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Charged defects reduction in gate insulator with multivalent materials

[1]Miyuki Kouda, [2]Naoto Umezawa, [1]Kuniyuki Kakushima,
[1]Parhat Ahmet, [3]Kenji Shiraishi, [2]Toyohiro Chikyow,
[4]Keisaku Yamada and [1]Hiroshi Iwai

[1]Tokyo Institute of Technology
[2]National Institute for Materials Science
[3]University of Tsukuba
[4]Waseda University

- Background
- Purpose of this work
- Theoretical approach
- Experimentally approach
- Conclusion

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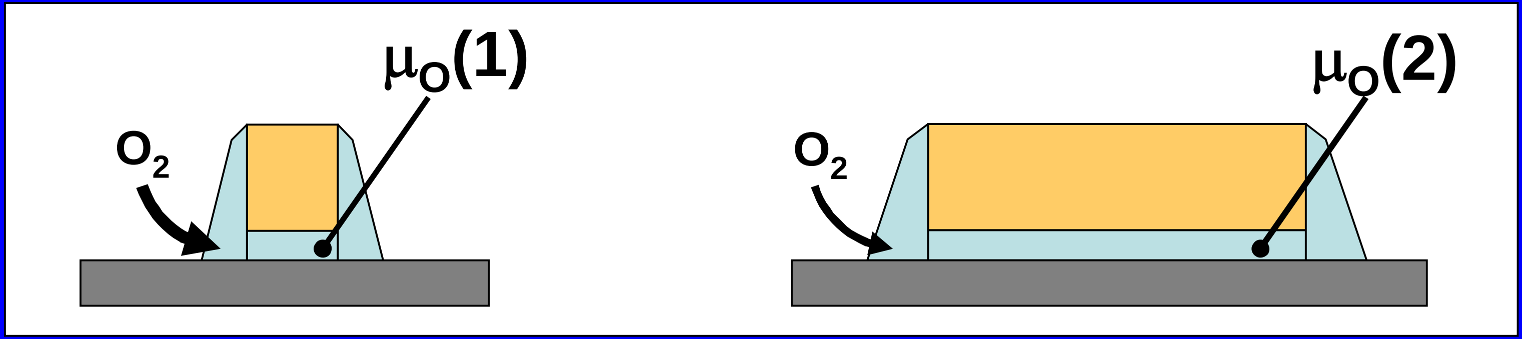
- Propose of this work
- Theoretical approach
- Experimentally approach
- Conclusion

1 Importance of oxygen chemical potential (μ_o) in gate oxide



$$\mu_O(1) \neq \mu_O(2)$$

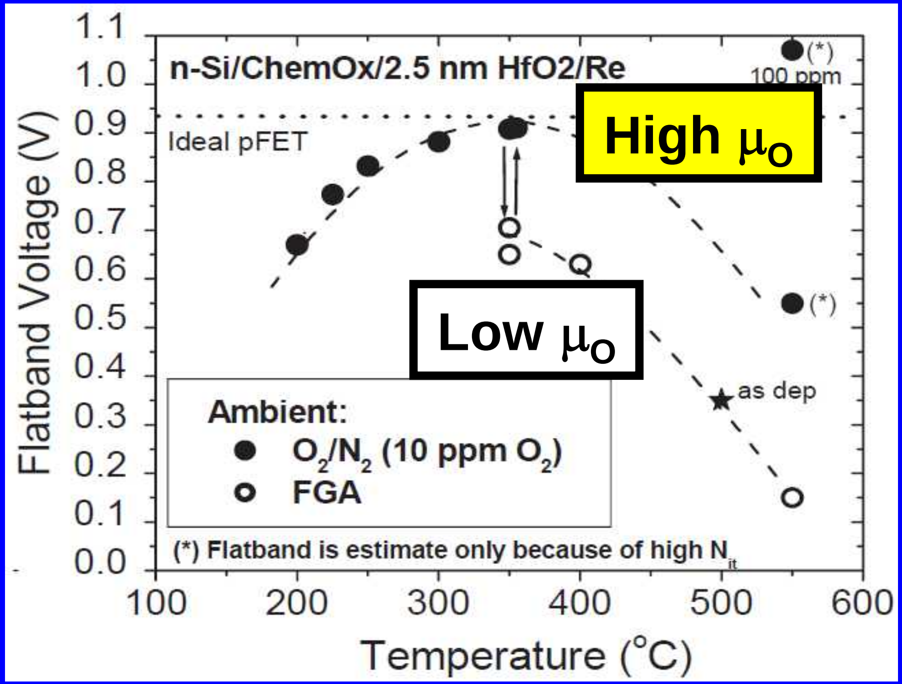
- Shape of gate edge
- Oxygen incorporated in metal electrode
- Device structure, etc

Variability of μ_O will change the density of defects

Precise control of μ_O is very difficult

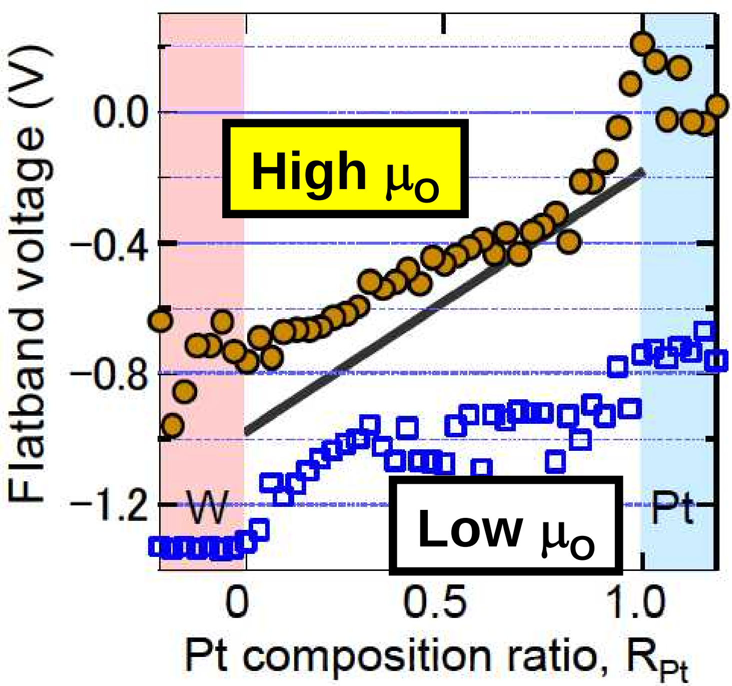
Instability of flatband voltage by μ_O

HfO_2



E. Cartier et al., Symp. on VLSI Technology, p.230 (2005)

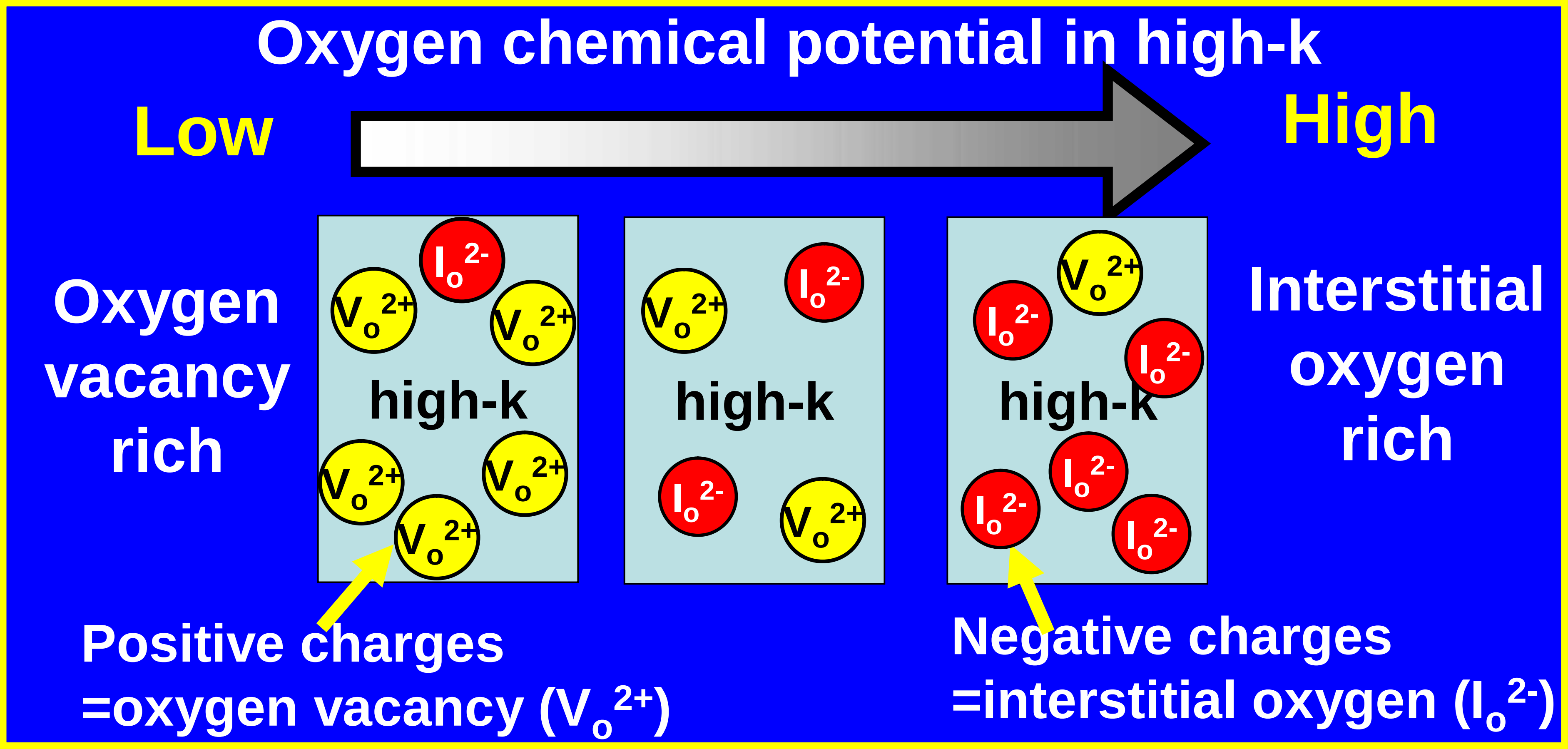
La_2O_3



K. Ohmori et al., SSDM (2006), p.210

Flatband voltage is very sensitive to oxygen chemical potential

Number of defects is sensitive to oxygen chemical potential (μ_O)



