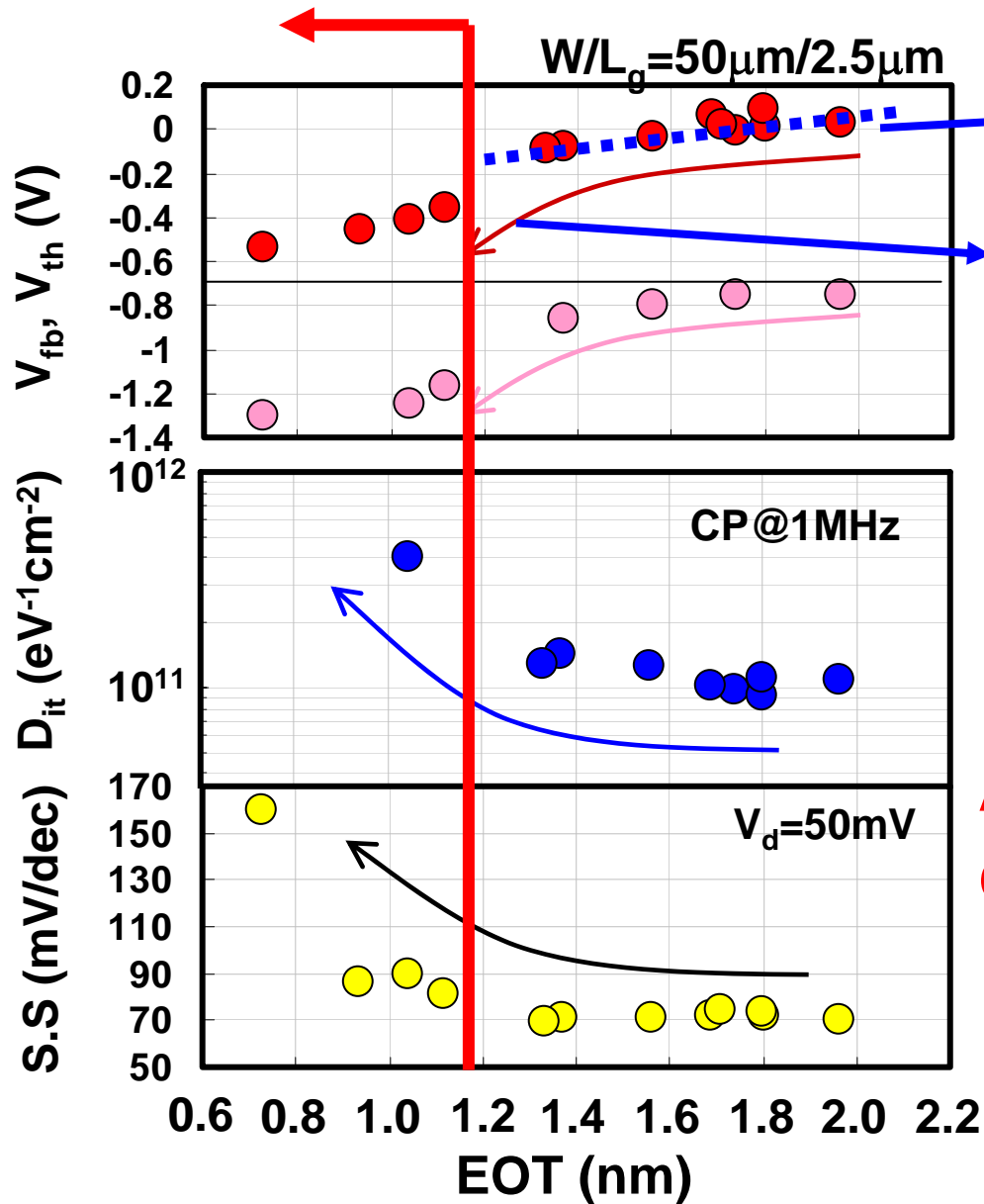
W/La₂O₃/nFET, 500°C anneal



Improvement in electrical characteristics
 SS=66mV/dec, µ_{eff}=300cm²/Vs

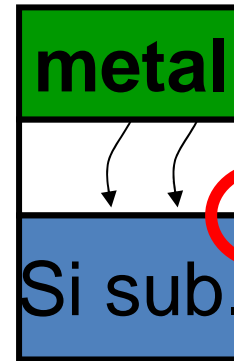
However, EOT grows from 0.5 to 1.3nm!

FET characteristics of W/La₂O₃ on EOT



$N_{fix} = 7 \times 10^{12} \text{ cm}^{-2}$

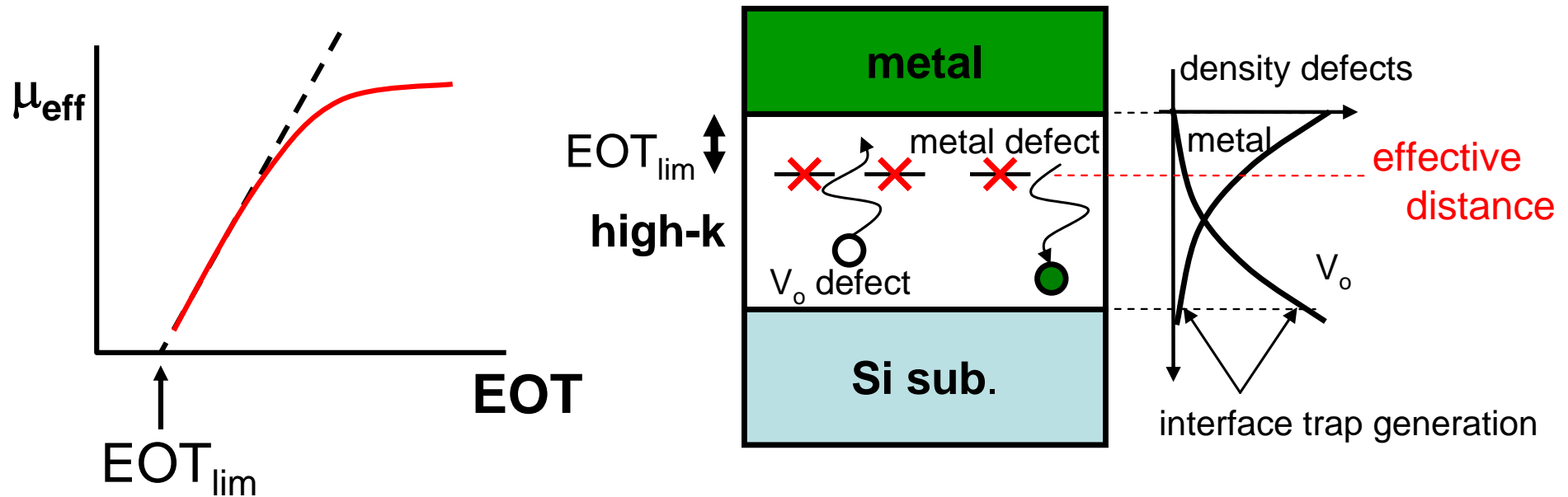
Aggressive N_{fix} generation
at EOT < 1.2 nm



N_{fix} and D_{it}

All characteristics start to
degrade or shift below
EOT = 1.4 nm

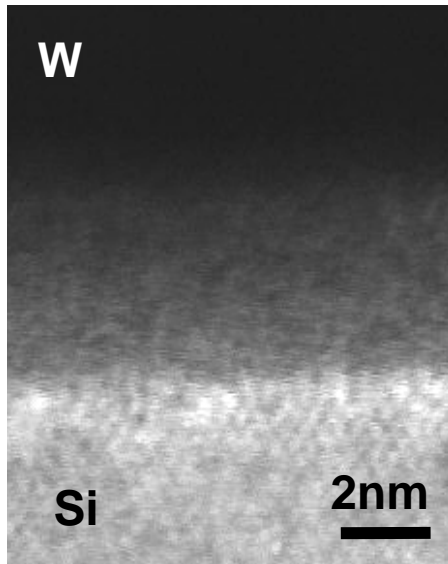
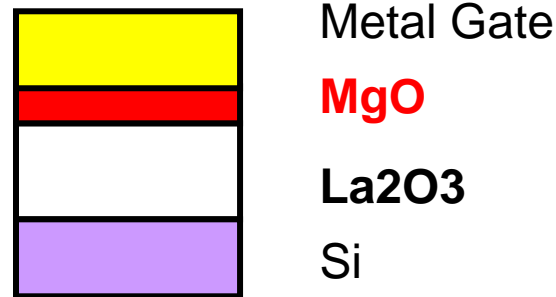
Schematic illustration of μ_{eff} reduction at small EOT



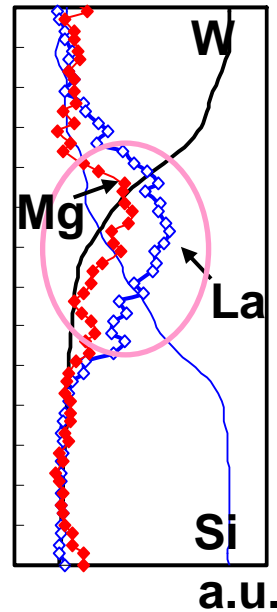
Spatial distribution of metal gate induced defects approaches to high-k/Si interface with small EOT

Some of the defects generates interfacial states

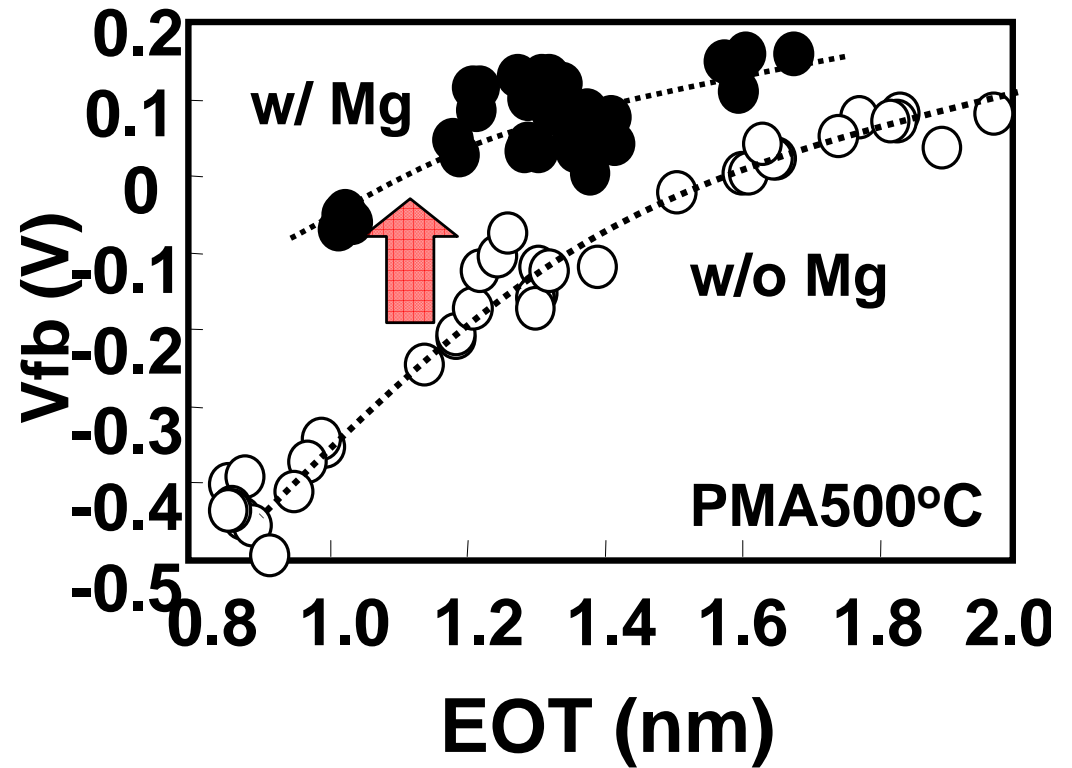
Gate Metal Induced Defects Compensation



TEM

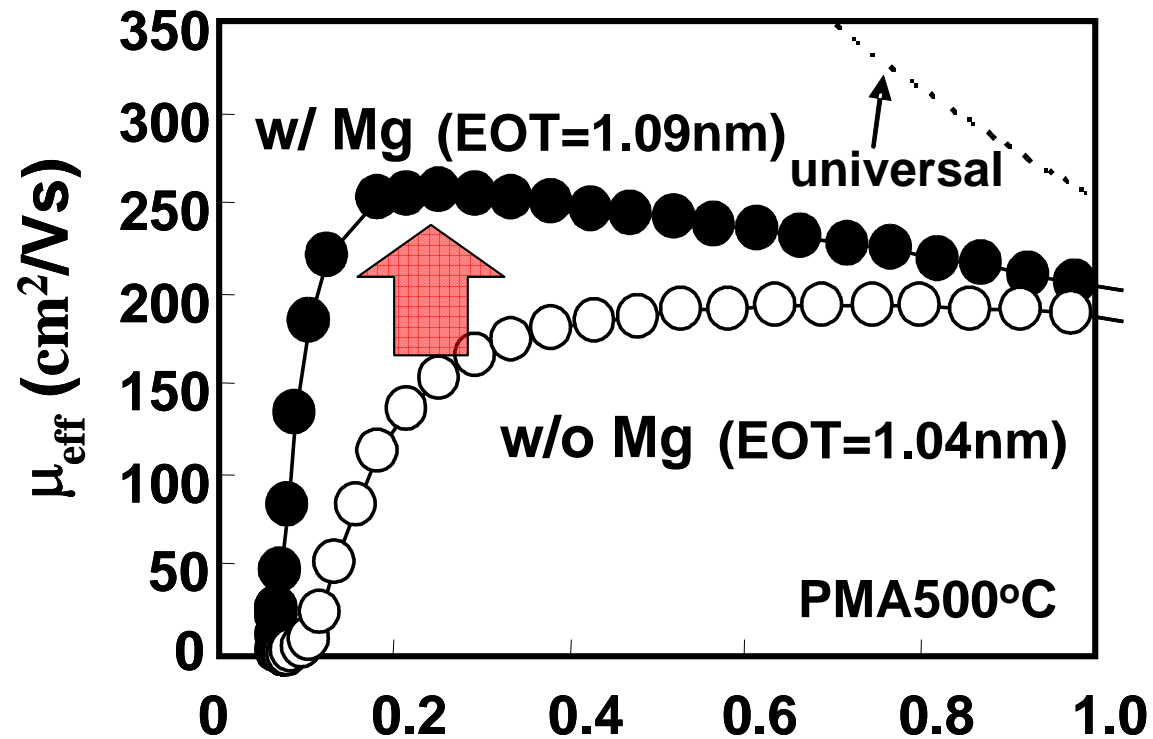


EDX



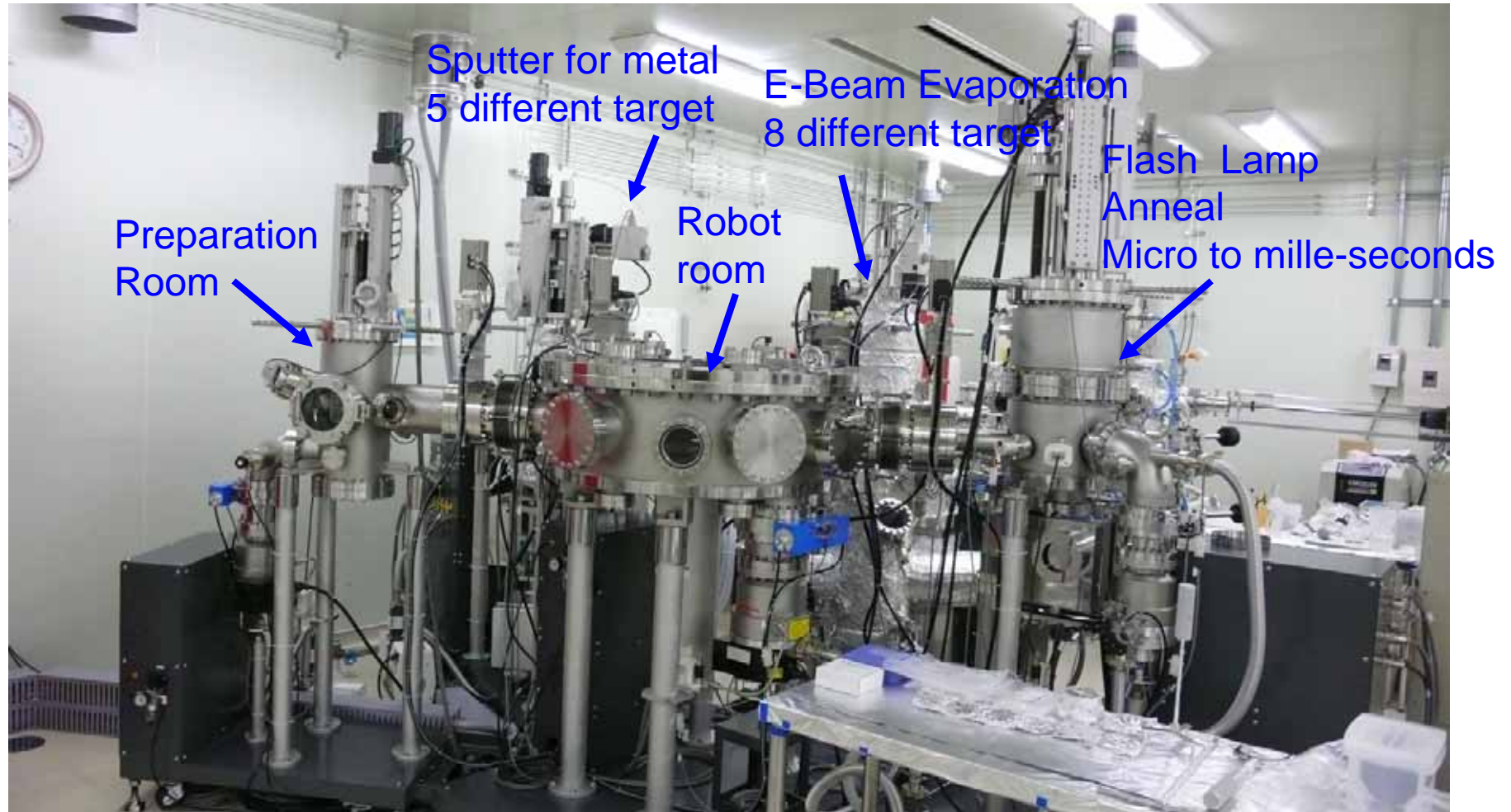
Suppression of aggressive shift in V_{fb}

Mobility Improvement with Mg Incorporation



Recovery of μ_{eff} mainly at low E_{eff}

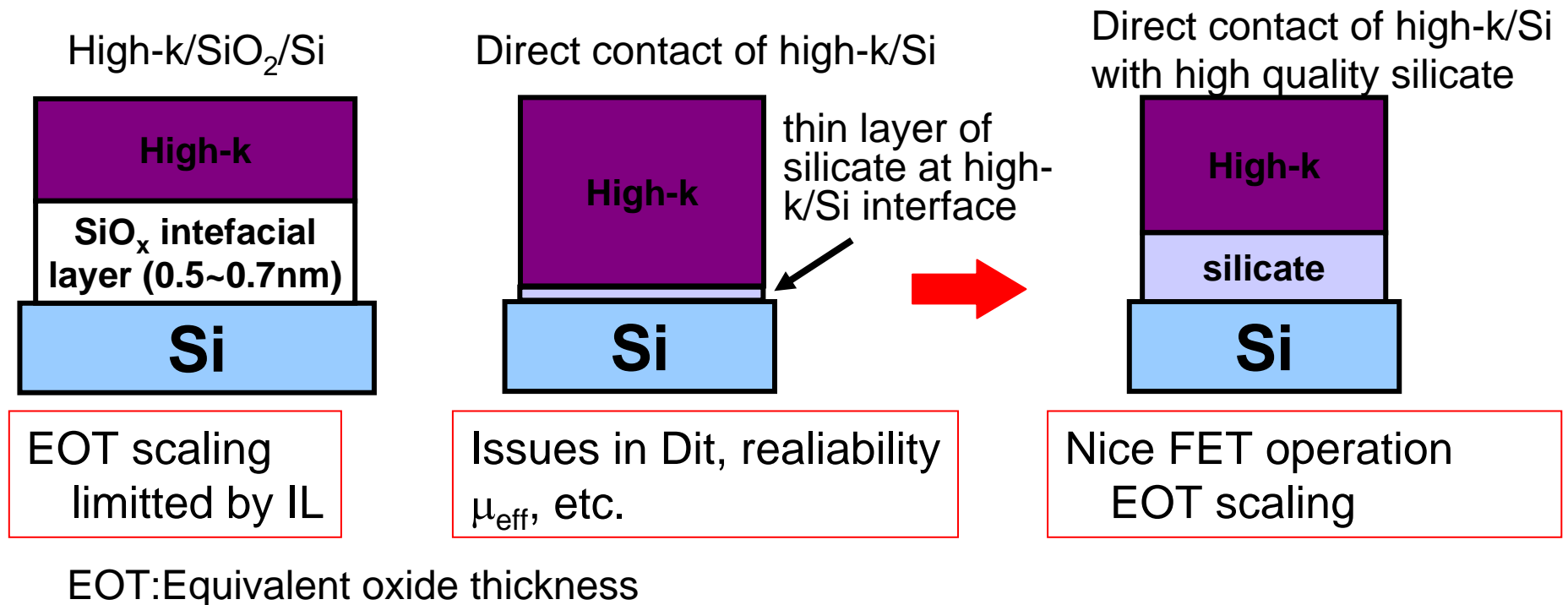
Cluster tool for high-k thin film deposition



Recent/Current Research Items in my group For High-k gate dielectrics

- (1) FET operation with EOT<0.5nm
- (2) High μ_{eff} with direct contact of La-silicate/Si
- (3) Origin of degradations at EOT<1.3nm
- (4) Modeling of defects in dielectrics
- (5) μ_{eff} recovery with Mg incorporation
- (6) Atomic structure of La-silicates
- (7) Small EOT with low leakage current
- (8) Interface dipole at high-k interface
- (9) Defect compensation with Ce-oxide capping

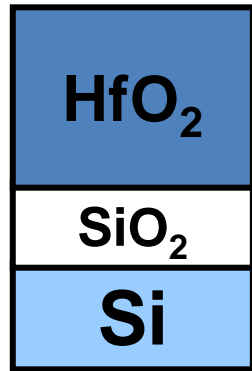
Direct contact of high-k/Si with La-silicate foramtion



