# Methods for Improving Electrical Properties of $La_2O_3$-based Gate Dielectric Films

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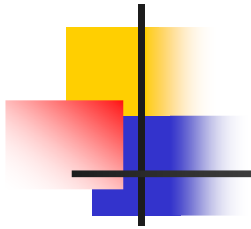


# Outline

1. Introduction

*Methods for Characteristic Improvement*

**2. Stoichiometric binary alloys**

**3. Pseudo-binary alloys**

**4. Doping**

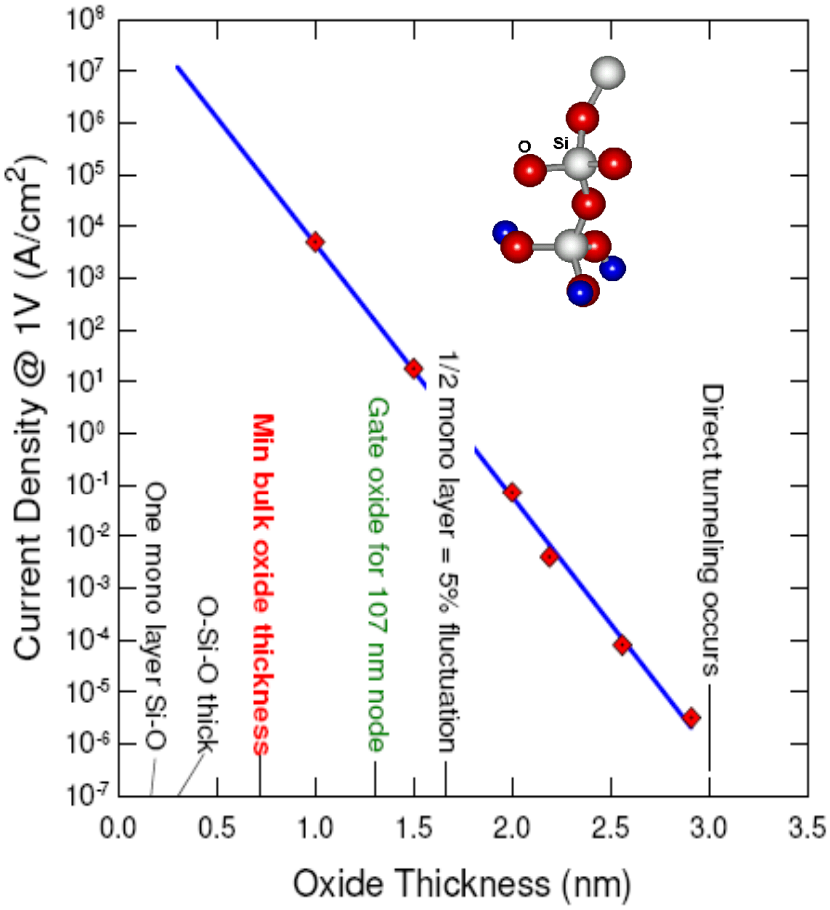
**5. Oxygen chemical potential control**

6. Concluding Remarks

- Higher dielectric constant ($\kappa$) materials *must be* used for

$$C = \frac{\kappa \varepsilon_0 A}{t_{diel}}$$

  - *having a larger capacitance for nanoscale devices;*
  - *reducing the leakage current while maintaining the same gate capacitance;*
  - *using of physical thicker high-k materials would also provide better process control.*




D. Misra, H. Iwai and H. Wong, *Interface (Electrochem. Soc.)*, **14**, (2005).

# Subnanometer EOT

- The physical thickness of 0.6 nm EOT $La_2O_3$ is less than 4 nm.
- Scaling closer bulk thickness limit (~1 nm?).
- Large leakage current are expected because of smaller band offsets at Si interface and high defect density.

# Some problems of high-κ dielectrics

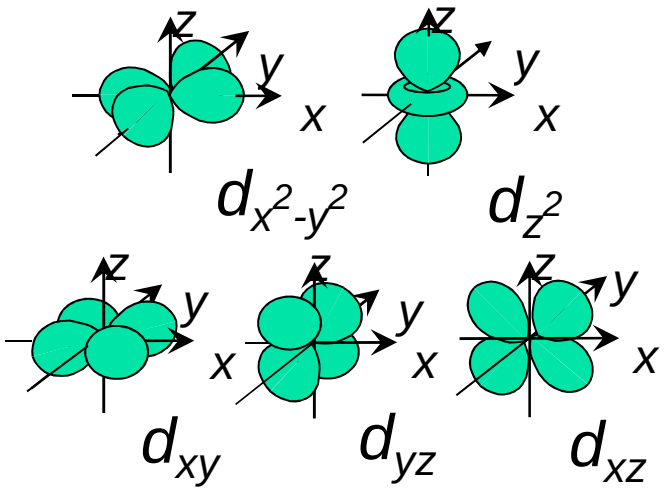
- Thermal instability 👎👎
- Low channel mobility 👎👎
- High interface trap density 👎👎
- High oxide trap density 👎👎
- Large leakage current 👎👎

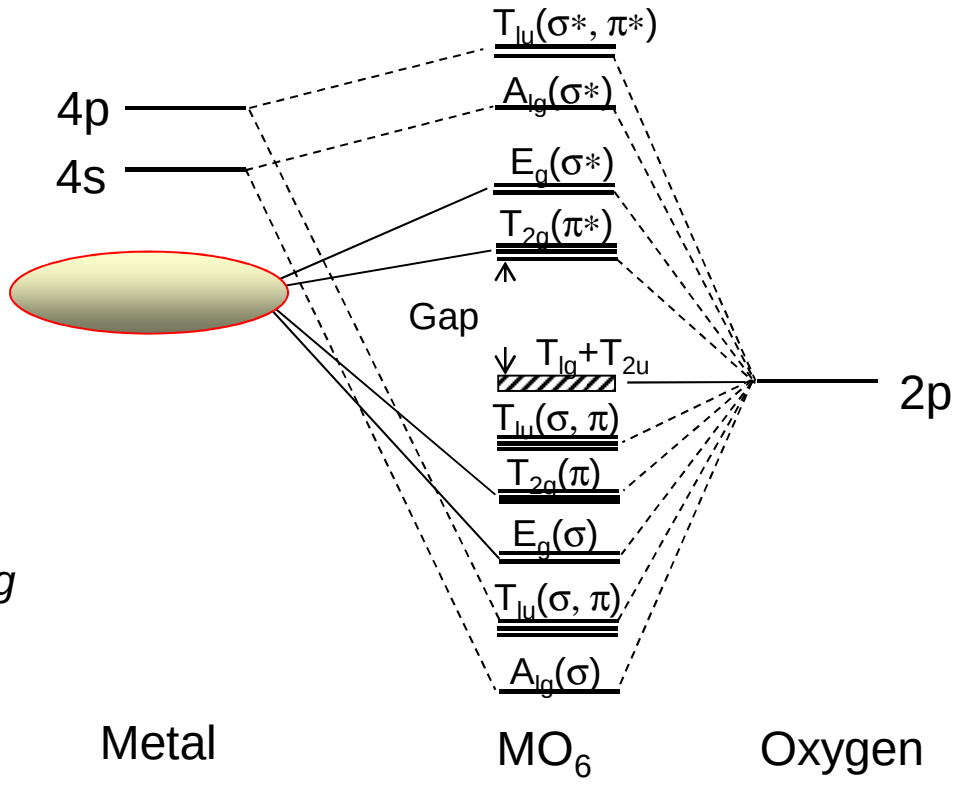
Instabilities !

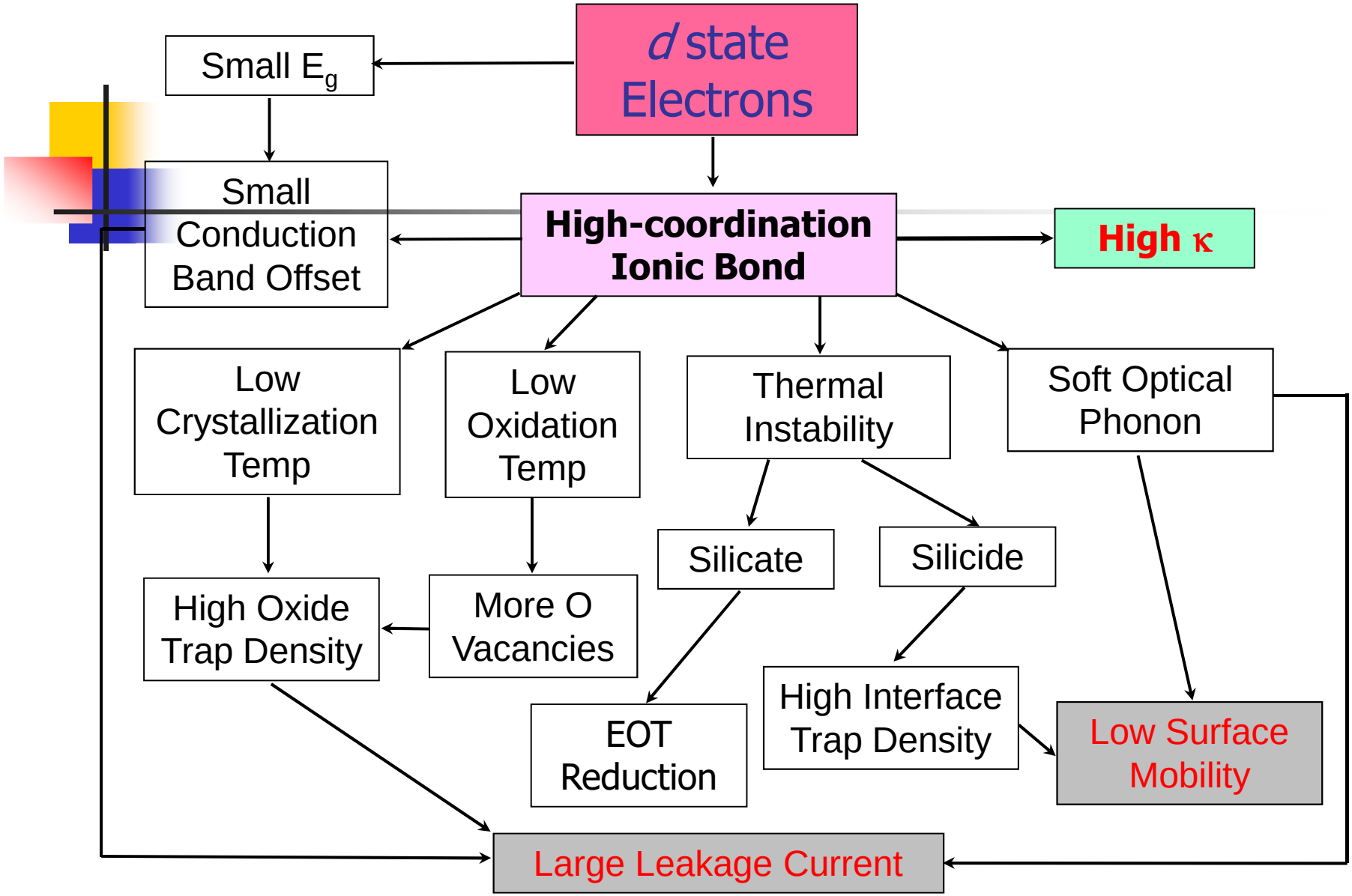
# Fundamentals

*Transition metal* forming bonding and anti-bonding molecular orbital with oxygen in TM oxide

