# Computational Science Studies toward Future Nano-Devices

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# Contents

1. Introduction
2. Key physics in ionic materials obtained by computational sciences.
3. Operation Mechanism of ReRAM
4. Physical Origin of Negative Fixed Charge by SiC Oxidation
5. Interface physics in high-k gate stacks
6. Summary

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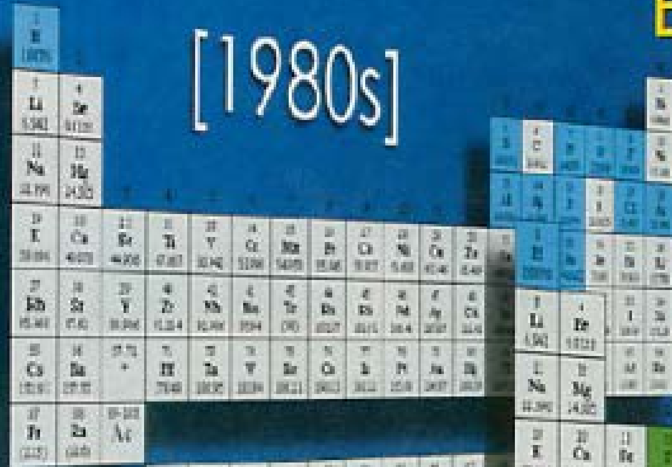
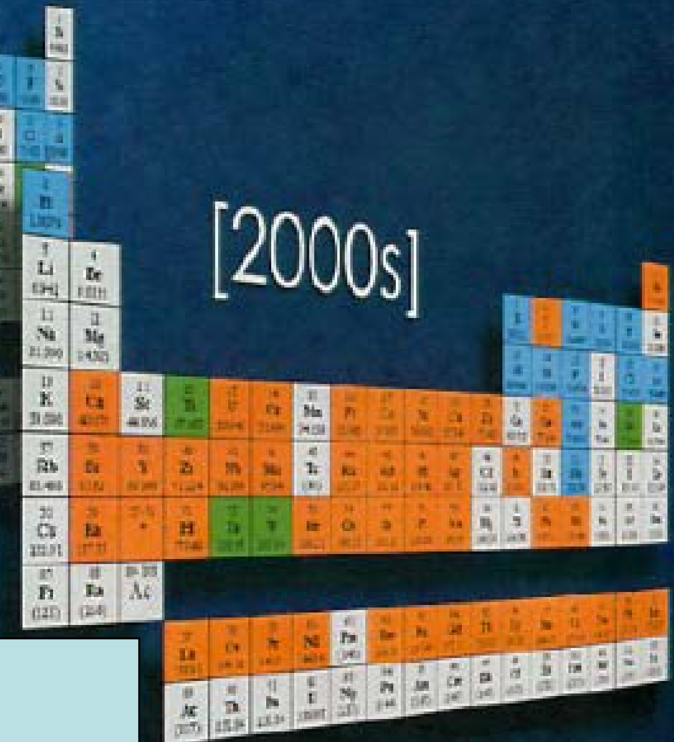
# 1. Introduction
# Recent LSI Devices Need Various Kinds of Elements

Silicon Technology: Complexity Increasing Exponentially






**Interfaces with various materials are inevitable**

**Computational material design becomes a crucial tool**

**By Intel**

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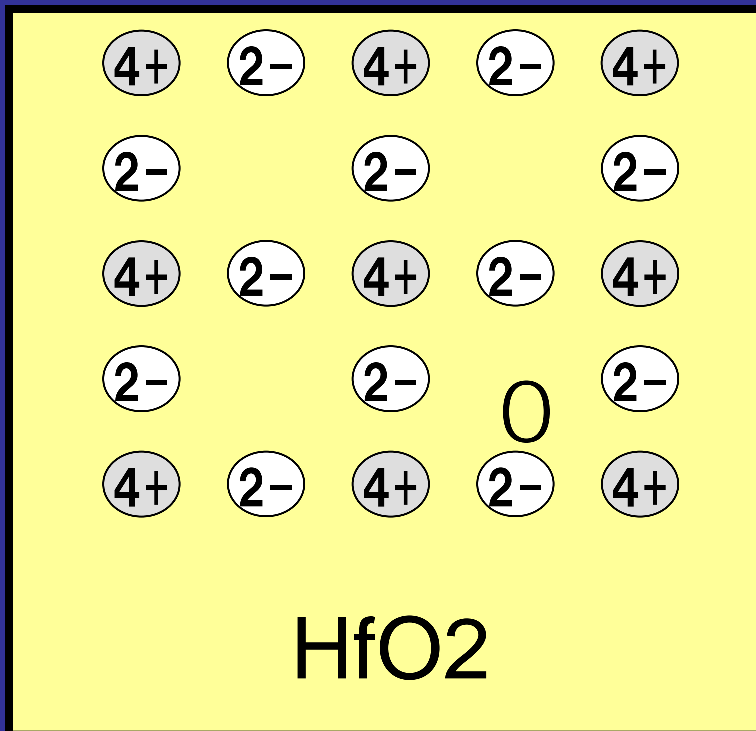
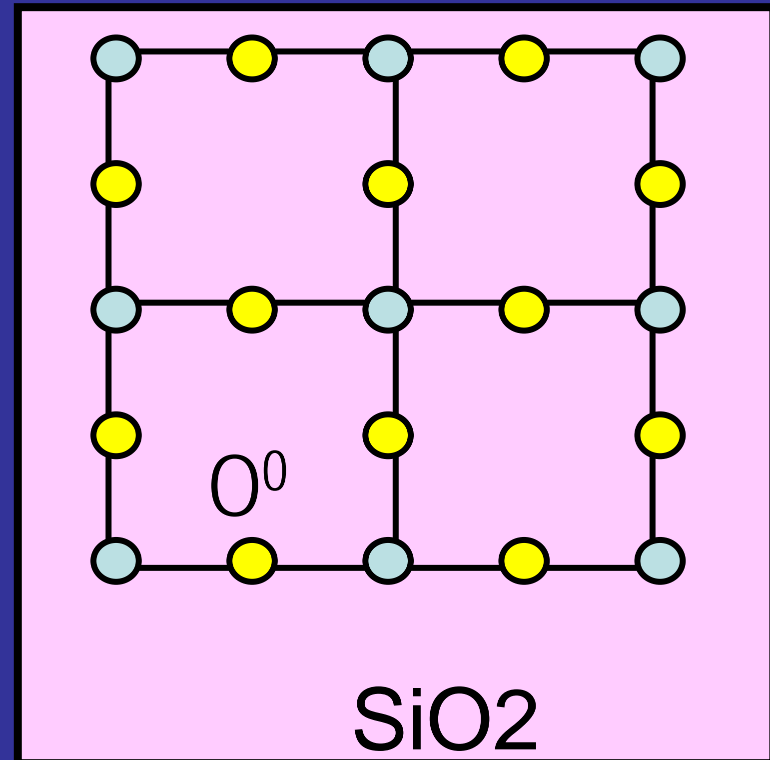
# 2. Key Interface physics between Ionic and covalent materials