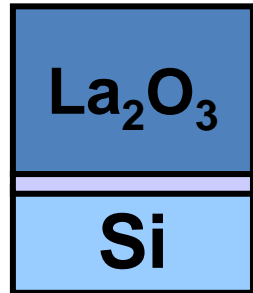
Originality

Foramtion of high-k quality La-silicate using the reaction of La_2O_3 and Si substrate

High quality La-silicate



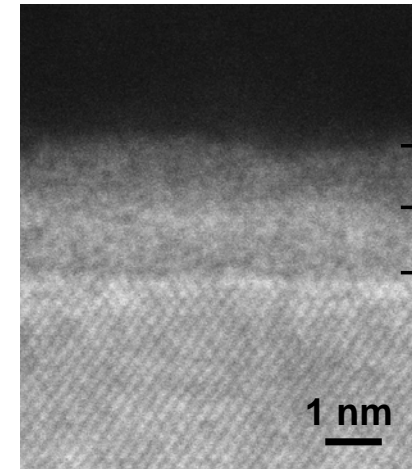
· HfO_2 forms SiO_2 at interface



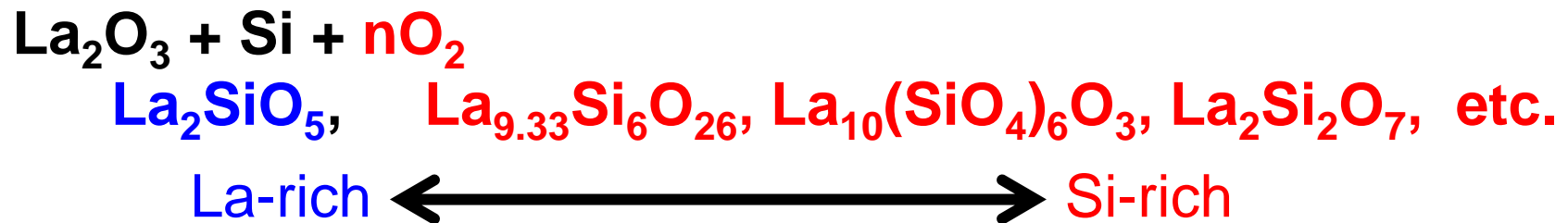
La-rich silicate
 La_2SiO_5

· μ_{eff} degradation
· defects in silicate (hysteresis)
· large D_{it} ($10^{13}\text{cm}^{-2}/\text{eV}$)

$\text{La}_2\text{O}_3/\text{Si}$ after 500 °C 30min

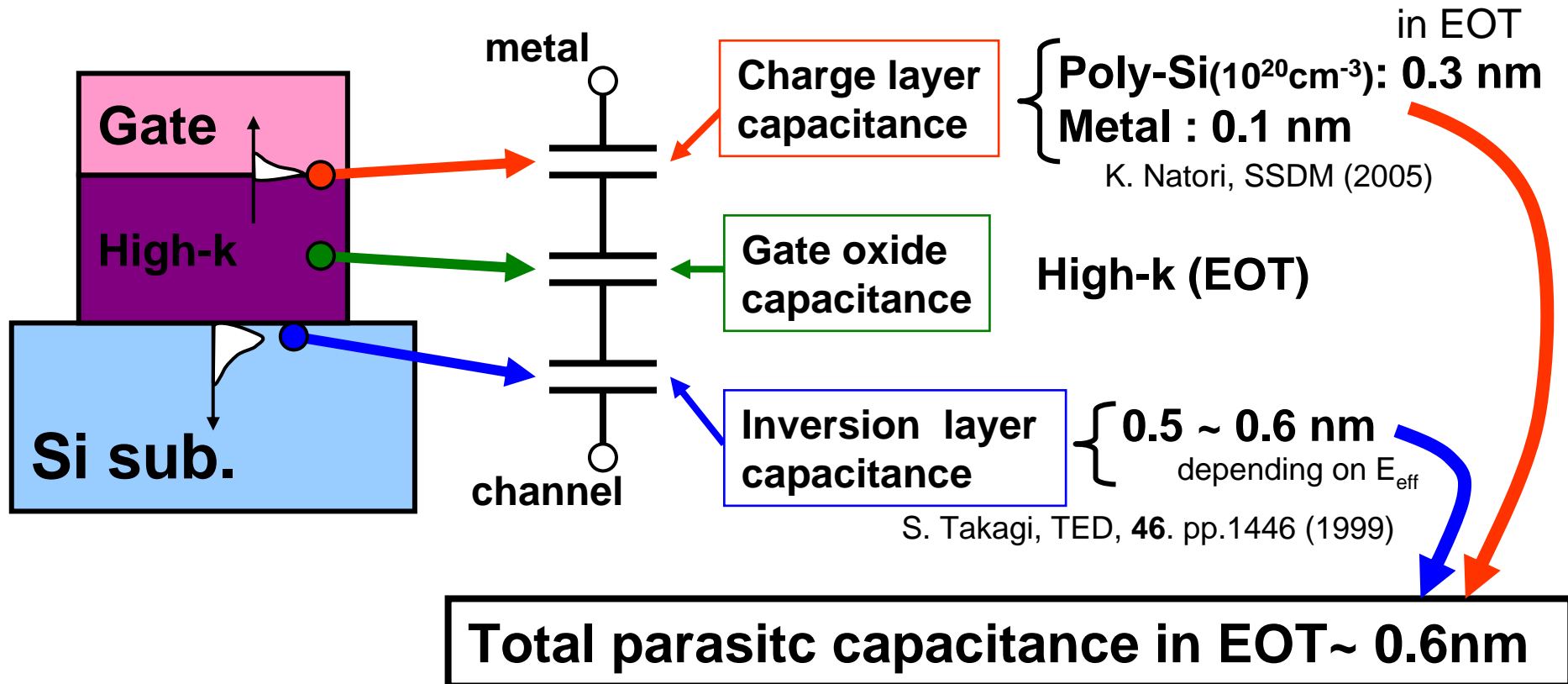


W
 La_2O_3 $k=23$
Si-rich silicate $k=8\sim 14$



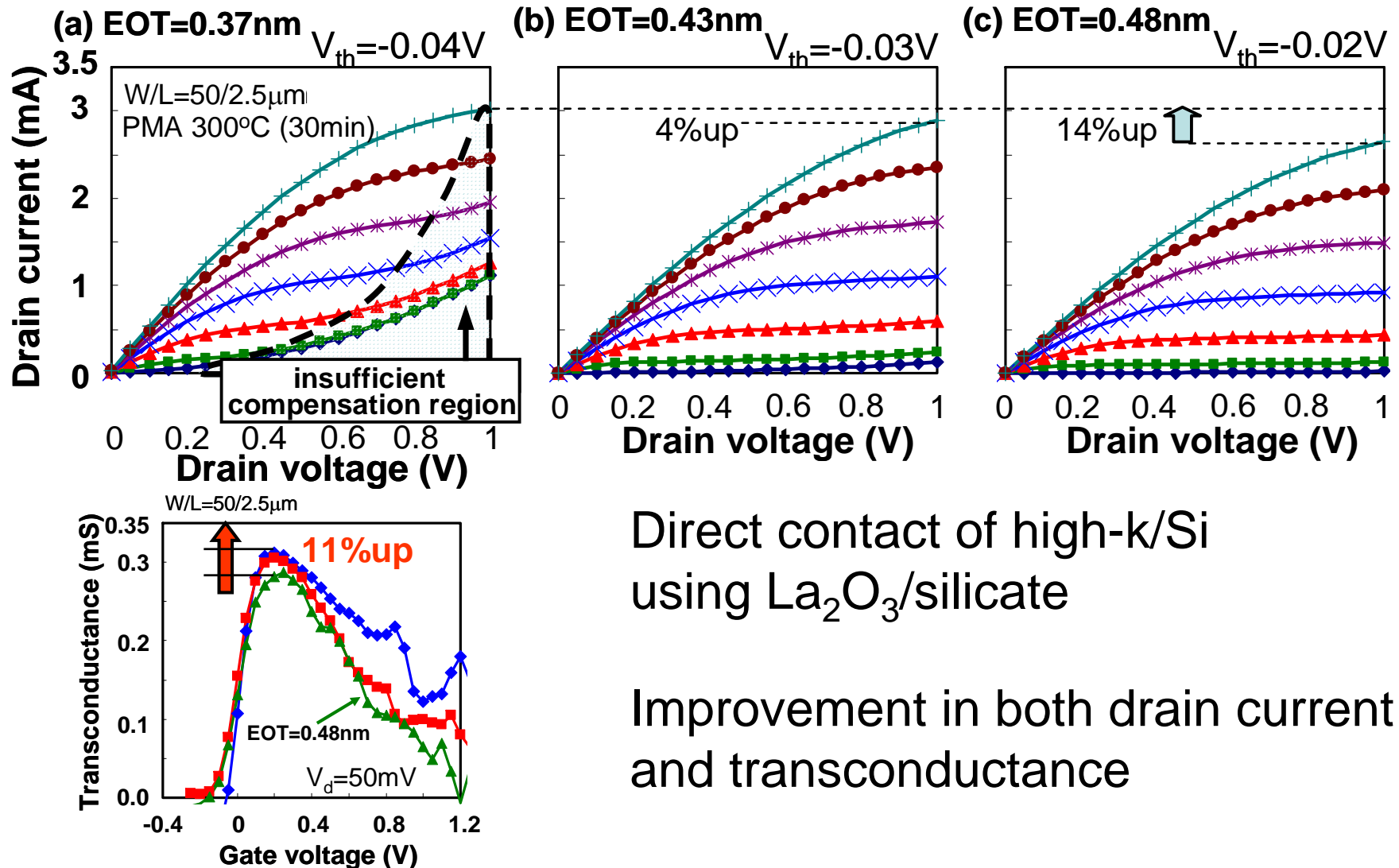
Proper oxygen atom supply to form high quality Si-rich La-silicate

(1) Overwhelming the EOT below 0.5 nm



- Question about device improvement below EOT=0.5nm (written in ITRS roadmap)
- Difficulty in fabrication process to achieve EOT<0.5nm

FET operation of EOT=0.37nm



Direct contact of high-k/Si
 using La_2O_3 /silicate

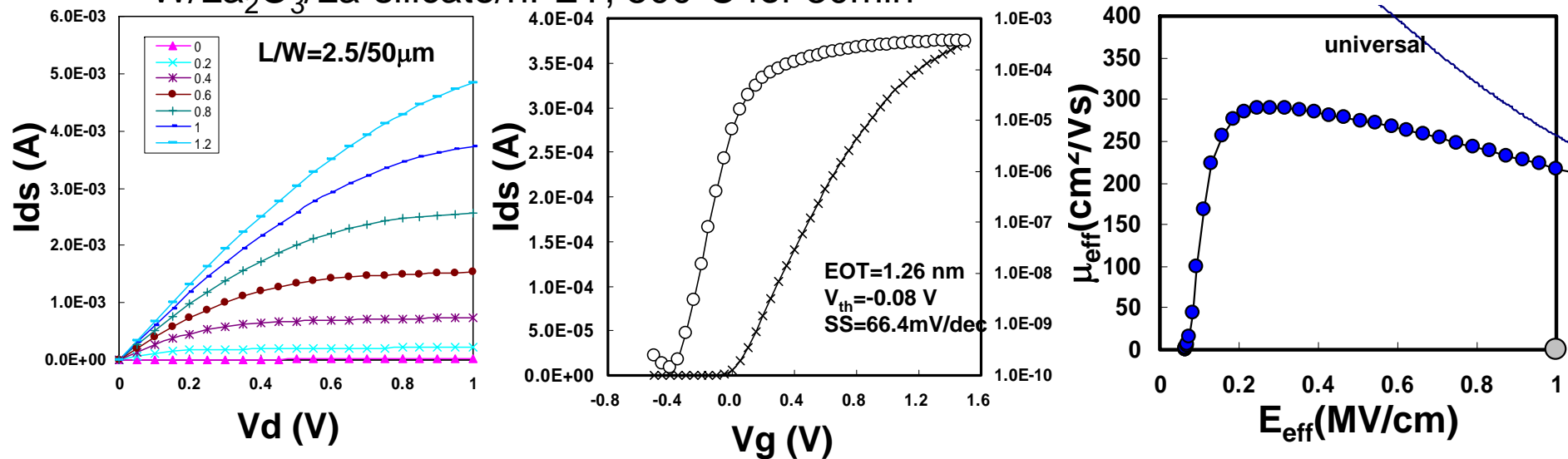
Improvement in both drain current
 and transconductance

EOT scaling below 0.5nm is still useful

(2) Direct high-k/Si using La-silicate/Si with high μ_{eff}

EOT=1.26nm

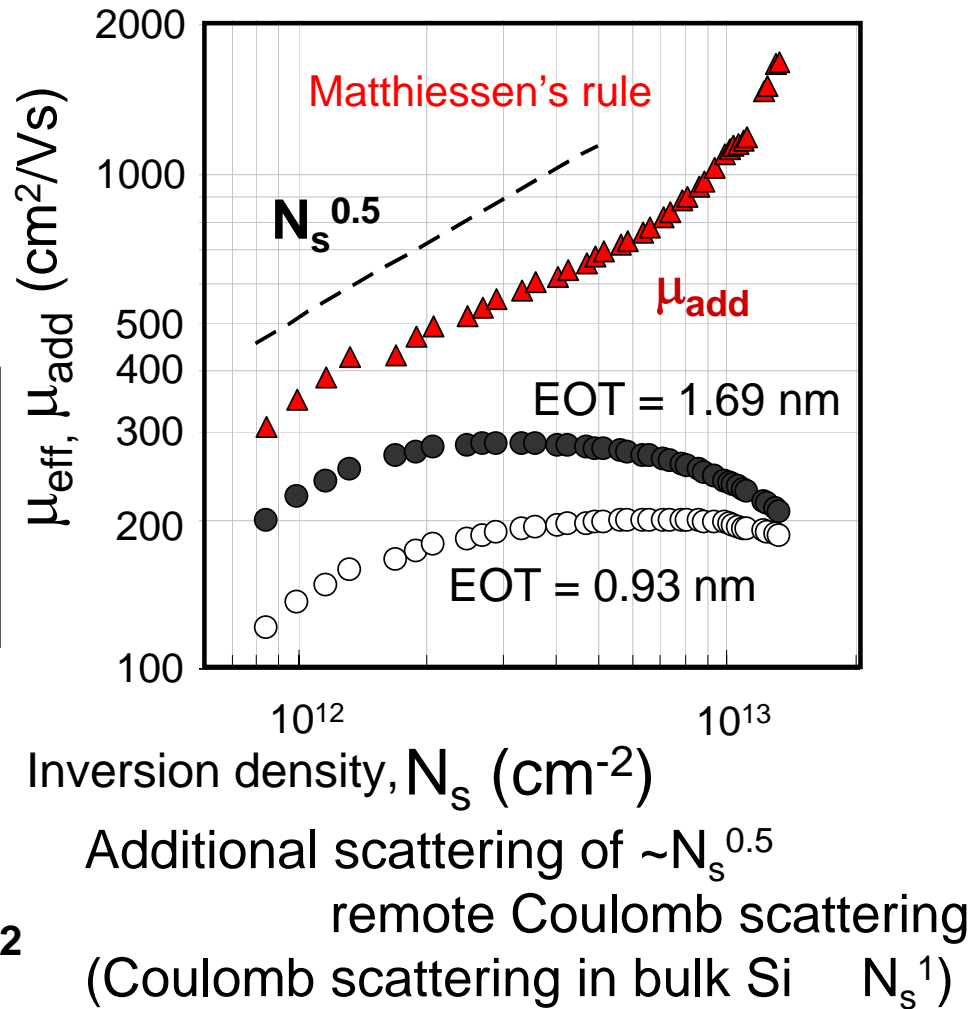
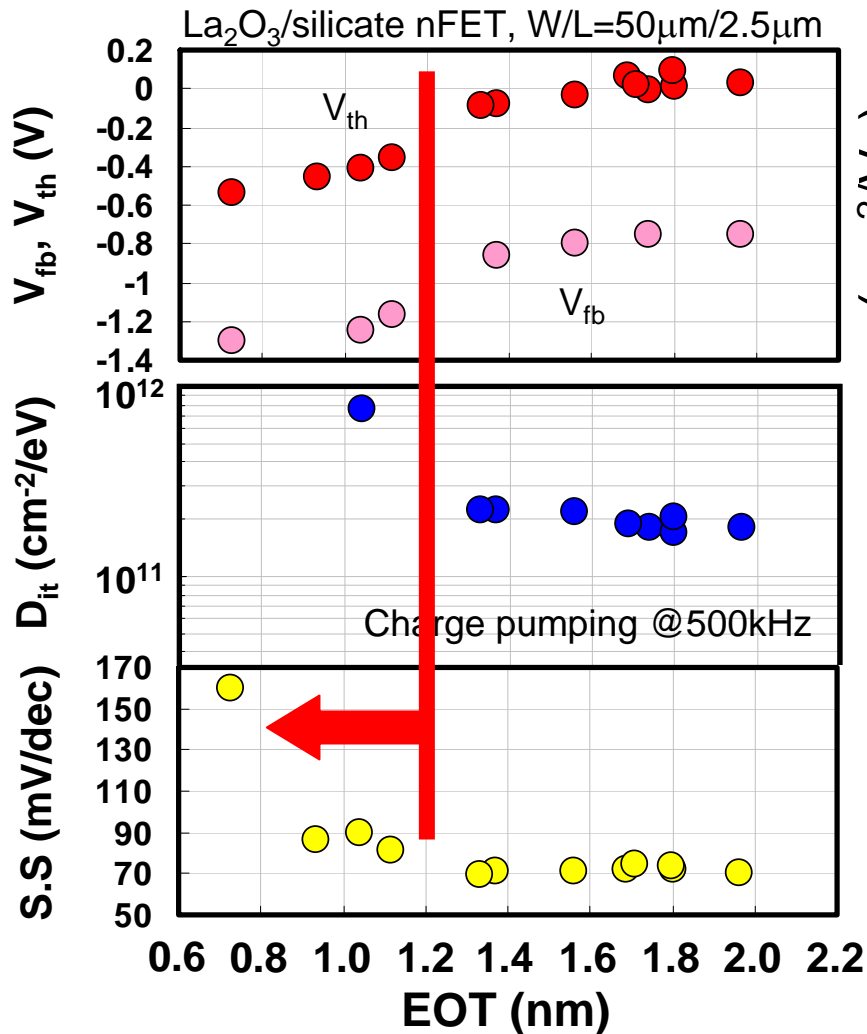
W/La₂O₃/La-silicate/nFET, 500°C for 30min



High peak μ_{eff} of 300cm²/Vs with 500°C annealing
nice properties of Si-rich La-silicate/Si interface

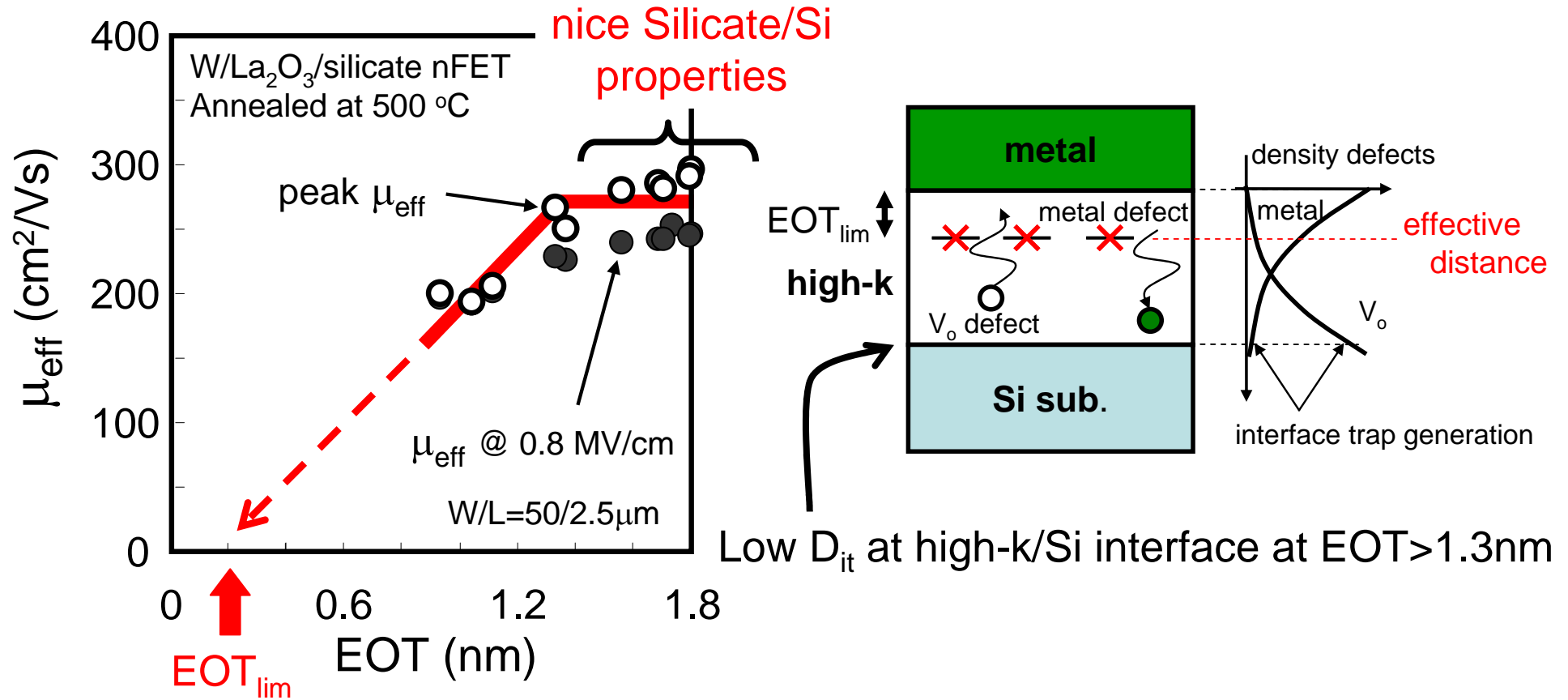
Fairly nice properties can be achieved even with
direct high-k/Si interface (EOT~1.2)