Degenerated *d*-orbital in typical transition metal

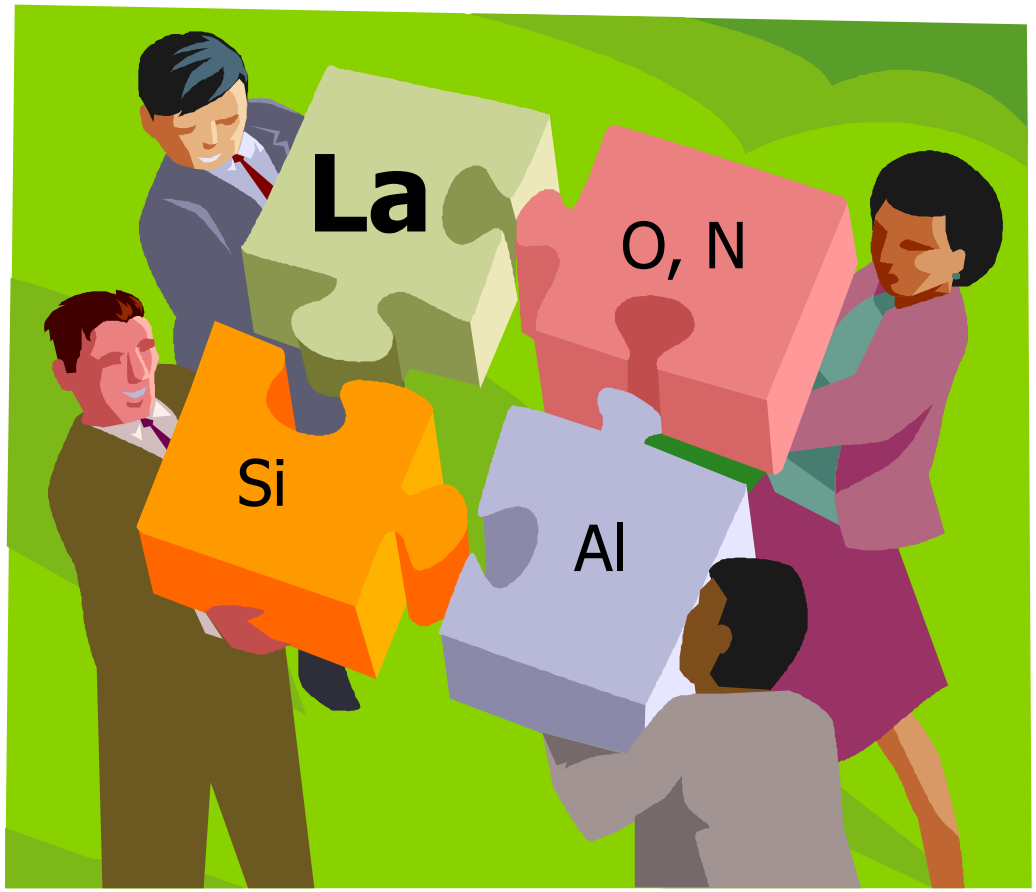





H. Wong and H. Iwai, Microelectron. Eng. 83, 1867 (2006).

# 2. Tailor-making the Dielectric Properties: Complex Oxides




**1. Stoichiometric binary alloys**

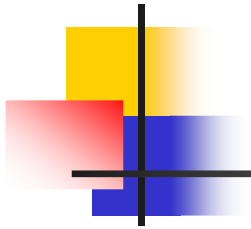
$LaAl_{11}O_{18}$, $LaAlO_3$

**2. Pseudo alloys**

LaSiON

**3. Doping, N, Al …**

**4. $\mu_o$ control**



# Outline

1. Introduction

Methods for Characteristic Improvement

**2. Stoichiometric binary alloys**

**3. Pseudo-binary alloys**

**4. Doping with Al and N**

**5. Oxygen chemical potential control**

6. Concluding Remarks

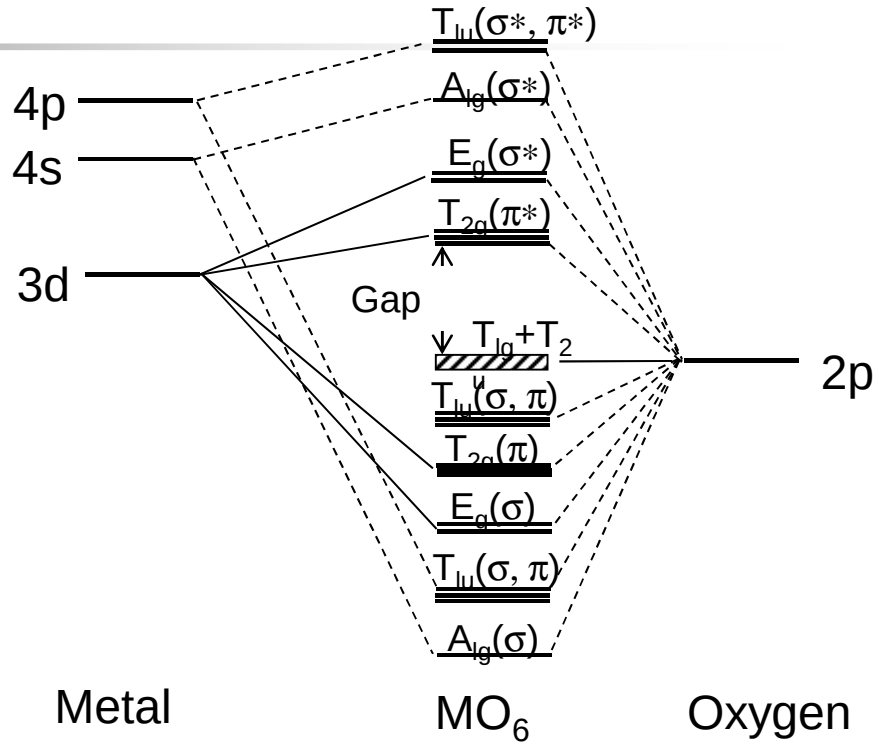
# 2. Stoichiometric binary alloys

- Stoichiometric binary alloys may be formed from two different metal, TM/RE elements.
- Two different metals sharing the same oxygen.
- *Titanium* and *scandium* can form stoichiometric binary alloys with many other TM/RE elements.

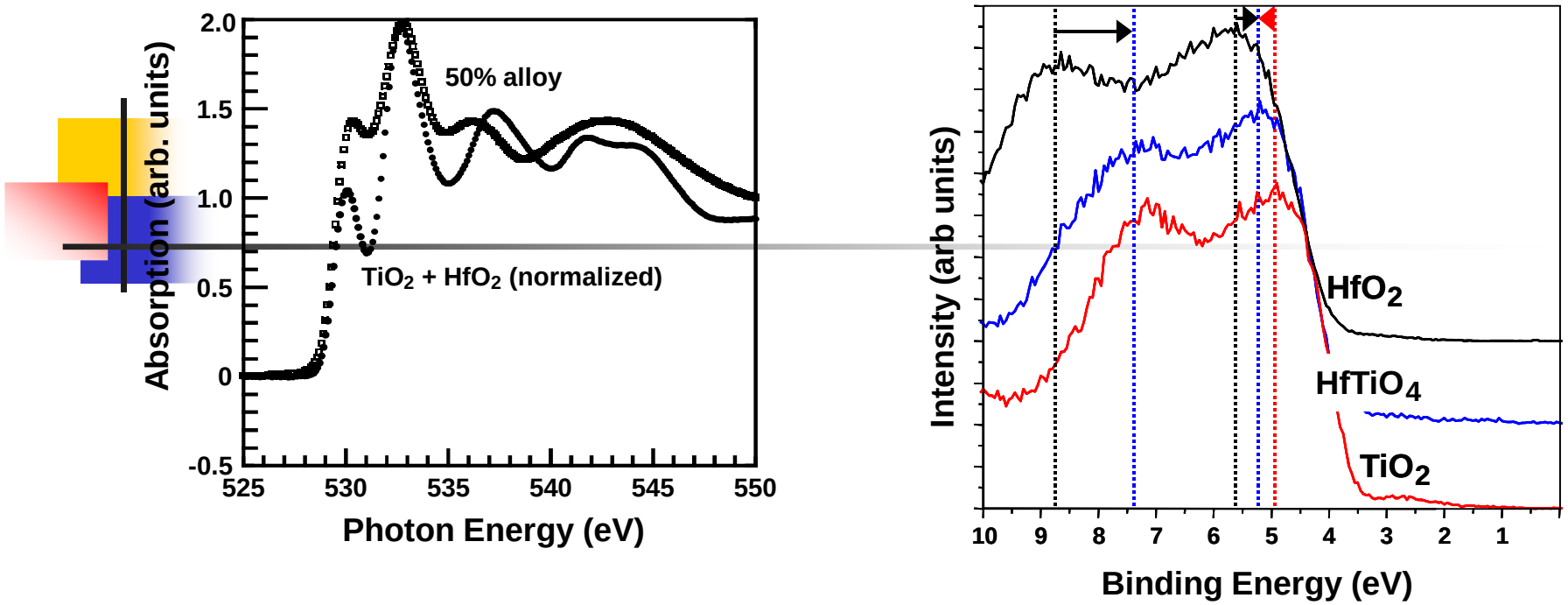
- The composition ratio of the two metal elements is limited to a certain value.
  - E.g, in Zr or Hf titanate, the compositional ratio of $TiO_2$ is limited to 1:2, 1:1, or 2:1;
  - In RE scandates, the ratio of the elemental oxides is 1:1.

# 2. Stoichiometric binary alloys

- **Ti is more ionic than most of the other TM/RE elements.**
  - It serves as a *polarizer* and produces a higher *k* value;
  - Sharing the same O with other metal. The bonding character is different from the elemental oxide;
  - $E_V$ is constituted by the TM p-states, and the $E_C$ is Ti-like.




- ***Not a good candidate for gate dielectric application !***




G. Lucovsky, Frontiers in Electronics, World Scientific, Singapore, 2006, 263.

O K1 edge features in Hf titanate can be approximated by a mixture of the individual $HfO_2$ and $TiO_2$ features.

*The ionicity of the overall metal-oxygen bond is changed nearly according to the averaging effect.*

# 2. Stoichiometric binary alloys

- **Stoichiometric La, Dy and Gd scandates have similar electronic structures.**

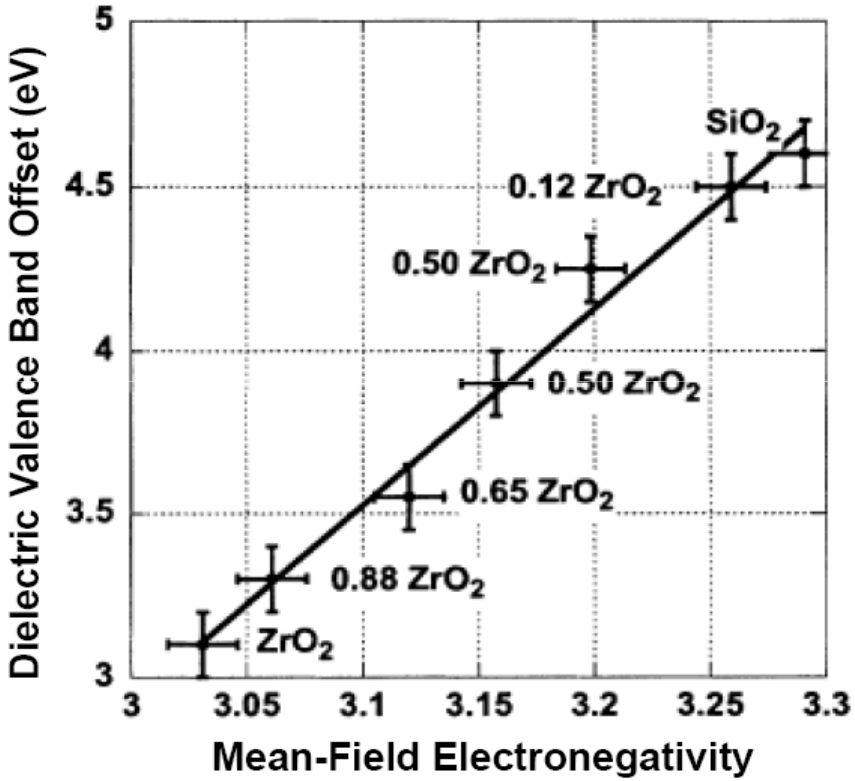
- *The stoichiometric oxides, except the $LaAlO_3$, generally lead to a larger k value and a smaller band gap value.*
  - *Effect of polarizer !*
  - *Not a good candidate because the conduction band is too small.*

# 2. Stoichiometric binary alloys

- *c*-$LaAlO_3$ may be the only possible stoichiometric binary alloy for gate dielectric applications;
- it is normally in the crystalline form;
- *c*-$LaAlO_3$ has a small lattice mismatch to Si;
- $LaAlO_3$/Si interface is also stable as both La and Al oxides are stable on Si;
- $LaAlO_3$ film cannot be directly grown on Si. Amorphous $LaAlO_3$ can be grown with a $SrTiO_3$ buffer layer. Alternatively, Si can be grown on *c*-$LaAlO_3$.