Oxygen chemical potential in high-k

Low

High

Oxygen vacancy rich

Interstitial oxygen rich

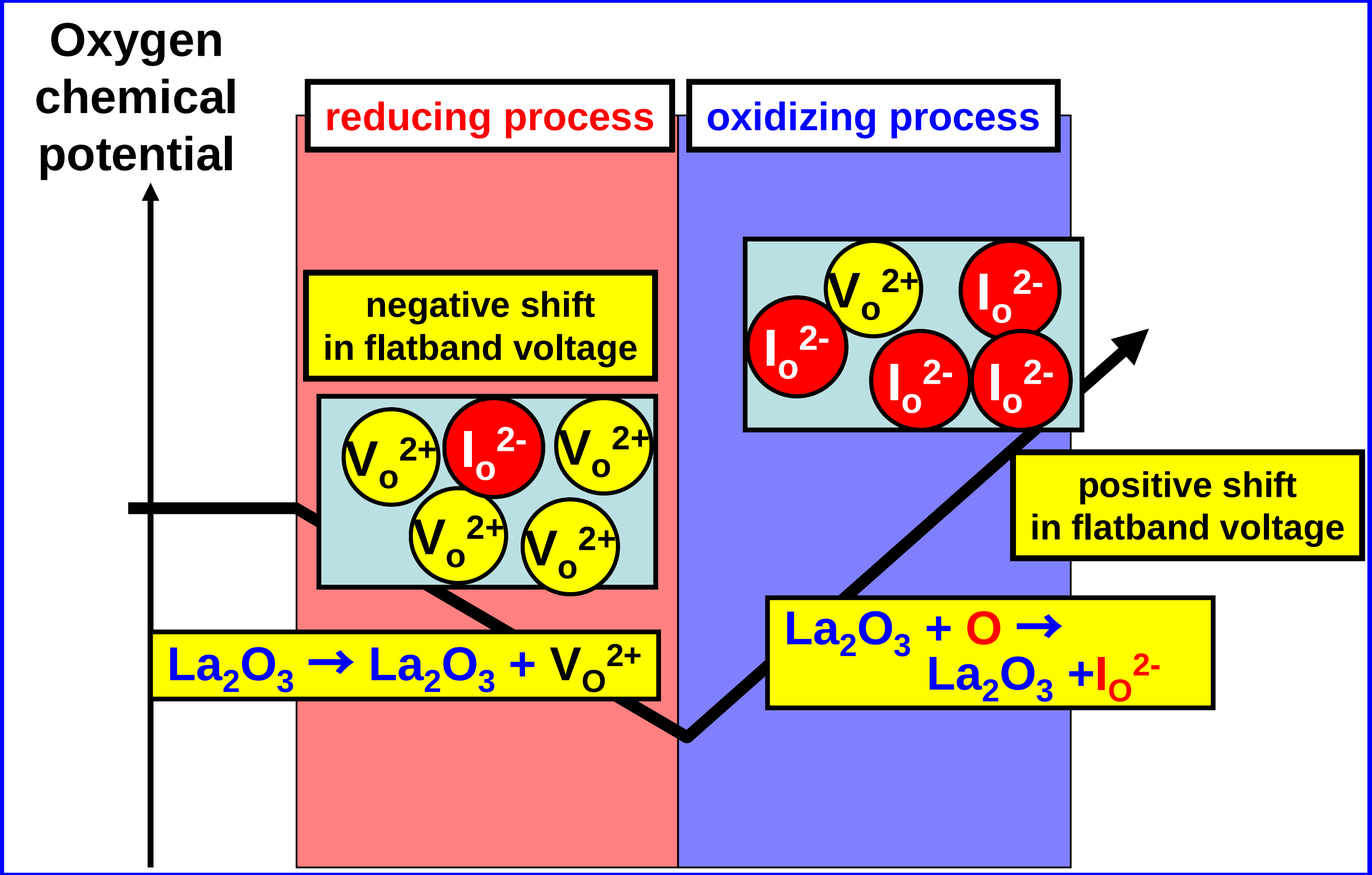
Positive charges
=oxygen vacancy (V_o^{2+})

Negative charges
=interstitial oxygen (I_o^{2-})

Degradation in MOSFET:

V_{th}, V_{fb} shift, Variability, mobility reduction

Process induced oxygen chemical potential shift



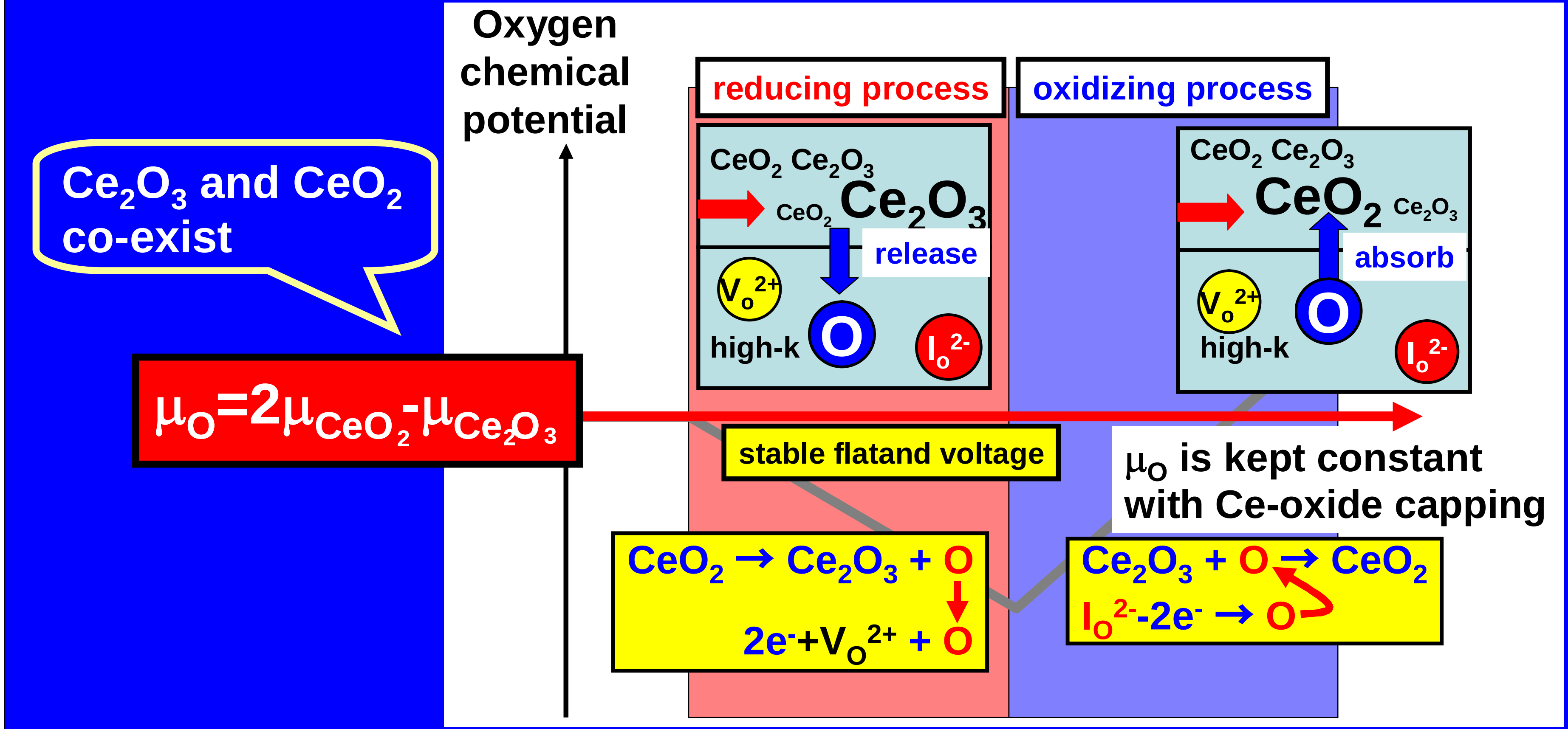
$La_2O_3 \rightarrow La_2O_3 + V_O^{2+}$

$La_2O_3 + O \rightarrow La_2O_3 + I_O^{2-}$

Oxygen chemical potential fluctuates by process condition

Purpose of this work

~Multivalent material capping for μ_O fixation~



Ce_2O_3 and CeO_2 co-exist

$$\mu_O = 2\mu_{CeO_2} - \mu_{Ce_2O_3}$$

μ_O is kept constant with Ce-oxide capping

$CeO_2 \rightarrow Ce_2O_3 + O$

$2e^- + V_O^{2+} + O$

$Ce_2O_3 + O \rightarrow CeO_2$

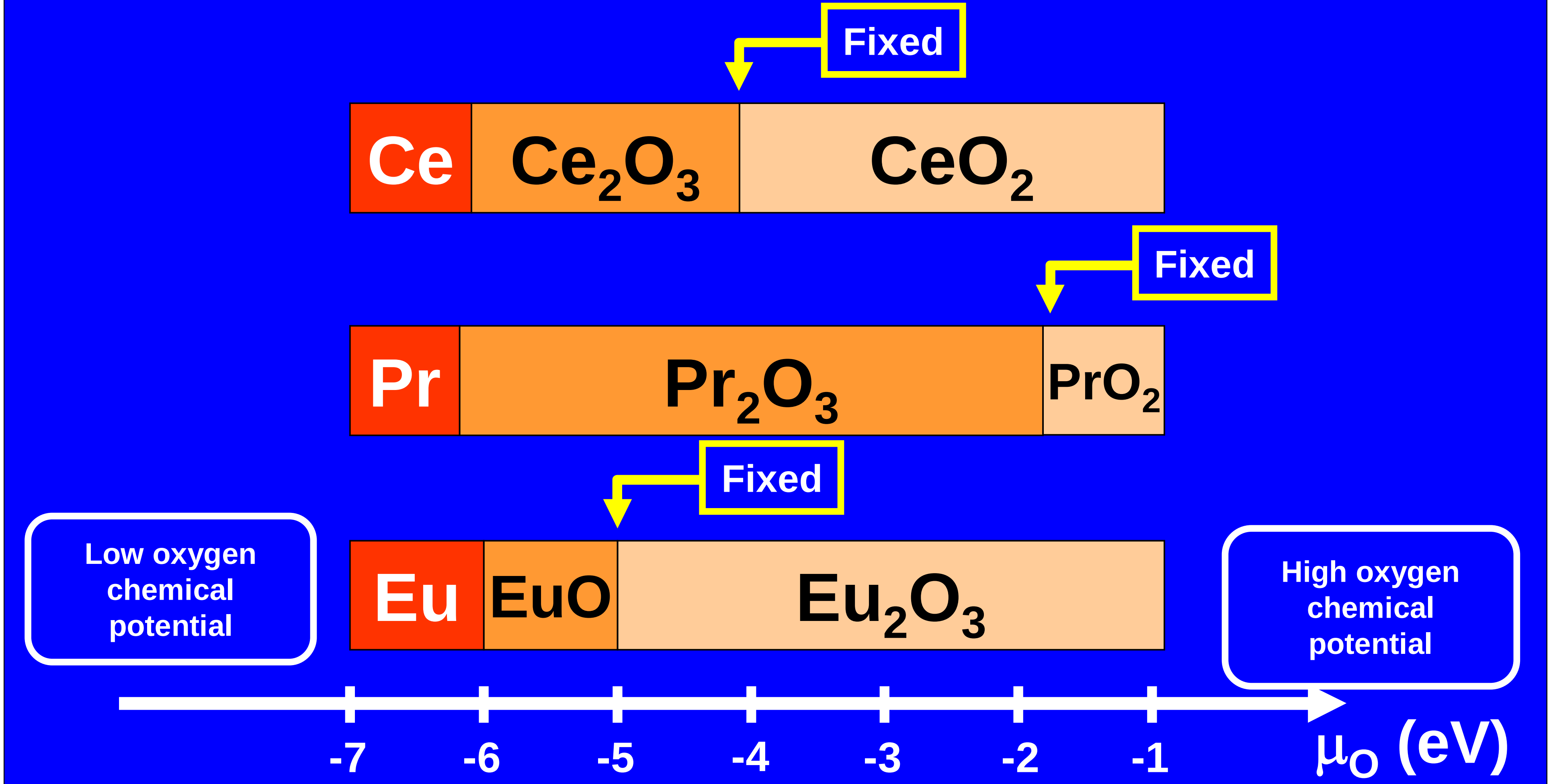
$I_O^{2-} - 2e^- \rightarrow O$

Multivalent material keep the chemical potential at intrinsic value by releasing and absorbing oxygen

➡ **Density of charged defects in high-k is kept constant**

➡ **V_{th} or V_{FB} is stable**

Intrinsic value of μ_O in multivalent materials



Fixed points depends on multivalent materials

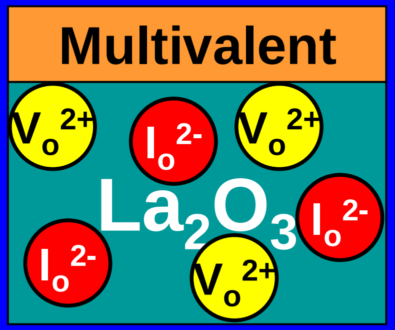
→ **Proper material selection for host high-k**

Two approaches in this work

Feasibility study of multivalent material capping to fix the oxygen chemical potential for charged defect reduction