(3) Origin of degradations at EOT < 1.3nm



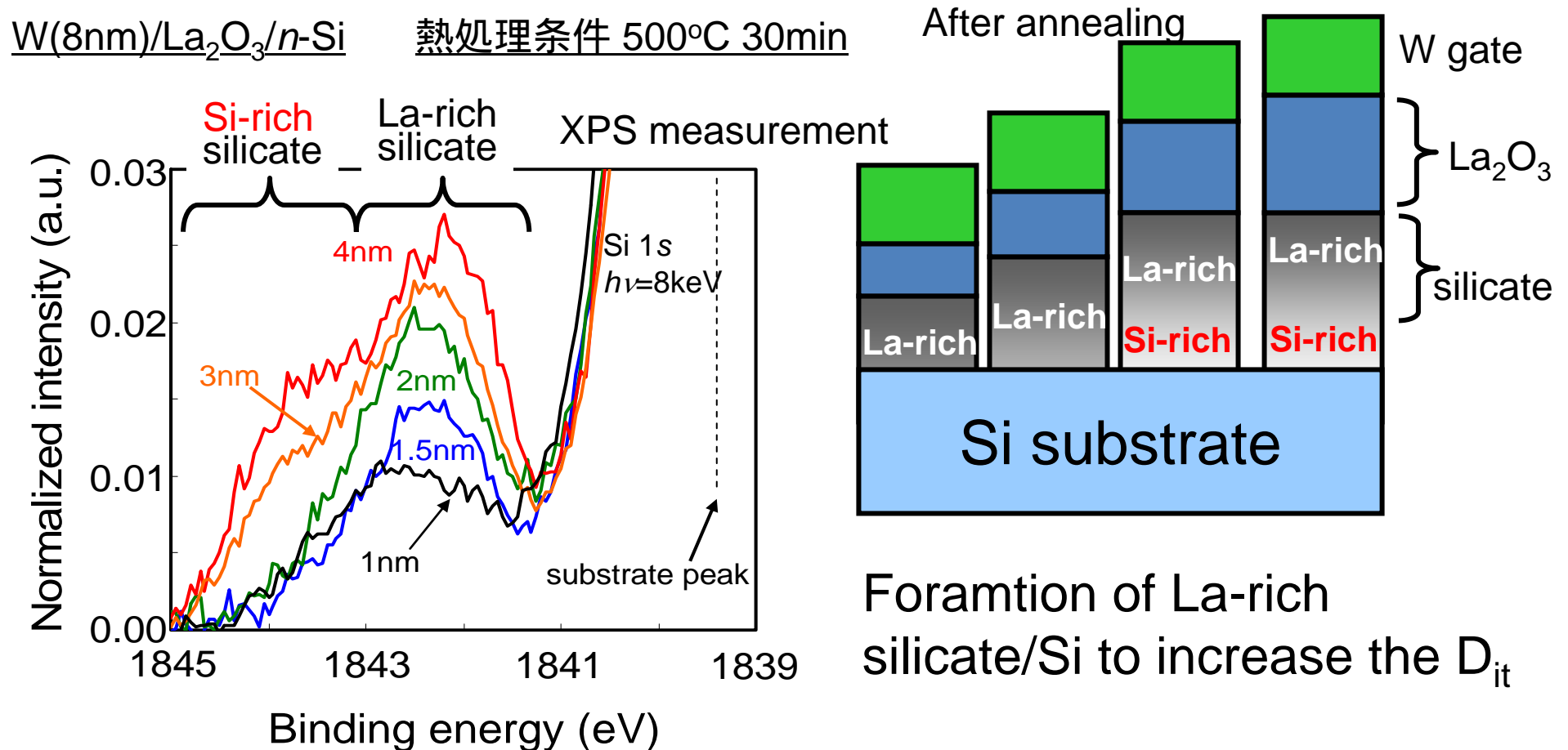
Coulomb scattering from high-k at EOT < 1.3nm

Defects from metal electrode



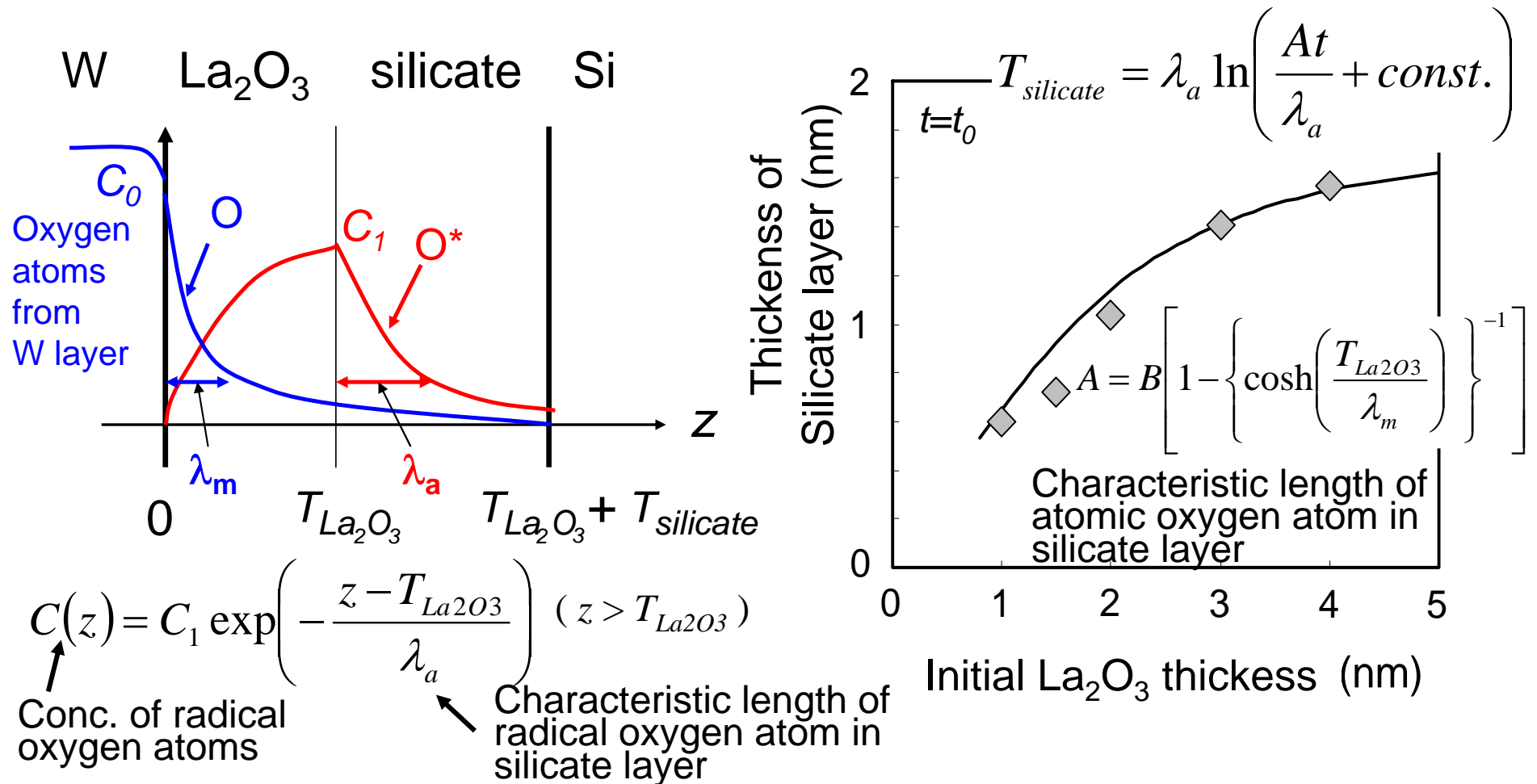
Metal atom diffusions to degrade the μ_{eff} in EOT < 1.3nm

(4) Modeling of defects in dielectrics



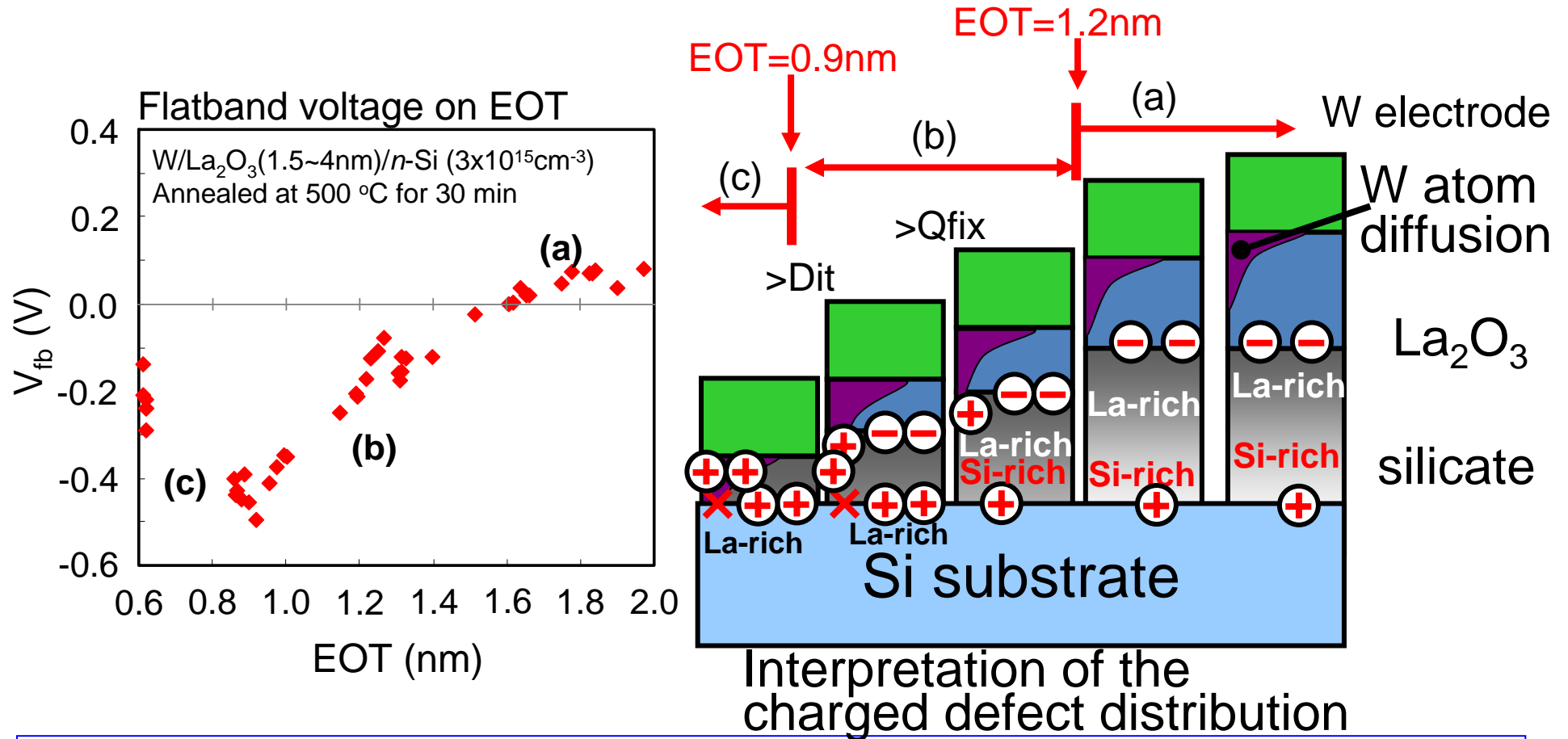
La-rich silicate formation with thin La₂O₃ layer
one of the reasons for μ_{eff} degradation

Thickness dependent silicate formation



Radical oxygen atoms produced by La_2O_3 determines the thickness of silicate layer
 thin layer of La_2O_3 makes thin La-rich silicate

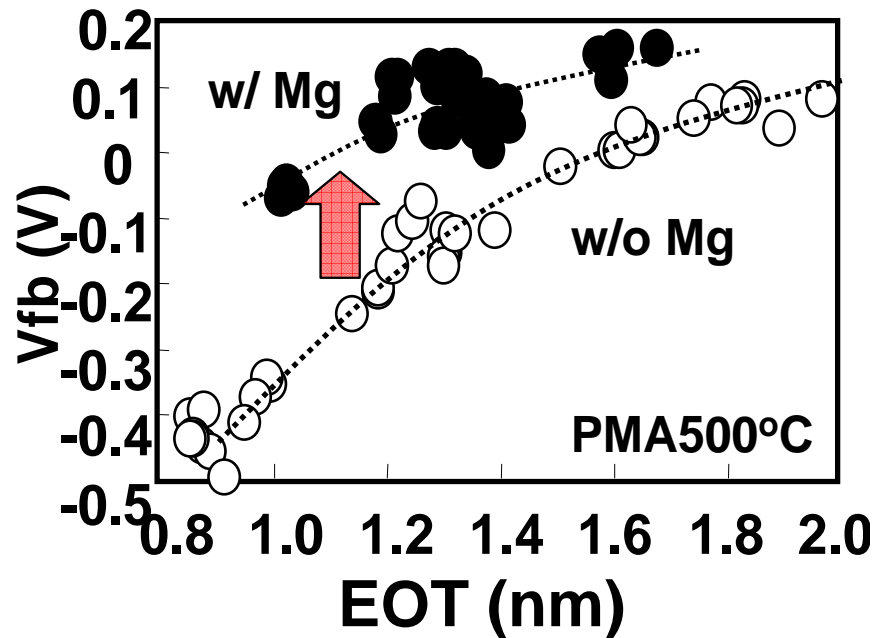
Modeling of the defect distribution in high-k



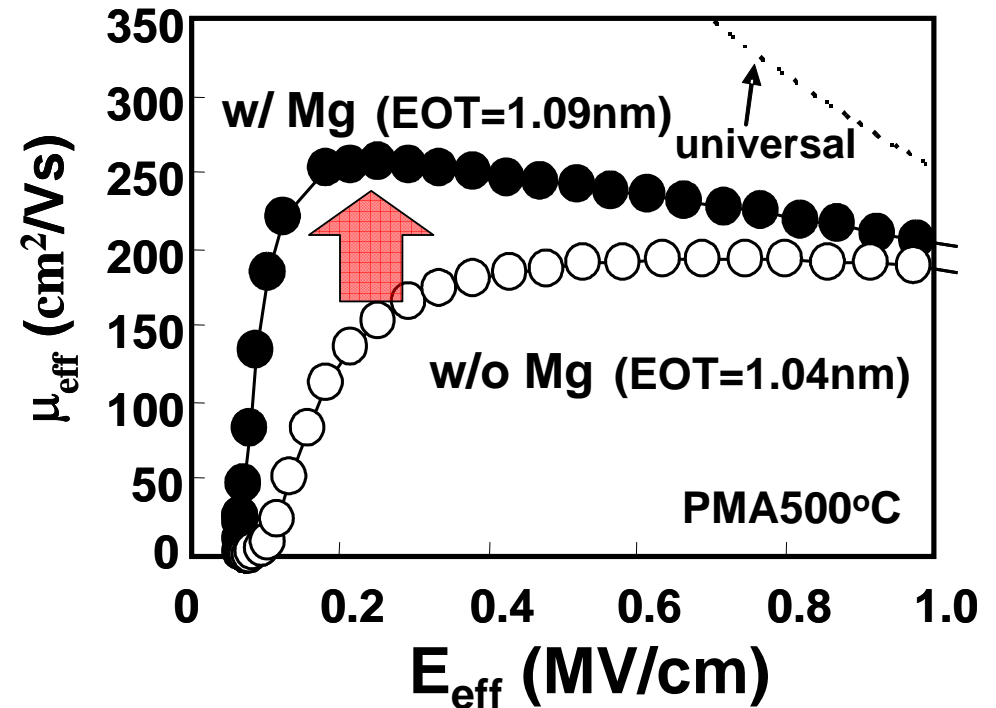
- W atom diffusion from electrode shift the V_{fb}
- Increase of D_{it} might be due to the diffusion of W atoms reaching to the high-k/Si interface and/or La-rich silicate formation

(5) μ_{eff} recovery with Mg incorporation

Mg incorporation into
La-silicate



Suppression of V_{fb} shift
at small EOT



μ_{eff} recovery

Incorporation of Mg into La-silicate can recover the μ_{eff}

Alkali earth incorporation into La-silicate 中

| Compound | Ionic conductivity (mS/cm) @500°C |
|--|--------------------------------------|
| $\text{La}_{9.33}\text{Si}_6\text{O}_{26}$ | 0.023 |
| $\text{La}_{10}\text{Si}_6\text{O}_{27}$ | 4.3 |
| $\text{La}_{10}\text{Mg}_{0.2}\text{Si}_{5.8}\text{O}_{26.8}$ | 14 |
| $\text{La}_{9.8}\text{Mg}_{0.3}\text{Si}_{5.7}\text{O}_{26.4}$ | 12 |

High La conc. ↓

ref: H. Yoshioka et al., SSI 179, 2165 (2008)

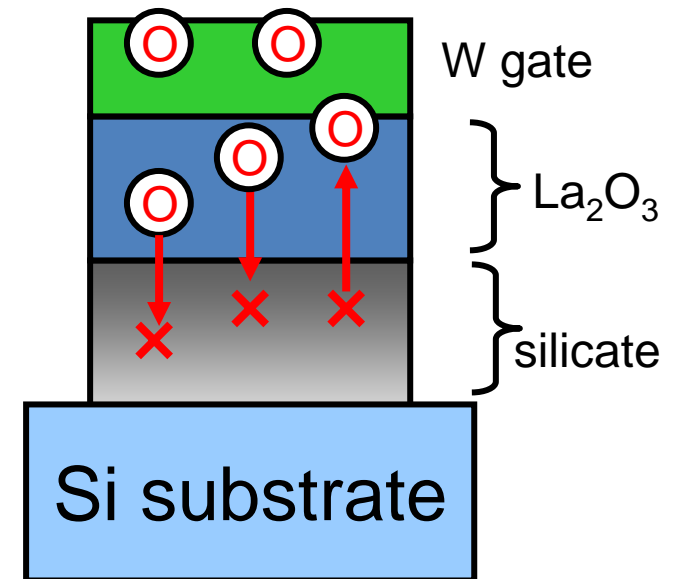
Oxygen ion conductivity

high easy V_o formation, easy to recover

low difficult to form V_o , difficult to recover

High ionic conductivity with Mg incorporation

Compensation of defects from W electrode



(6) Atomic structure of La-silicates

Purpose

Investigation of the atomic structure of La-silicate

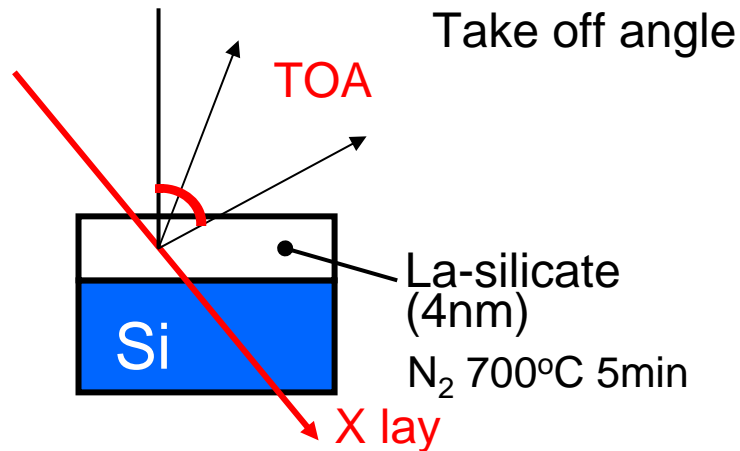
La-silicate for gate dielectric (<4nm)