# 3. Pseudo-binary alloys

- Most TM/RE *silicates* and *aluminates* are in the form of pseudo-binary alloy or in the form of solid solution.
- The compositions of $SiO_2$ and $Al_2O_3$ in the TM/RE alloys vary continuously .
- TM/RE *d*-states do not mix with the lowest conduction band *s* states of Si or Al.




G. Lucovsky, Frontiers in Electronics, World Scientific, Singapore, 2006, 263.

***The material properties are still different to elemental constitution oxides.***

# 3. Pseudo-binary alloys

- $SiO_2$ is an *amorphizer* for TM/RE oxides; crystallization temperature increases because:
  - The ionic metal atom bonds in silicate alloys can be disrupted and modified by the covalent Si-O bonds ➔ modified continuous random network.
- It reduces the *effective k* value.

- However, pseudo-binary alloys may be less stable at very high temperature;
- Si can be a donor to $La_2O_3$ and enhance electron conduction.

# Comparison of Different Forms of Complex Oxides

| Properties | Pseudo-Binary Alloy | Stoichiometric Alloy | Doping |
|---|---|---|---|
| **Typical Materials** | Silicates, aluminates, $(HfO_2)_x(SiO_2)_y$, $(HfO_2)_x(Al_2O_3)_y$ | Titanates, scandates, $Hf_mTi_nO_{2(m+n)}$, $LaScO_3$, $LaAlO_3$ | $HfO_2$ with ~5% N<br>$La_2O_3$ with ~5% N<br>$La_2O_3$ with 10% Al |
| **Dielectric Constant** | ↓ | ↑ | -- |
| **Conduction Band** | -- | ↓ | -- |
| **Valance Band** | -- | little effect | -- |
| **Crystallization Temperature** | ↑ | ↓ | ↑ |
| **Phase Separation** | Yes | -- | At interface |
| **Si Interface** | Better | -- | Better |

# 4.1 Nitrogen Doping

# 4.1 Nitrogen Doping

***Bulk La oxynitride***

- Large amount of N incorporation in $La_2O_3$ oxides will change the material properties such as bandgap narrowing.
- Bulk type TM/RE oxynitride is unstable. It was found that the bulk La-N bonds can be readily replaced by oxygen with thermal annealing in oxygen ambient.

***Doping***

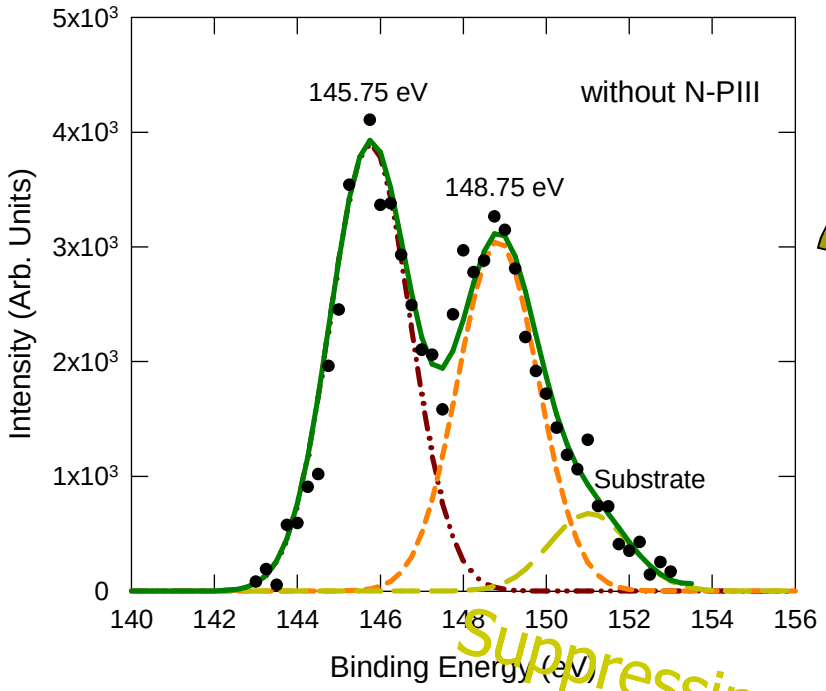
- Dopant with amount of < 10 at.%
- Does not change the electronic structure of host dielectric
- But still have significant impact on some of the electrical and material properties:
  - Increases the crystallization temperature remarkably.
  - Suppresses the boron penetration.
  - Reduces the leakage current by reducing the oxygen vacancies.

# 4.1 N Doping

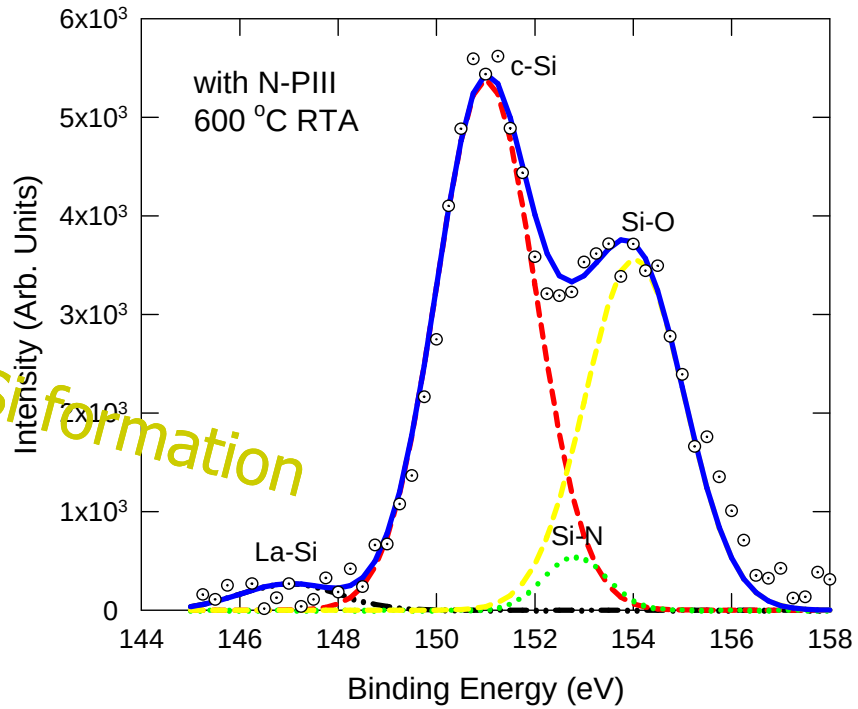
- **Mechanisms of nitrogen incorporation:**
  - filling of the O vacancies ($V_O$) in the bulk;
  - replacement of O atoms of the $V_O$ neighbors and making the $V_O$ centers inactive;
  - nitridation of the interfacial La-Si bonds; and
  - nitridation of the interfacial Si-Si bonds and substrate Si.

- ***Note:*** **Different to $SiO_2$ nitridation.**
  - N incorporation in $SiO_2$ mainly occurred on the surface and at the $SiO_2$/Si interface by nitridation of Si-Si and silicon dangling bonds.