Theoretical approach

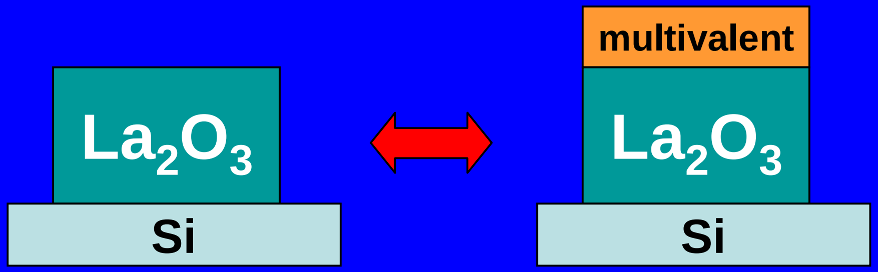
First-principles calculation



Estimate the density of charged defects in high-k

Experimental approach

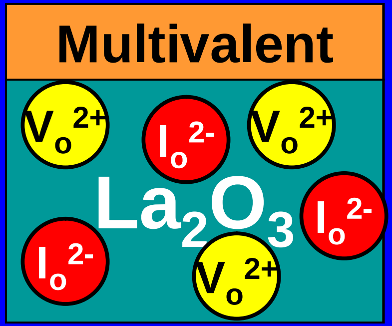
Device fabrication



Quantity of the charged defects in high-k film with multivalent material capping

- Back ground
- Propose of this work
- Theoretical approach

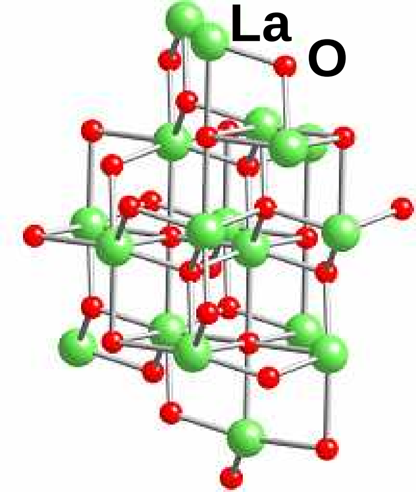
First-principles calculation



Ce, Eu, Pr-oxide were used as capping materials

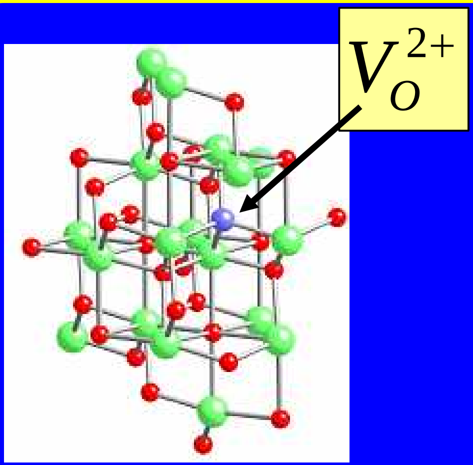
Calculation of charged defect density

La_2O_3: 50atoms , Hexagonal

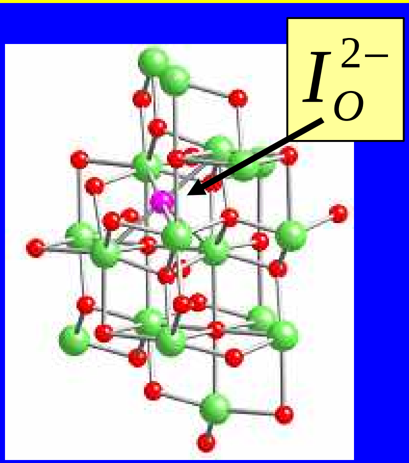


Perfect crystal

no defect



Oxygen vacancy



Interstitial oxygen

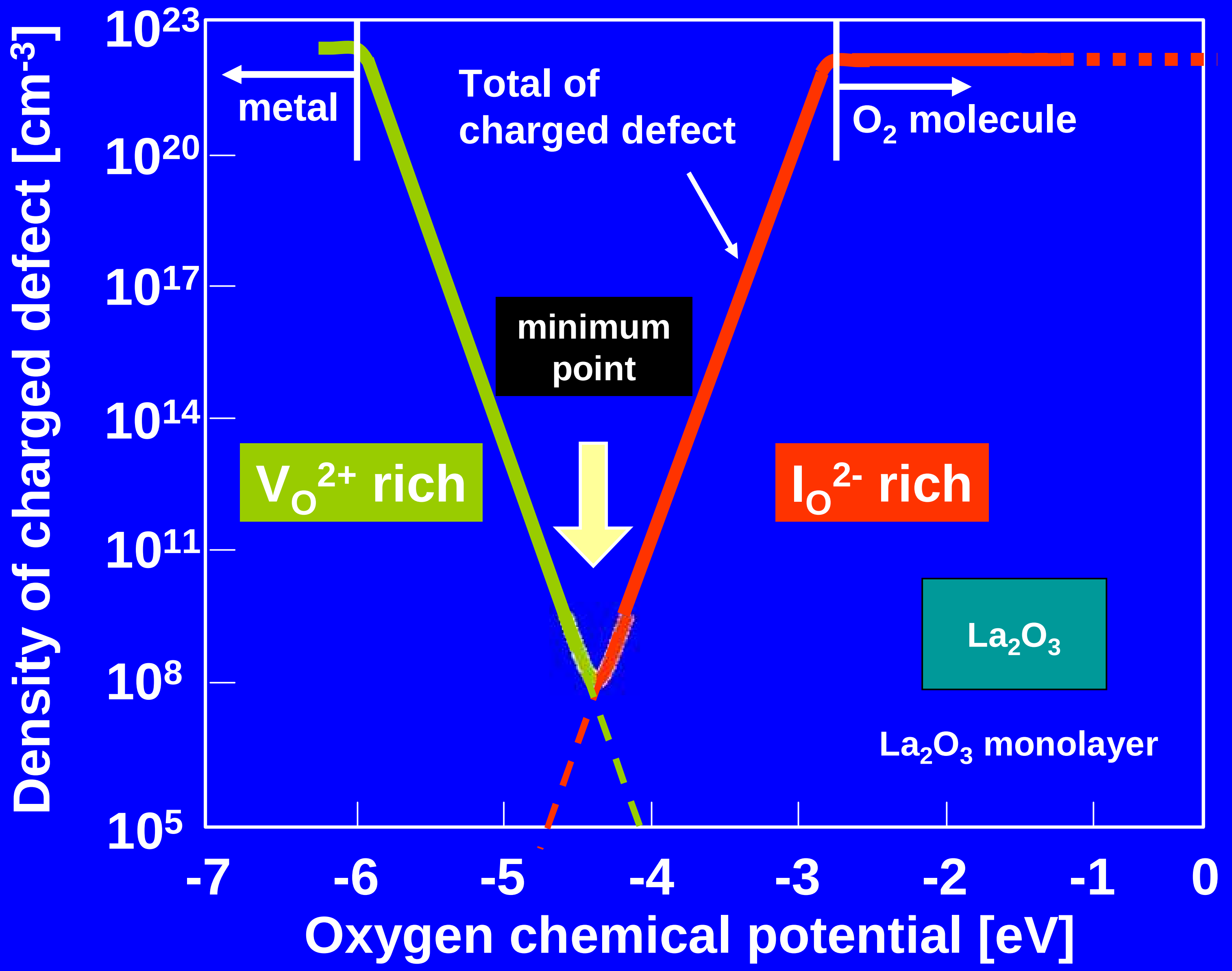
$$E_f[X^Q] = E_{tot}[X^Q] - E_{tot}[no\ defect] - n_o\mu_o + Q(e_f + e_v)$$