Compositional gradient normal to the surface

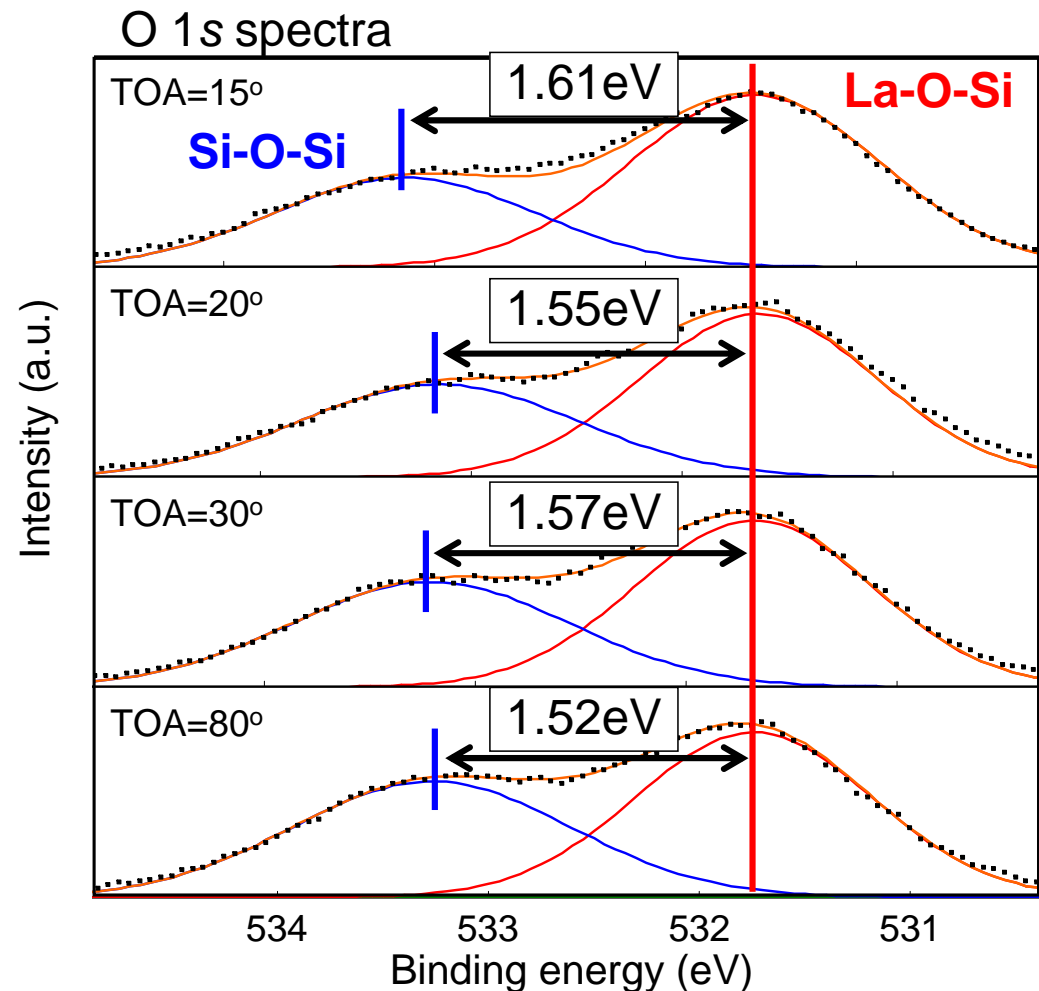
Method

Angle-resolved XPS measurement

O 1s spectra of La-silicate on different TOA



Binding energy of Si-O-Si and La-O-Si differs on the TOA

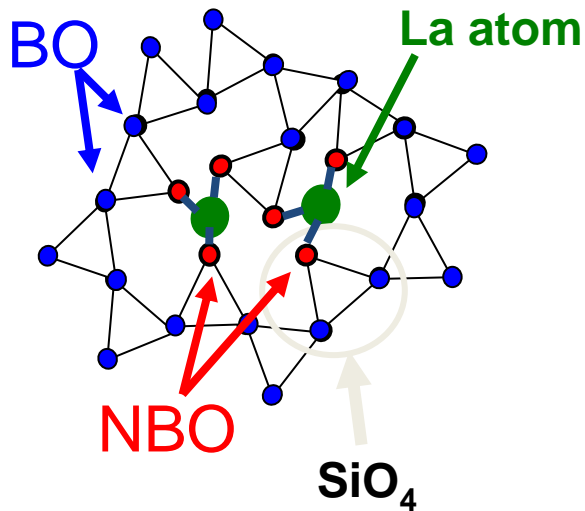


Difference in the binding energy of La-O-Si and Si-O-Si should be constant

Lack of physics based interpretation

Atomic structure of La-silicate

Network of tetrahedrons (SiO_4)
amorphous

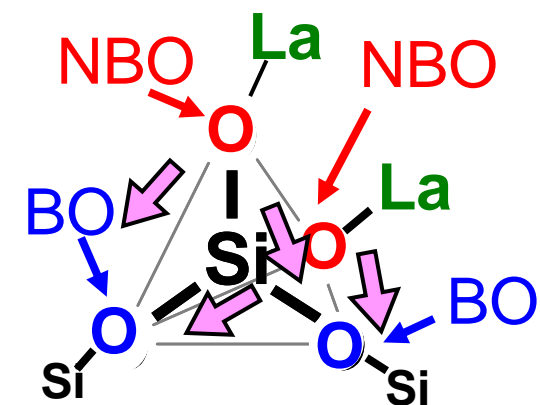
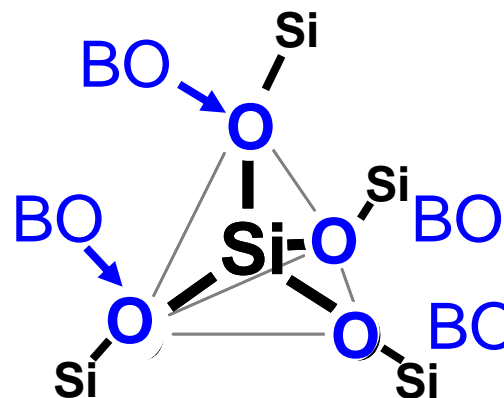


Si-O-Si bonding

BO: bridging oxygen atom

La-O-Si bonding

NBO: non-bridging oxygen atom



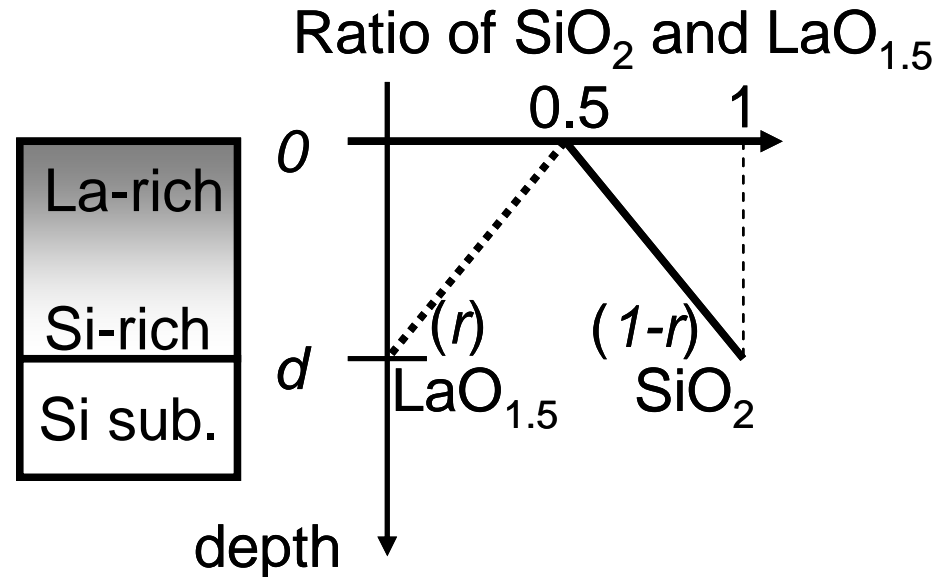
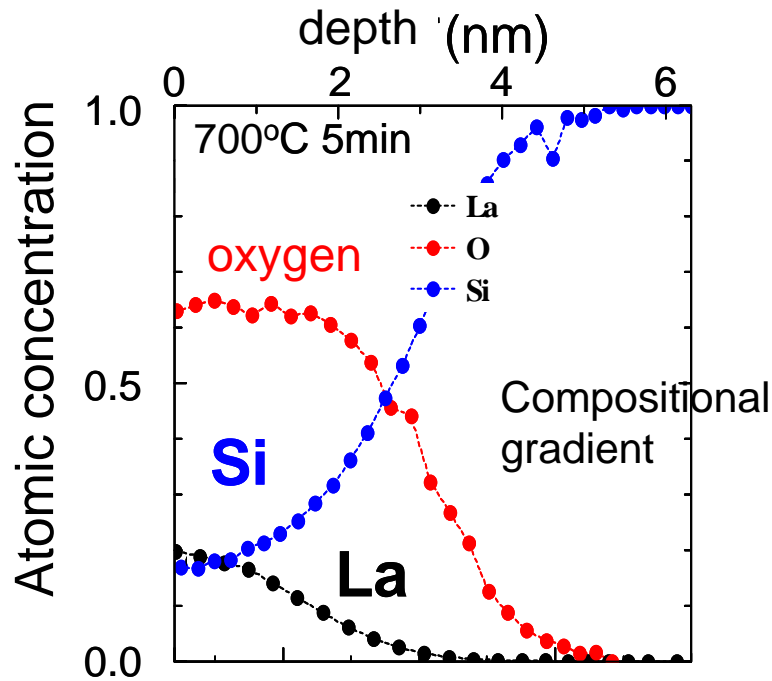
The influence of second neighbor atom should be accounted

La atom concentration dependent binding energy shift

A common method for Na-dope glass

La atom distribution in La-silicate

Atomic distribution determined by RBS



Surface is $\text{La}_{0.2}\text{Si}_{0.16}\text{O}_{0.64}$

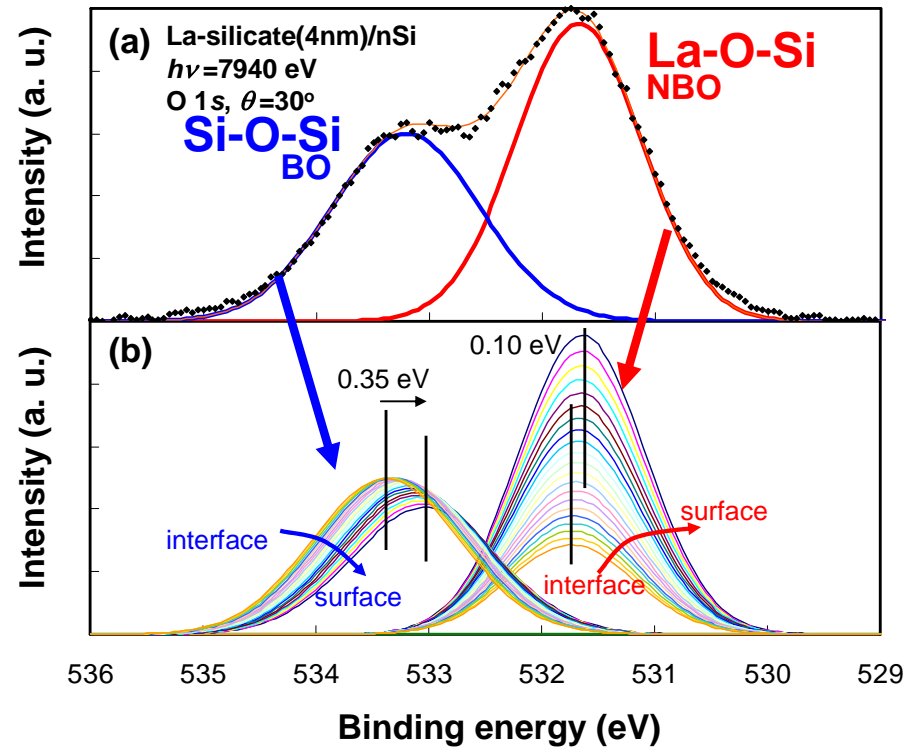
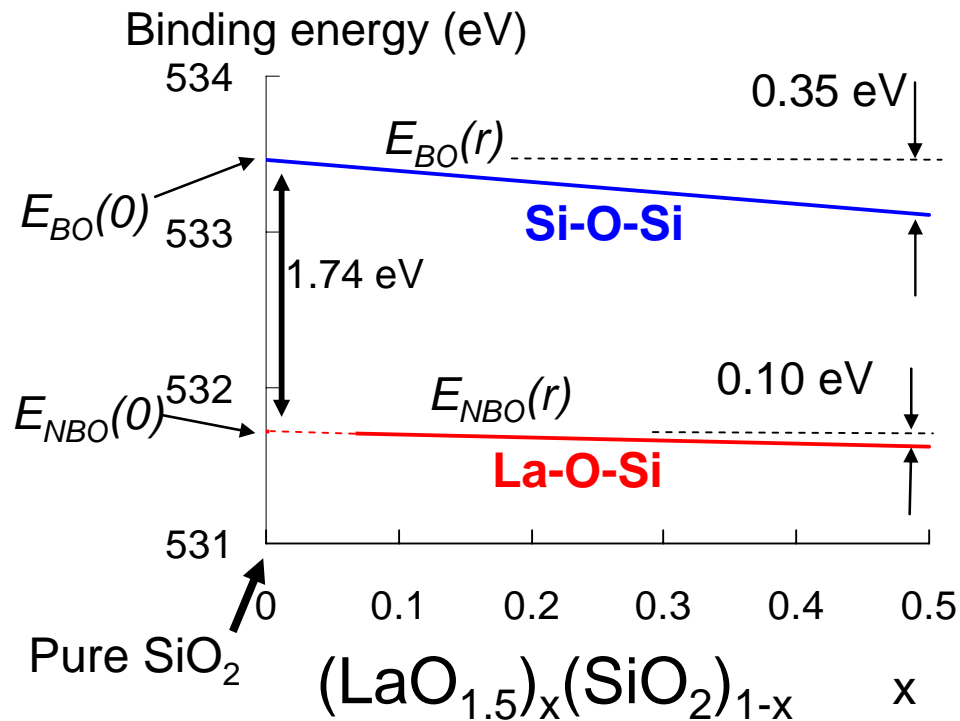
K. Kimura, et al, Proc. IWNC, pp. 89 (2005)

A simple model for the distribution used in this study

Extraction of concentration dependent binding energy shift

Concentration dependent binding energy shift

BO: bridging oxygen atom
NBO: non-bridging oxygen atom



Reconstruction of the obtained O 1s spectrum

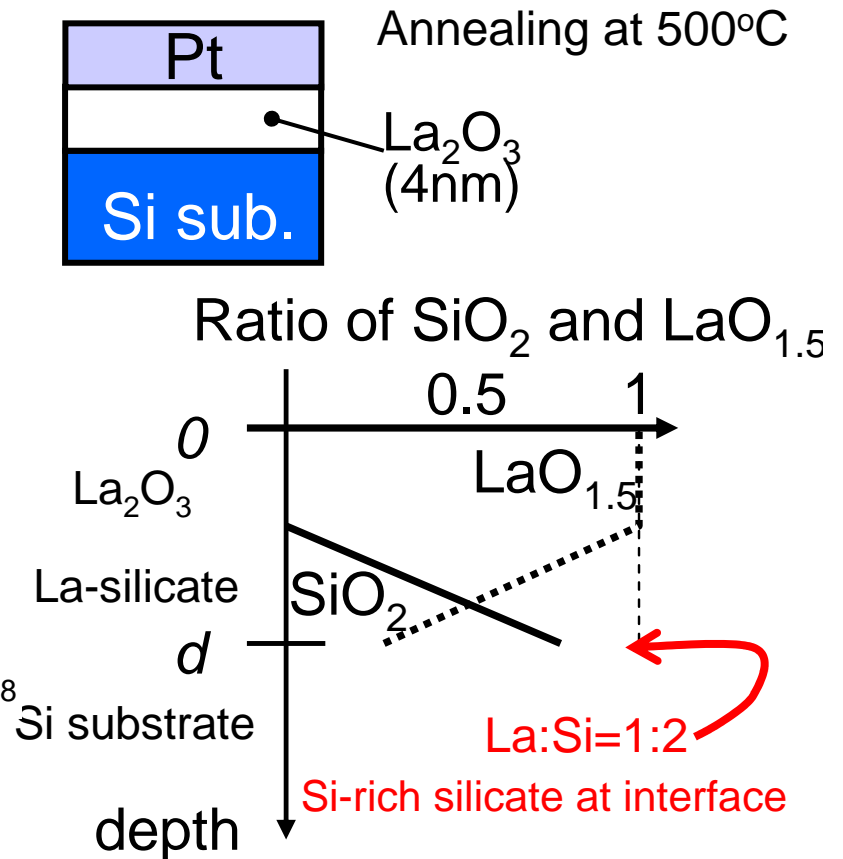
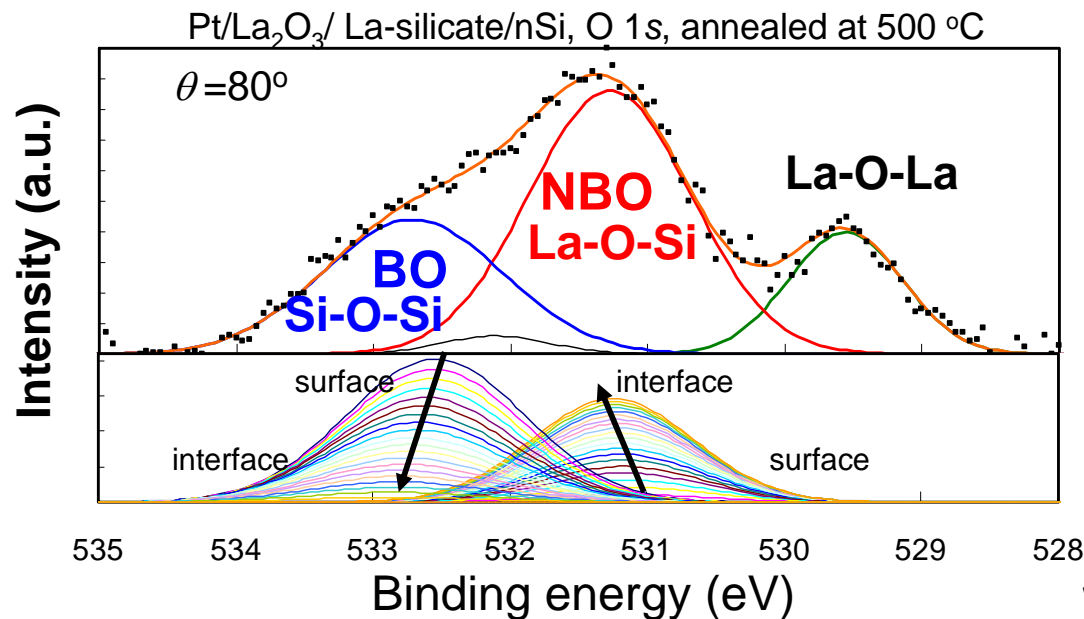
Summary of the deconvolution

| | Binding energy of O 1s, eV (FWHM, eV) | Take-off angle (degree) | | | | |
|-----------------------------|---|-------------------------|------------------|------------------|------------------|------------------|
| | | 15 | 20 | 30 | 52 | 80 |
| Conventional fitting | NBO 1s | 531.49 (1.57) | 531.63 (1.57) | 531.71 (1.48) | 531.76 (1.57) | 531.75 (1.53) |
| | BO 1s | 533.10 (1.46) | 533.18 (1.41) | 533.28 (1.41) | 533.26 (1.34) | 533.27 (1.29) |
| | ΔE_{BO-NBO} | 1.61 | 1.55 | 1.57 | 1.50 | 1.52 |
| This work | NBO 1s at $r=0$, $E_{NBO}(0)$ | 531.42 (1.32) | 531.60 (1.32) | 531.64 (1.32) | 531.72 (1.32) | 531.70 (1.32) |
| | BO 1s at $r=0$, $E_{BO}(0)$ | 533.17 (1.53) | 533.33 (1.53) | 533.38 (1.53) | 533.46 (1.53) | 533.45 (1.60) |
| | $\Delta[E_{BO}(0)-E_{NBO}(0)]$ | 1.75 | 1.73 | 1.74 | 1.74 | 1.75 |

A constant binding energy difference between BO and NBO
Physical meaning

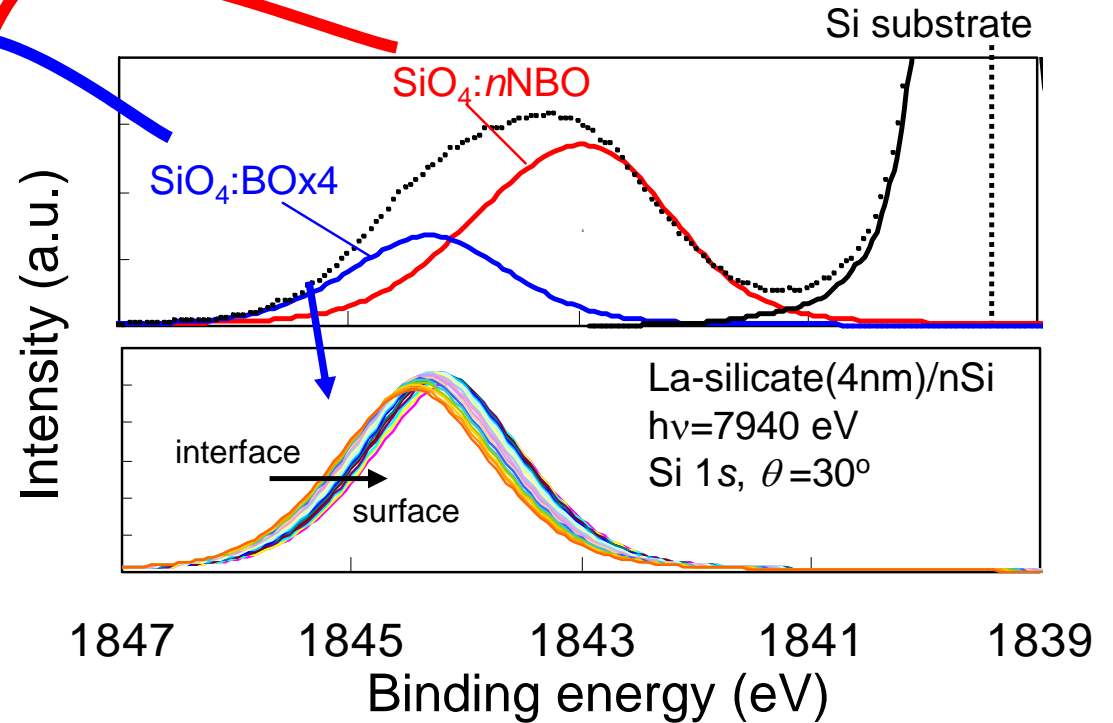
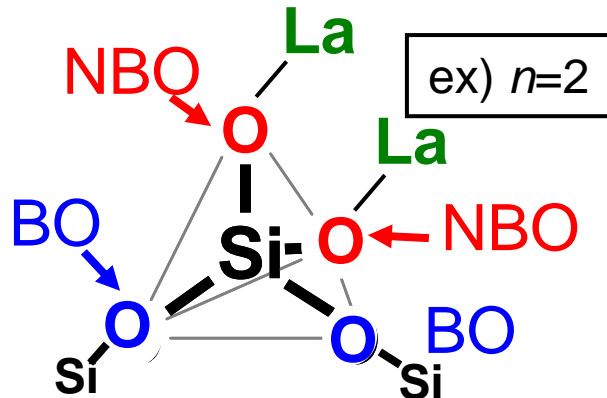
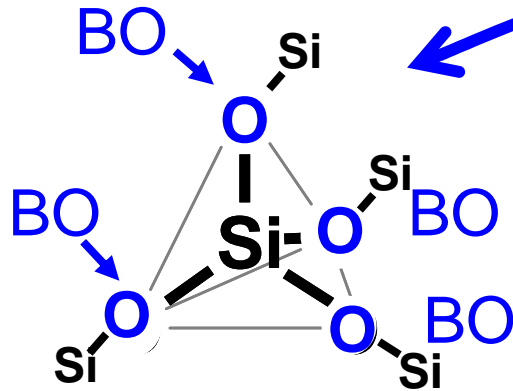
Extraction of La concentration from a spectrum