# N Doping on $La_2O_3$ : Si 2s interface XPS

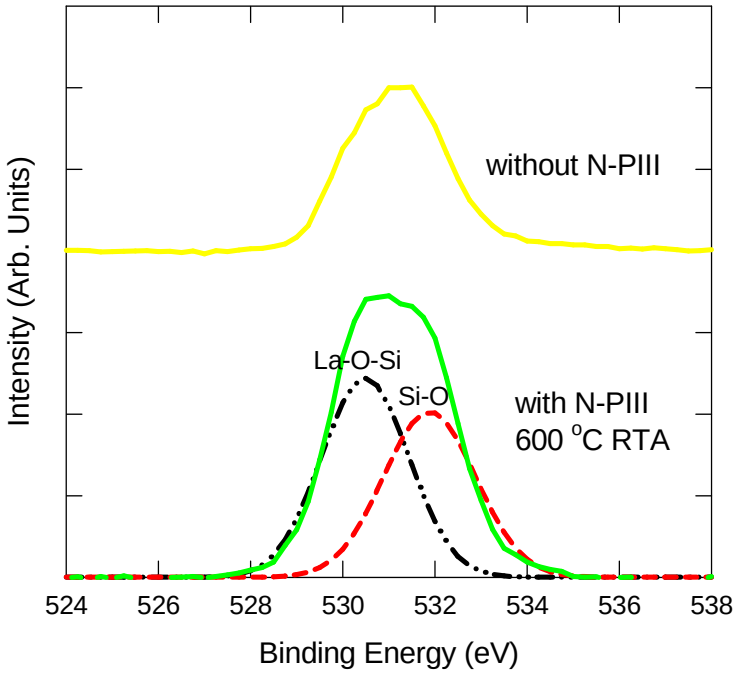


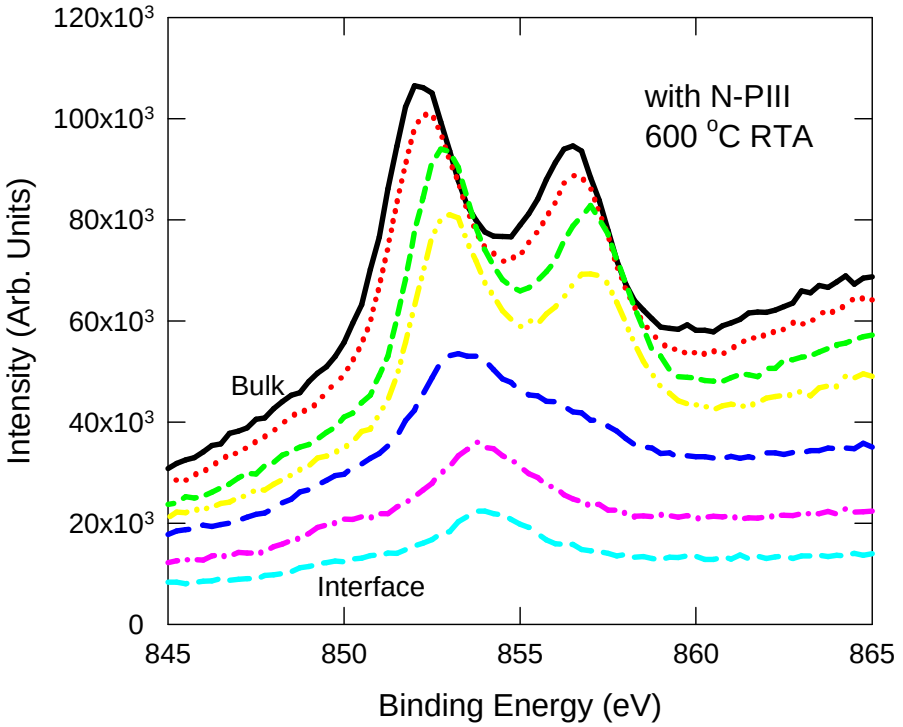

Suppressing La-Si formation




- **Reduce La-Si,**
- **Increase Si-N and Si-O.**

# Nitrogen Doping

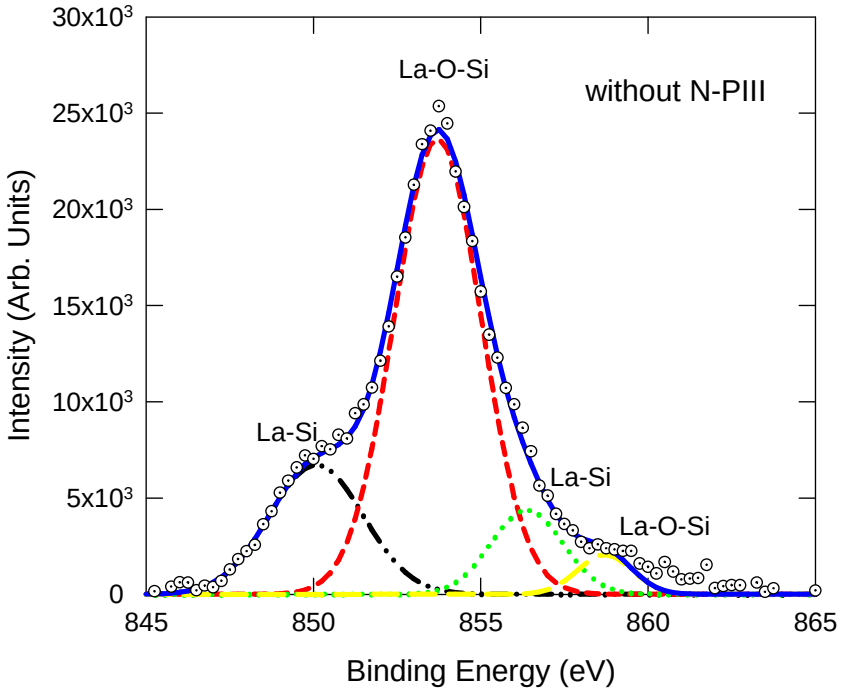


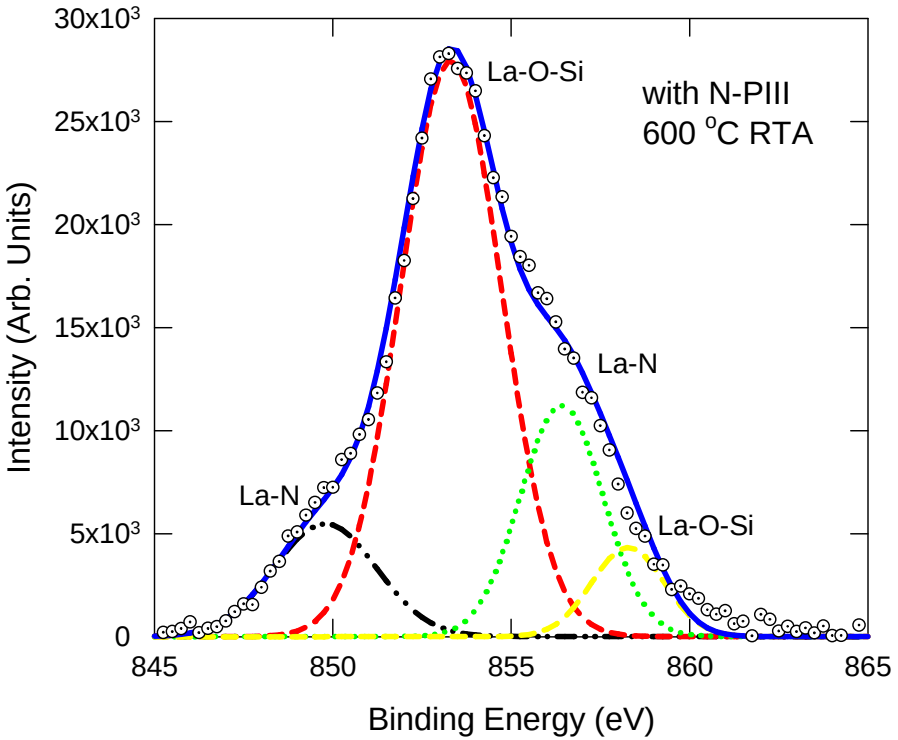

- **O 1s shows two kinds of bonding at interface of N-PIII sample.**

- **La 3d shows the exist of silicates at the interface of N-PIII sample.**

# La 3d at interface

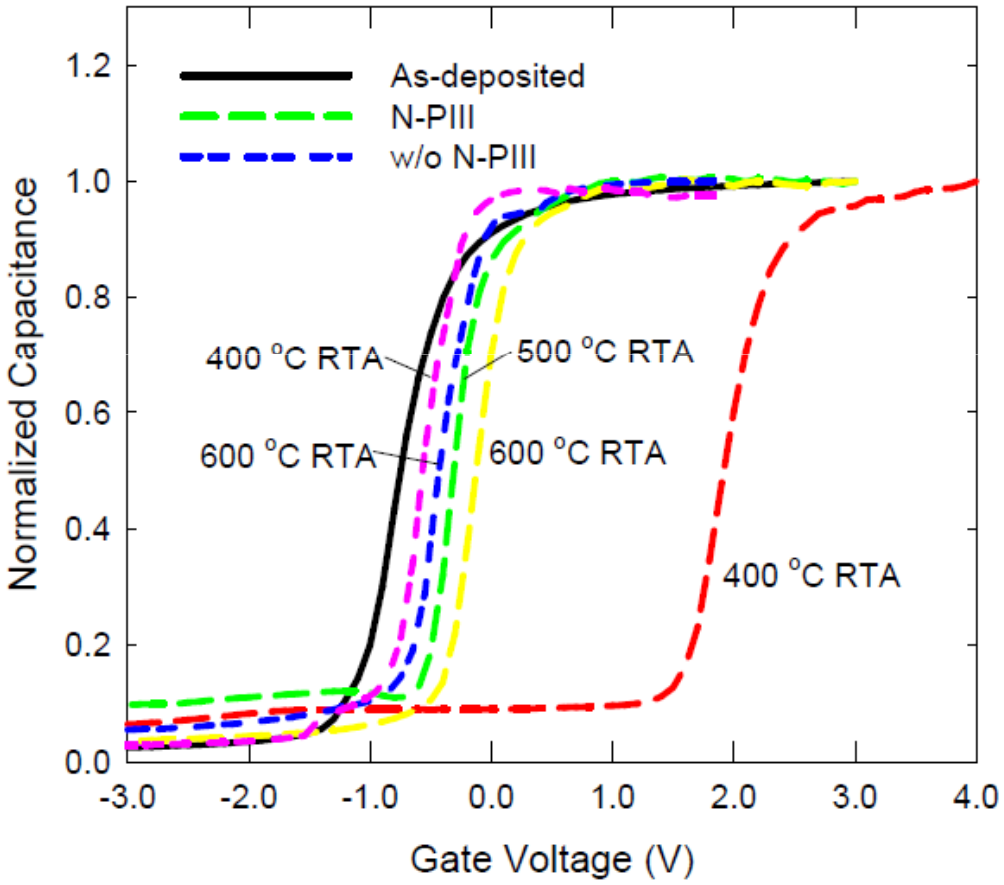



- **La-Si reduces,**
- **La-N and La-O-Si increase.**



# C-V Characteristics

- Smaller flatband shift ➔ low oxide trap density
- Steeper slope ➔ low interface trap density



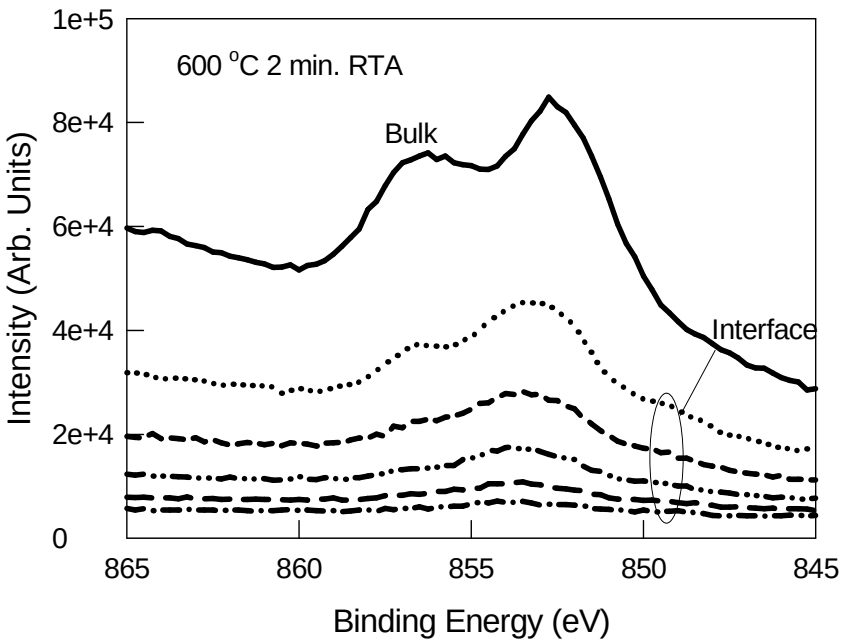
# 3.3 Summary

- Properties of $La_2O_3$ were improved by incorporating a trace amount of N atoms.
- $La_2O_3$ reduces the O vacancies in the bulk, distorts the lattice structure and thus enhances the thermal and electrical stabilities of $La_2O_3$ films.
- N incorporation also improves the interface. It reduces the amount of silicide bonds at the interface by forming La-N bonds and causes the interface oxidation.