**Difference in O forms in ionic HfO2 and covalent SiO2**

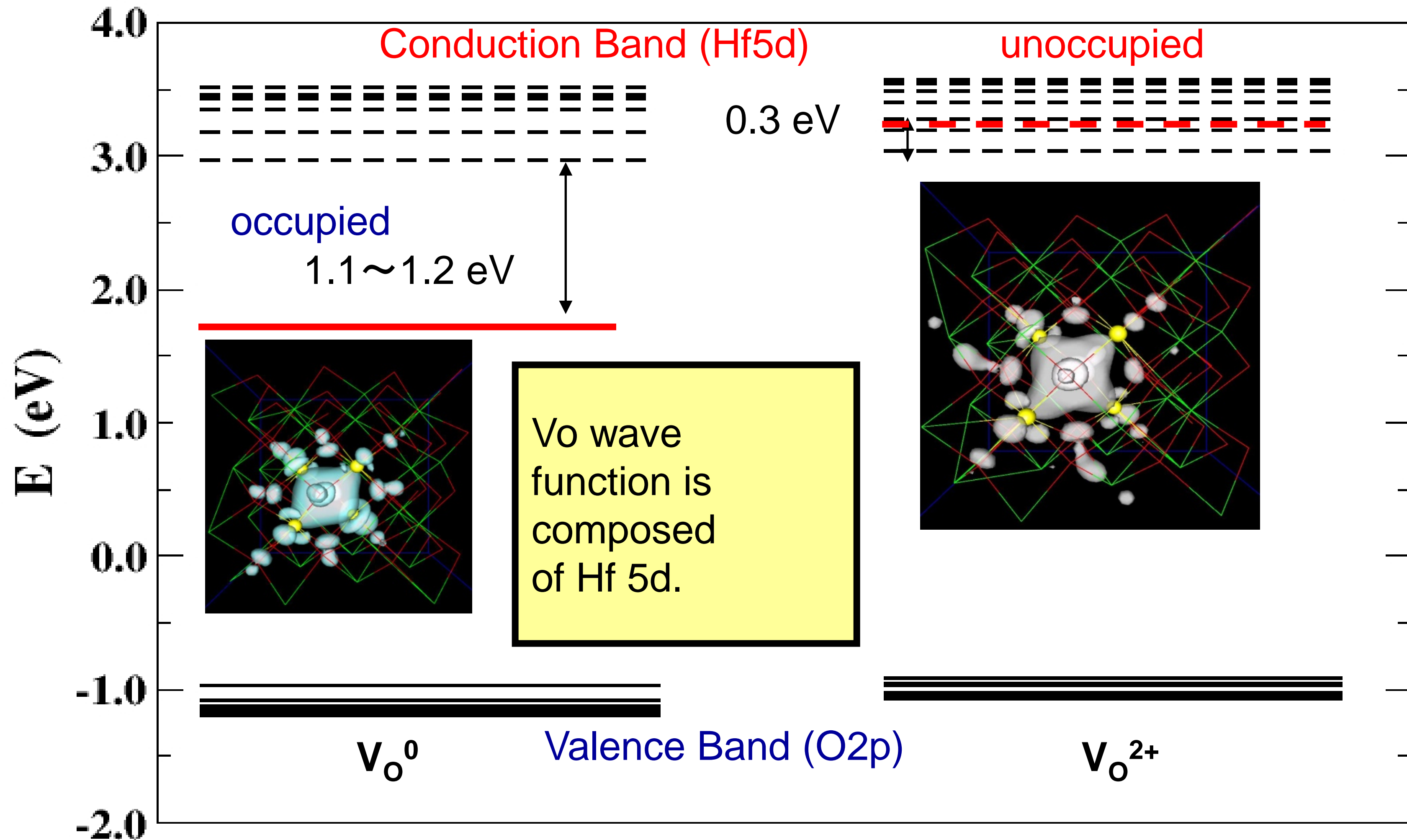


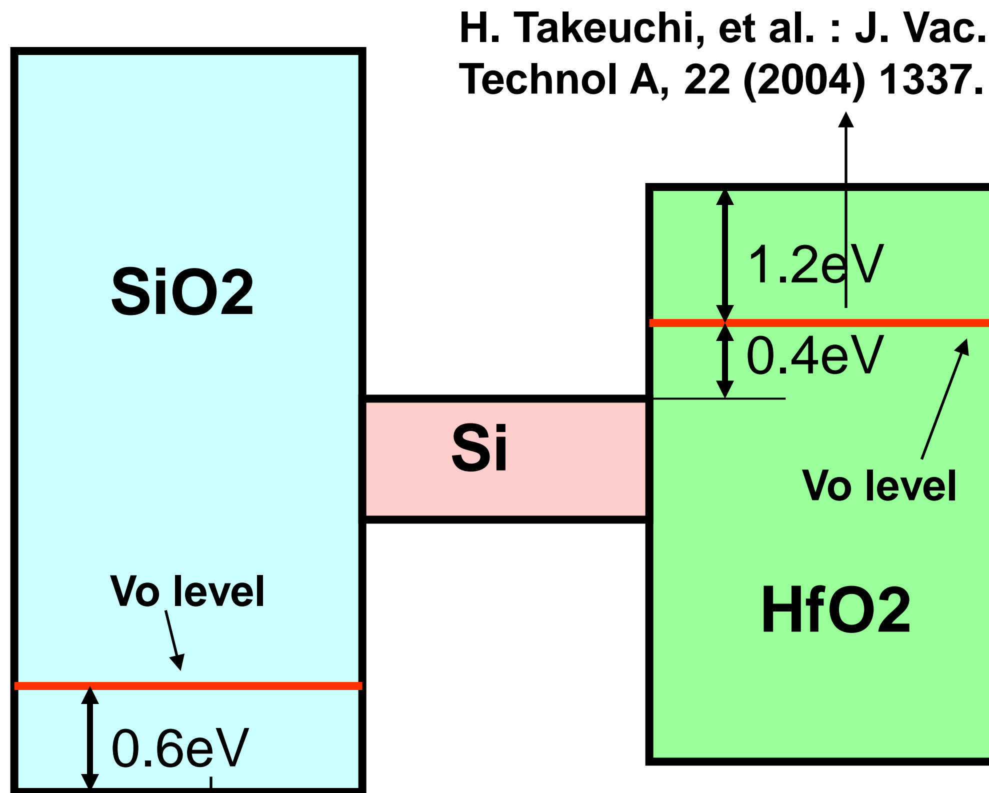

**$O^{2-}$ form in HfO2.** **$O^0$ form in SiO2.**

K. Shiraishi et al. VLSI 2004

# Computational Science Knowledge for O Vacancies in $HfO_2$ -First Principles results-



What is the crucial difference between covalent $SiO_2$ and ionic $HfO_2$ from microscopic viewpoint: (Energy level position of Vo) Relatively higher energy level position is the origin of the large Vfb shift of $HfO_2$ dielectrics as well as the easy formation of Vo




Spectroscopic ellipsometry experiments

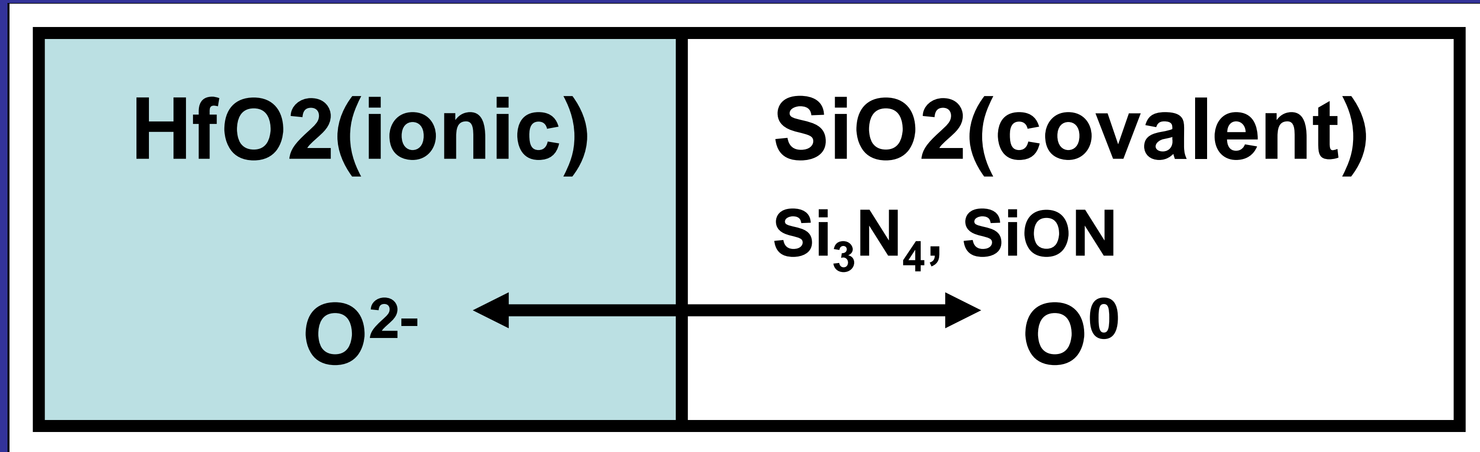
In $HfO_2$, Vo energy level is located much higher position compared to Vo energy level of $SiO_2$.

(additional electron generation is difficult in $SiO_2$)



**Isolated Vo in an ionic materials tends to become 2+.**

# Coexistence of Covalency and Ionicity → new interface physics




O atoms in ionic crystals such as $HfO_2$ are $O^{2-}$ ion. However, they change into the $O^0$ form, when they enter inside the covalent crystals such as $SIO_2$. This causes a lot of unusual interface phenomena such as Fermi level pinning, and maybe interface dipole formation between HfO2 (La2O3)/SiO2 interfaces.

# Coexistence of Covalency and Ionicity → new interface physics

| $HfO_2$(ionic) | $SiO_2$(covalent) |
| --- | --- |
| $O^{2-}$ | |

# Coexistence of Covalency and Ionicity → new interface physics

| $HfO_2$(ionic) | $SiO_2$(covalent) |
| --- | --- |
| $O^{2-}$ | |

# Coexistence of Covalency and Ionicity → new interface physics

| $HfO_2$(ionic) | $SiO_2$(covalent) |
| --- | --- |
| $O^{2-}$ | |

# Coexistence of Covalency and Ionicity → new interface physics

| HfO2(ionic) | SiO2(covalent) |
| --- | --- |
| Vo+2e | $O^{0}$ |

# Coexistence of Covalency and Ionicity → new interface physics

| HfO2(ionic) | SiO2(covalent) |
|---|---|
| $Vo^{2+}$ + 2e | $O^0$ |

When $O^{2-}$ ion moves from ionic HfO2 into covalent SiO2, two surplus electrons are generated. These two electrons tends to transfer into gate metals, leading to formation of Vo(2+).

TiO2 and ZrO2 also have above tendency.

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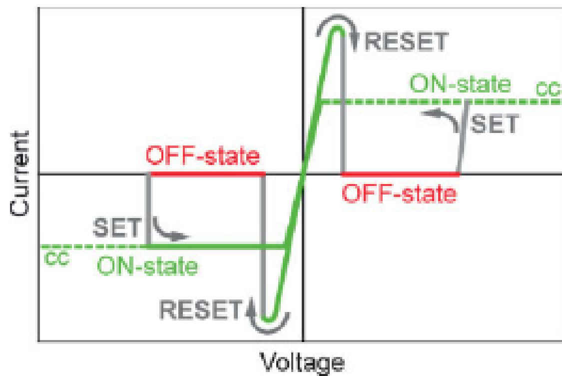
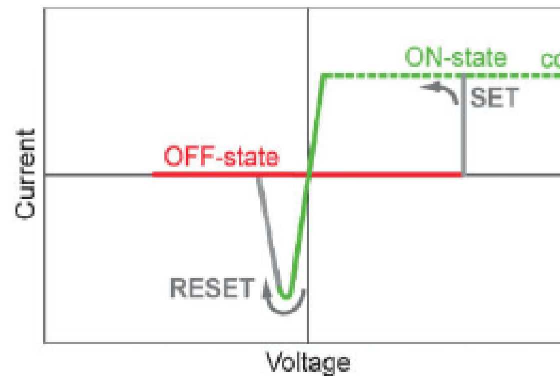
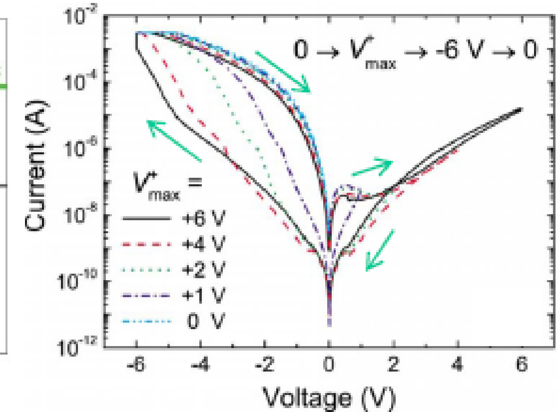
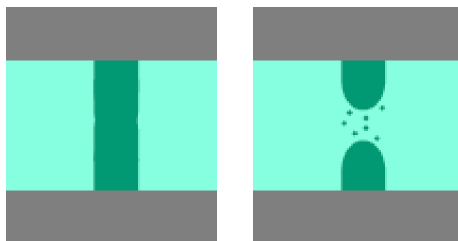
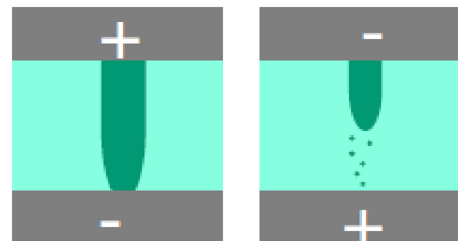
# RRAM types