BO: bridging oxygen atom
 NBO: non-bridging oxygen atom



La atom distribution can be detected from one O 1s spectrum

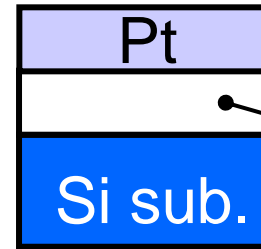
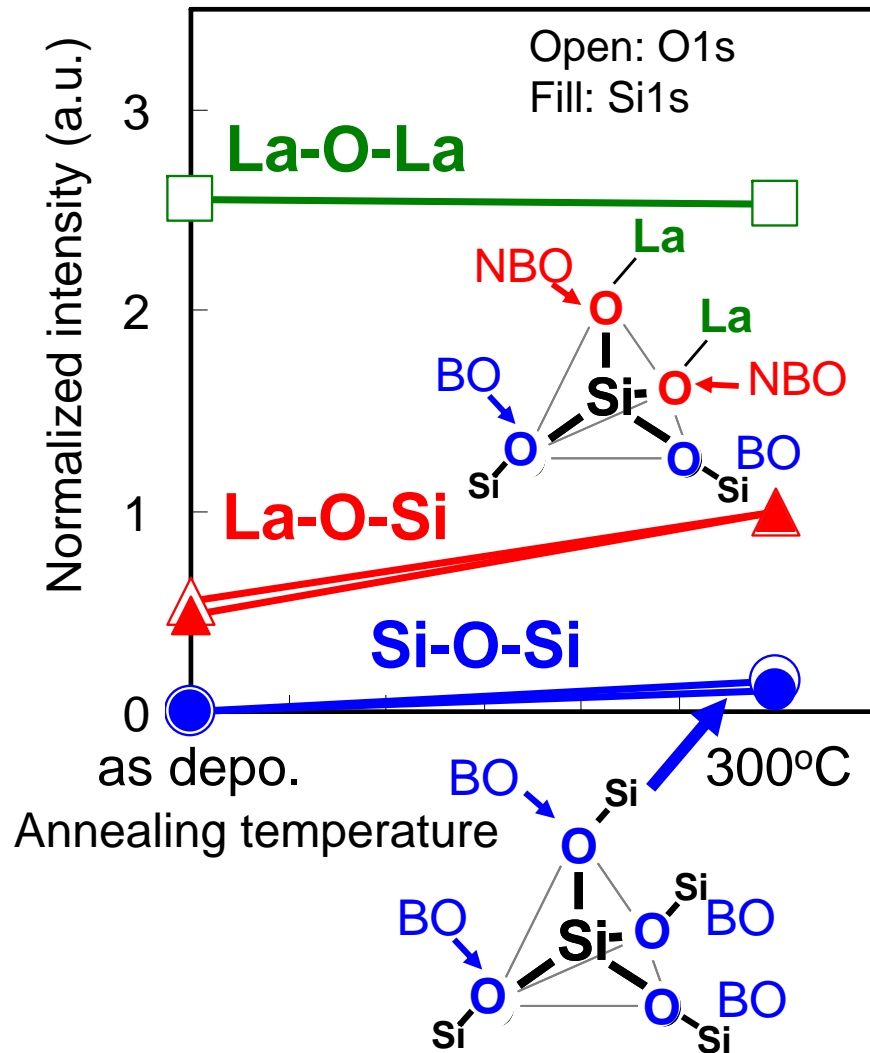
Analysis of Si 1s spectra



Distinguish
SiO₄:BOx4 and SiO₄:nNBO (n=1~3)

O 1s spectra: the amount of **BOs** and **NBOs**
 Si 1s spectra: the amount of SiO₄ with four **BOs**
 the amount of SiO₄ with **NBO(s)**

Determination of oxygen sites after annealing



samples

- as-depo.
- 300°C 5min

After annealing at 300°C

O1s

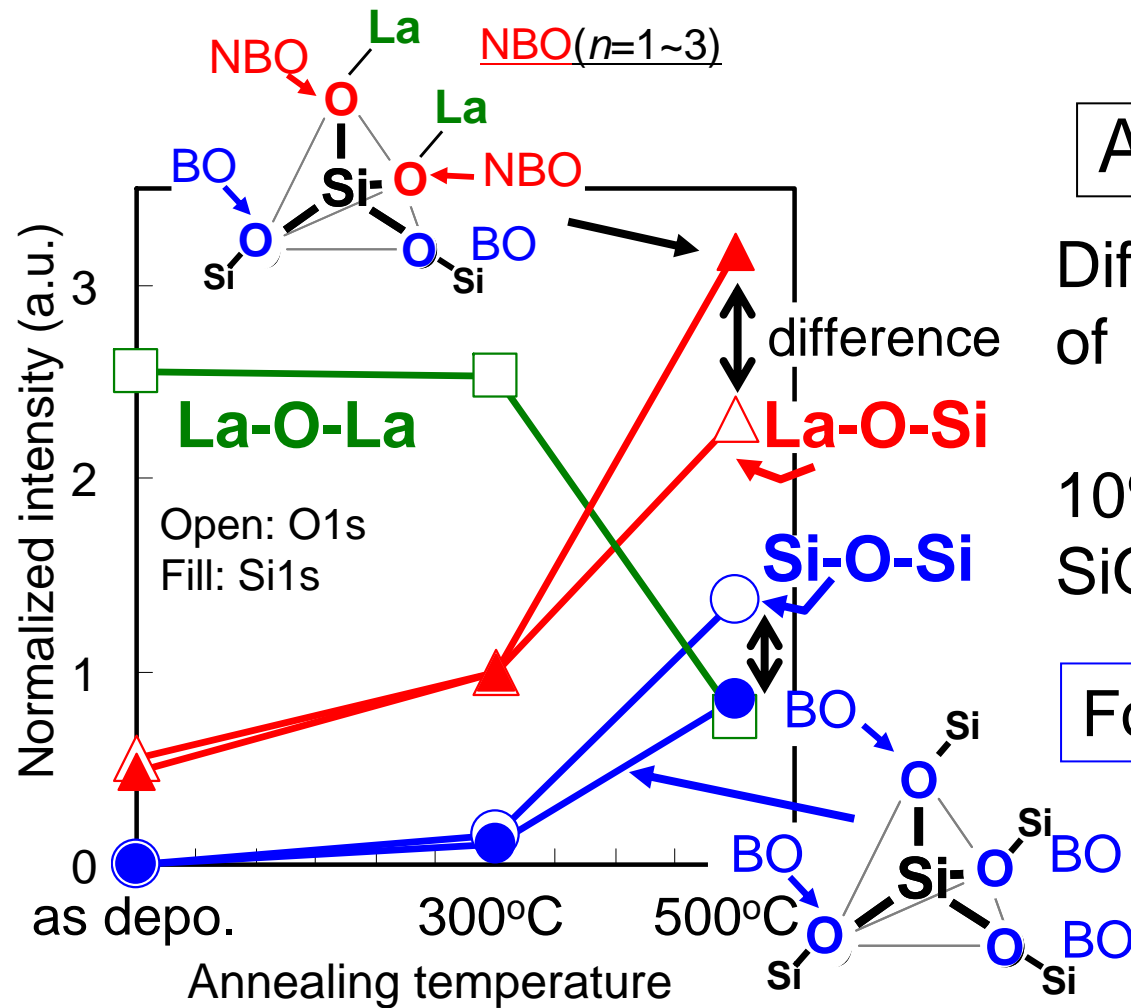
Increase in NBO(La-O-Si)

Si1s

Same increase amount of
SiO₄:nNBO

formation of La-rich silicate

Formation of Si-rich silicate



Annealing at 500°C

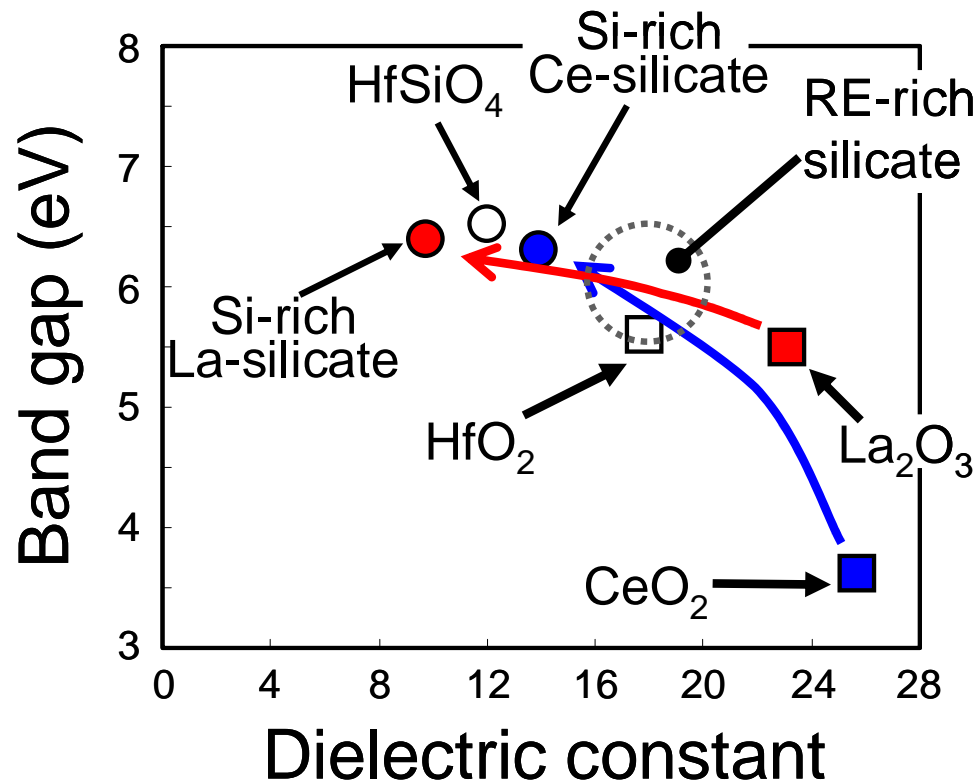
Difference in the increase of NBO and $\text{SiO}_4:n\text{NBO}$

10% of the newly created SiO_4 is in $\text{SiO}_4:\text{BO} \times 4$ phase

Formation of Si-rich silicate

This method enables us to see the oxygen site in the newly created silicate

(7) Small-EOT with small-leakage current



- high k -value
- wide E_g

La₂O₃: k -value decreases with excess silicate reaction

CeO₂: small E_g

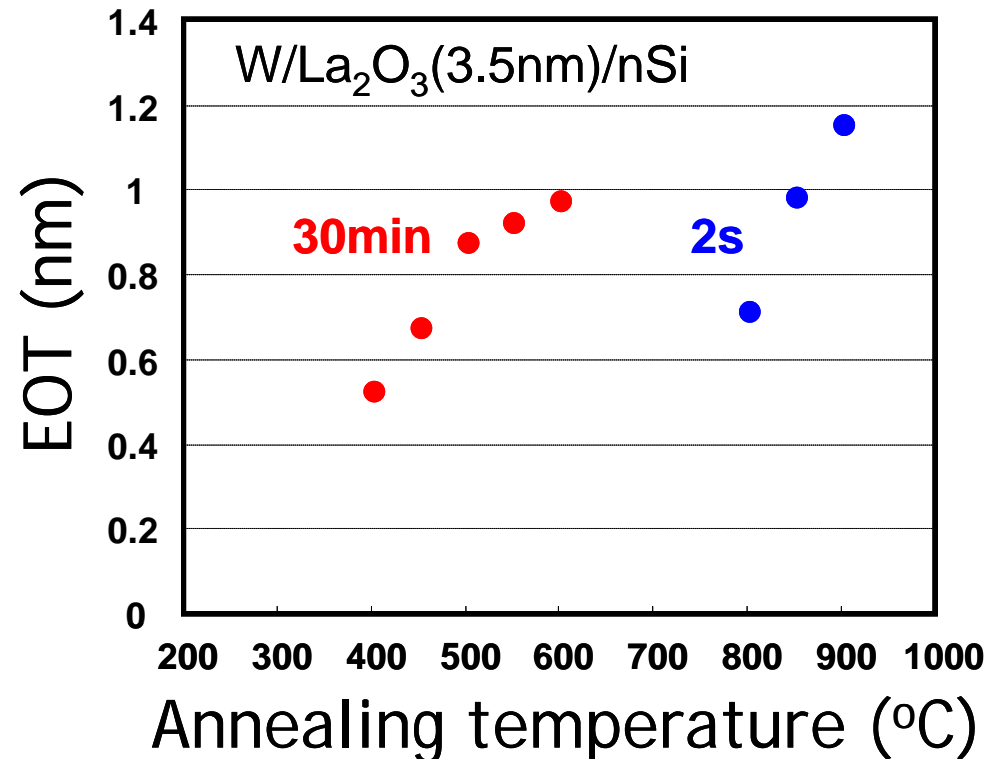
combination of
La₂O₃ and CeO₂

Formation of rare earth-rich silicate with nice interface properties

Excess silicate formation with La_2O_3

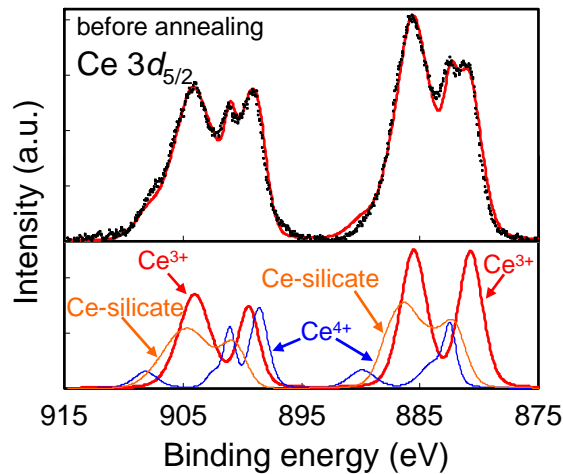
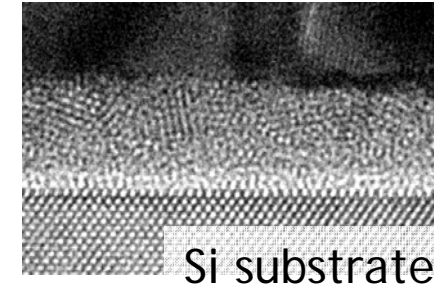
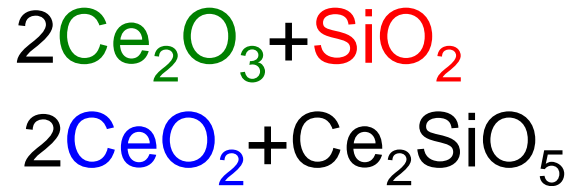
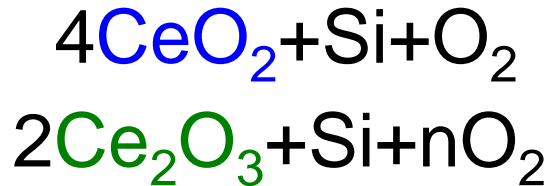


High temperature annealing
promotes the reaction
increase in the EOT

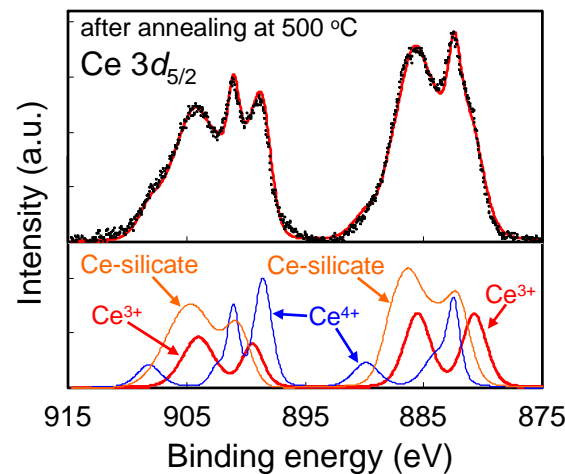


Annealing for short period before thermal equilibrium
Suppression of the EOT increase

Issues in CeO_x



| | | |
|-------------------------|----------------|----------|
| Ce_2O_3 | CeO_2 | silicate |
| 47% | 19% | 34% |



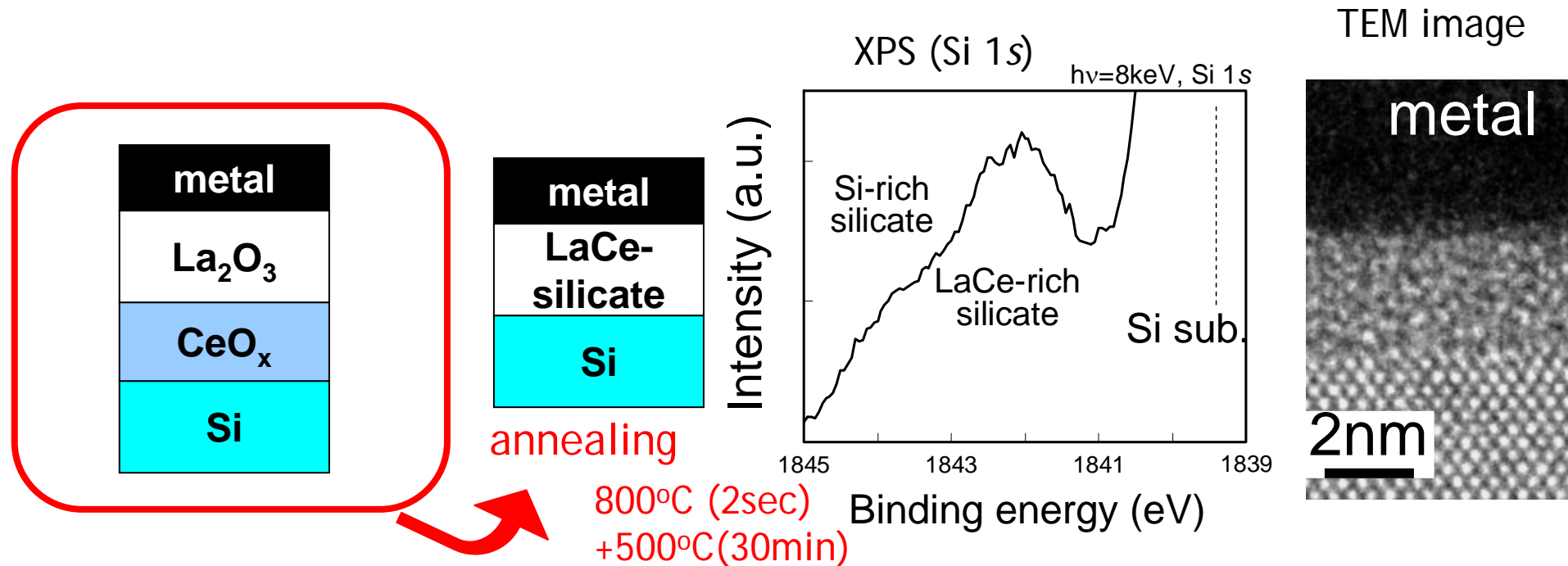
| | | |
|-------------------------|----------------|----------|
| Ce_2O_3 | CeO_2 | silicate |
| 26% | 26% | 48% |

Valence number changes with annealing

Ce^{3+} , Ce^{4+} and silicate

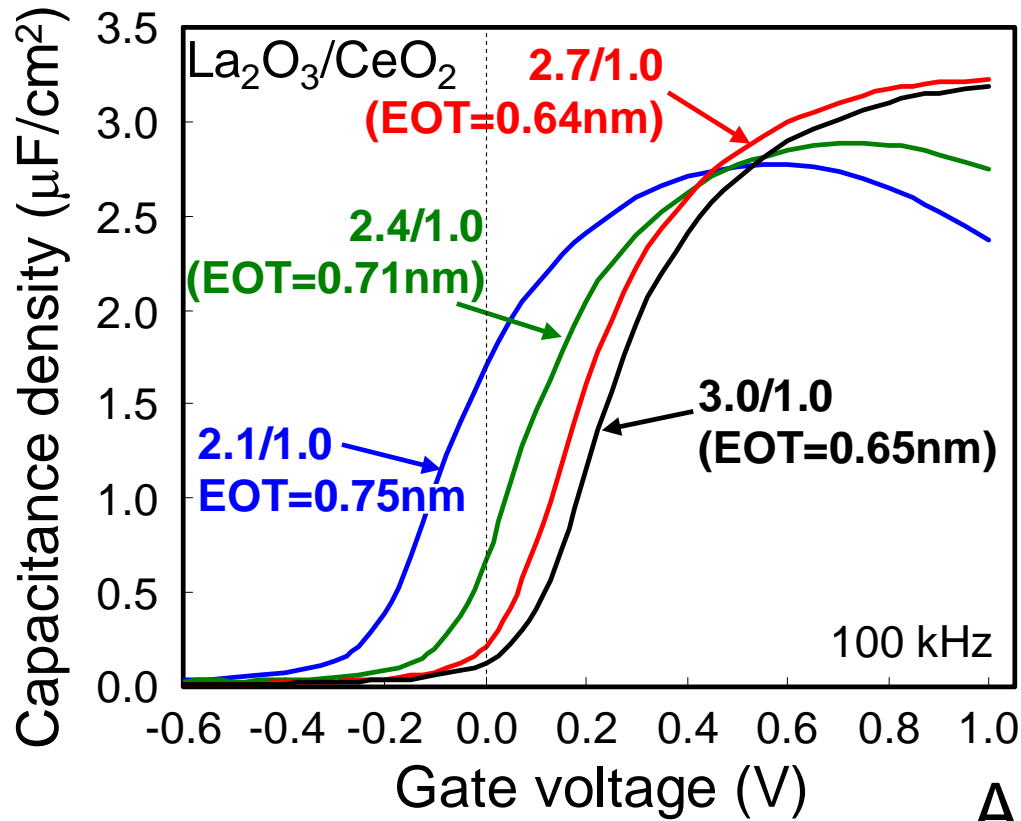
CeO_2 within CeO_x forms SiO_2 as an interfacial layer

LaCe-silicate using La_2O_3 and CeO_x

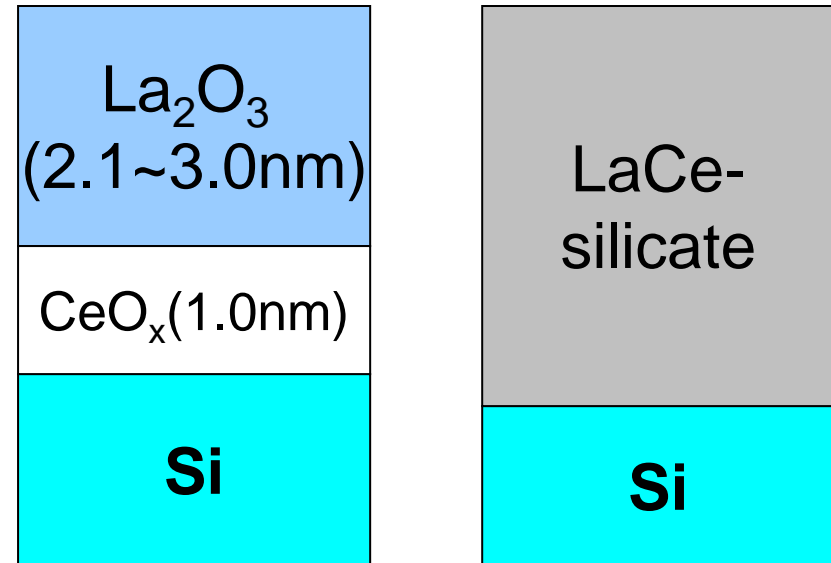


- Intermixing of La, Ce and Si atoms with high temperature annealing
- Uniform LaCe-silicate with sharp interface