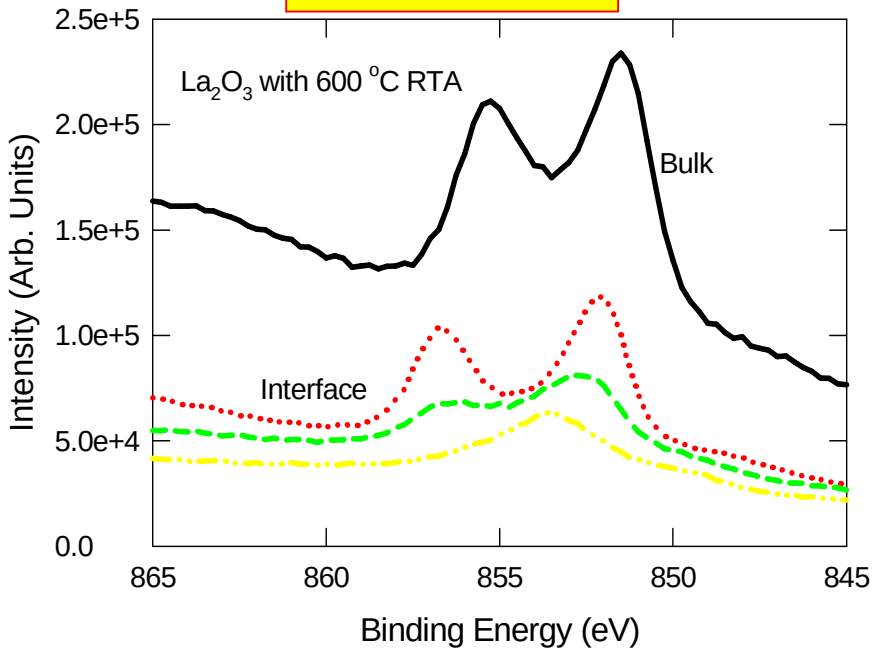
# 4.2 Aluminum Doping

# 4.2.1 XPS: La 3*d* XPS

w/o Al-implanted



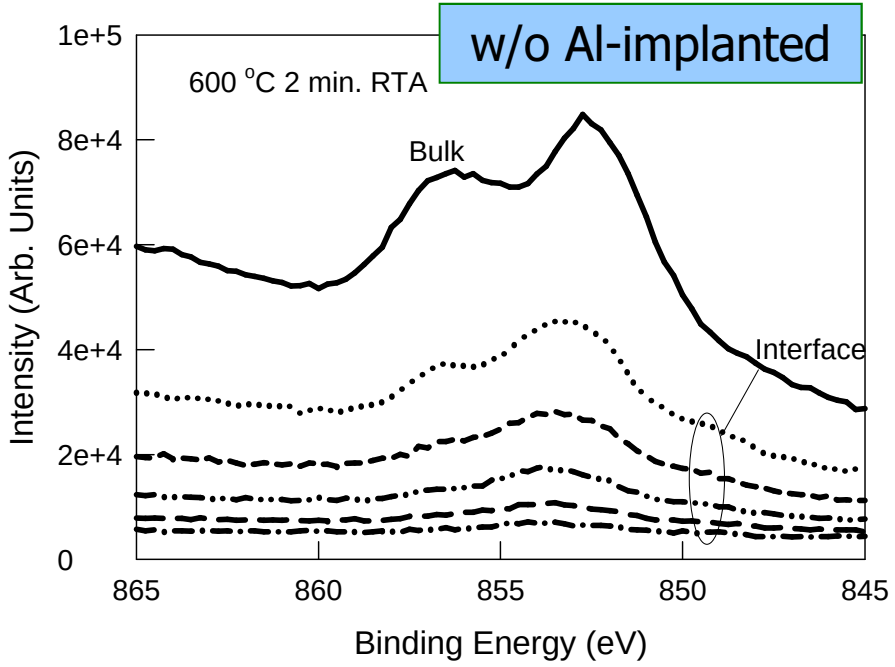

Al-implanted

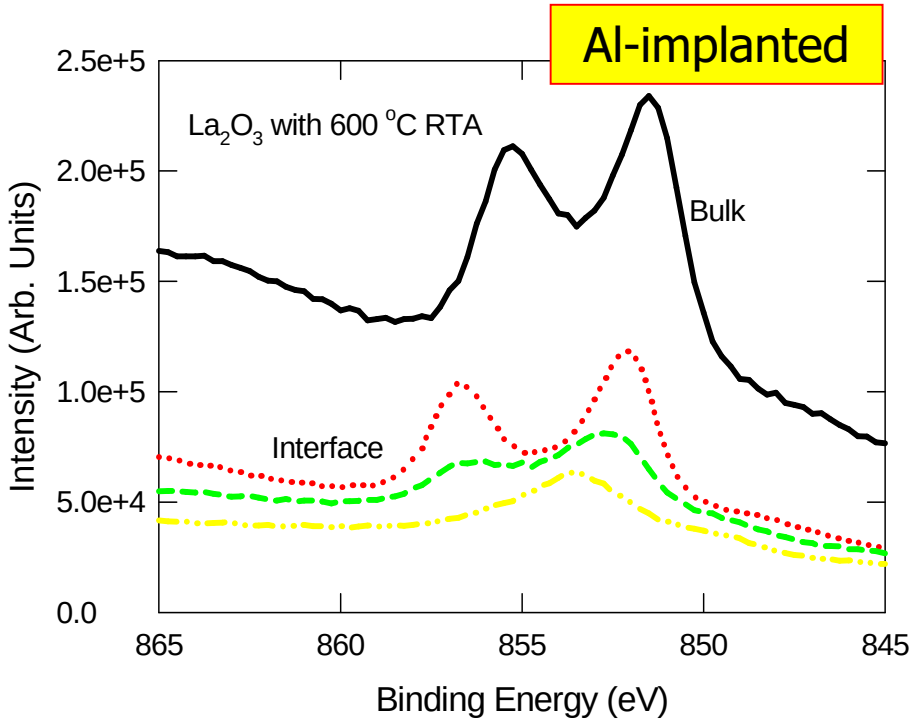



- Bulk La $3d_{2/3}$ has a doublet at 851.4 eV and satellite energy of 855.2 eV.

- Bulk La $3d_{2/3}$ doublet shift to 852.7 eV and 856.2 eV because of the La-O-Al bonding.

# 4.2.1 XPS: Interface La 3*d*

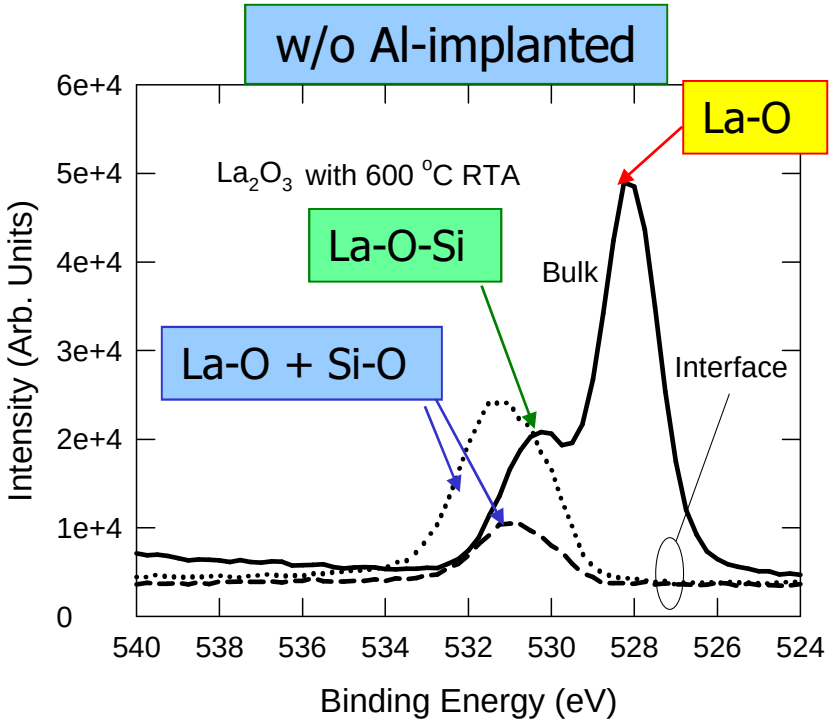


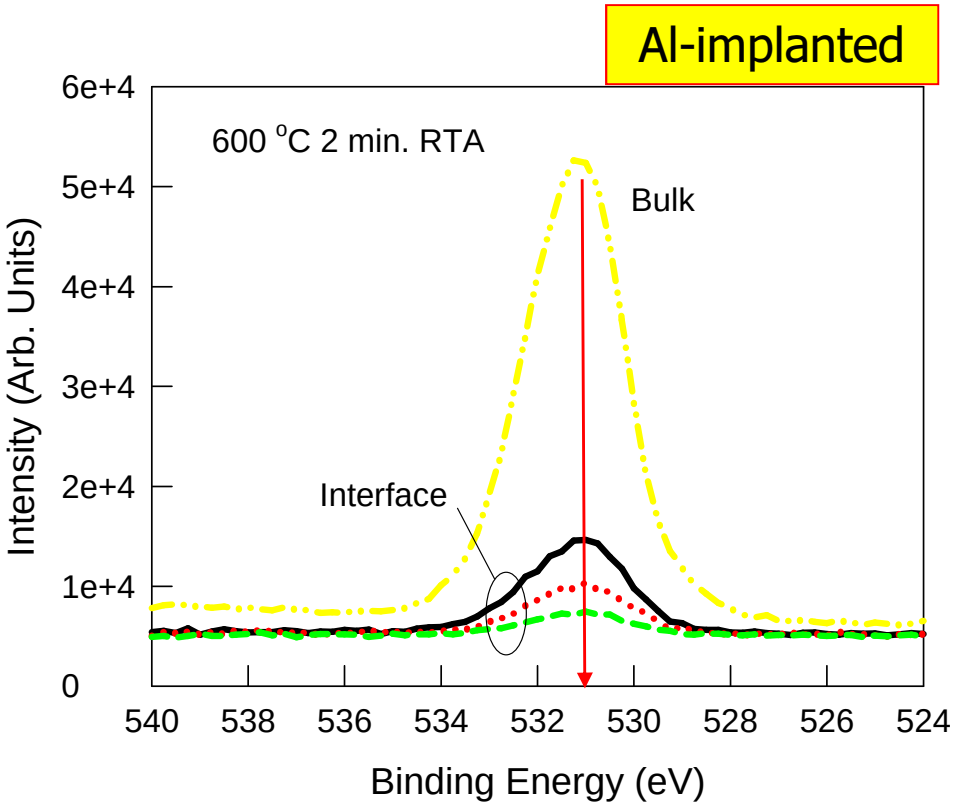




- La $3d_{2/3}$ shifts to higher energy side because of the existence of interfacial silicate layer.
- Weaker satellite peak.

- The shift of La $3d_{2/3}$ peak reduce.
- Stronger satellite peak.

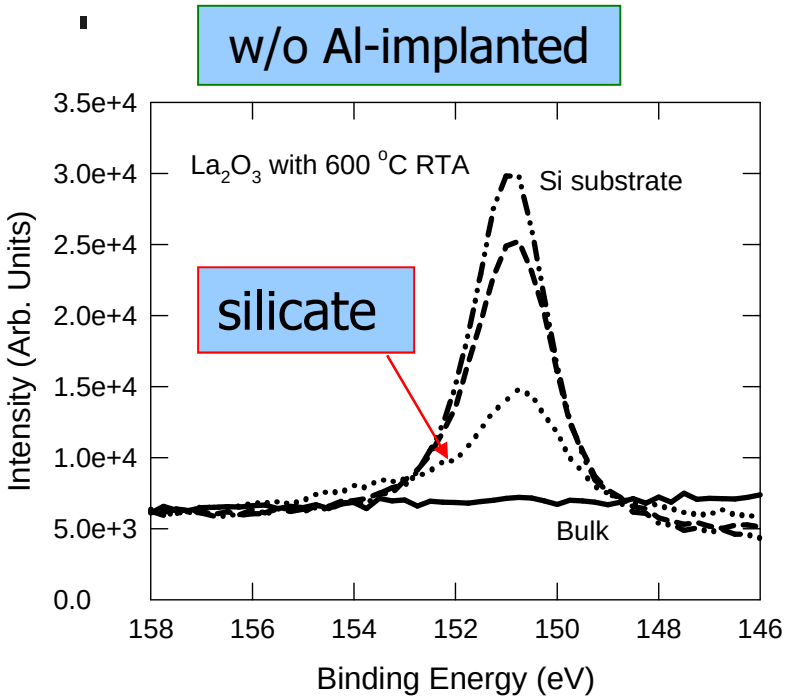
# 4.2.1 XPS O 2*p*

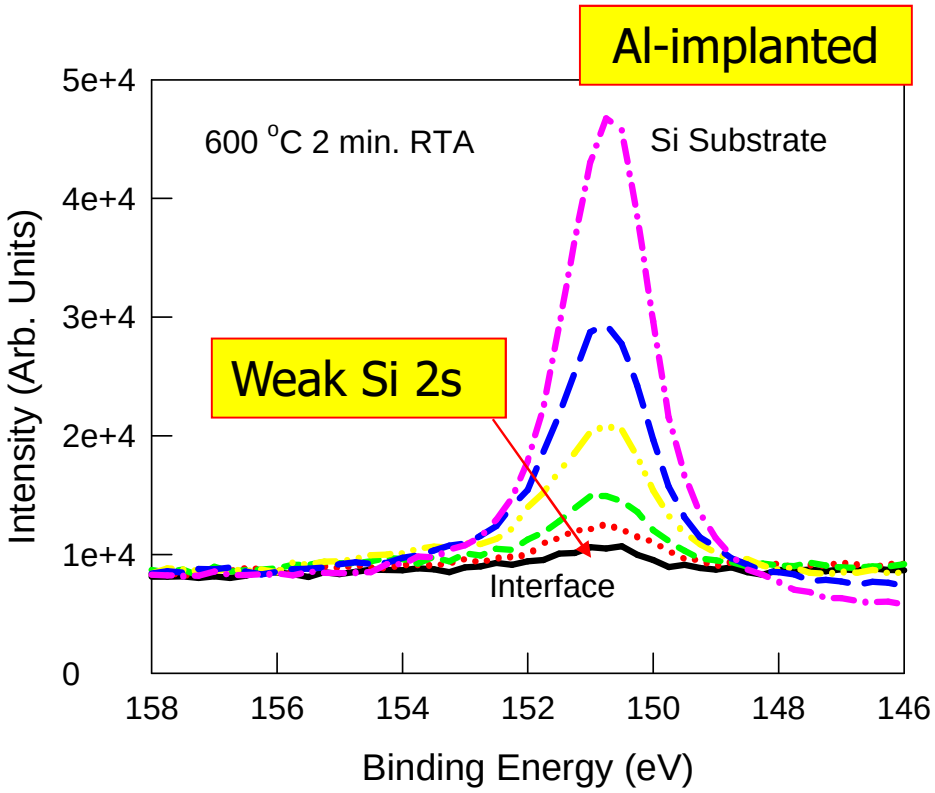



- In Al-implanted sample, O 2*p* at both bulk and interface has a dominant peak at about 531.4 eV due to $Al_2O_3$.
- The 531.4 eV O 2*p* peak are not due to the random mixing of La-O and Si-O bonds partially because we did not detect the $La_2O_3$ peak at the interface.