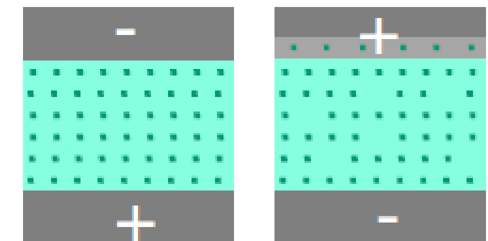



Unipolar (filamentary)

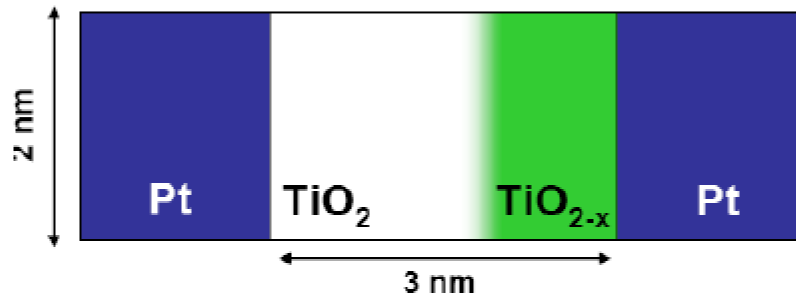
Bipolar (filamentary)

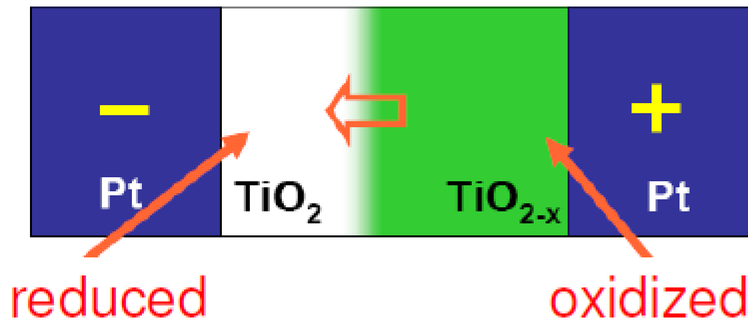
Bipolar/analog (interface)

From D. Ilemini Lecture

# Conventional Model of ReRAM Operation

## Dopant = oxygen vacancy $V_O^{2+}$




- Insulating $TiO_2$ + low-resistivity $TiO_{2-x}$
- $V_O^{2+}$ drift toward the cathode: $TiO_2$ reduction lowers resistance (n doping by $V_O^{2+}$) while $TiO_{2-x}$ is not majorly affected by oxidation

- *Series* model as opposed to *parallel* model in filamentary switching (e.g. NiO)
- Experimental evidence for TiO2-TiO2-x model?

From D. Ilemini Lecture

# Question

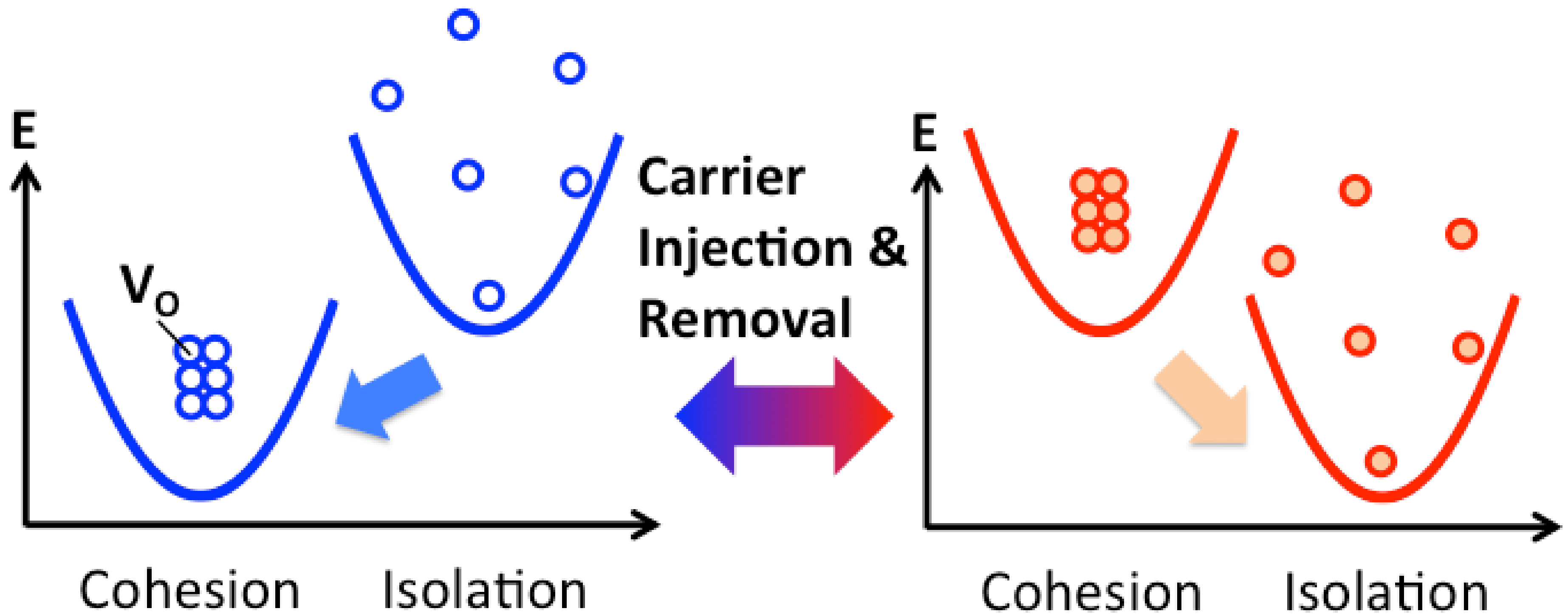
- Is it a simple drift of charged Vo(2+) by electric field?
- Do electrons play significant roles?

- Our proposal is that electrons induces phase transition of Vo based nanostructures (Vo filaments)

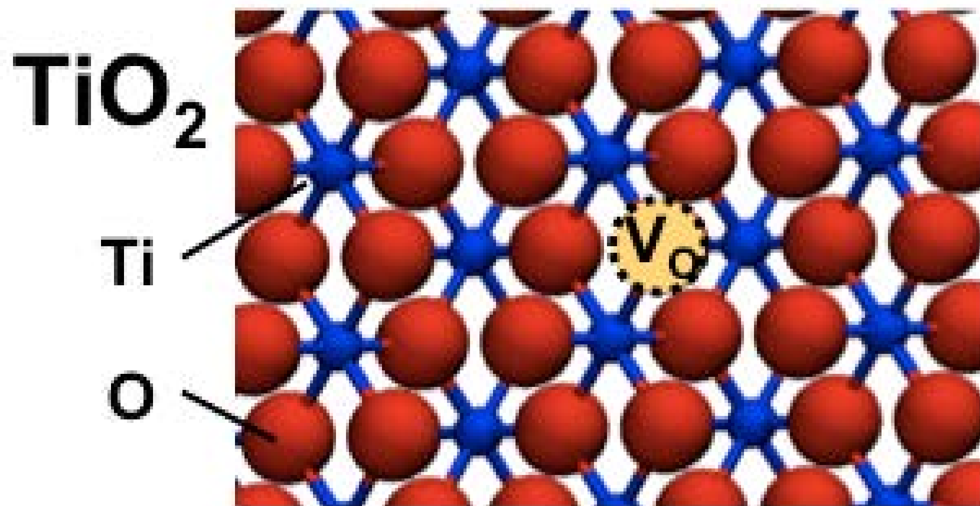
# Purpose

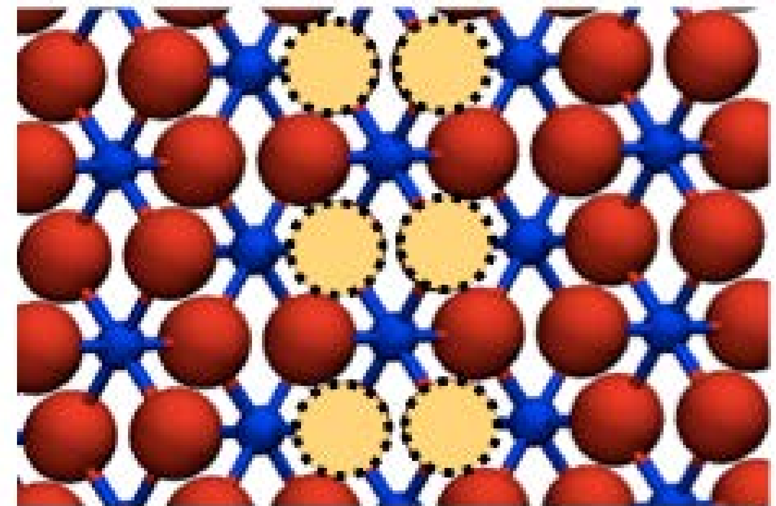
- We propose new ReRAM operation model by investigating $TiO_2$ based ReRAM by LDA+U method.