LaCe-silicate with different La concentration



$$D_{it} \sim 10^{11} \text{cm}^{-2}/\text{eV}$$

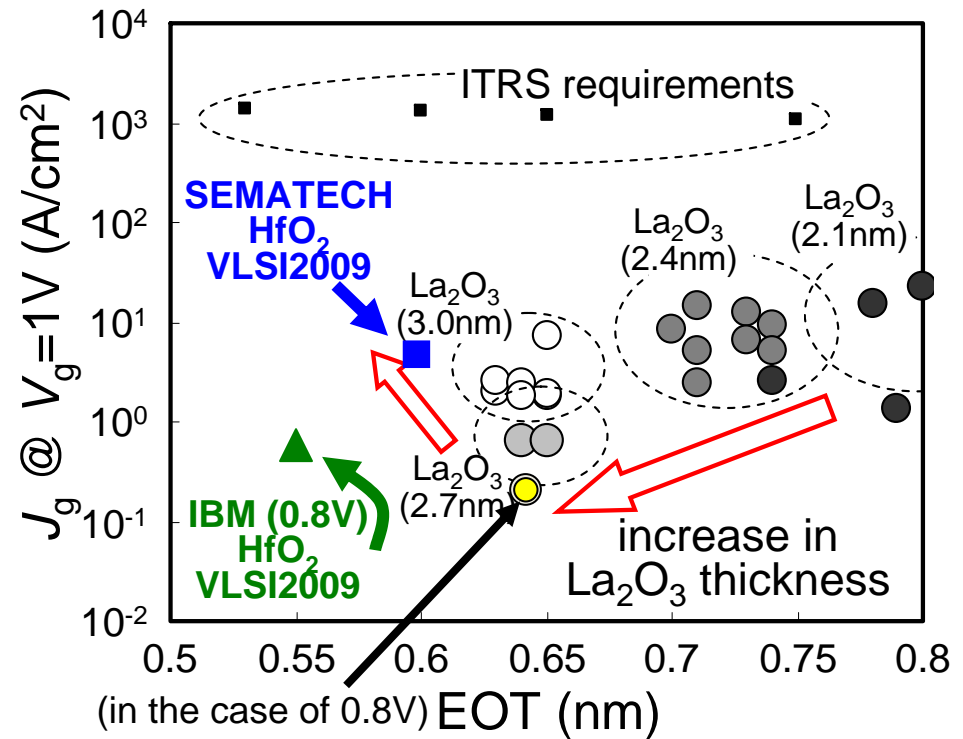
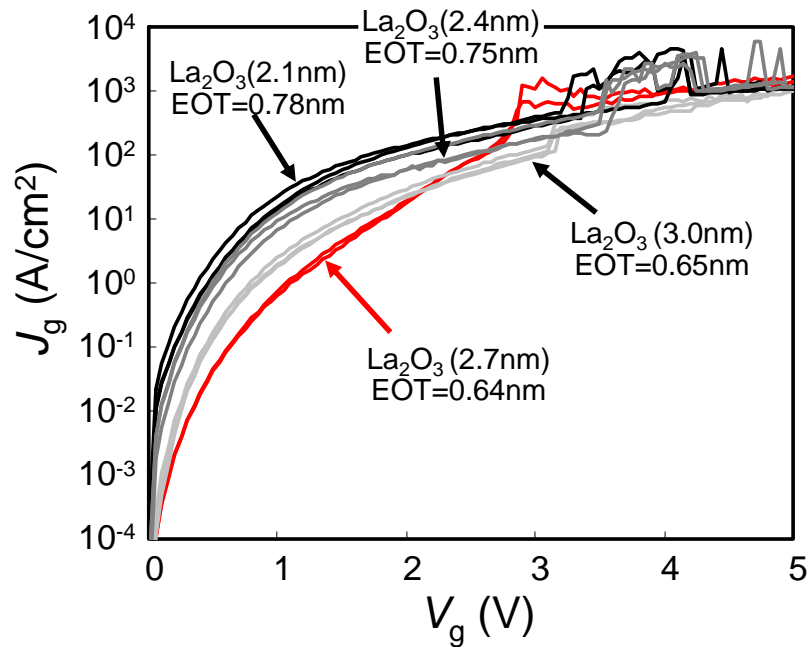


Annealing condition

800°C (2sec)+ 500°C (30min)

k -value of 17.4 with $\text{La}_{1.5}\text{Ce}_{0.5}\text{SiO}_5$

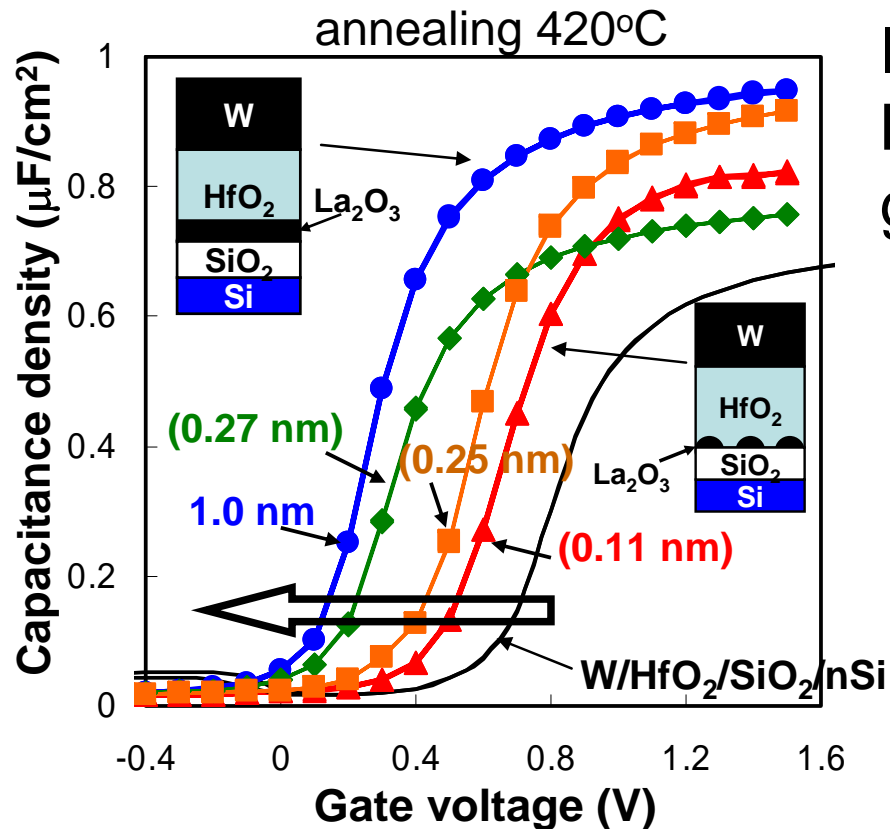
Gate leakage current with LaCe-silicate



$J_g=0.65A/cm^2$ at EOT=0.64nm

(世界最小レベル)

(8) Interface dipole at high-k interface



Incorporation of La atoms:
Negative flatband shift for HfO₂
gate dielectrics

Reported mechanism

1. La capping on HfO₂

X. Wang, VLSI symp. tech. 2006

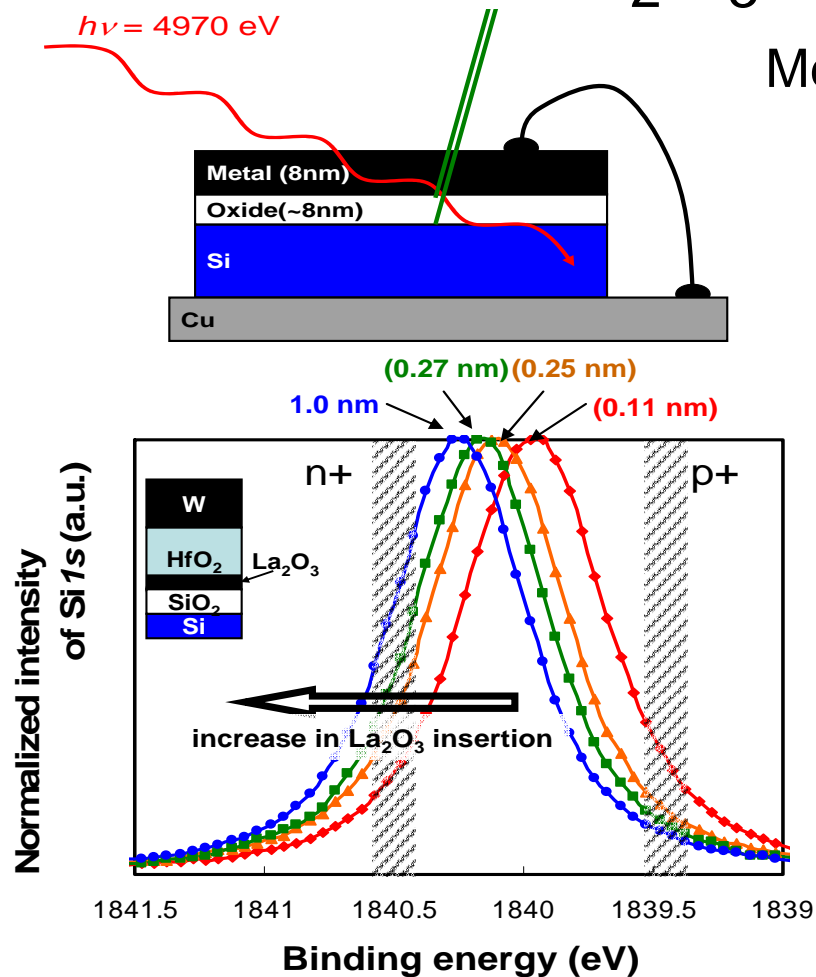
2. La concentration in HfLaO_x

Y. Yamamoto, SSDM 2006

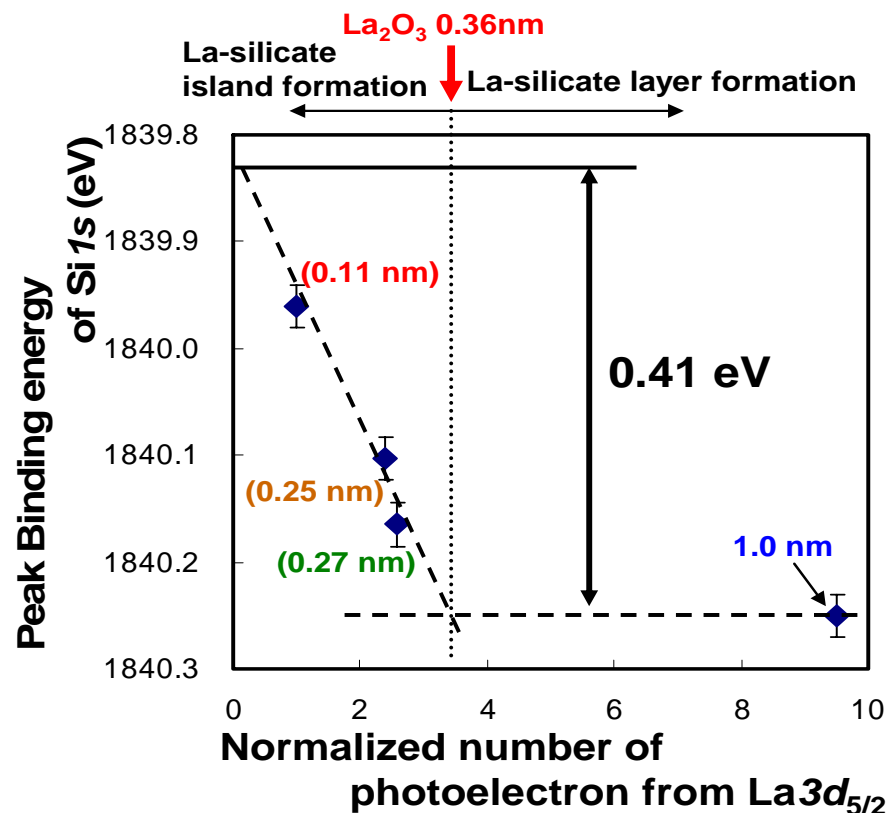
The amount of La atoms at HfO₂/SiO₂ determines
the V_{fb}

An interface dipole at high-k/SiO₂

Binding energy shift of the substrate with the amount of La_2O_3 insertion

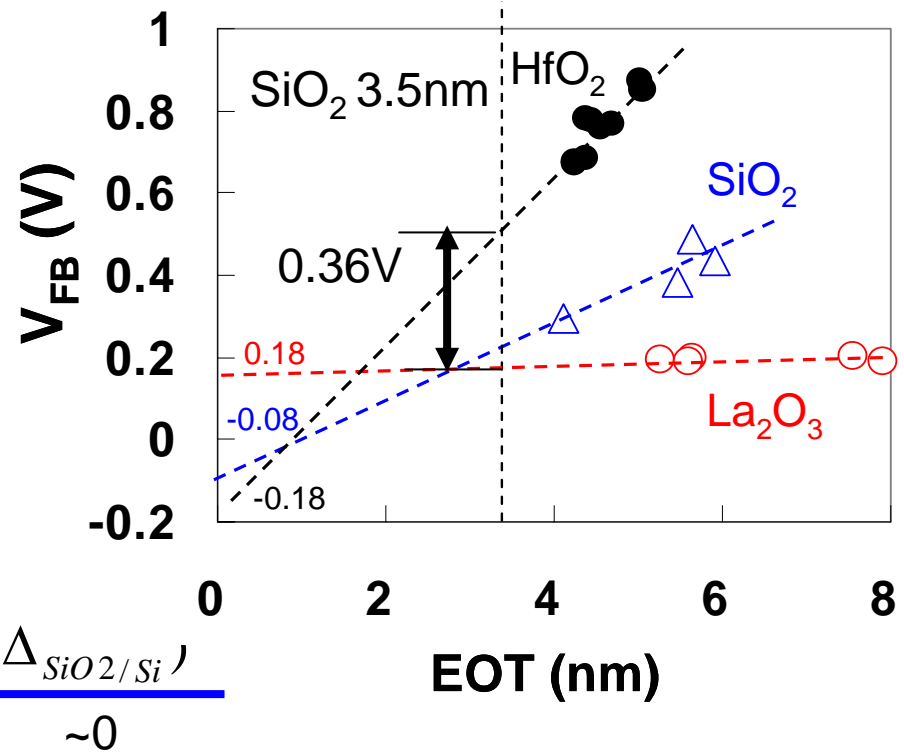
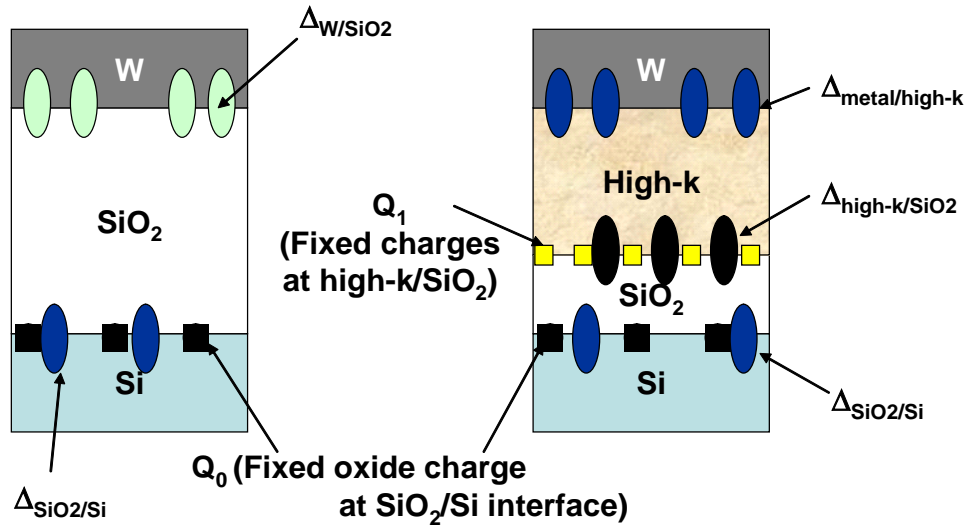


Measurement with XPS
No influence of Dit



- Direct observation of the band bending of the substrate
- The amount of La atoms at High-k/ SiO_2 determines the V_{FB}

Dipole extraction from HfO₂/SiO₂/Si and La₂O₃/SiO₂/Si



Metal/SiO₂/Si

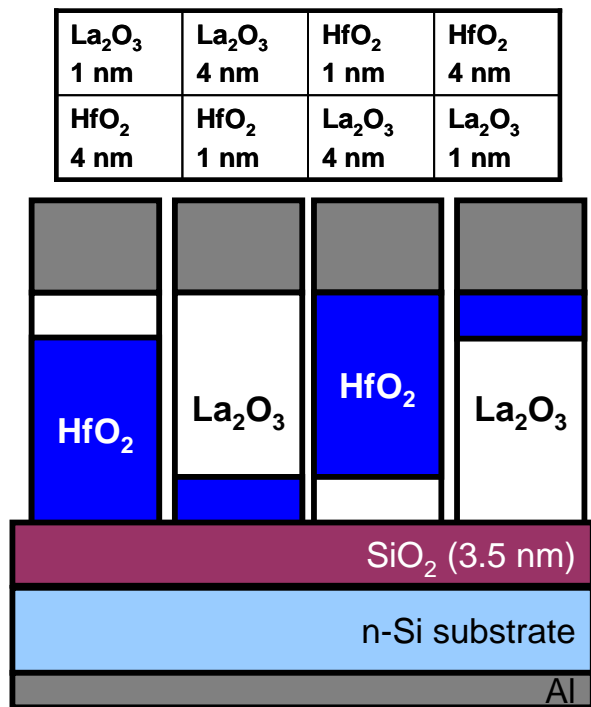
$$V_{FB} = -EOT \left(\frac{Q_0}{\epsilon_0 \epsilon_{ox}} \right) + \frac{\varphi_{ms}}{q} + \underbrace{(\Delta_{metal/SiO_2} + \Delta_{SiO_2/Si})}_{\sim 0}$$

Metal/high-k/SiO₂/Si

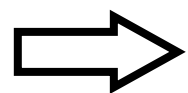
$$V_{FB} = -EOT \left(\frac{Q_0 + Q_1}{\epsilon_0 \epsilon_{ox}} \right) + \frac{Q_1 \cdot EOT_{IL}}{\epsilon_0 \epsilon_{ox}} + \frac{\varphi_{ms}}{q} + \underbrace{(\Delta_{metal/high-k} + \Delta_{high-k/IL} + \Delta_{IL/Si})}_{\sim 0}$$

$$(\Delta W/HfO_2 + \Delta HfO_2/SiO_2) - (\Delta W/La_2O_3 + \Delta La_2O_3/SiO_2) = 0.36 \text{ V}$$

Dipole at metal interface : W/HfO₂, W/La₂O₃



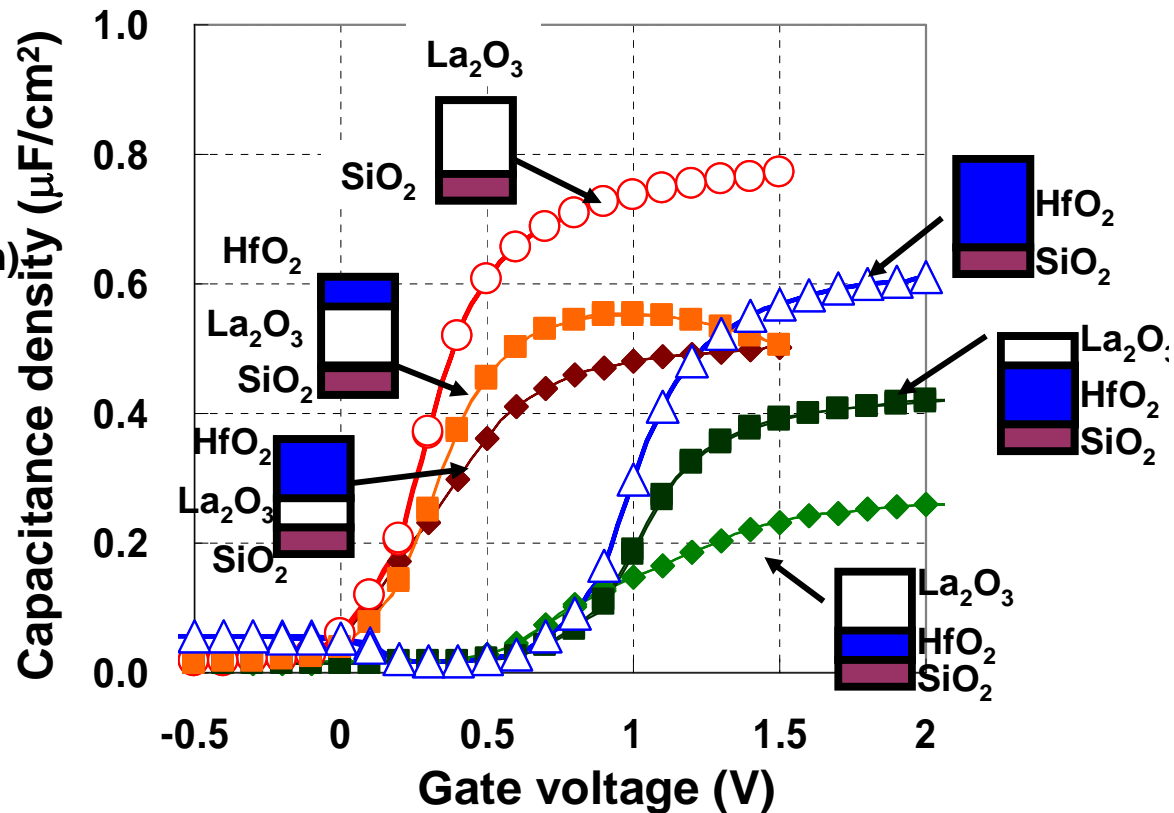
$$\Delta W/\text{HfO}_2 = \Delta W/\text{La}_2\text{O}_3$$



$$\Delta \text{HfO}_2/\text{SiO}_2 - \Delta \text{La}_2\text{O}_3/\text{SiO}_2 = 0.36 \text{ V}$$