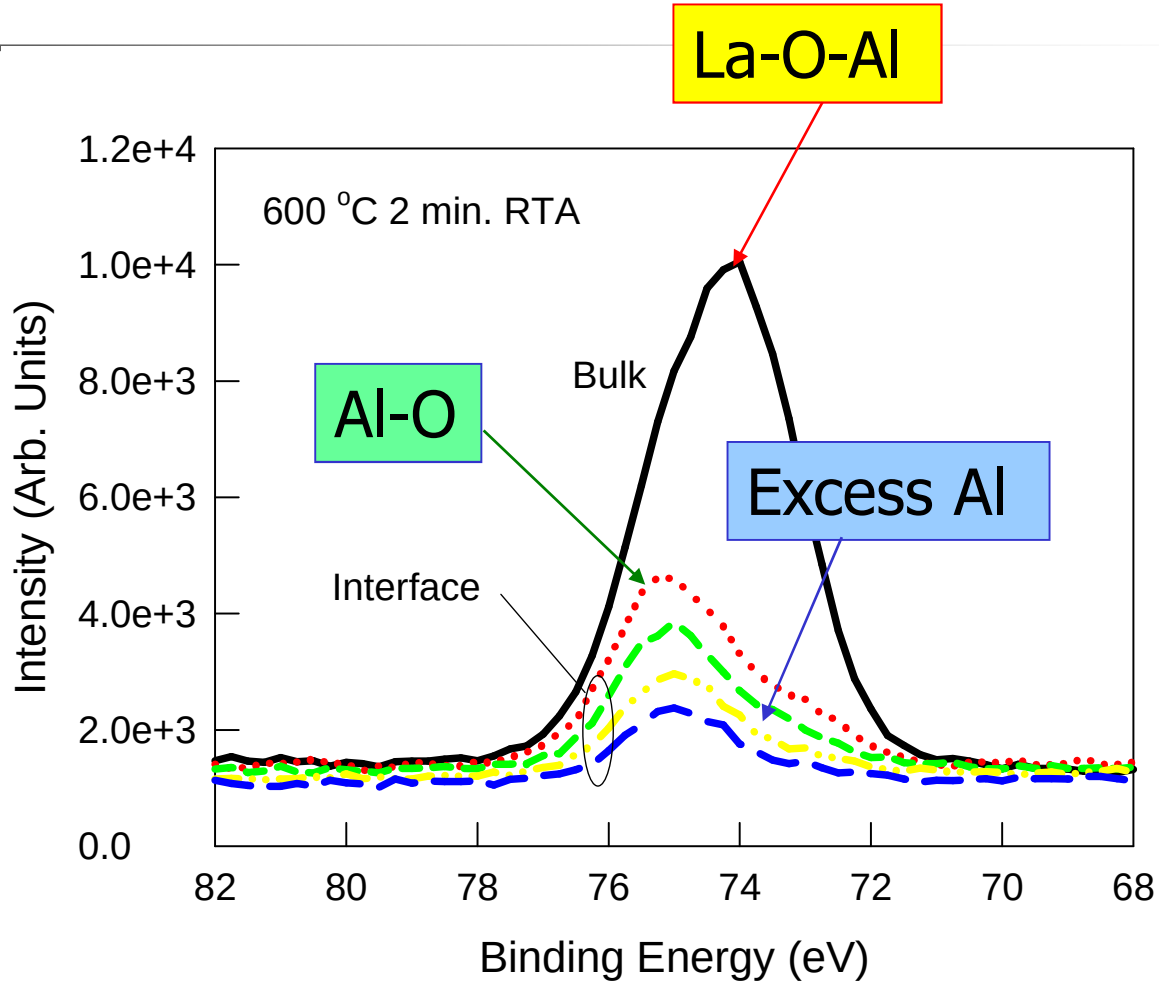
# 4.2.1 XPS: Si 2*s*



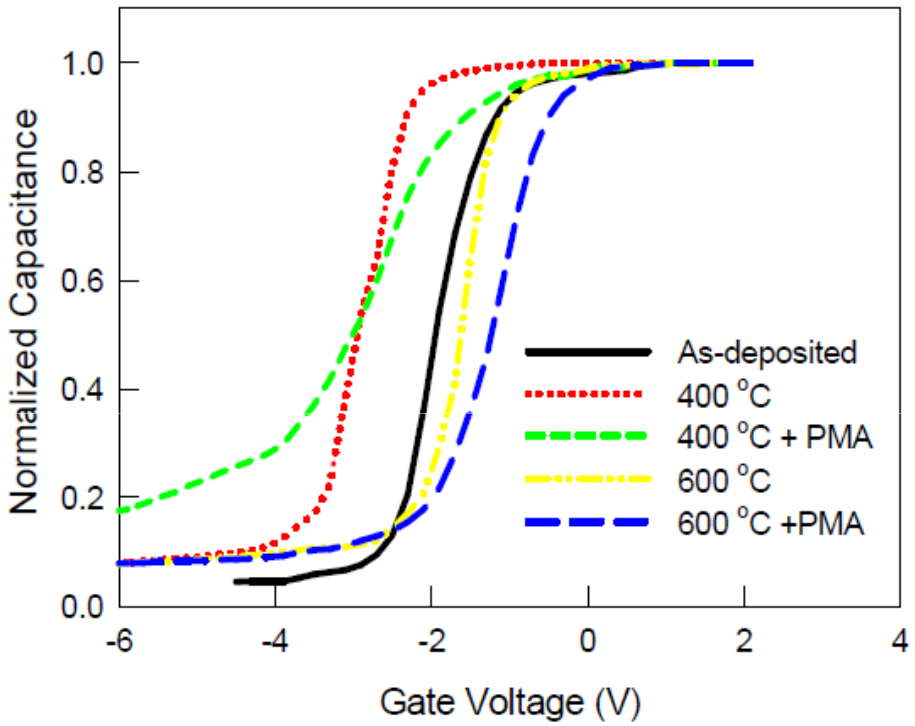




- Neither $SiO_2$ peak (153.9 eV) nor silicate peak (152–153 eV) was found.
- The low conc. of Si-O and La-Si bonding in Al-implanted samples are due to the formation of $Al_2O_3$ layer at the $La_2O_3$/Si interface.

# 4.2.1 XPS: Al 2*p*


La-O-Al
600 °C 2 min. RTA
Al-O
Bulk
Excess Al
Interface
Intensity (Arb. Units)
1.2e+4
1.0e+4
8.0e+3
6.0e+3
4.0e+3
2.0e+3
0.0
82
80
78
76
74
72
70
68
Binding Energy (eV)

# 4.2.2 Electrical Characteristics: C-V

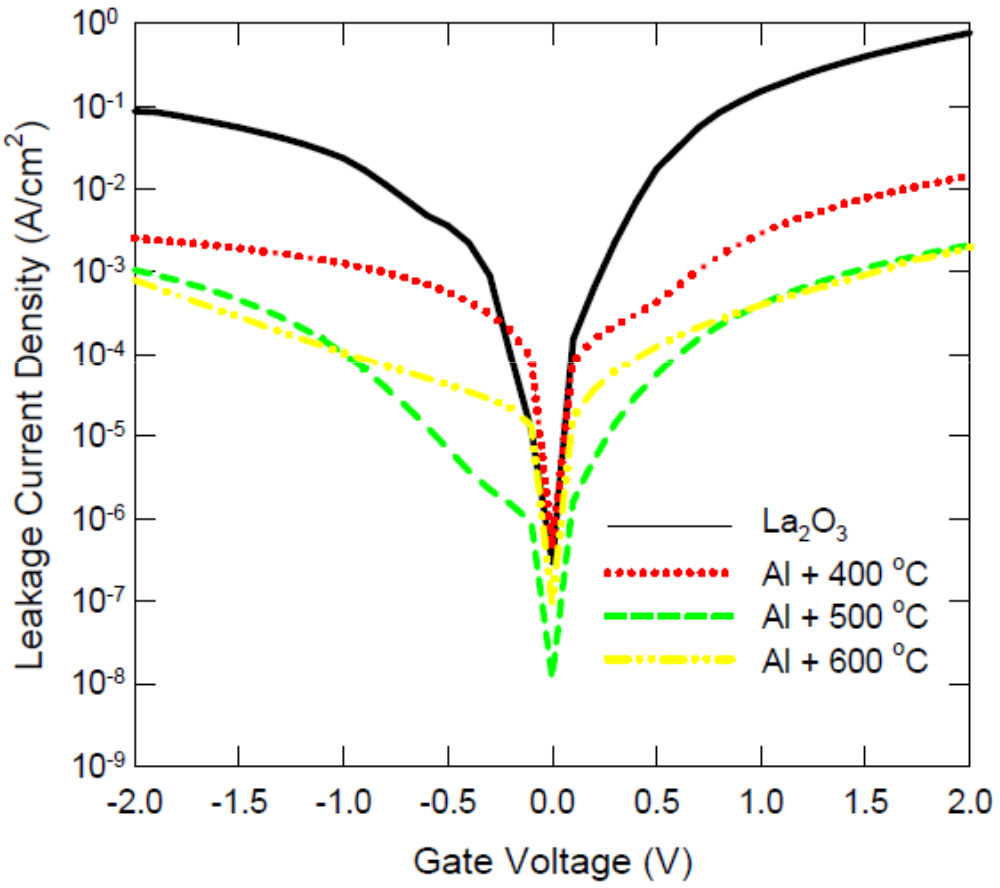



- With 600 °C RTA+PMA, $V_{FB}$ reduces to about -0.9 V indicating the trapped charge density has been reduced pronouncedly.
- The reduction +Q is due to oxidation of Al at the interface and the forming of complex $LaAlO_3$ in the bulk during RTA.
- 600 °C RTA ➔the lowest $D_{it}$ as revealed by the steepest transition between the accumulation region and the strong inversion.

- $V_{FB}$ shifts to more -ve side for T < 500 °C because the implanted Al ions had not been fully activated and the interstitial atoms serve as +Q.

- *These effects result in significant reduction in $J_g$.*

# 4.2.2 Electrical Characteristics: I-V




The I-V characteristics of $La_2O_3$ films were found to be quite unstable because of the present of large amount O vacancies and the hydroscopic nature of $La_2O_3$.

$J_g$ of Al-implanted films have been reduced by a couple orders of magnitude.

The current reduction is more significant for RTA at 500 °C and 600 °C.

Reduction of bulk $V_O$ + formation of interfacial $Al_2O_3$ layer.

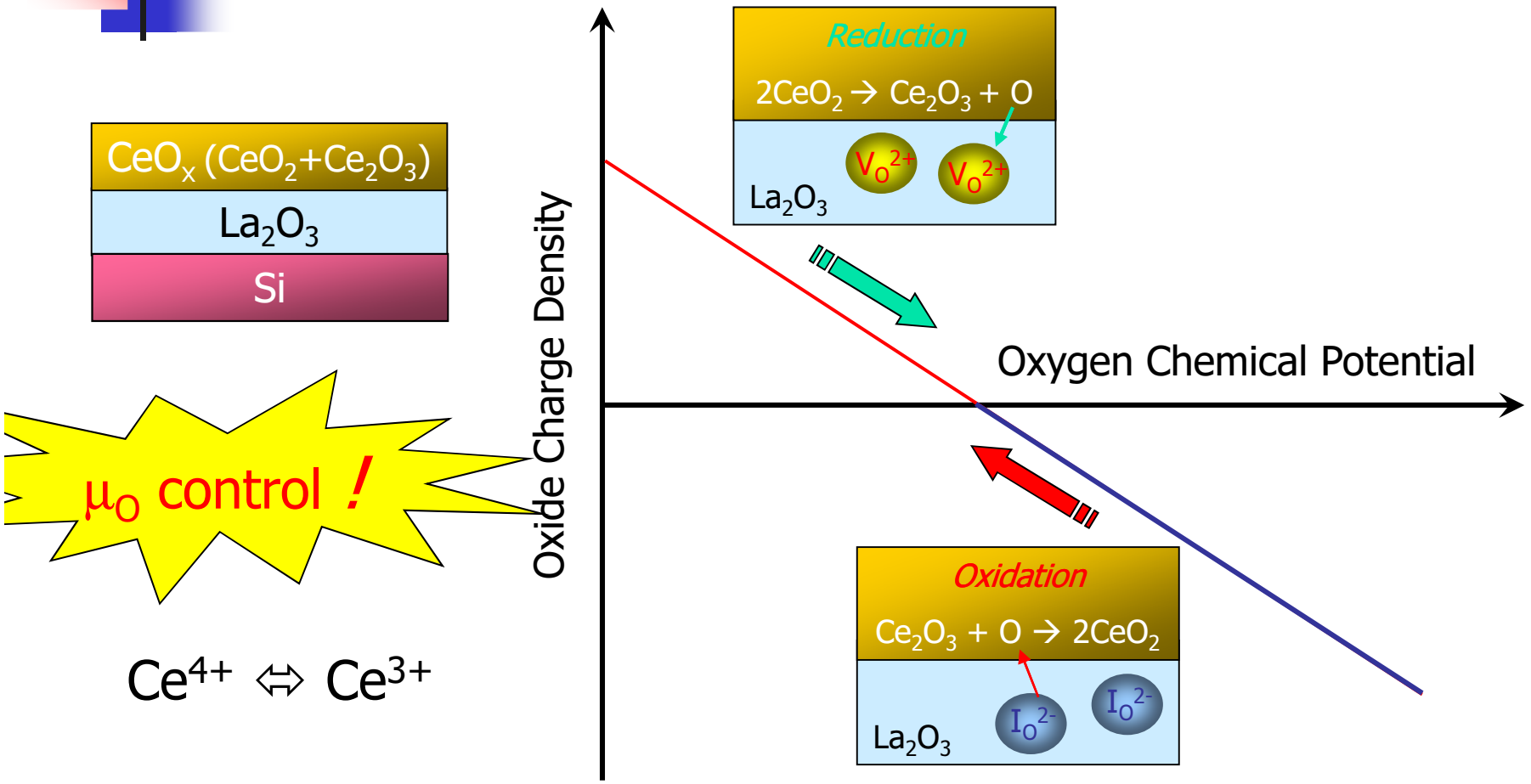
# 4.3 Summary

- A trace amount of Al doping has significantly improved the material and interface properties of $La_2O_3$/Si structure while keep most other desirable high-k properties unchanged.
- Al atoms were incorporated into the $La_2O_3$ network in the bulk and forming a thin $Al_2O_3$ layer at the $La_2O_3$/Si interface.
- The interfacial $Al_2O_3$ layer suppressed the out-diffusion of substrate Si and the formation La silicate and La silicide bond at the interface.
- Both the bulk and interface defect densities were reduced with this process.