# Message:
# Carrier injection/removal induces Cohesion-Isolation transition
## (K.Kamiya et al. Appl. Phys. Lett. (2012) in press)



# We investigated isolated Vo and Vo chain by first principles calculations.



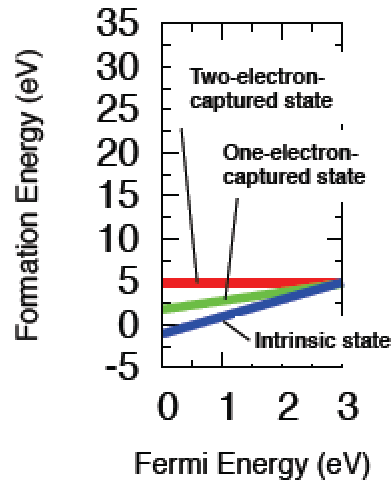
Isolated Vo

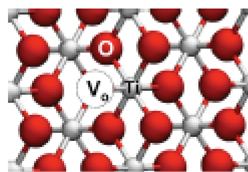
Vo chain

# Isolated Vo and Vo chains are calculated 108 atom supercell, LDA+U, 4Vo in supercell

Isolated Vo

(a)

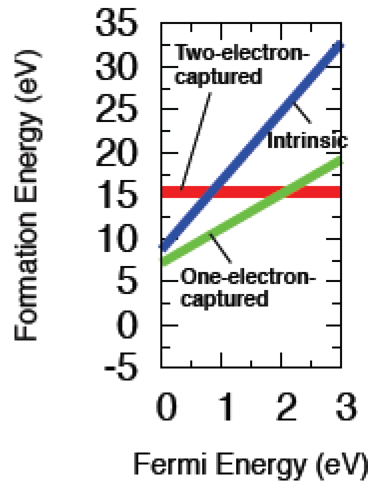


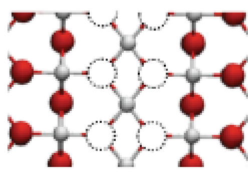



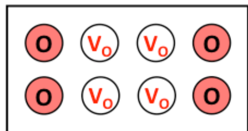
Isolated Vo

Vo chain

(b)

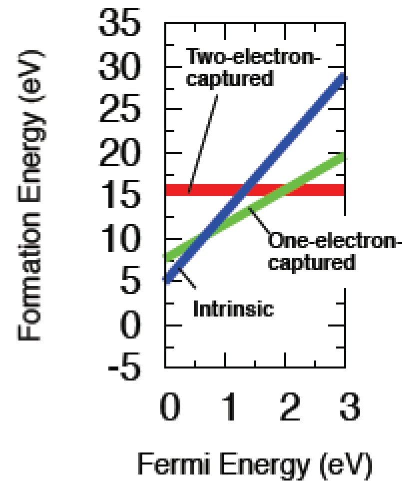


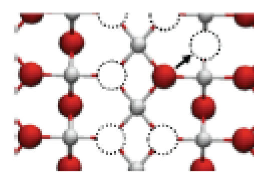



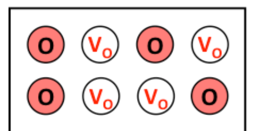


Vo chain with 1 Vo disruption

(c)

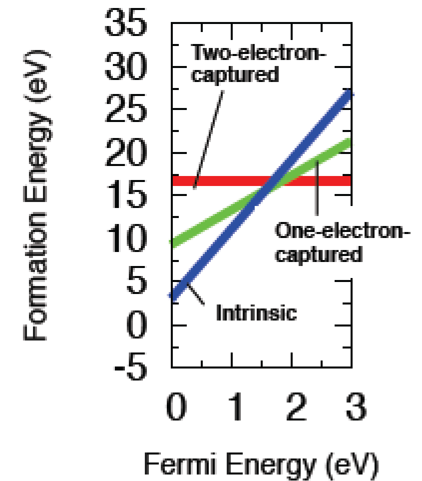


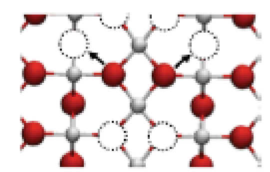



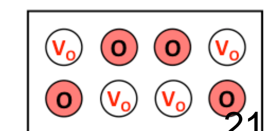


Vo chain with 2 Vo disruption

(d)