$$n[X^Q] = \frac{N_{site}[X^Q]}{1 + \exp(\frac{E_f[X^Q]}{k_B T})}$$

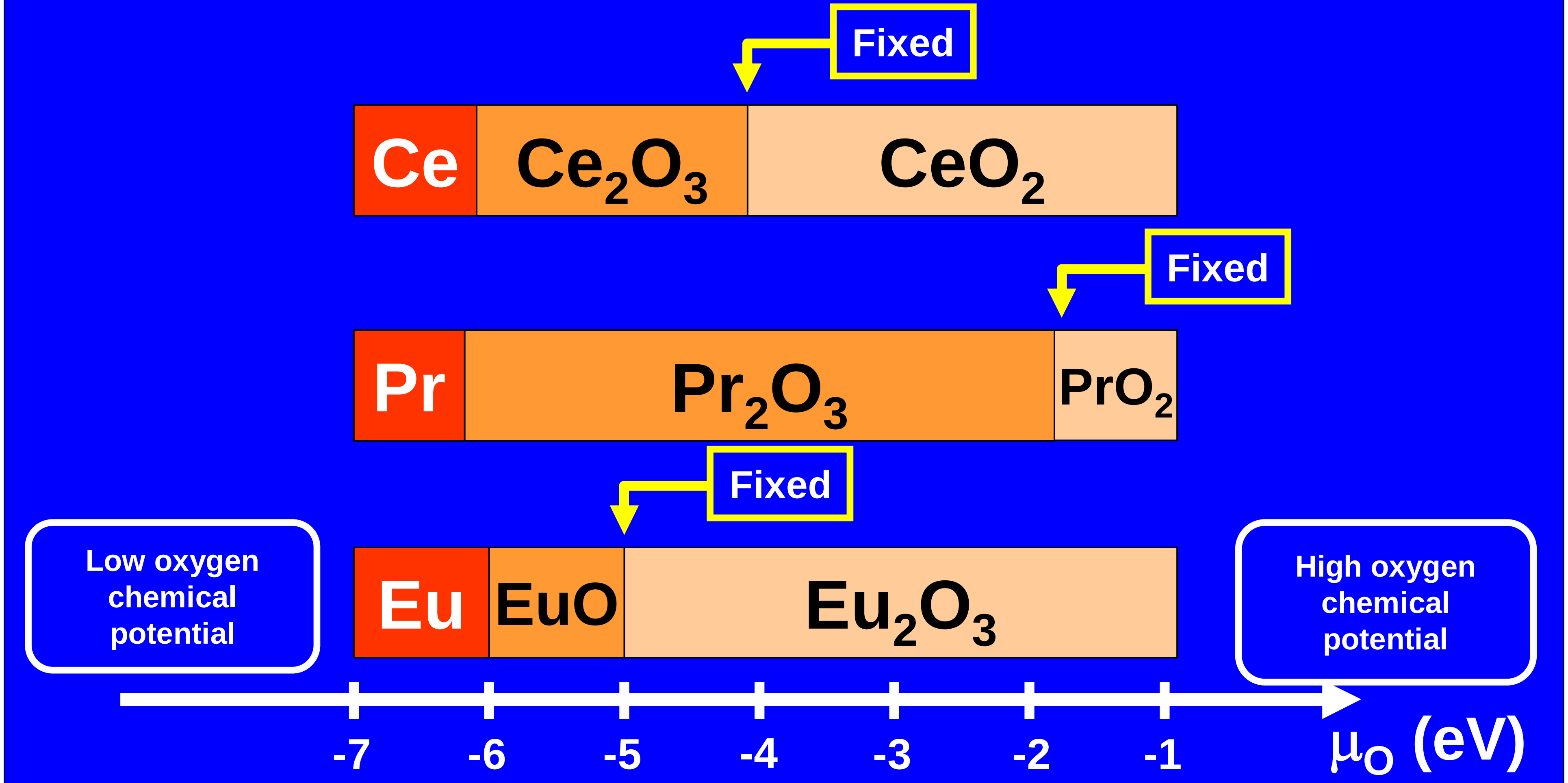
Oxygen chemical potential

$n[I_o^{2+}]$+ $n[V_o^{2+}]$: total of charge density

Density of charged defects in La_2O_3



Fixed μ_O point in multivalent materials



Fixed

Ce | Ce_2O_3 | CeO_2

Fixed

Pr | Pr_2O_3 | PrO_2

Fixed

Low oxygen chemical potential

Eu | EuO | Eu_2O_3

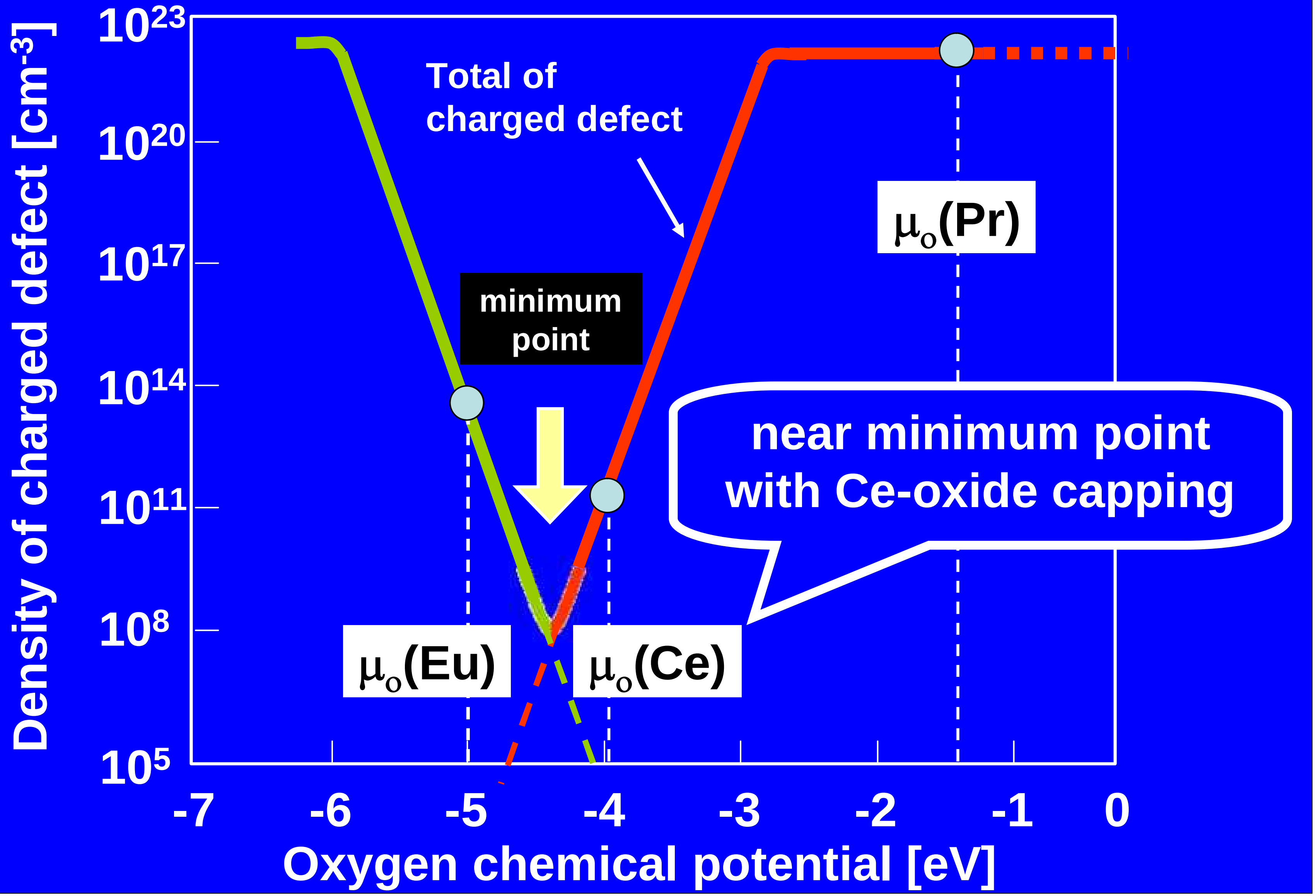
High oxygen chemical potential

-7 -6 -5 -4 -3 -2 -1 μ_O (eV)

Fixed points depends on multivalent materials

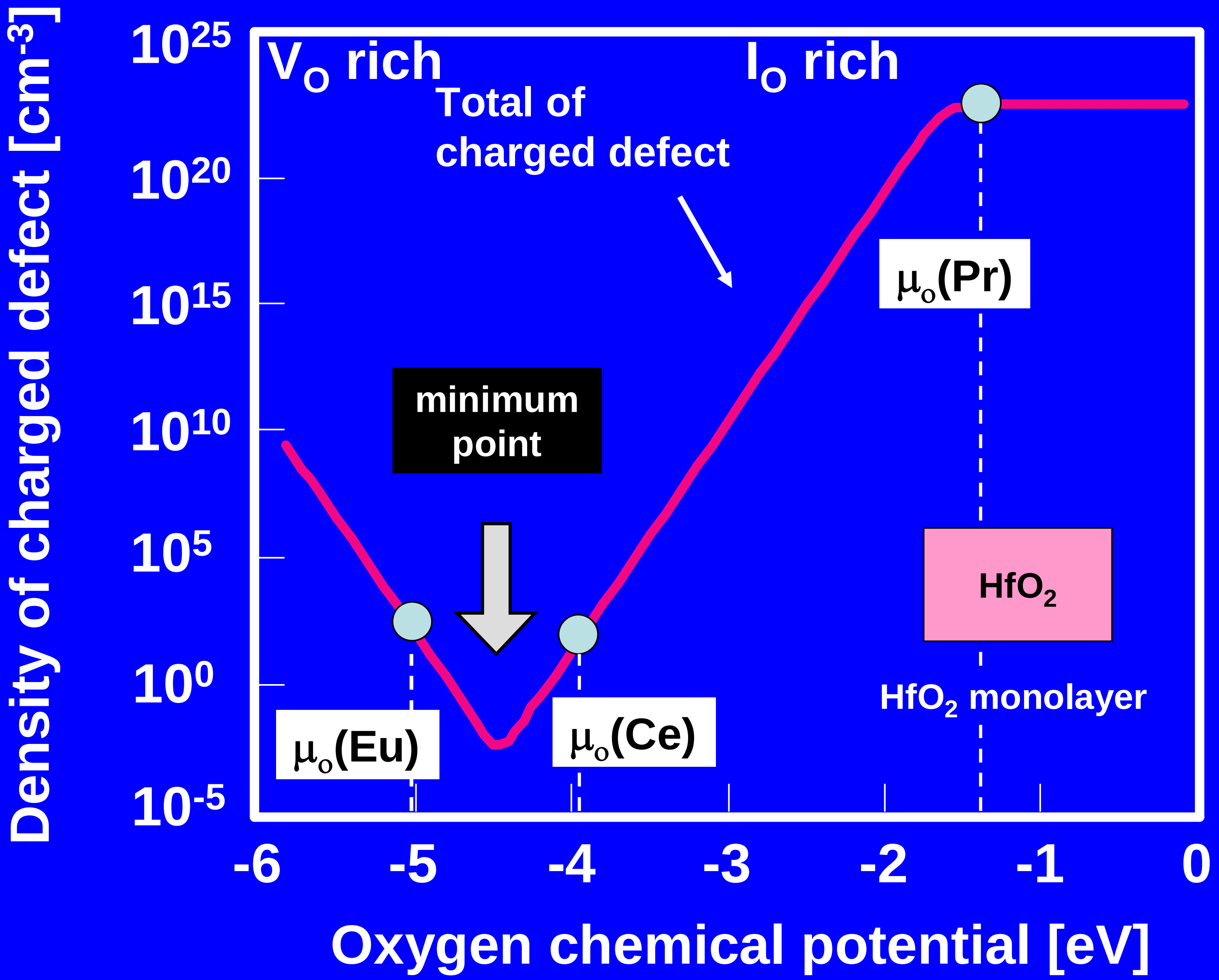
→ **Proper material selection for host high-k**

Fixation of μ_O with Eu, Ce and Pr oxides in La_2O_3

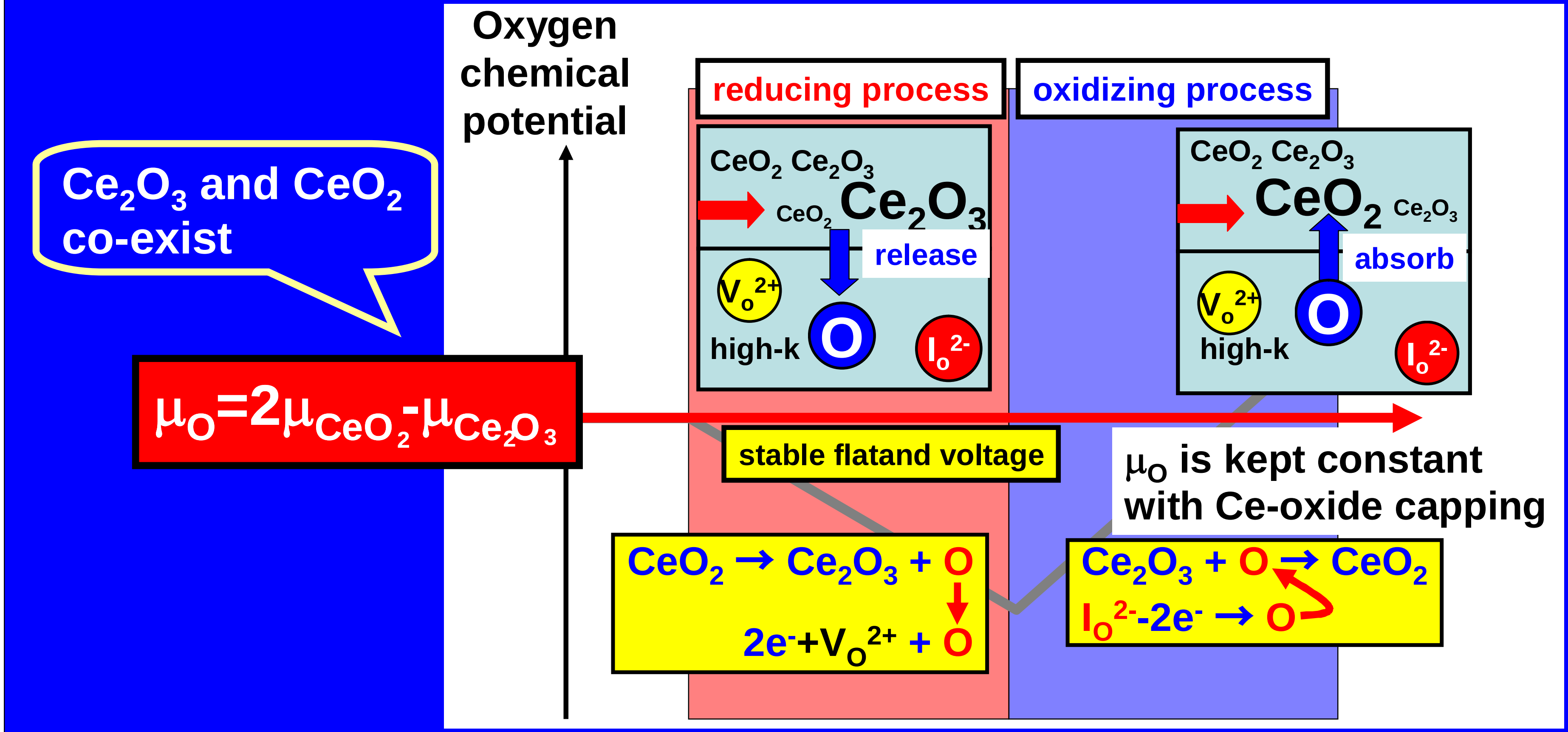


near minimum point with Ce-oxide capping

Density of charged defects in HfO_2



Message from theoretical calculation



Oxygen chemical potential

Ce_2O_3 and CeO_2 co-exist

$\mu_O=2\mu_{CeO_2}-\mu_{Ce_2O_3}$

reducing process

oxidizing process

CeO_2 Ce_2O_3 CeO_2 Ce_2O_3 release V_o^{2+} high-k O I_o^{2-}

CeO_2 Ce_2O_3 CeO_2 Ce_2O_3 absorb V_o^{2+} high-k O I_o^{2-}

stable flatand voltage

μ_O is kept constant with Ce-oxide capping

$CeO_2 \rightarrow Ce_2O_3 + O$

$2e^-+V_O^{2+} + O$

$Ce_2O_3 + O \rightarrow CeO_2$

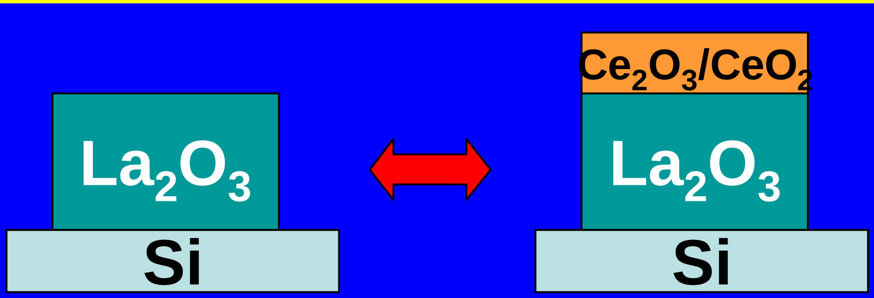
$I_O^{2-}-2e^- \rightarrow O$

Fixation of μ_O with multivalent oxide, can control the density of charged defect