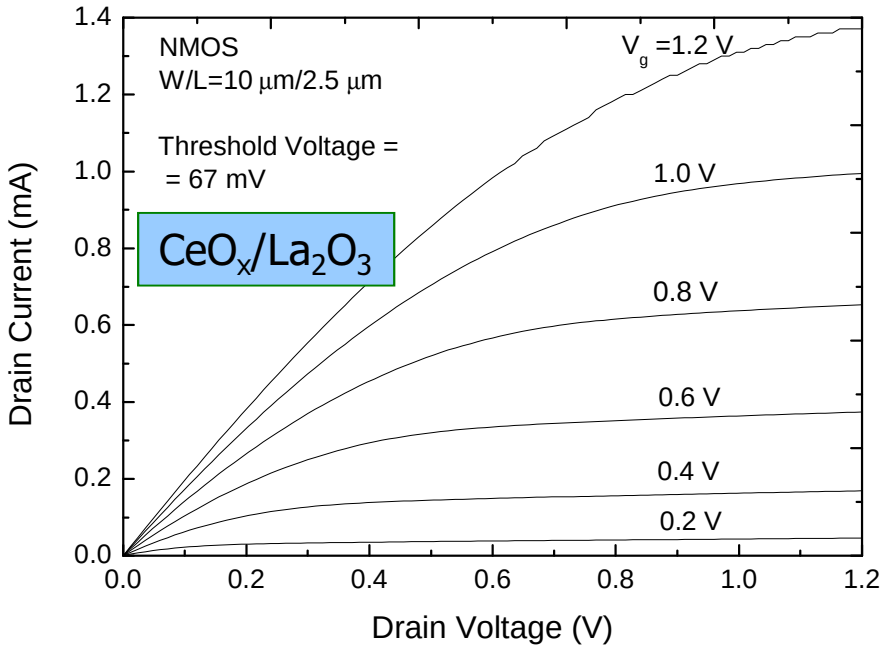
# 5. Oxygen Chemical Potential Control

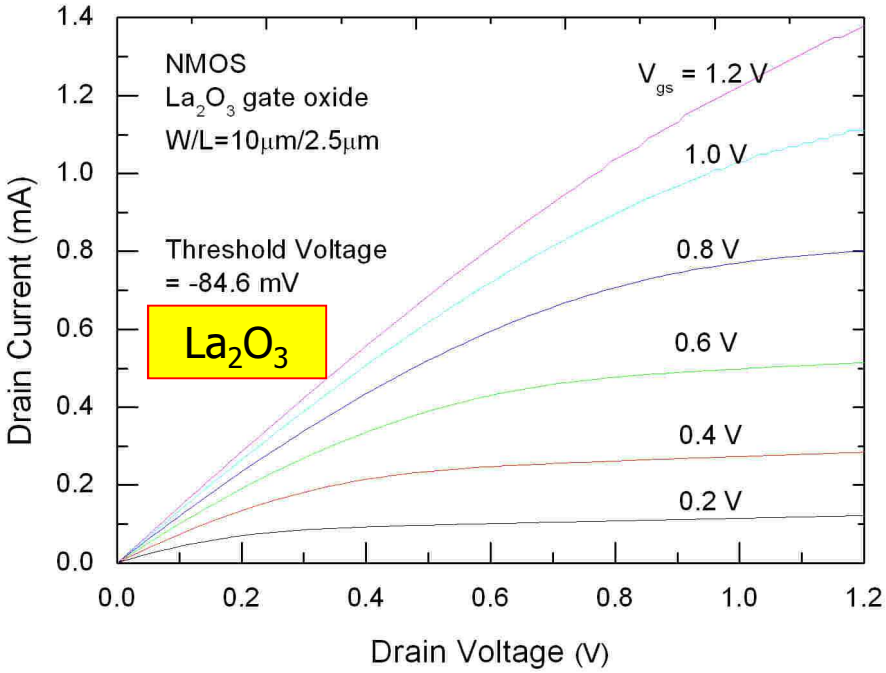
Using MgO, SrO, $CeO_2$ …

# Illustration of using $CeO_x$ for Oxygen Chemical Potential Control for $La_2O_3$



# 5.1 Electrical Characteristics: I-V



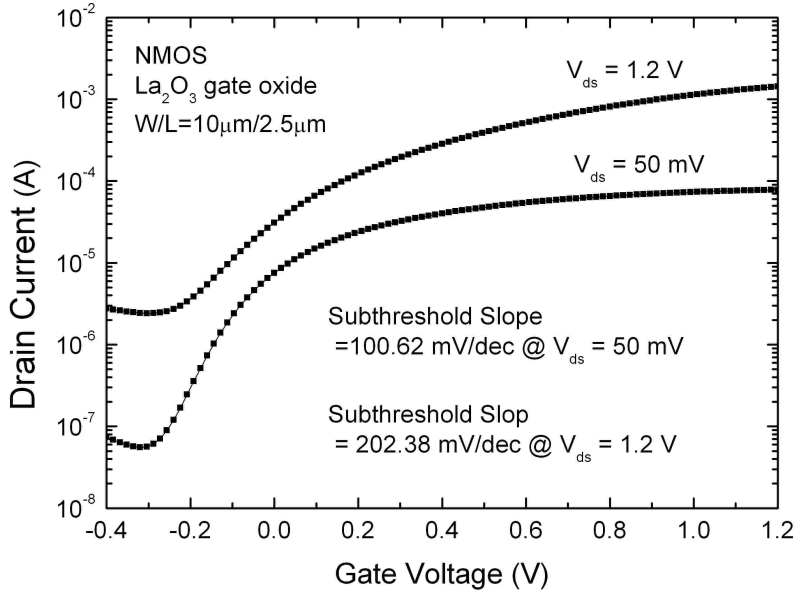



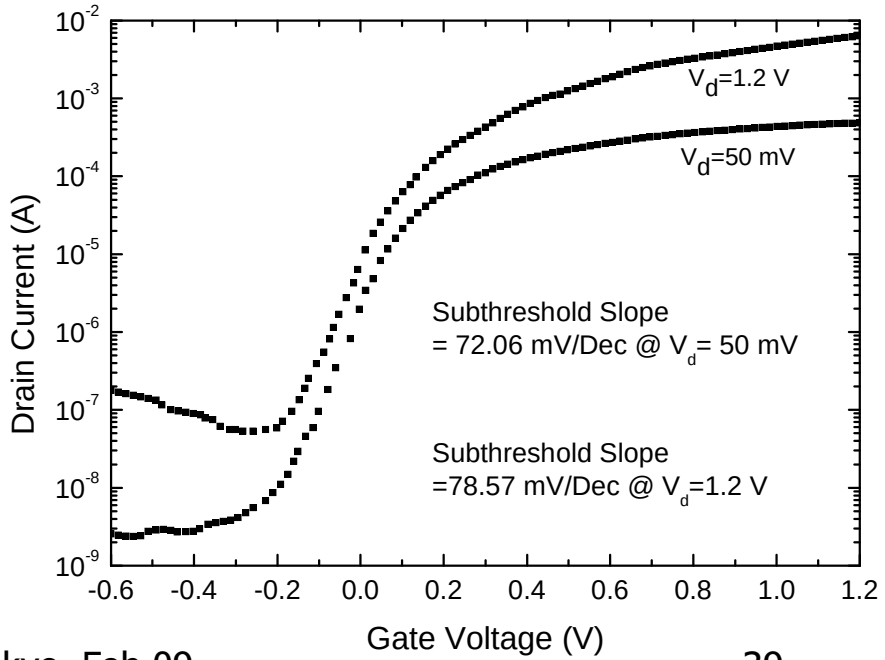

- $V_t$ and $g_m$ were significantly improved as compared with transistors with $La_2O_3$ only.

➔ suppression of fixed oxide charge in the $CeO_x$ capped $La_2O_3$ film and enhancement of channel mobility.

# 5.1 Electrical Characteristics: I-V

- Subthreshold slope (SS) is much better than the device using $La_2O_3$ only:
  - 72 mV/dec for NMOS
  - 73 mV/dec PMOS
- ~ 100 mV/dec for NMOS with $La_2O_3$ gate oxde.



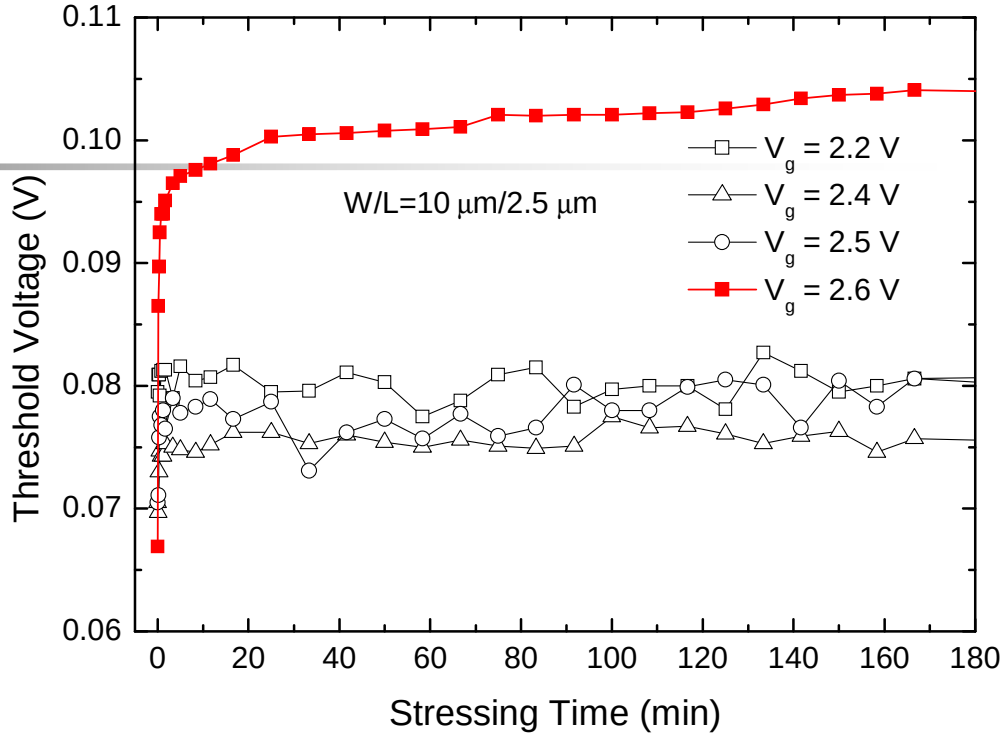



# Parametric Comparison

| Parameter | $La_2O_3$ | | $CeO_x/La_2O_3$ | |
|---|---|---|---|---|
| | NMOS | PMOS | NMOS | PMOS |
| $V_t$ (V) | -0.085 | -1.064 | 0.067 | -0.840 |
| SS (mV/dec) | 101 | 195 | 72 | 73 |