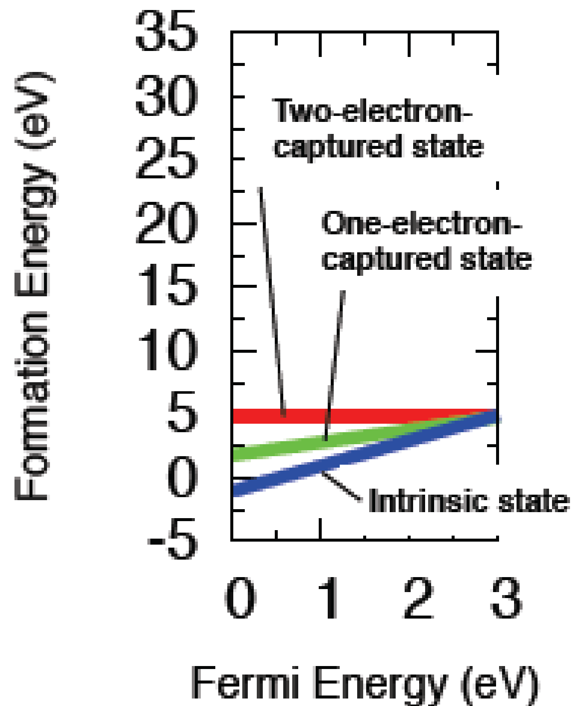


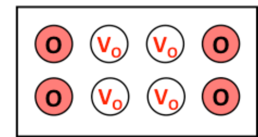



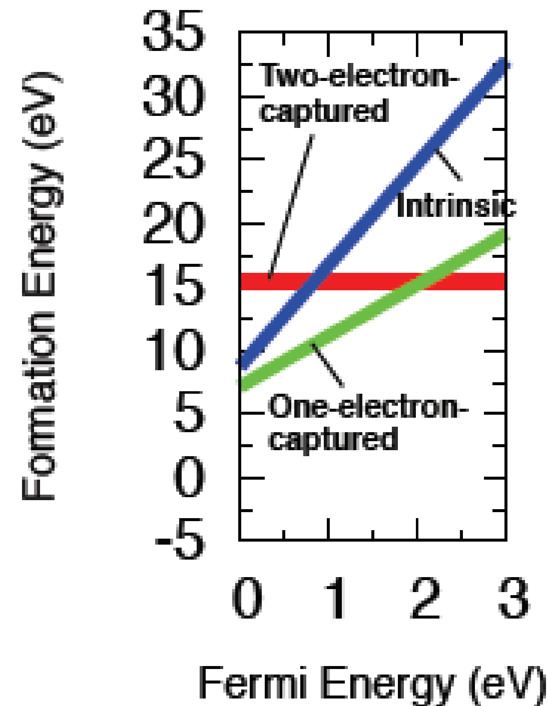


# Favorable charge state difference between isolated Vo and a Vo chain (filament).

Isolated Vo



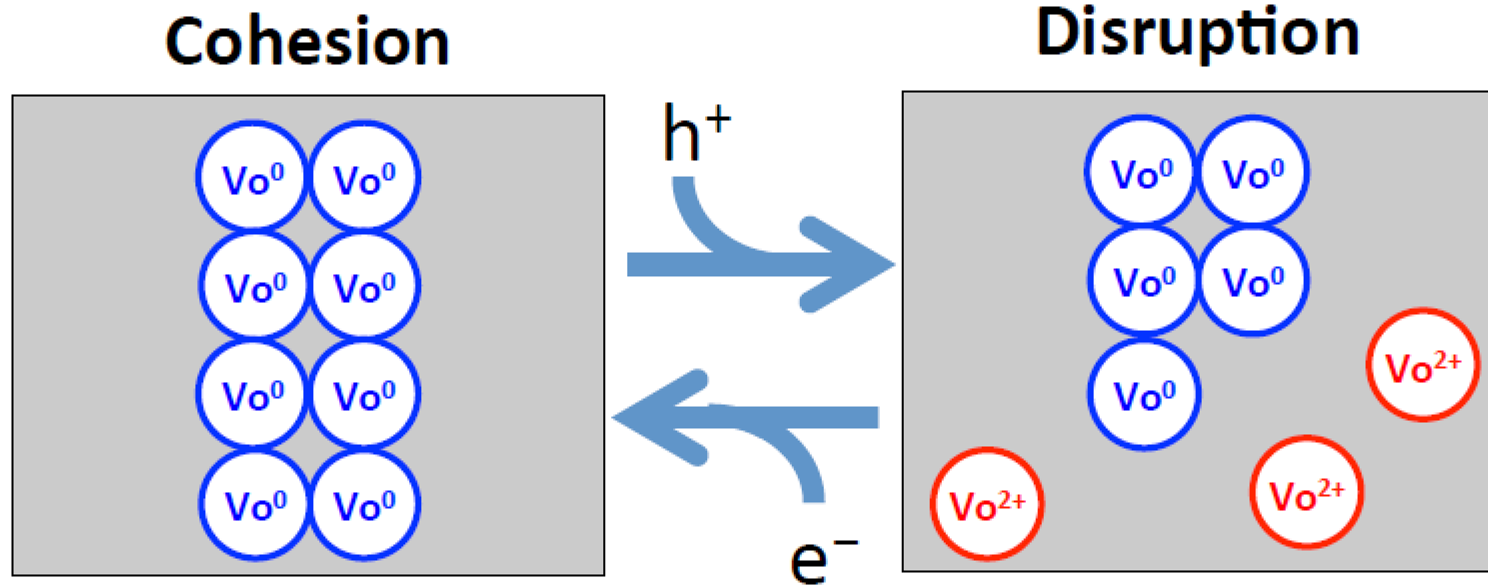




Isolated Vo tends to be 2+

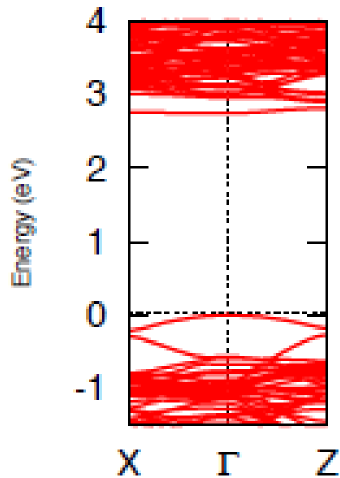
Vo chain tends to capture electrons

# Carrier injection can cause Cohesion-Disruption(Isolation) transition



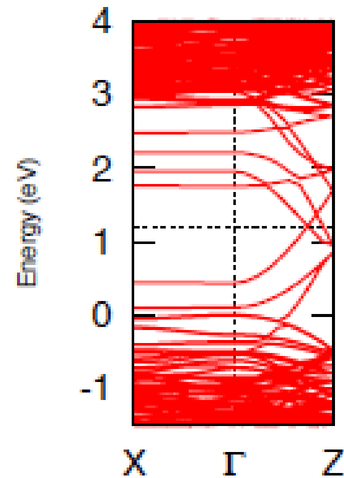
# Band structures of each model

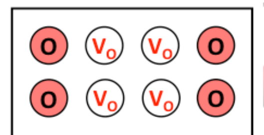
Insulating



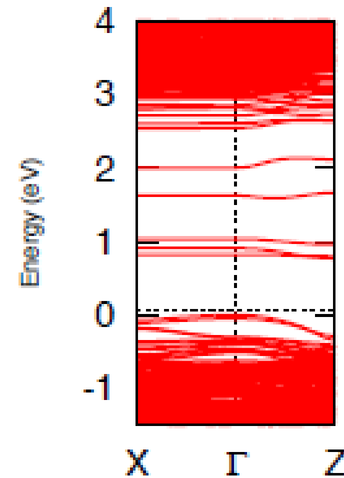

Isolated Vo

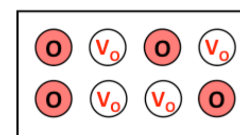
Metallic



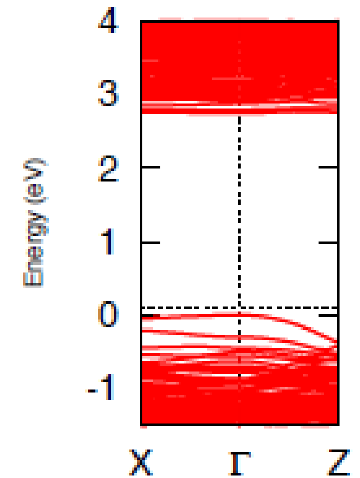



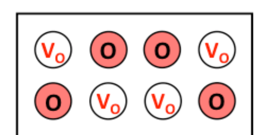

Semi-insulating



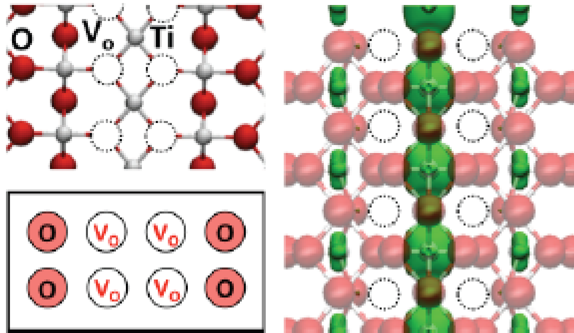

Insulating



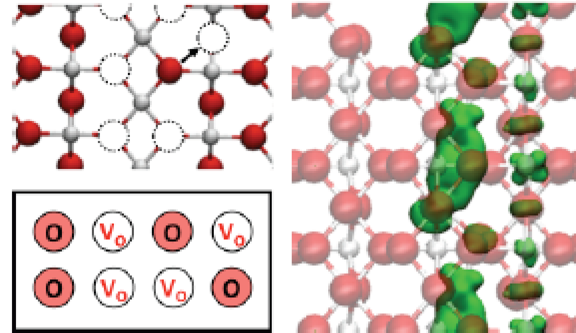



# Charge density of each model

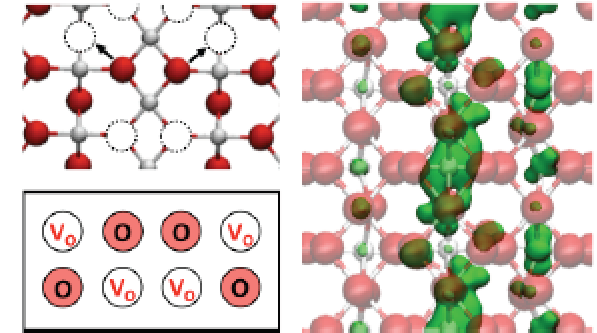
Chain




Partial Disruption



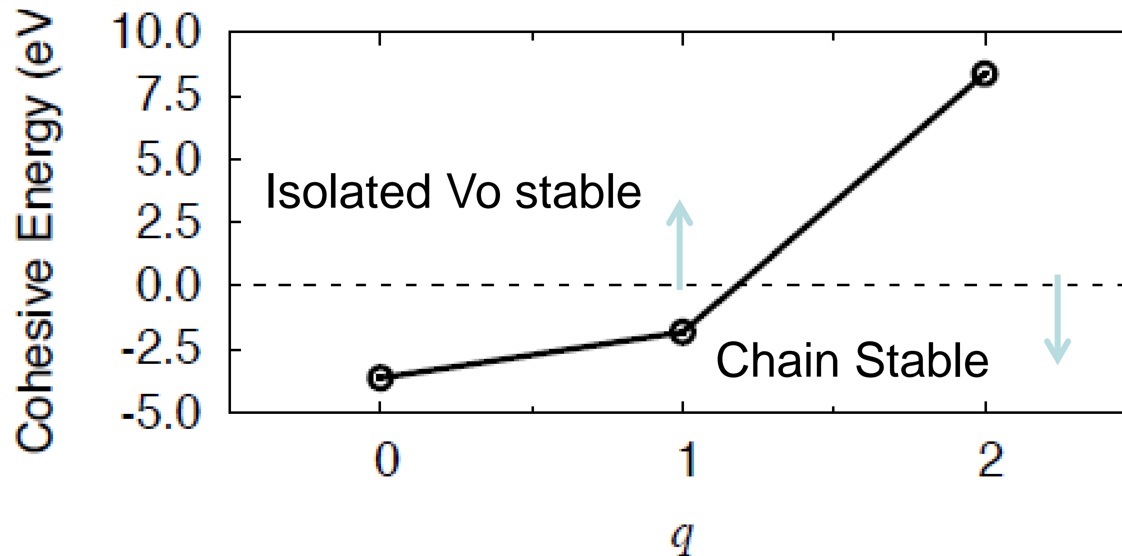

Disruption

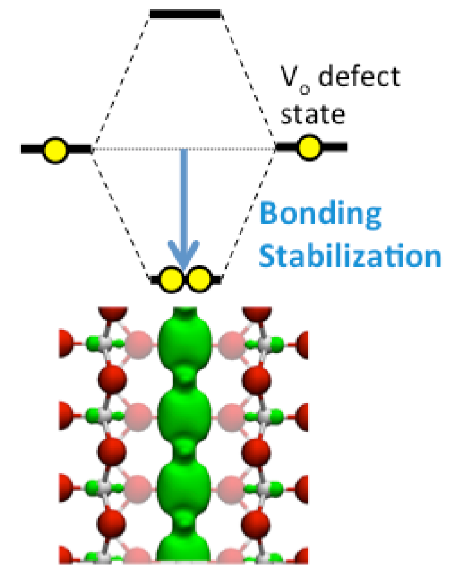



Also from charge density distributions, only chain model reveals conductive feature

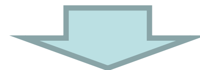
# Formation Energies of Vo Chain as a Function of Electron Fermi Energies.

$$E_c(q) = E(V_O^q\text{–chain}) + 3 \times E(\text{bulk}) \\ -4 \times E(\text{isolated–}V_O^q),$$




**Vo chain (filament) becomes stable when system charge states becomes neutral or 1+.**



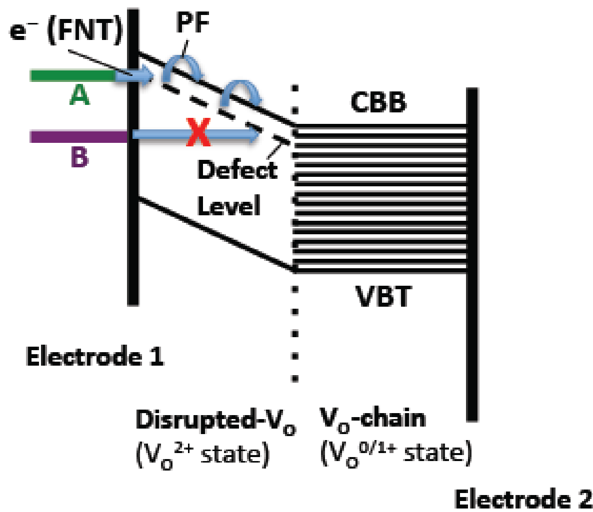
**By changing system charged states, cohesion-Isolation transition (filament formation and disruption) can be controlled.**