Total density of charged defects can be minimized with Ce oxide capping for both La_2O_3 and HfO_2

- Back ground
- Propose of this work
- Theoretical approach

○ **Experimental approach**



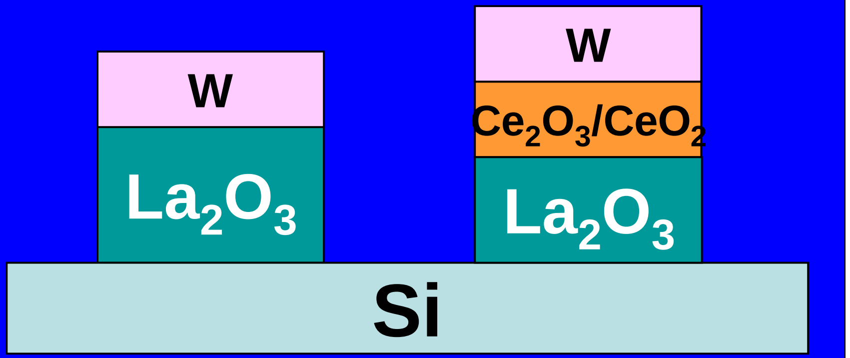
Quantify the charged defects in high-k film with and w/o multivalent capping

Device fabrication

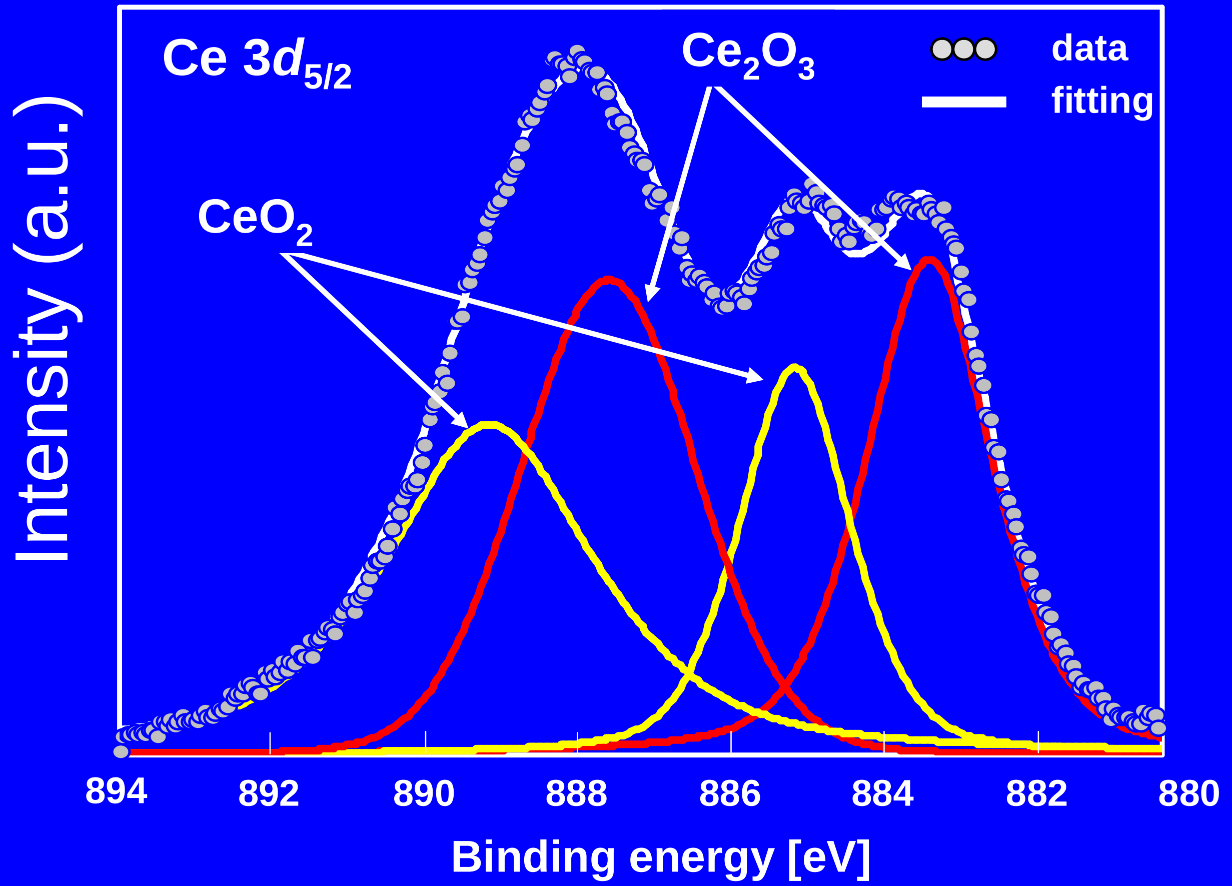
- n-type Si substrate (3×10^{15} cm^{-3})
- SPM, HF last treatment
- High-k materials deposition by EB evaporation (La_2O_3 single, 2-nm thick Ce-oxide-cap/La_2O_3 layer)
- Tungsten (W) metal gate electrode deposition by RF sputtering

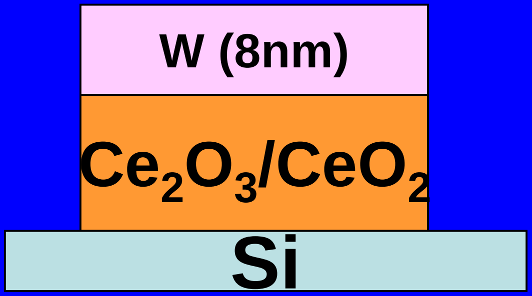
In situ

- PMA (Post Metallization Annealing) 500℃ 30min (FG:3%H_2)
- Bottom electrode Al deposition



Detection of Ce_2O_3 and CeO_2 in Ce-oxide layer



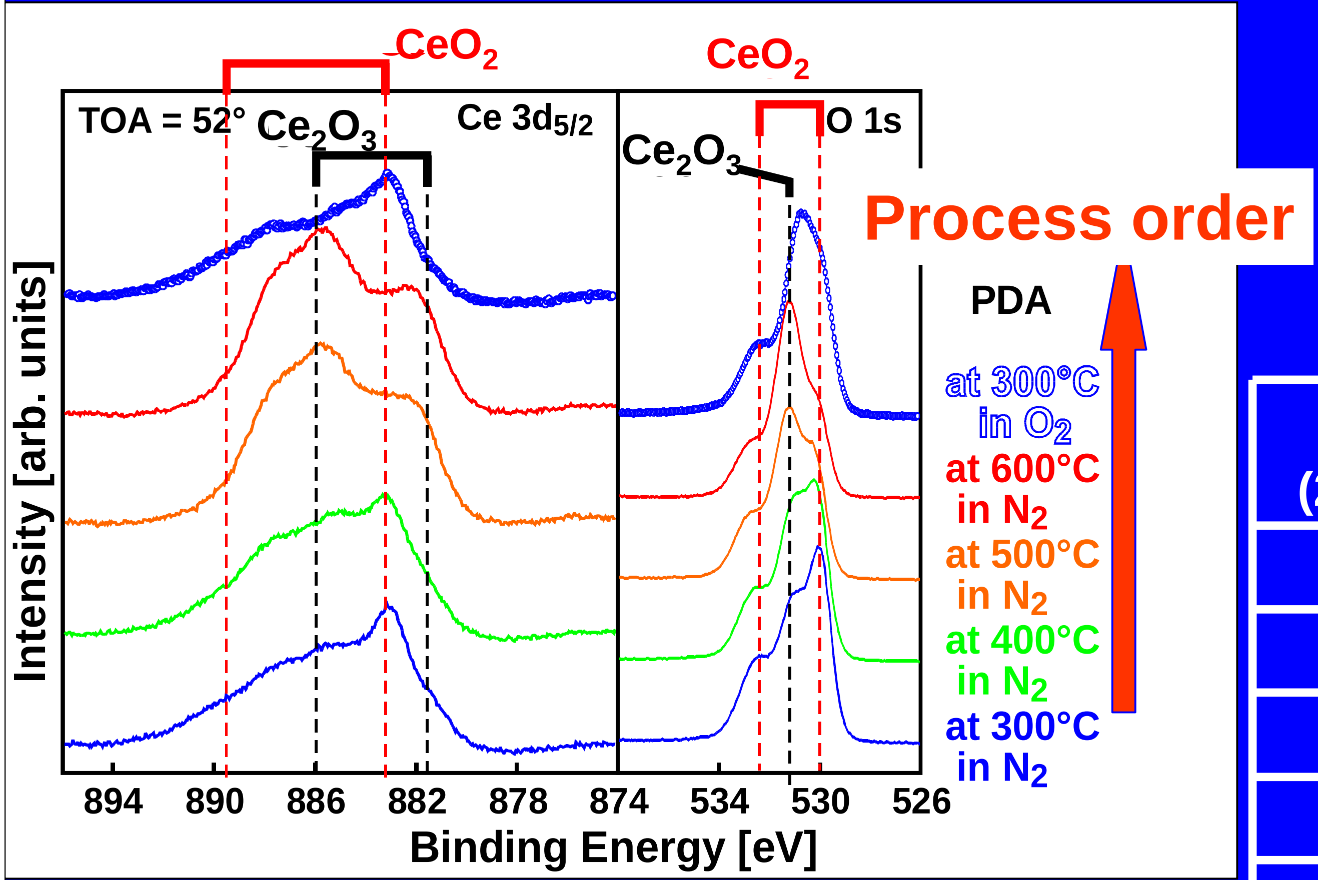


Ce-oxide 4nm
Annealed in
F.G. for 30min

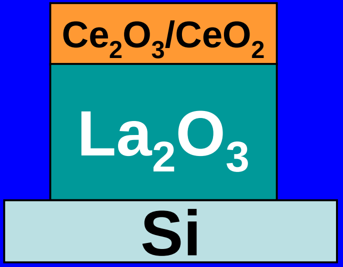
Ce_2O_3 and CeO_2 co-exist in a Ce-oxide layer