No difference at metal interface

High-k/SiO₂ is the reason for V_{FB} shift

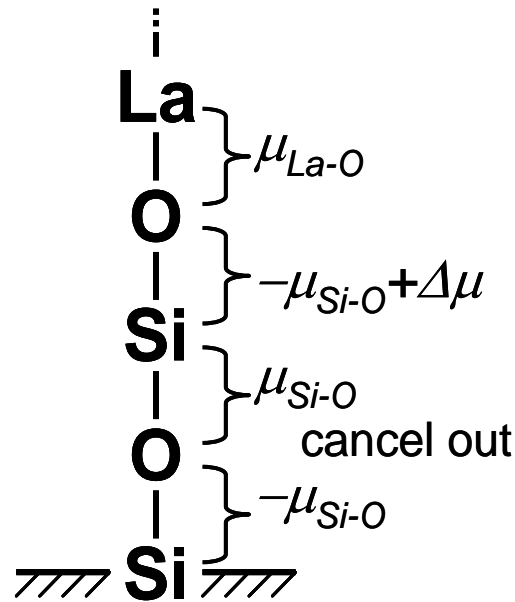


Modeling of the interface dipole

La₂O₃/IL/Si

μ : dipole moment

(electronegativity) \times (bonding length)



$$\mu_{all} = \frac{2}{3} \mu_{La-O} - \frac{2}{4} \mu_{Si-O} + \Delta\mu$$

Valence number
of O and Si

O and Si

Second neighbor
of O and SiO
molecule

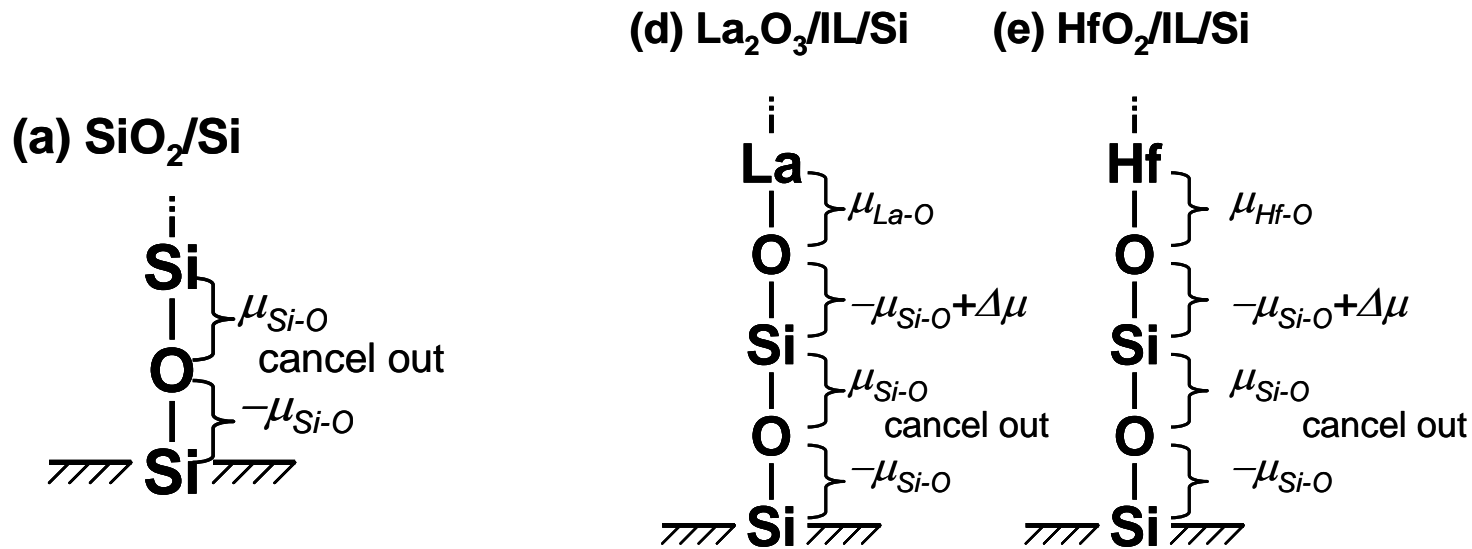
$$= \frac{2}{3} \times 0.604 - \frac{2}{4} \times 0.246 + 0.141$$

$$= 0.169 \text{ (nm)}$$

electronegativity
O: 3.44
Si: 1.90
La: 1.10

Definition of dipole moment for electron transfer

Estimation of V_{FB}



| | <i>calculation</i> | μ_{all} | V_{FB} (V) |
|--|---|-------------|--------------|
| (a) SiO_2/Si | $1/2\mu_{\text{Si-O}} - 1/2\mu_{\text{Si-O}}$ | 0 | 0.40 |
| (d) $\text{La}_2\text{O}_3/\text{SiO}_2$ | $2/3\mu_{\text{La-O}} - 1/2\mu_{\text{Si-O}} + \Delta\mu$ | 0.169 | 0.08 |
| (e) $\text{HfO}_2/\text{SiO}_2$ | $1/2\mu_{\text{Hf-O}} - 1/2\mu_{\text{Si-O}} + \Delta\mu$ | -0.023 | 0.44 |

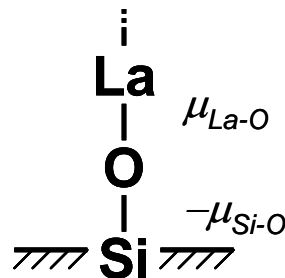
0.36V

$$V_{FB} = \eta \mu_{all} + \phi_{ms} \quad \phi_{ms} = 0.4 \text{ eV}$$

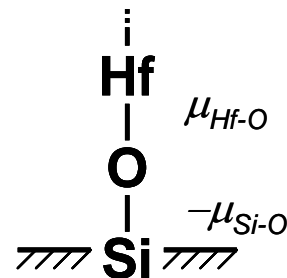
$\eta = -1.87$ using experimentally deduced 0.36V

Estimation of V_{FB} for direct high-k/Si

(b) $\text{La}_2\text{O}_3/\text{Si}$



(c) HfO_2/Si



$$V_{FB} = \eta \mu_{all} + \phi_{ms}$$

$$\eta = -1.87 \quad \phi_{ms} = 0.4 \text{ eV}$$

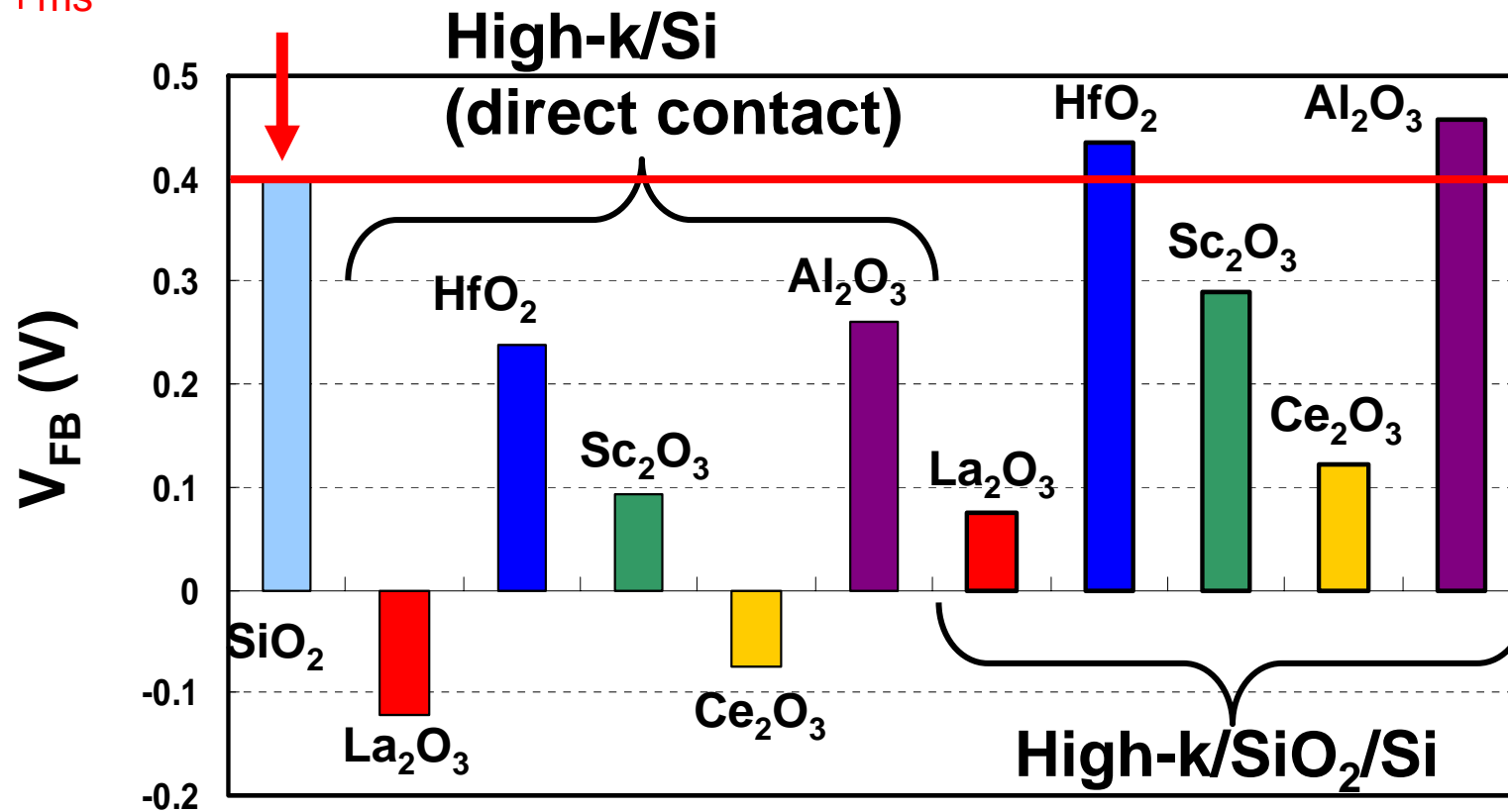
estimation

| | <i>calculation</i> | μ_{all} | V_{FB} (V) |
|---------------------------------------|-----------------------------------|-------------|--------------|
| (b) $\text{La}_2\text{O}_3/\text{Si}$ | $2/3 \mu_{La-O} - 1/2 \mu_{Si-O}$ | 0.279 | -0.12 |
| (c) HfO_2/Si | $1/2 \mu_{Hf-O} - 1/2 \mu_{Si-O}$ | 0.087 | 0.24 |

Proposed model can predicts the V_{FB} even with direct contact of high-k/Si

V_{FB} estimation on wide materials

$$\phi_{ms} = 0.4 \text{ eV}$$

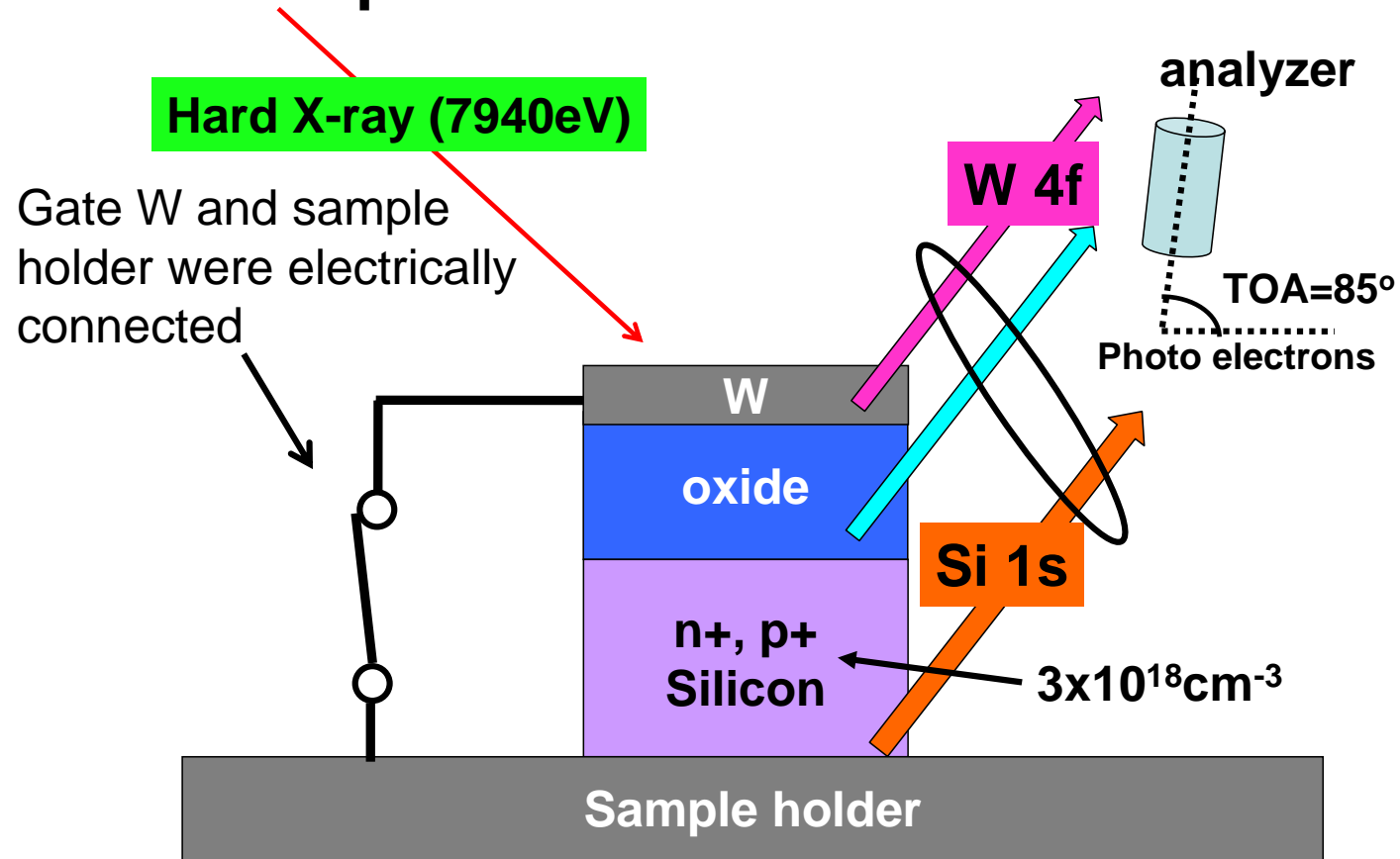


Measured and modeled V_{FB}

| Oxide | Measured V_{fb} (V) | Modeled V_{fb} (V) | EOT (nm) |
|--------------------------------|-----------------------|----------------------|----------|
| SiO ₂ | 0.38 | 0.40 | 5.46 |
| La ₂ O ₃ | -0.13 | -0.12 | 1.15 |
| HfO ₂ | 0.34 | 0.24 | 0.90 |
| Sc ₂ O ₃ | 0.18 | 0.09 | 1.40 |
| Ce ₂ O ₃ | -0.04 | -0.07 | 1.11 |

A fairly nice mode to predict the V_{FB}

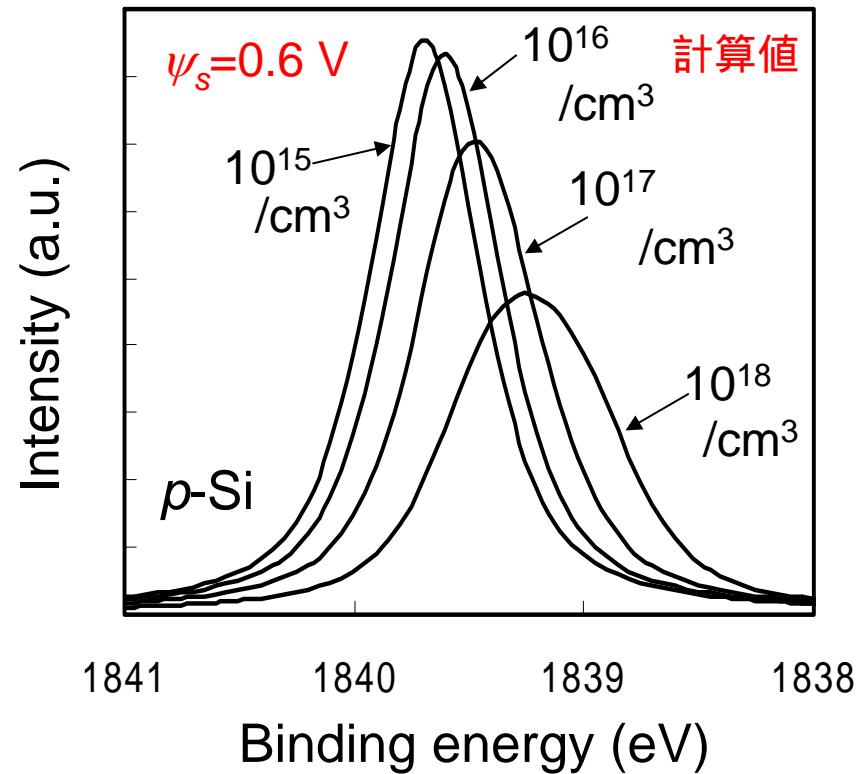
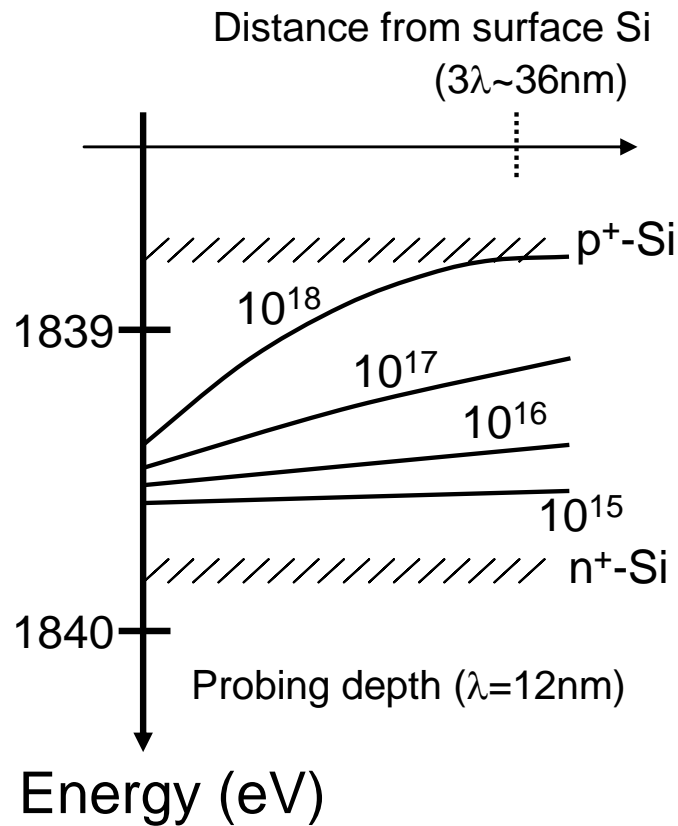
Interface dipole measurement with XPS



Fermi level of metal and Si are fixed to the ground potential

No influence of Dit

An example of Si 1s XPS spectra on different doping



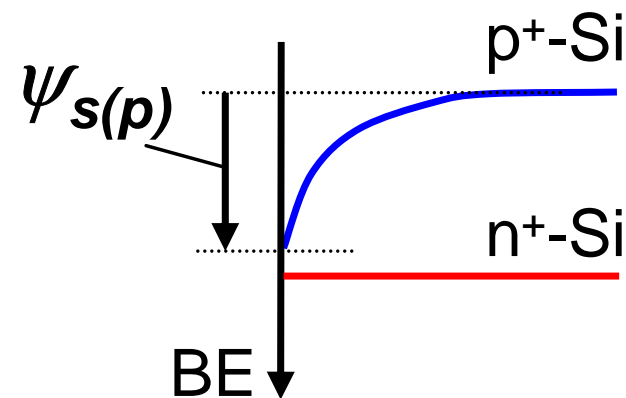
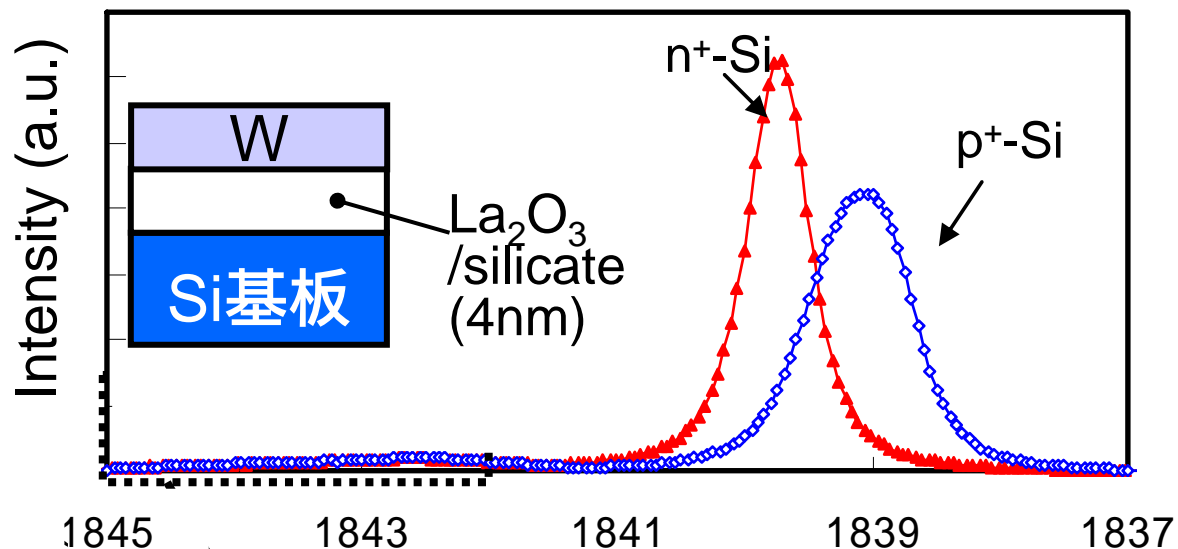
$$\psi(z) \approx \psi_s \left(1 - \sqrt{\frac{qN_b}{2\epsilon_{Si}\psi_s}} \cdot z \right)^2$$