# 5.2 Hot-Carrier Effects

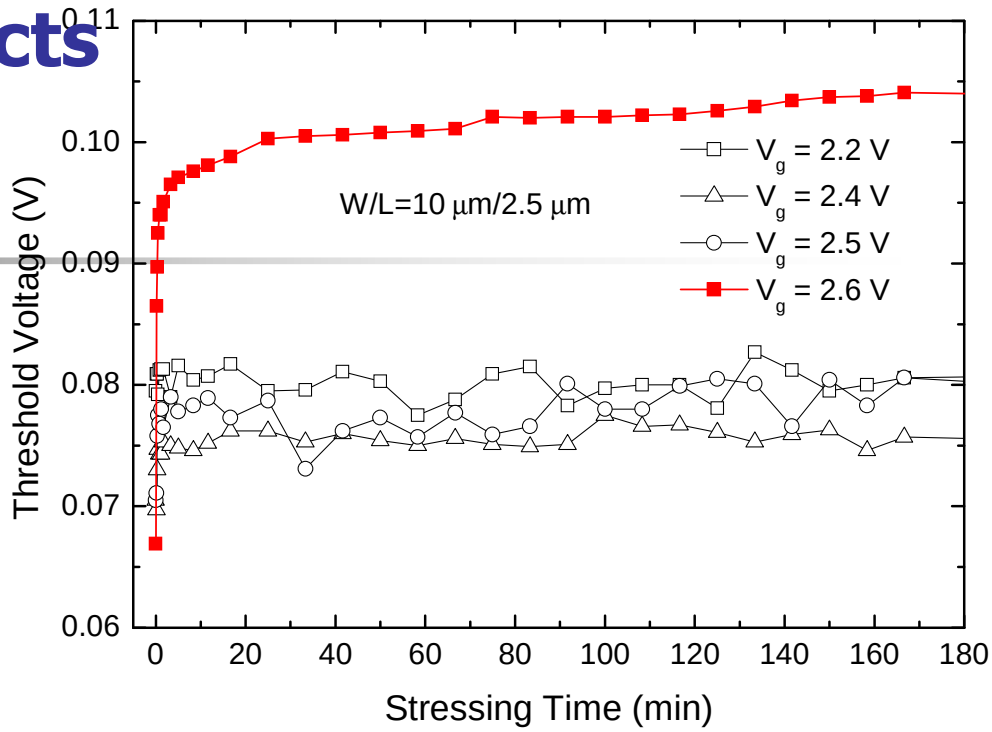
- $V_t$ increases rapidly after a brief "stressing" of 10 s.
  - ➔ charge trapping at the interface.




- For $V_{gs} = V_{ds} \leq 2.5$ V, $V_t$ does not have much change for different stressing voltages.
- $V_t$ remains almost the same for stressing duration up to 24 hrs.
  - The transistor was biased at $V_{gs} = V_{ds}$ to have maximum hot carrier injection.
  - $V_t$ = 0.067 V before the stressing being taken place.

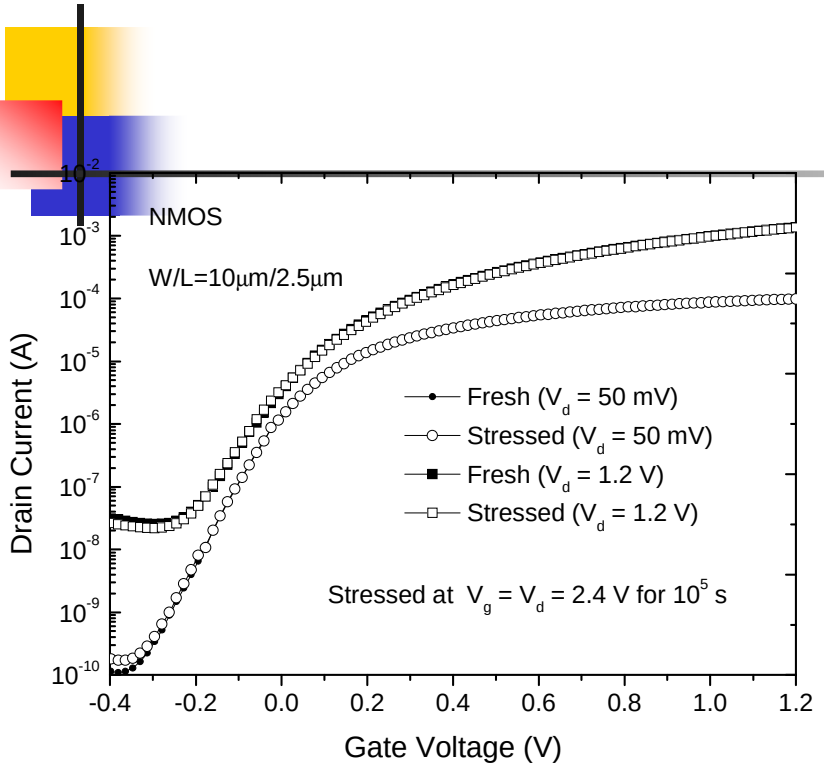
# 5.2 Hot-Carrier Effects

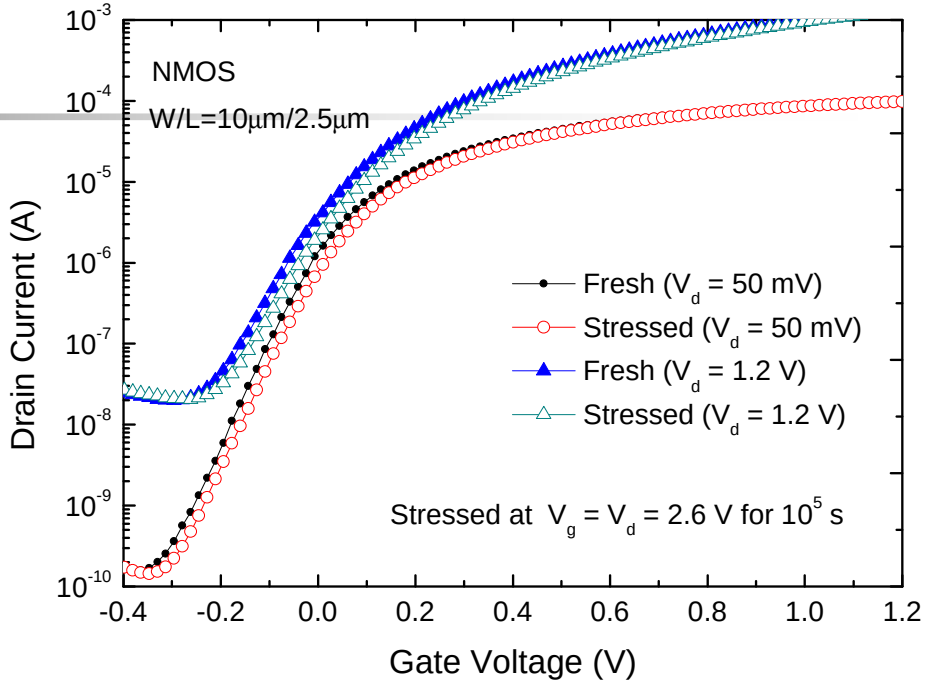
- Abrupt jump of $V_t$ shift for stressing at $V_{gs}$ = $V_{ds}$ = 2.6 V because the onset of FN conduction.
- Gradual increasing of $V_t$ up to 0.105 V for 180-min stressing is due to stress induced defects.




- Stressing at 2.6 V ➔
  - filling of $V_O$ in $La_2O_3$ and the interface trap at $CeO_x/La_2O_3$ interface;
  - generation of oxide charges or interface charges for prolonged stressing.
- $V_t$ did not increase further for stressing up to 24 hrs.

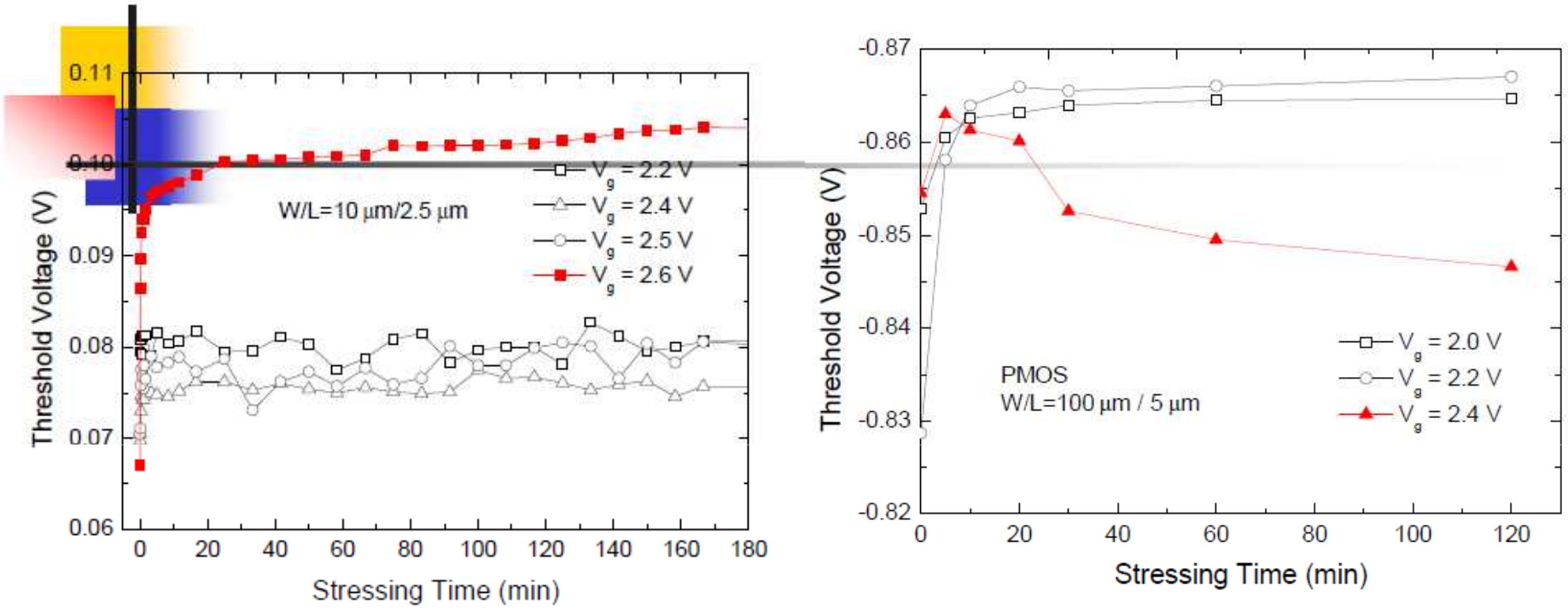
# 5.2 Example of stressed $I_{ds}$-$V_{gs}$ Characteristics




- Notable change, but still small, for HC stressing at $V_{gs} = V_{ds} = 2.6$ V.
  - band bending of the $Si/La_2O_3$ interface is large enough to cause FN conduction over the $E_C$ edge.
  - able to cause O- species to have a notable drift?

# 5.2 Hot-Carrier Effects




- HC stressing has larger impact on the PMOS.
- A large +ve $V_t$ shift was found for sample stressed at $V_{gs} = V_{ds} = -2.4$ for 30 min !
- The present results demonstrate much better robustness against the HC stressing than the transistor using $La_2O_3$ only.

# 5.3 Summary

- The transistors with W/$CeO_x$/$La_2O_3$ gate stack have:
  - smaller threshold voltage,
  - larger transconductance,
  - smaller subthreshold slope, and
  - better hot-carrier robustness

  when compared with devices using $La_2O_3$ gate dielectric only.

- These improvements were ascribed to the filling of O vacancies in $La_2O_3$ film with the O atoms released from ***partial reduction reaction*** of the capping $CeO_2$ film.

# 6. Conclusions

*La-based high-κ dielectric can be a promising candidate for sub-nanometer EOT for future nanoscale MOS devices.*

*The instability issues can be alleviated by several methods such as doping or stacked structure.*