⇒ **Fixation of oxygen chemical potential**

15 Valence number transition on process condition



H. Nohira et al., to be presented at 216th ECS meeting



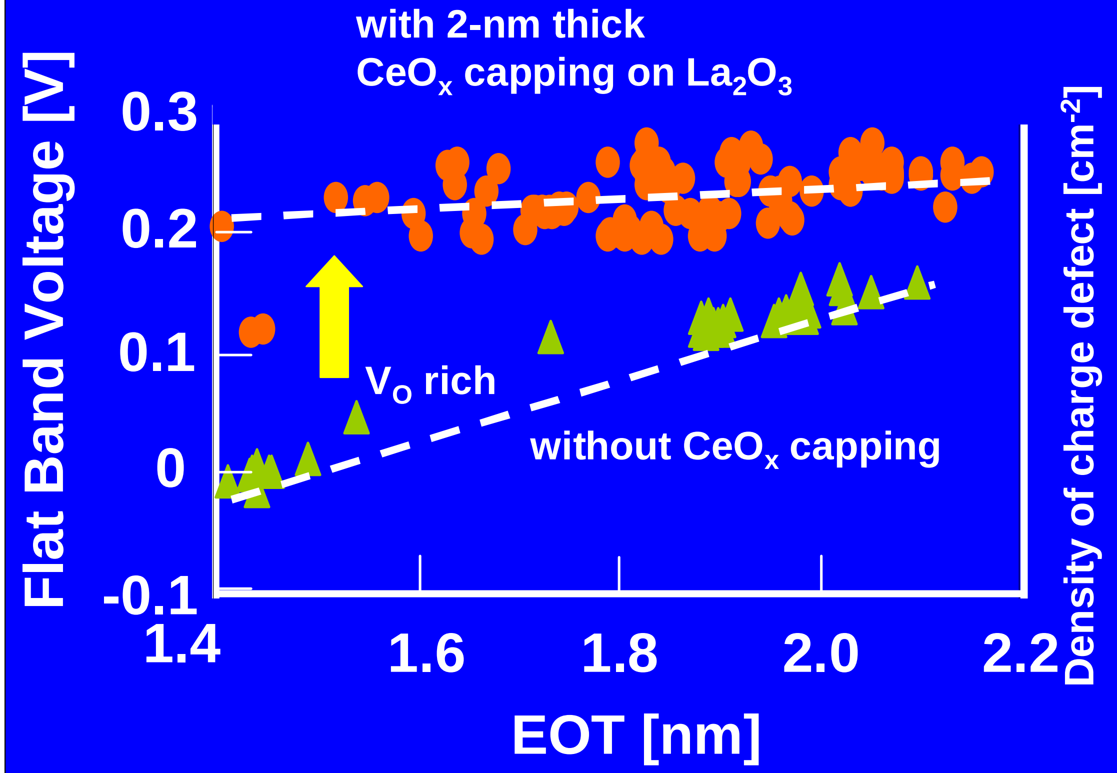
Annealing (20min 1Torr)	Ce_2O_3 (%)
O_2 300 °C	40
N_2 600 °C	69
N_2 500 °C	61
N_2 400 °C	48
N_2 300 °C	40

Ce_2O_3 increases at N_2 annealing and CeO_2 with O_2 annealing

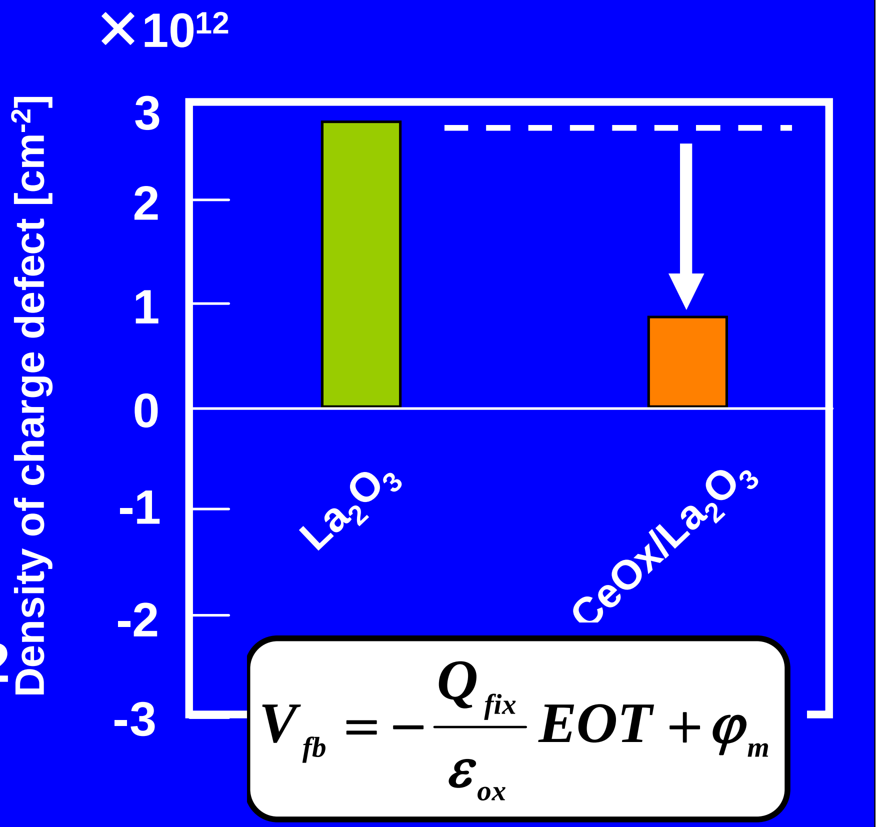
⇒

Suppression of charged defect formation
Oxygen chemical potential is fixed

Effective Fixed charge estimation



Annealing in F.G. at 500 ºC for 30min



$$V_{fb} = -\frac{Q_{fix}}{\varepsilon_{ox}} EOT + \varphi_m$$

Charged defects reduction was demonstrated with Ce-oxide capping on La$_2$O$_3$

Fixation of oxygen chemical potential by multivalent material capping

- Back ground
- Propose of this work
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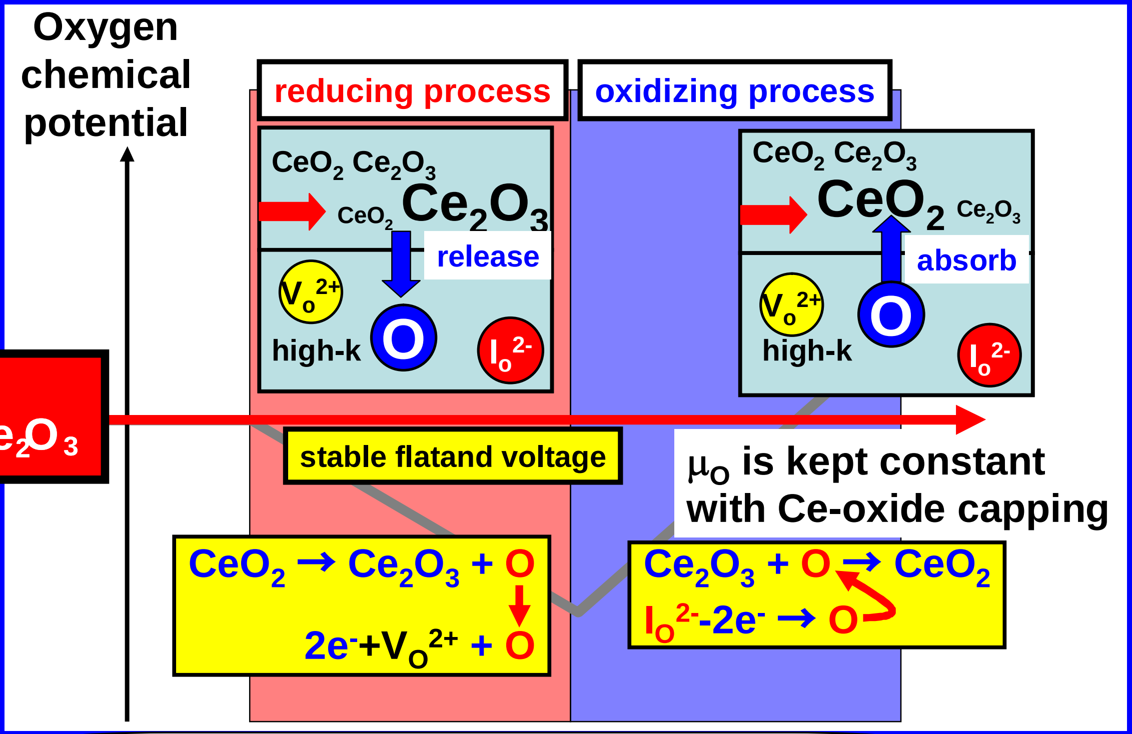
- **Conclusion**

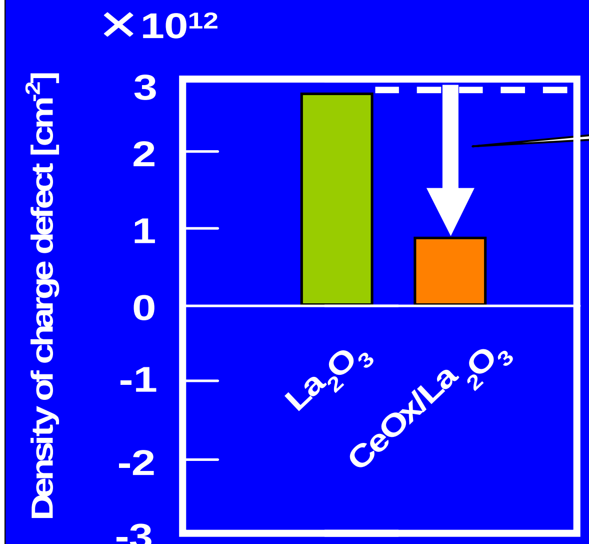
Conclusion

Ce_2O_3 and CeO_2 co-exist

$$\mu_O = 2\mu_{CeO_2} - \mu_{Ce_2O_3}$$



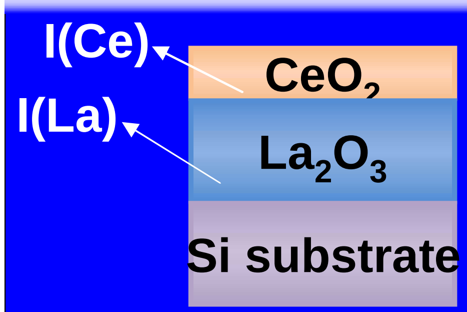
60% reduction of positive charges



Multivalent material capping fixes the oxygen chemical potential of host high-k

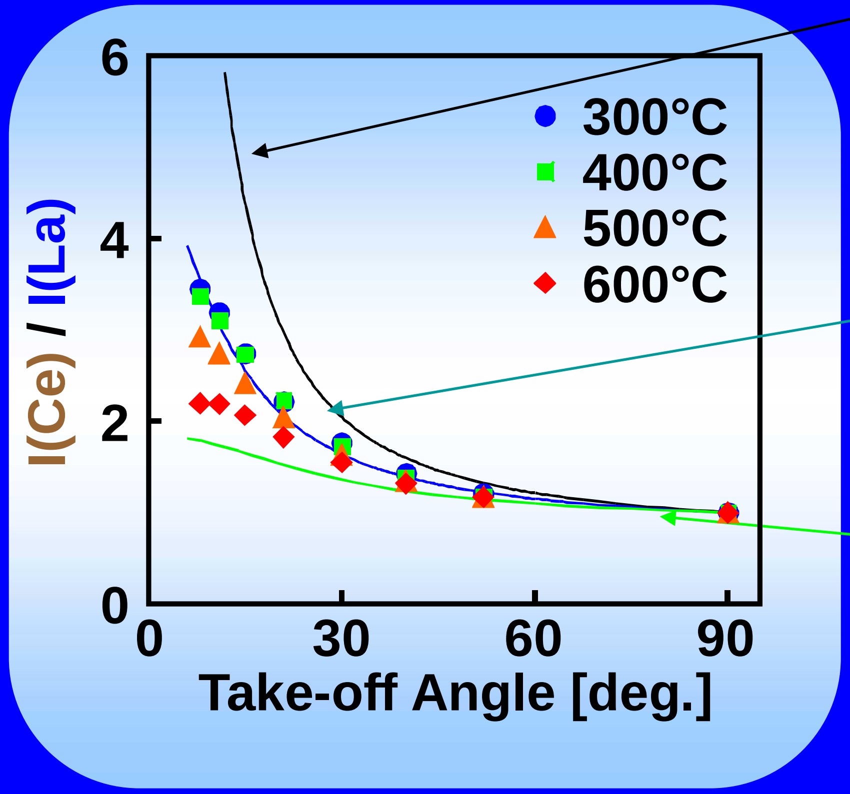
Stable V_{th} or V_{FB} can be obtained by selecting a proper multivalent material for host high-k