N_b : doping concentration
 ψ_s : surface potential

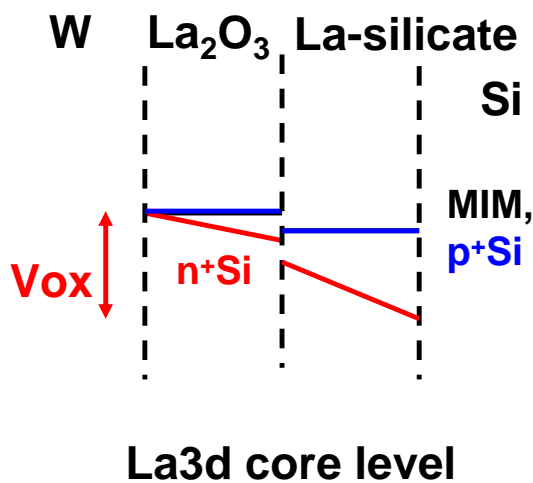
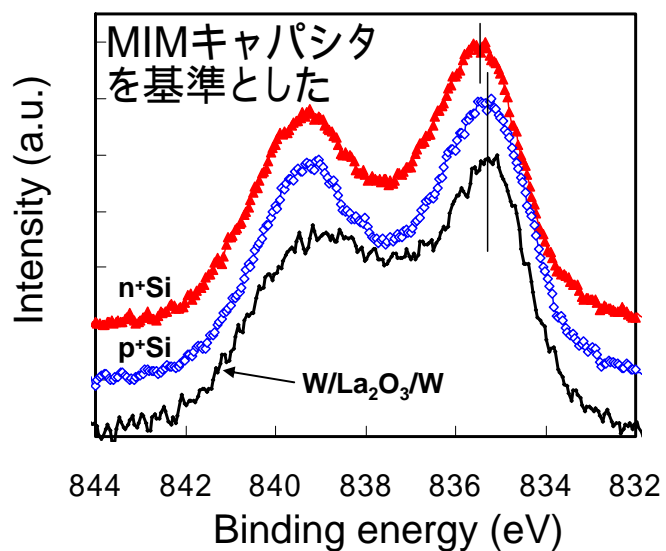
Spectra broadening due to band bending at surface

Extraction of surface potential

Quantitative estimation of interface dipole

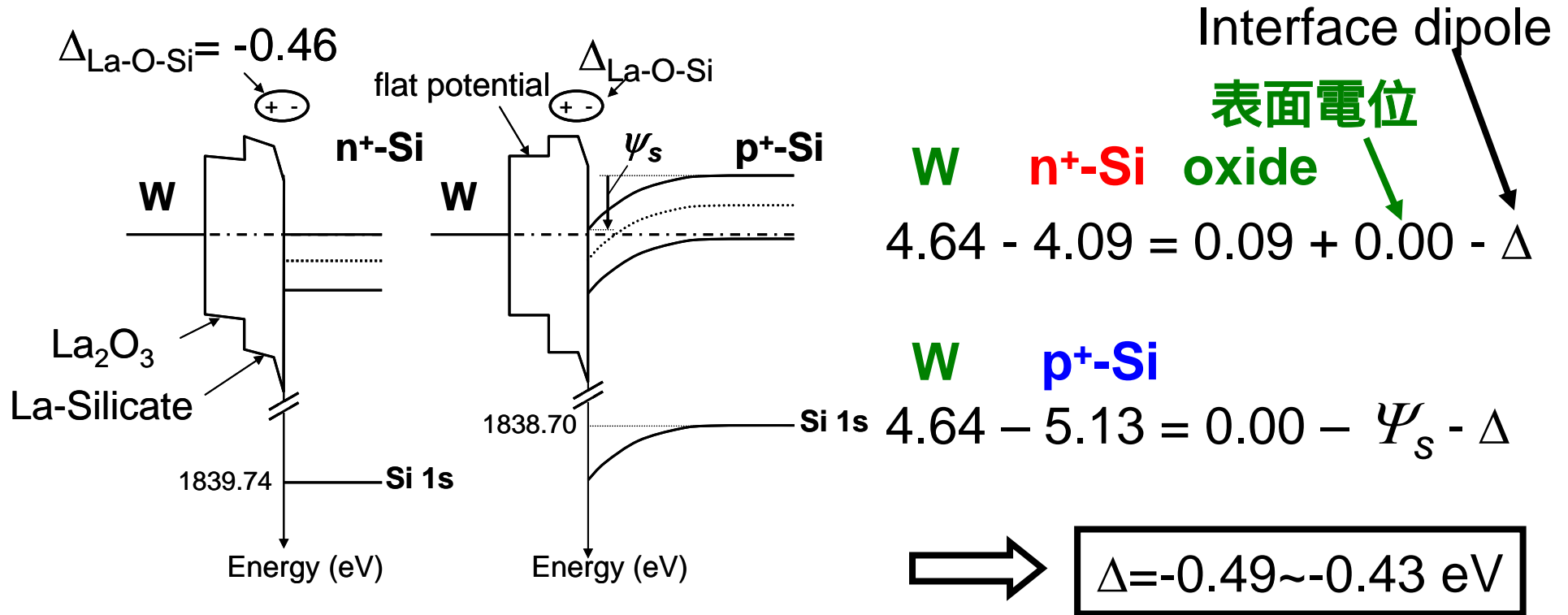


Surface potential extraction from Si 1s



Voltage in the oxide from La3d_{5/2} spectra

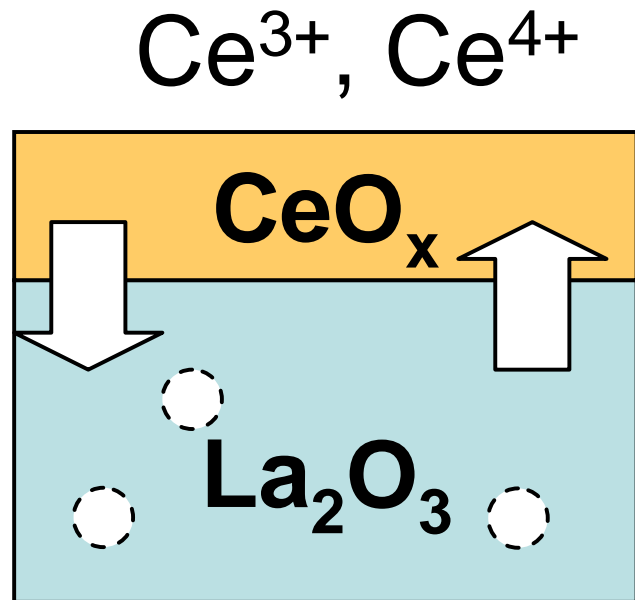
Band diagram of $\text{La}_2\text{O}_3/\text{La-silicate}/\text{Si}$



Dipole extracted from capacitors: -0.52 eV

Good agreement with electrical measurements

(9) Defect compensation with CeO_x capping



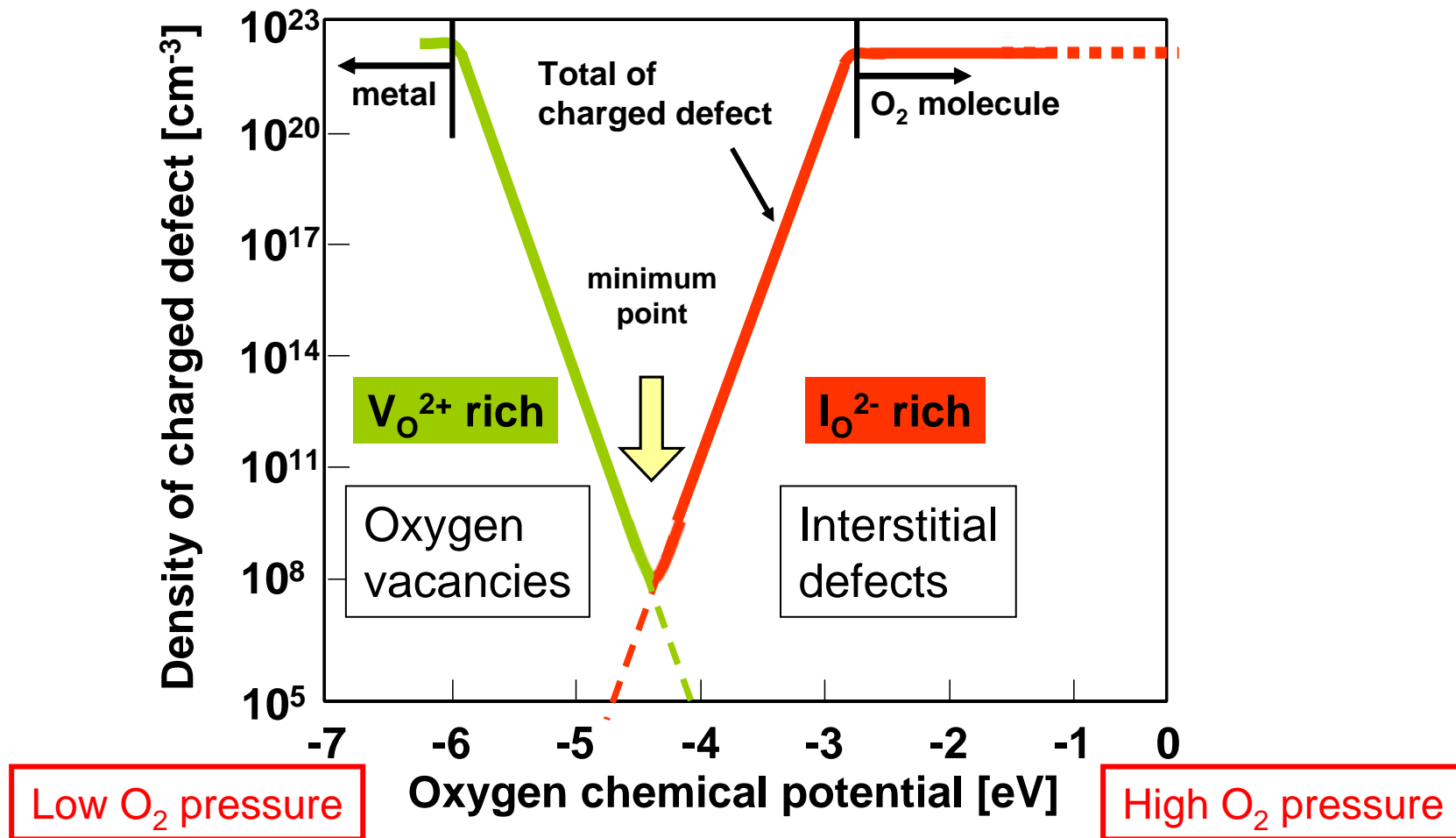
Valence number changes
to fix the oxygen partial
pressure



Keeps the defects in the
 La_2O_3 to a certain value

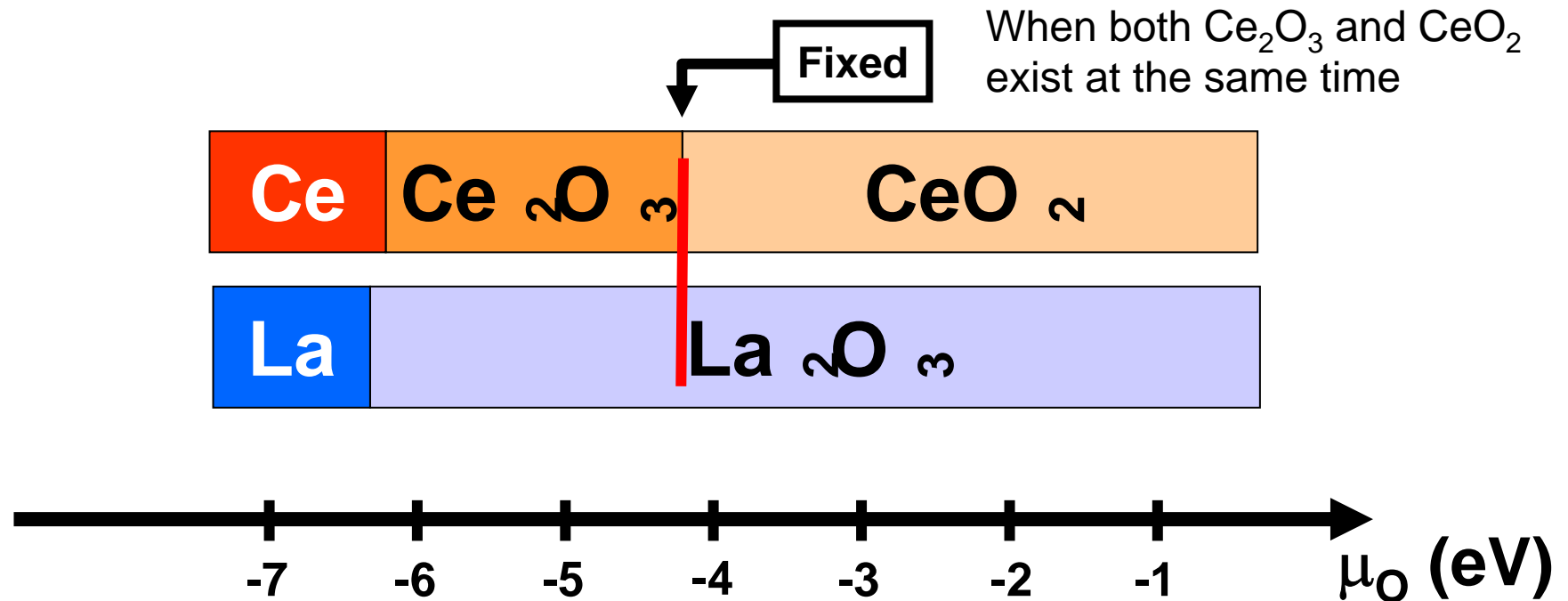
Control of the defect concentration with capping
recovery of μ_{eff} and V_{FB} shift

Theoretical study of the defects in La_2O_3



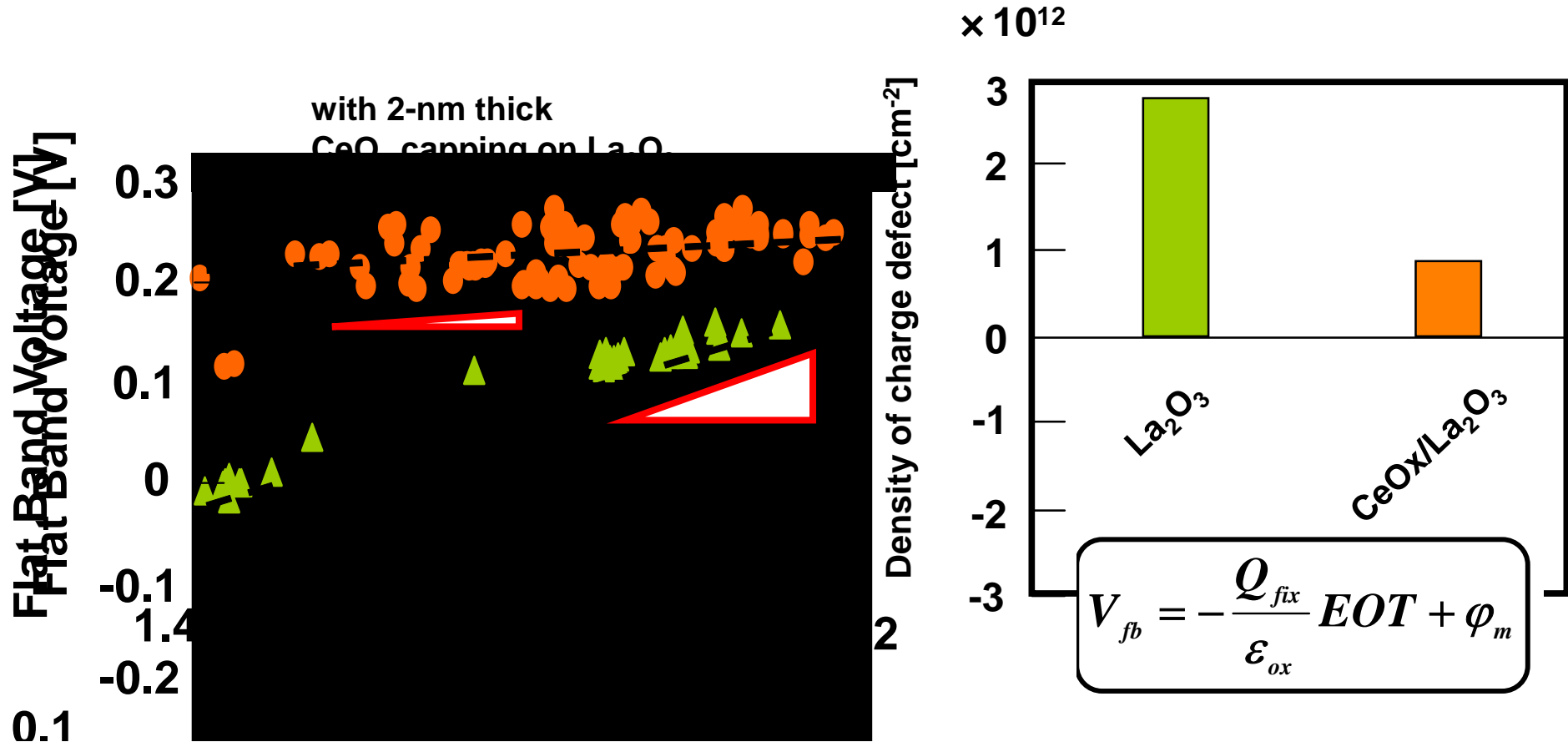
Smallest charged defect can be achieved at oxygen chemical potential of -4.2eV

Fixation of the chemical potential with CeO_x



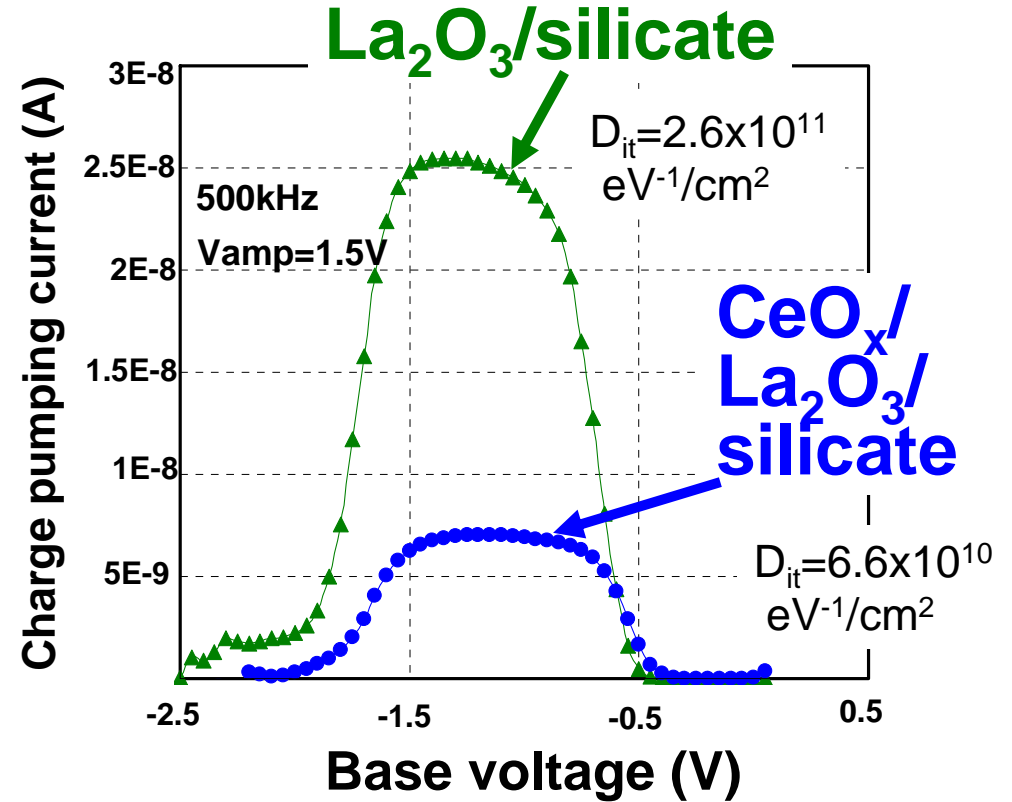
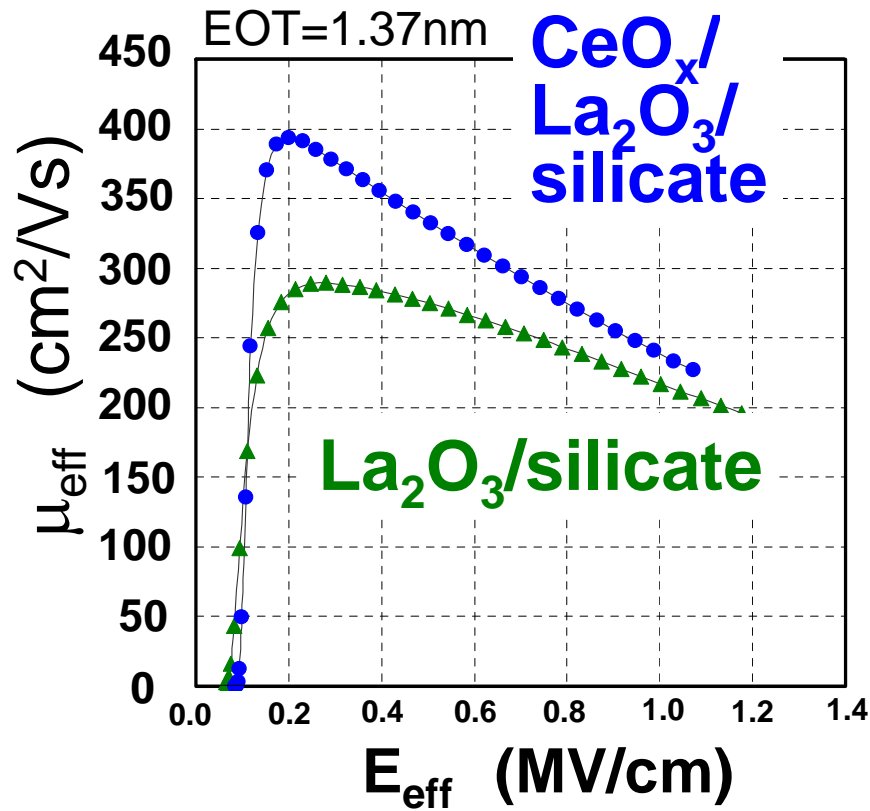
Adjacent high-k has the same chemical potential
 CeO_x shows μ_0 where smallest defects can be achieved with La_2O_3

Suppression of fixed charge with CeO_x capping



Fixed charge density reduction by 66%

μ_{eff} and D_{it} improvement with CeO_x capping



Improvement in the low field μ_{eff} and D_{it}