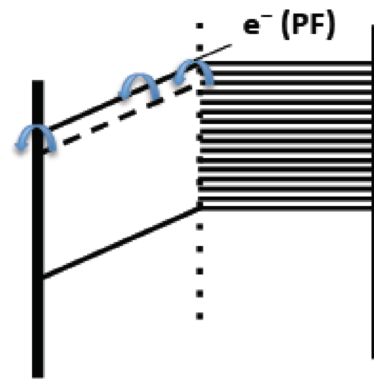
# Physical Origin of Bipolar and Unipolar Operation

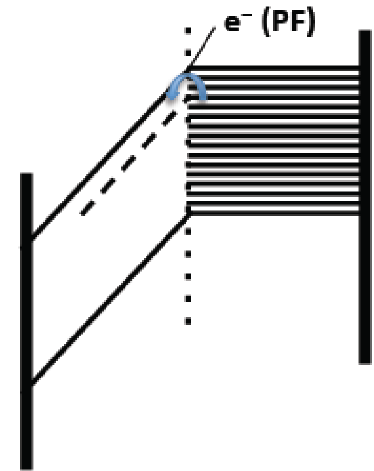
(a) Bipolar (Set)

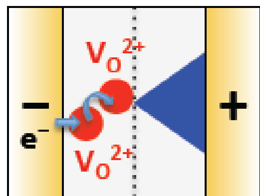
(b) Bipolar (Reset)

(c) Unipolar (Set)



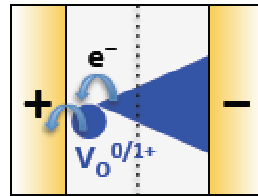



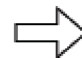

Electron injection from electrode 1

−
$V_O^{0/1+}$
+

Filament growth

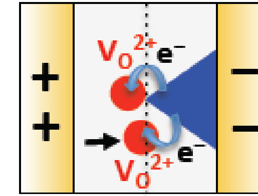



hole injection from electrode 1

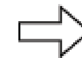


+
$V_O^{2+}$
$V_O^{2+}$
−

Filament disruption




Electron injection from filament



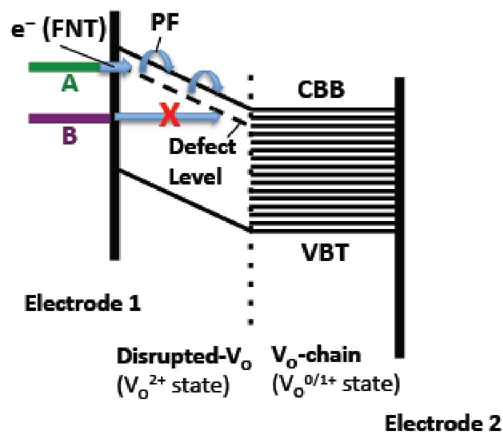
+
+
$V_O^{0/1+}$
−
−

Filament growth

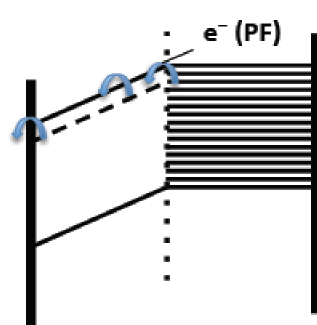
Bipolar: Carriers are injected from both electrodes and filaments
Unipolar: Carriers are injected only from filaments

# Guiding principles for electrode material selection for bipolar operations.

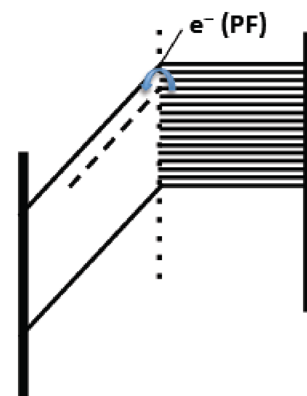
(a) Bipolar (Set)

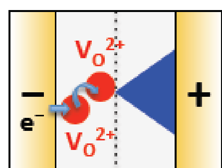



(b) Bipolar (Reset)

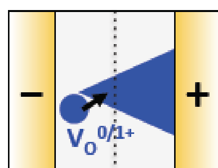



(c) Unipolar (Set)

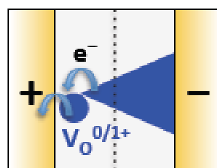


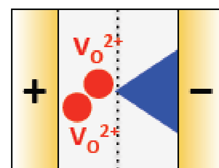

Electron injection from electrode 1



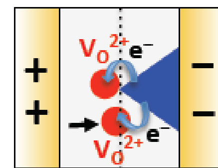

Filament growth



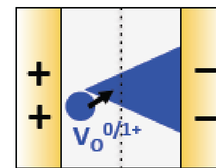

hole injection from electrode 1




Filament disruption



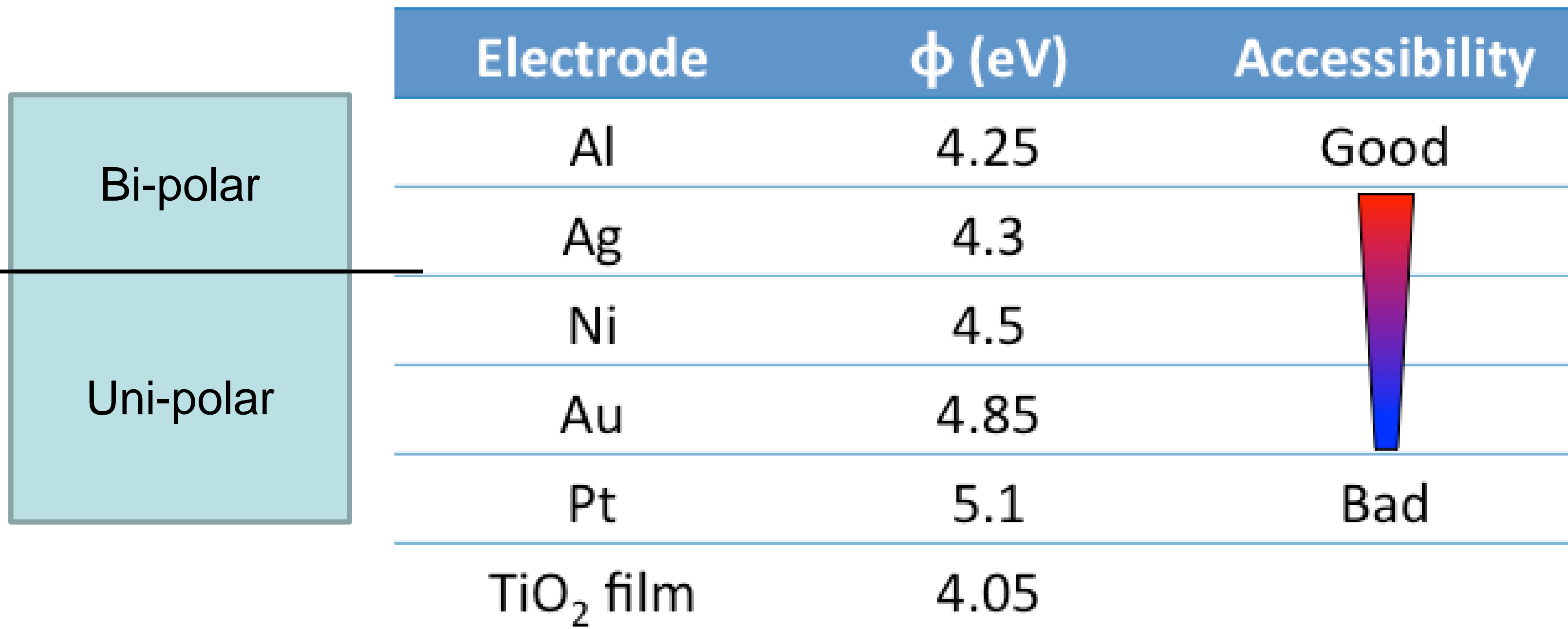

Electron injection from filament




Filament growth

**Fermi level position of electrodes should be similar to Vo energy level**

# Guiding principles for TiO2 based ReRAM




| Electrode | ϕ (eV) | Accessibility |
|---|---|---|
| Al | 4.25 | Good |
| Ag | 4.3 | |
| Ni | 4.5 | |
| Au | 4.85 | |
| Pt | 5.1 | Bad |
| $TiO_2$ film | 4.05 | |

Low work function metal are suitable for TiO2 based ReRAM

# Summary of ReRAM computation

- Computational science has clarified that the ON-OFF switching in $TiO_2$-based ReRAMs via Vo based conducting channels is ascribed to the cohesion-isolation nature of Vo upon carrier injection and removal.
- We have found that bipolar or unipolar switching is governed by the way of the carrier injection into Vo. Moreover we give a guideline for the electrode material selection. (Matching between the electrode Fermi level to Vo levels is essential)

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1. Introduction
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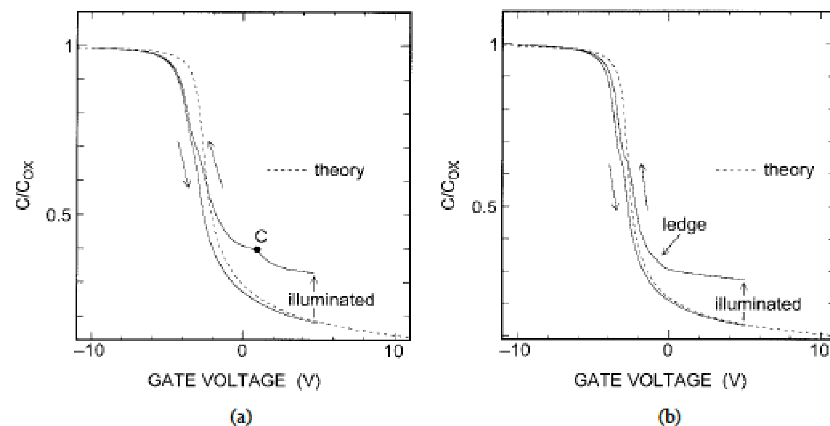
# Negative Fixed Charge of SiC-MOSFET

- SiC-MOSFET is the candidate for Power devices due to the large break down voltages and high thermal conductivity.
- SiC oxidation process is complicated and we can not create the good interfaces.
- Moreover, wet oxidation which has more advantages than dry oxidation. However, it causes the creation of negative fixed charges.