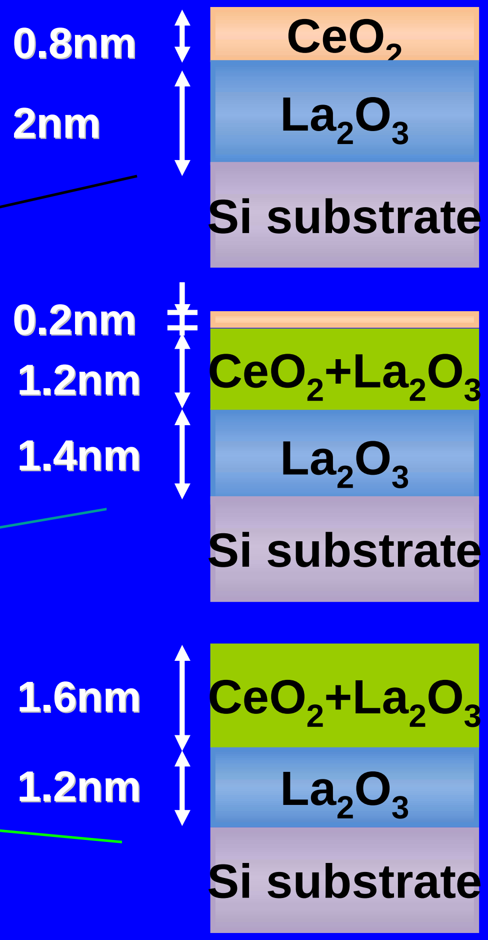
The diffusion at CeO_2/La_2O_3 interface



I(Ce):Ce $3d_{5/2}$ photoelectrons at CeO_2

I(La)︰La_2O_3La $3d_{5/2}$ photoelectrons at La_2O_3



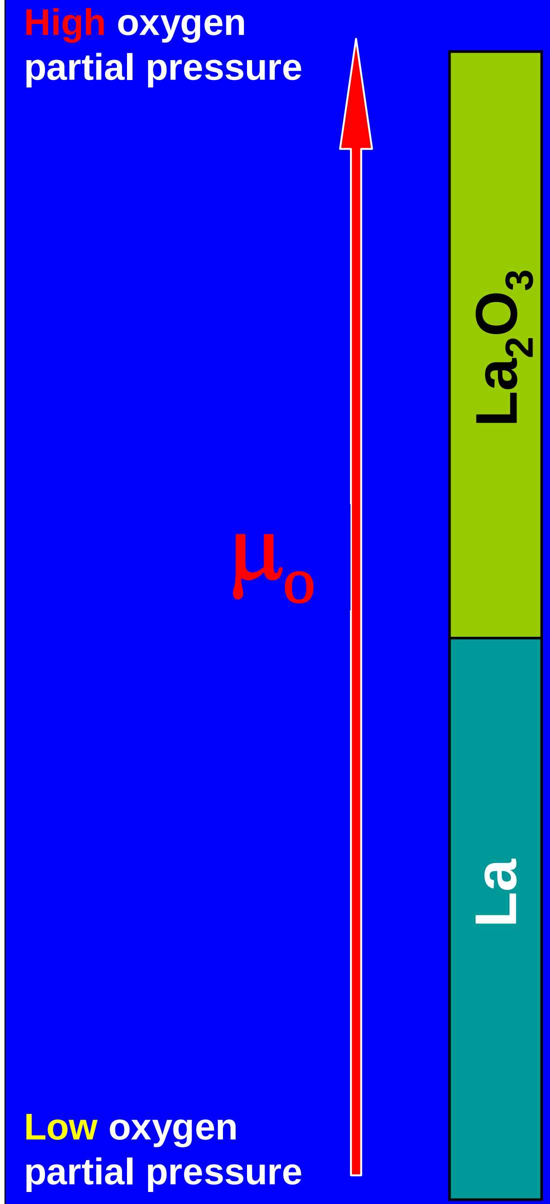


Diffusion layer : Ce:La=1︰1

The diffusion of Ce and La atom occurs at CeO_2/La_2O_3 interface by PDA at 500°C

[Ref] H. Nohira et al., J.S.A.P. 69th Autumn Meeting 2008, 3a-CB-7

Oxygen chemical potential diagram



$$\mu_o = E_{tot}(O_2)/2 = \mu_o^{O_2}$$

Vary in a wide range

$$\mu_o = (\mu_{La2O3} - 2\mu_{La}^{bulk})/3 = \Delta H(La_2O_3)/3 + \mu_o^{O_2}$$

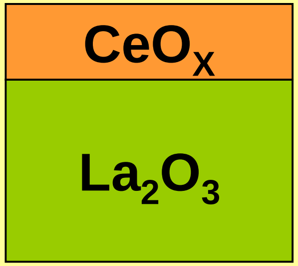
μ_{La2O3} , μ_{La}^{bulk} **: chemical potential of bulk La_2O_3 and La**

$\Delta H(La_2O_3)$: Enthalpy of formation value

Ref: O. Kubaschewski, et al., in Materials Thermochemistry 6th edition (Pergamon Press, April 1993)