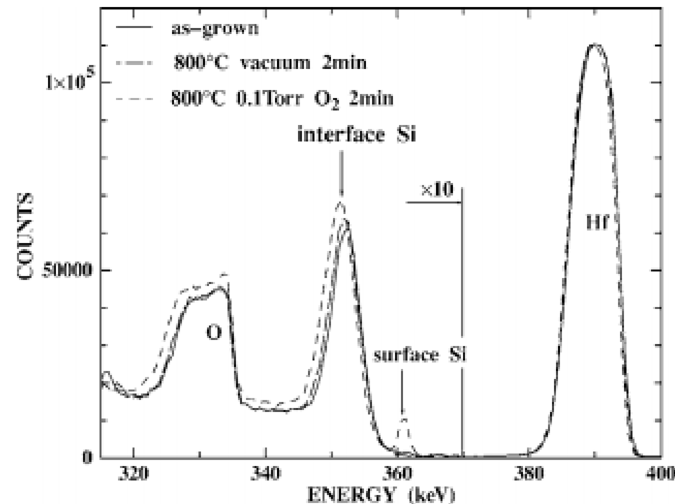
(H. Yano, F. Katafuchi, T. Kimoto and H. Matsunami, IEEE Transaction on erectron devices **46**, 3 (1999) )



# Background

It was reported experimentally and theoretically that one-third Si atoms are inevitably emitted from the interface to release the stress induced by Si oxidation.

(H. Kageshima and K. Shiraishi, Phys. Rev. Lett.,81, 5936 (1998). Z. Ming et al. Appl. Phys. Lett., 88, 153516 (2006).)

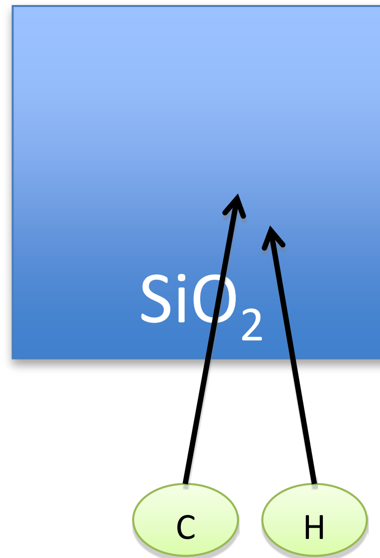



It is a natural extension that the emitted C atom gives the unexpected effects to SiC devices that lead to unfavorable performances.

**To obtain high quality $SiO_2$/SiC interfaces, investigation of C atom's behavior during oxidation is one of the most important issues !**

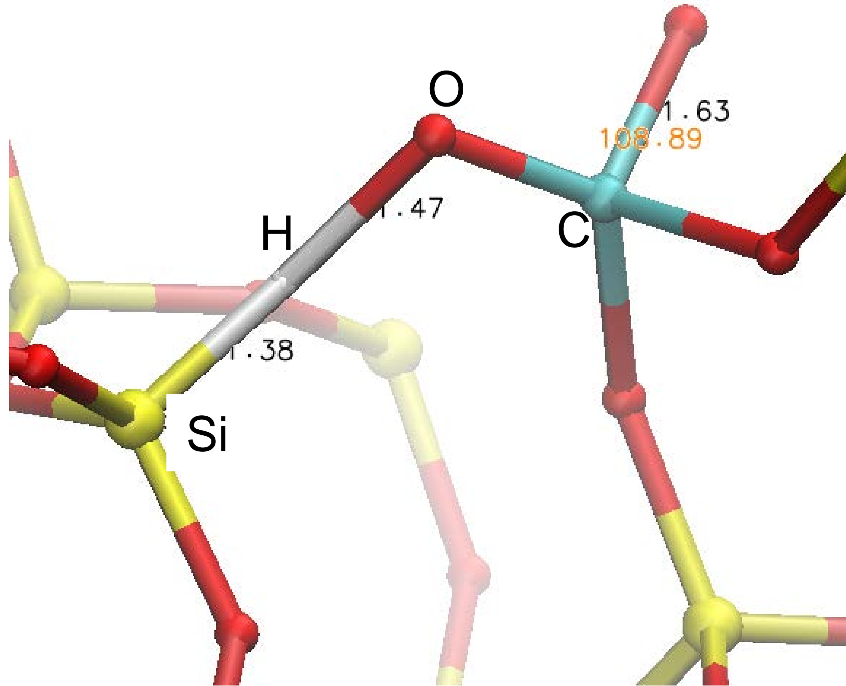
# Purpose

We investigated the energetics, geometry, and electronic structures of C-substituted $SiO_2$ under wet oxidation conditions (H insertion) by using first-principles calculations.

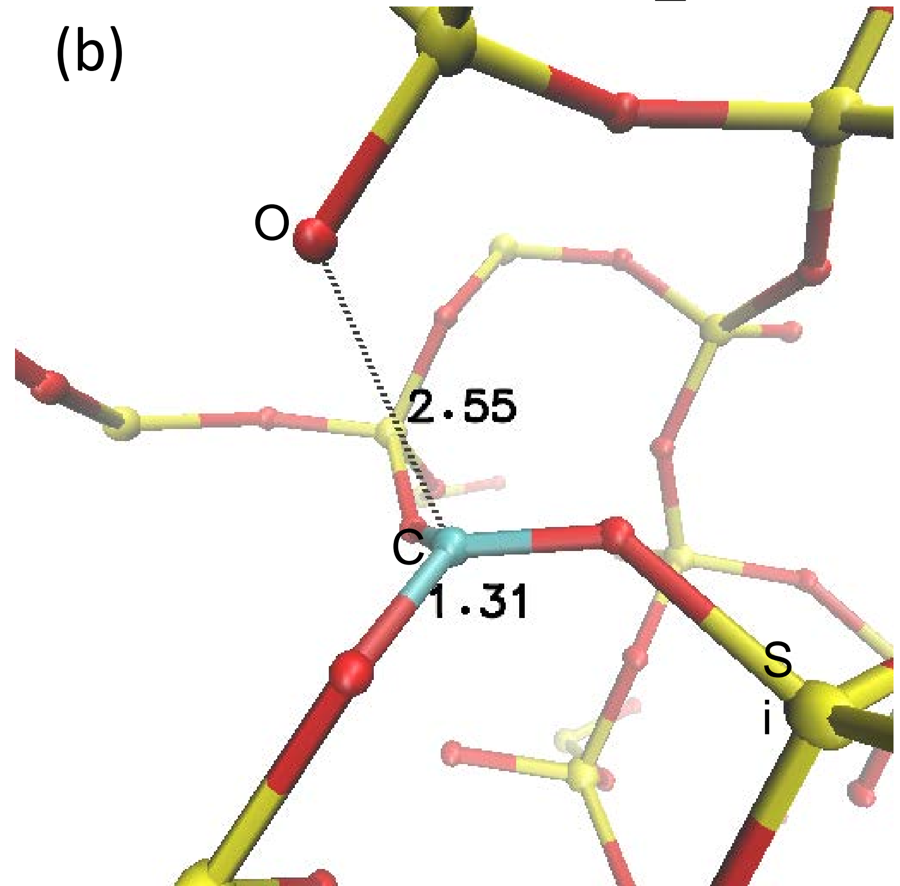


# Calculation model of bulk $SiO_2$

(a)




(b)



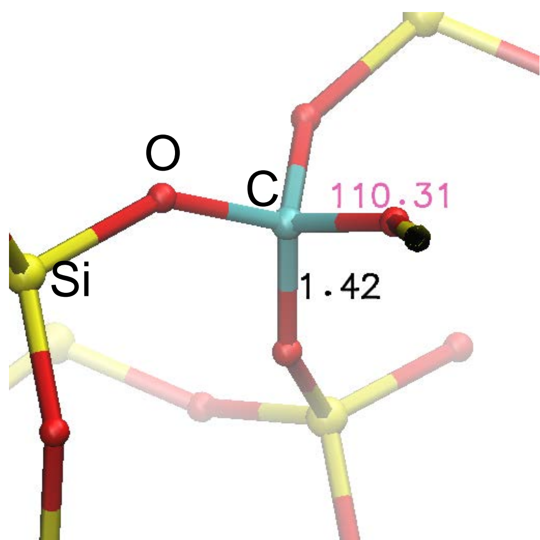

**-A inserted Carbon atom replace a Si atom in $SiO_2$.**
**-Carbon atom and H atom is (a) inserted or (b) not inserted into 72 atoms alpha quartz.**

# Calculation method

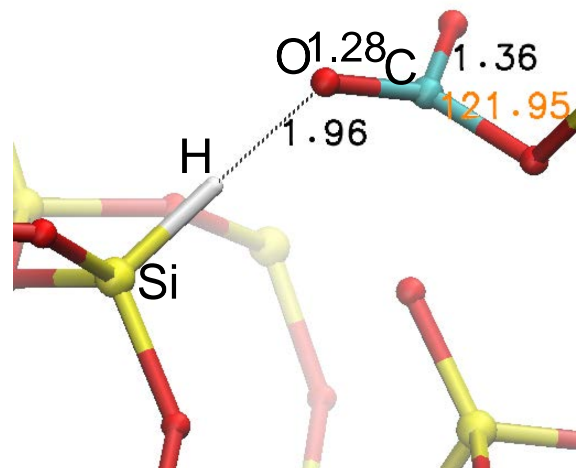
- First-principles calculations（GGA）
- Ultrasoft pseudo potential
- Plane wave expansion
- Cutoff energy 64 (Ryd.)
- Sample k points 2x2x2
- Force convergence $10^{-3}$ (Ht./a.u.)