Multivalent High-k capping ~ an example with Ce-oxide ~

CeO_x capping

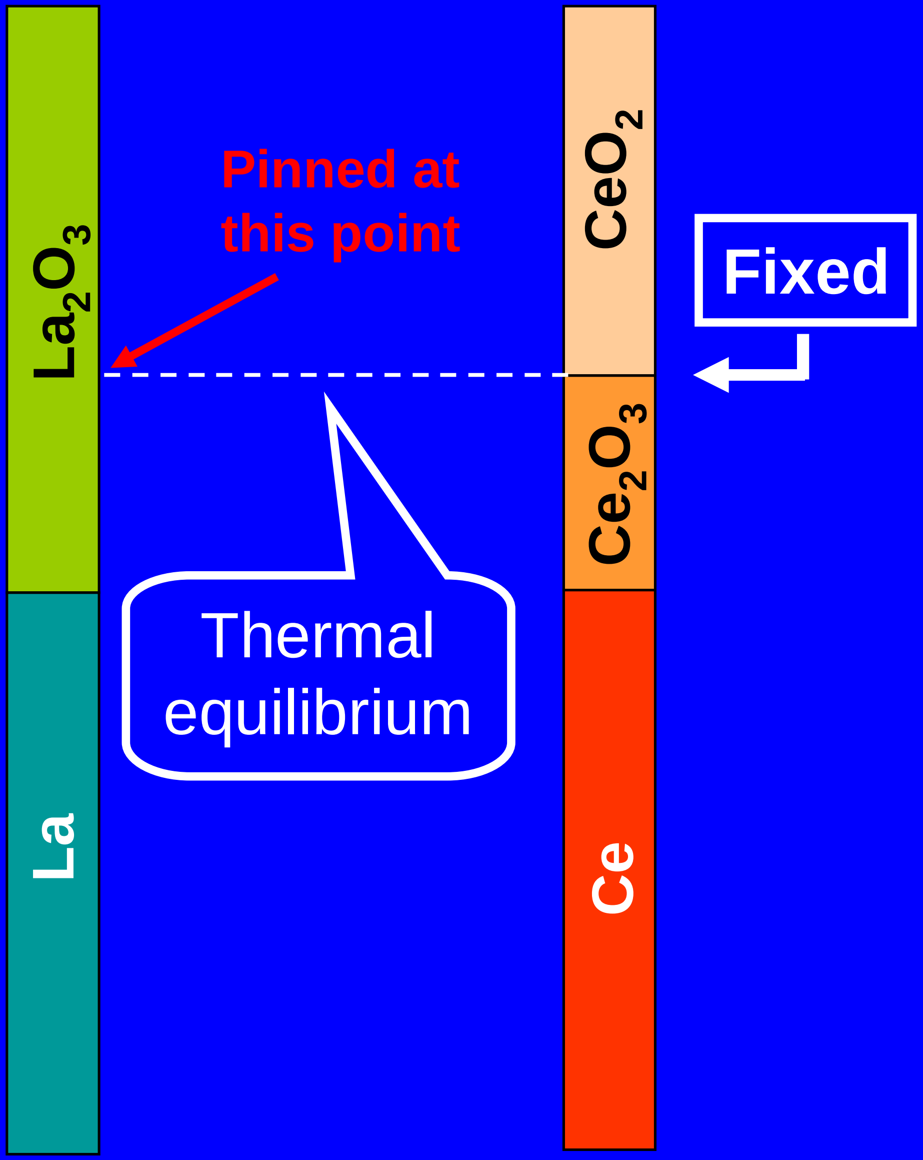


Ce^{3+},Ce^{4+} co-exist

Different valence states exist

Oxygen chemical potential in the La_2O_3 film is fixed

$$\mu_o=\mu_{CeO2}-2\mu_{Ce2O3}$$

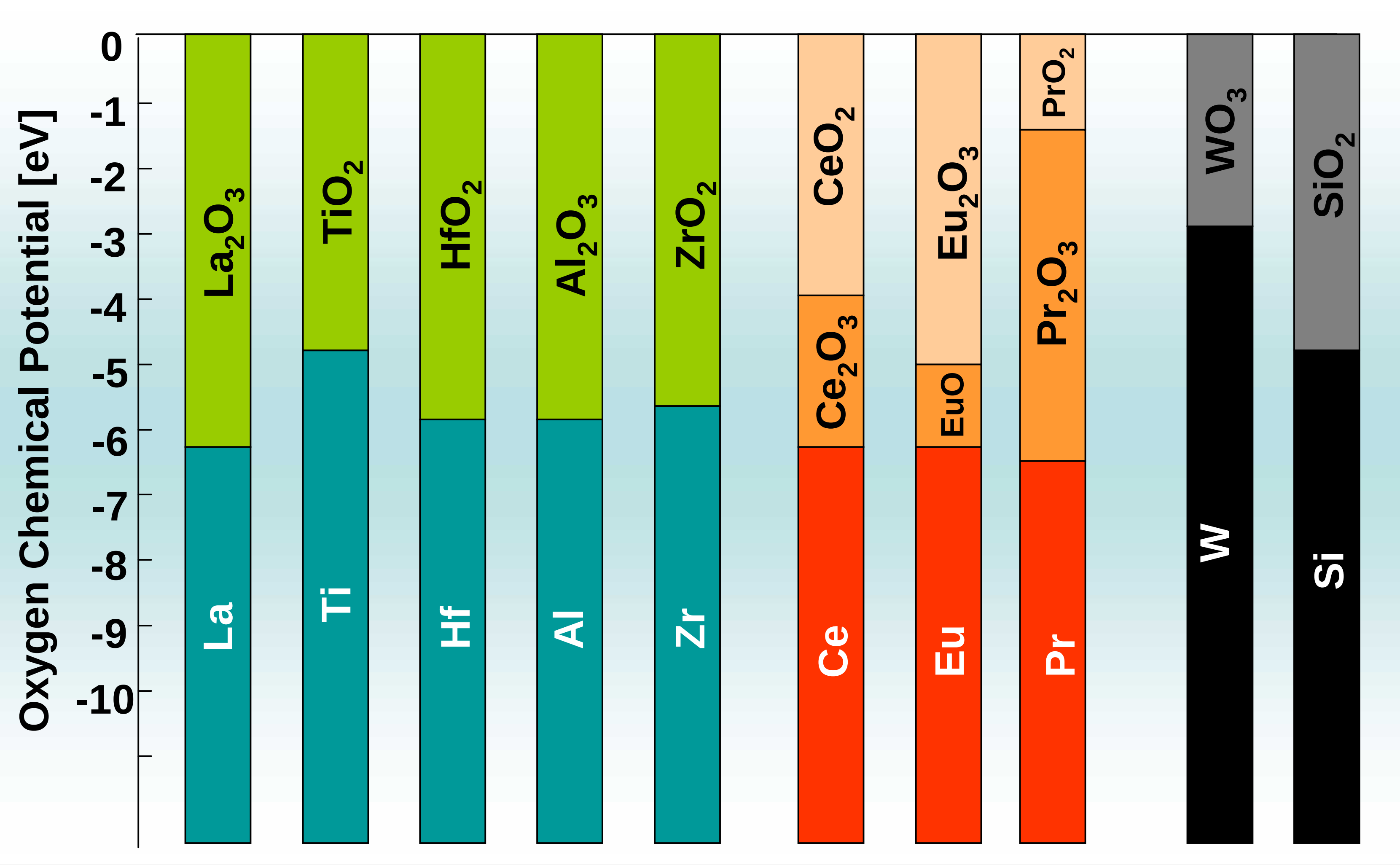


Pinned at this point

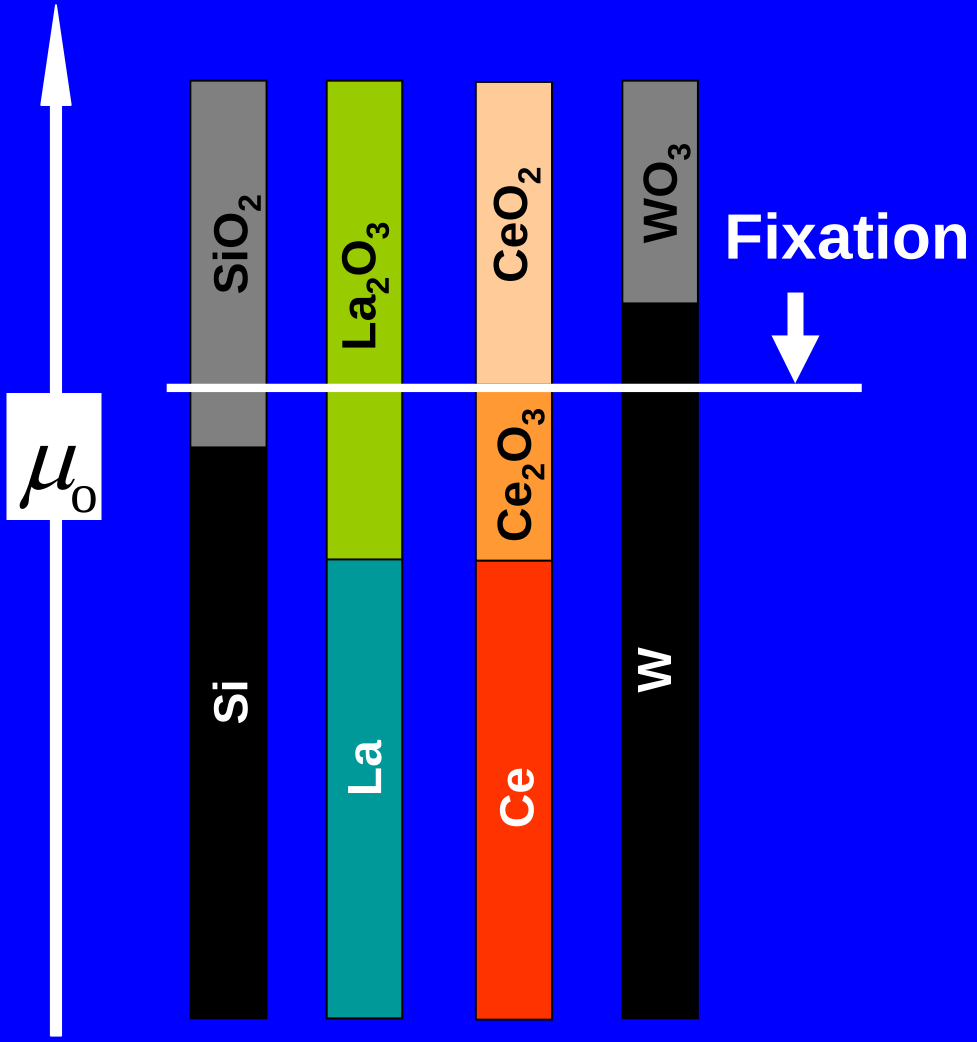
Fixed

Thermal equilibrium

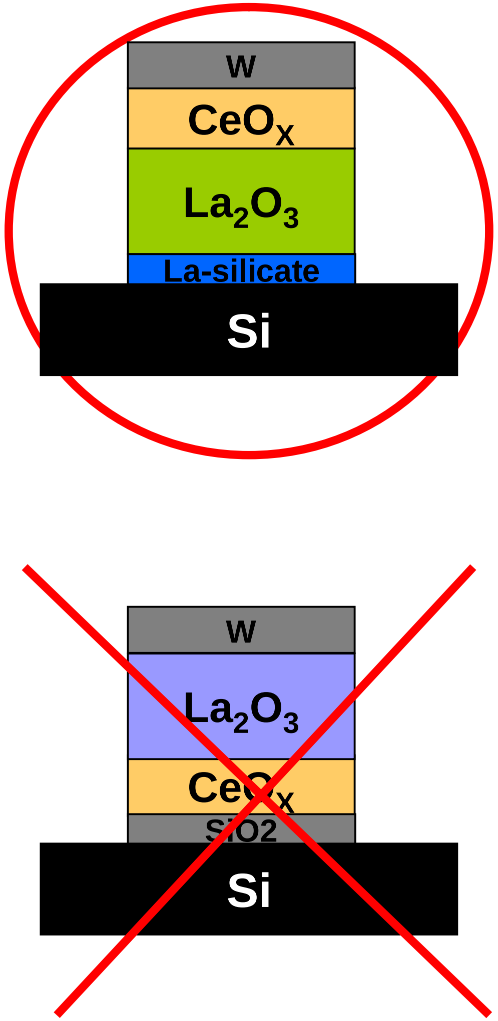
Oxygen chemical potential diagram

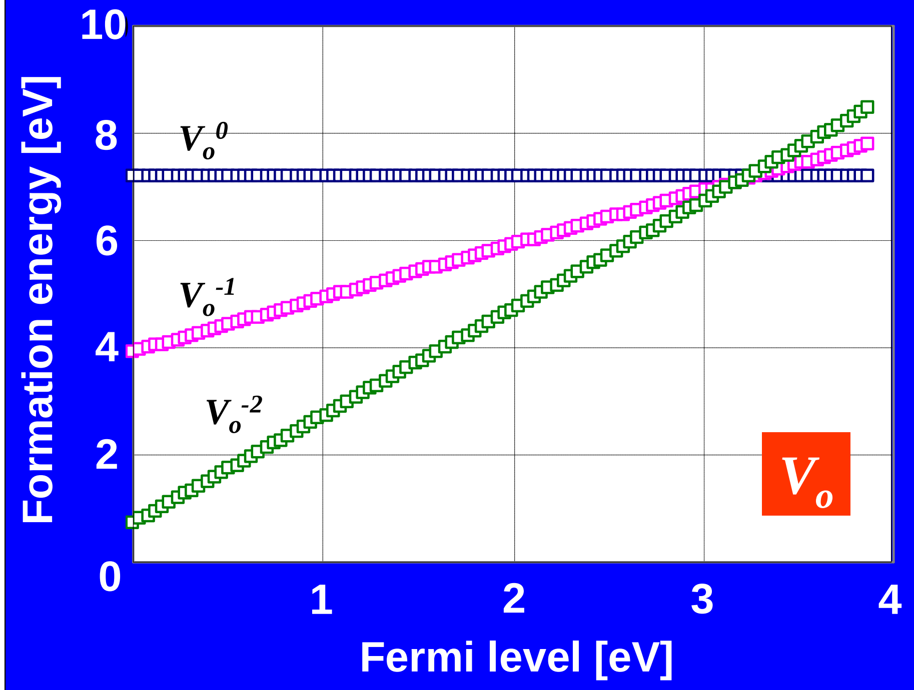


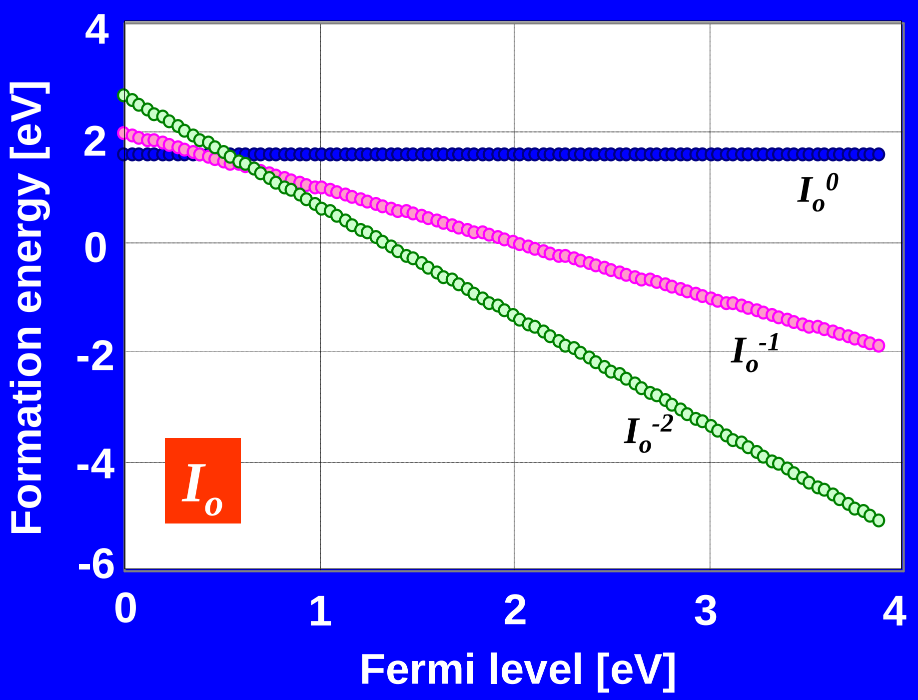
Selection of gate stack material for multivalent oxide capping technique

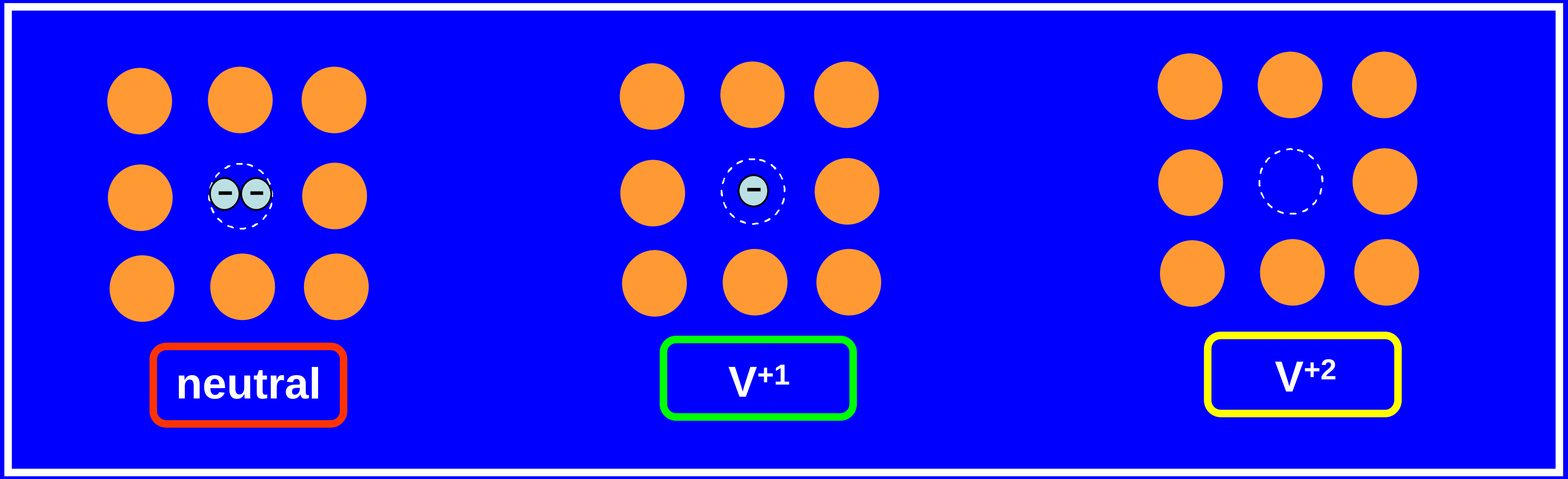


W/CeO_X/La_2O_3 structure is the best




Formation energy [eV]
10
8
6
4
2
0
1
2
3
4
Fermi level [eV]
V_o^0
V_o^{-1}
V_o^{-2}
V_o


Formation energy [eV]
4
2
0
-2
-4
-6
0
1
2
3
4
Fermi level [eV]
I_o^0
I_o^{-1}
I_o^{-2}
I_o


neutral
V+1
V+2

Formation energy