# Results of C,H atom inserted in $SiO_2$

(Y. Ebihara et al. ISSS5 Tokyo (2011))



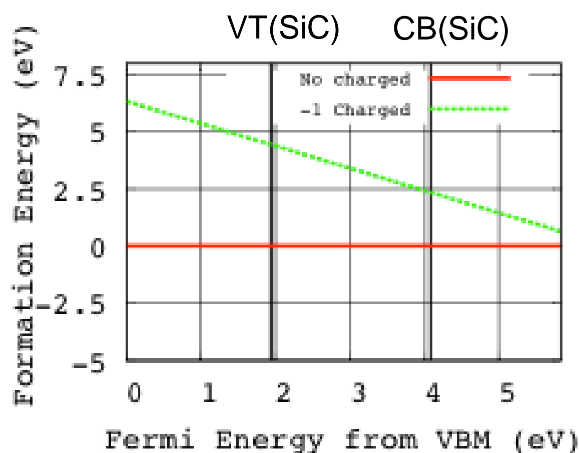

(a) Only C atom was inserted (0 state)



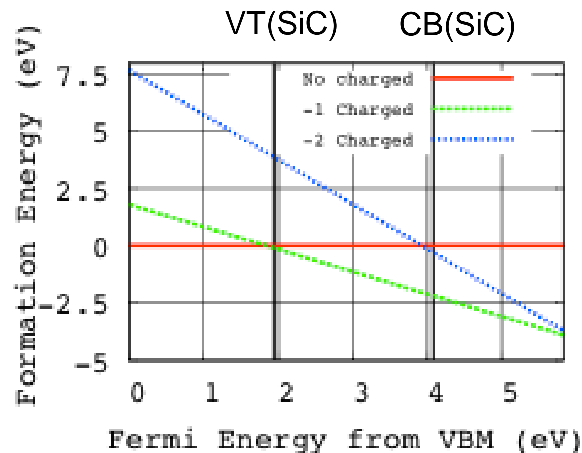

(b) C,H atom were inserted (-1 state)

C-O:1.43Å
C=O:1.23 Å

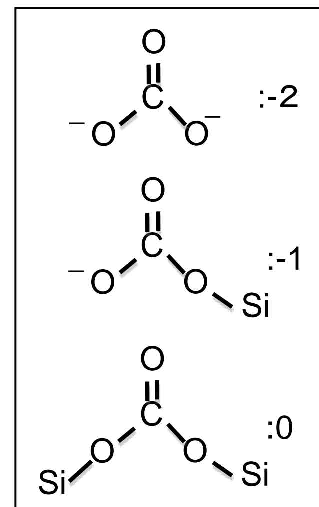
C-O(carbonate)
:1.29 Å




Formation energy for (c) only C atom was inserted

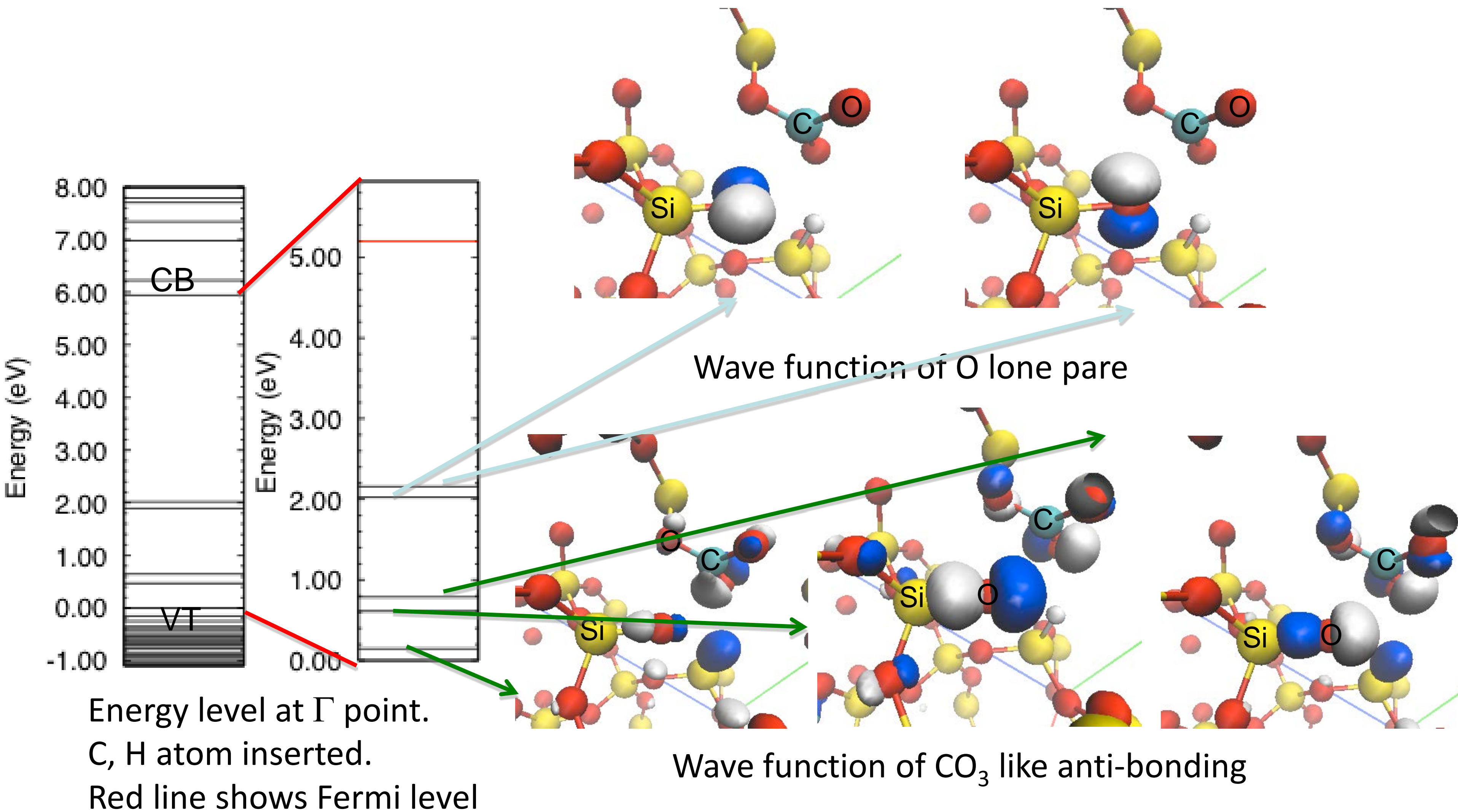



(d) C, H atom were inserted




-Carbonate-like ion was created in $SiO_2$ which a C, O and H atom was inserted.
-Therefore, negative charge state was most stable in SiC band gap.
-C takes intrinsically preferred $sp^2$ network in $SiO_2$ assisted by the H atom.

# Results: C and H atom incorporated in $SiO_2$

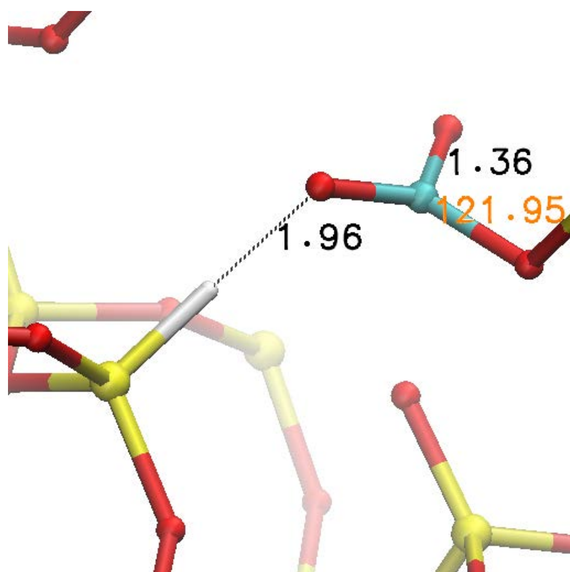


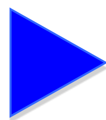

Energy level at Γ point.
C, H atom inserted.
Red line shows Fermi level

Wave function of $CO_3$ like anti-bonding

-We found that carbonate-like anti-bonding state and O lone pare state was formed in the $SiO_2$ band gap.

# Results: C incorporation with 3H atoms

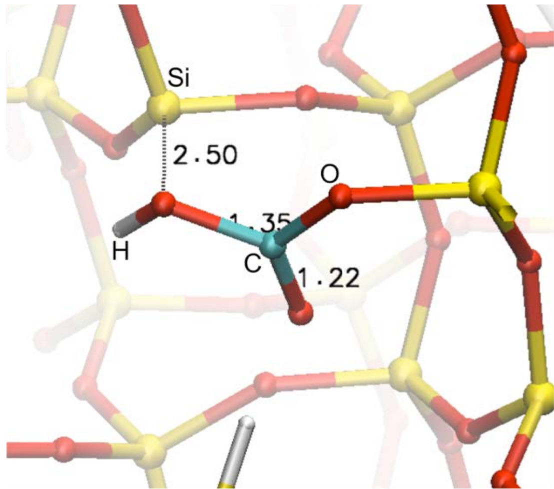


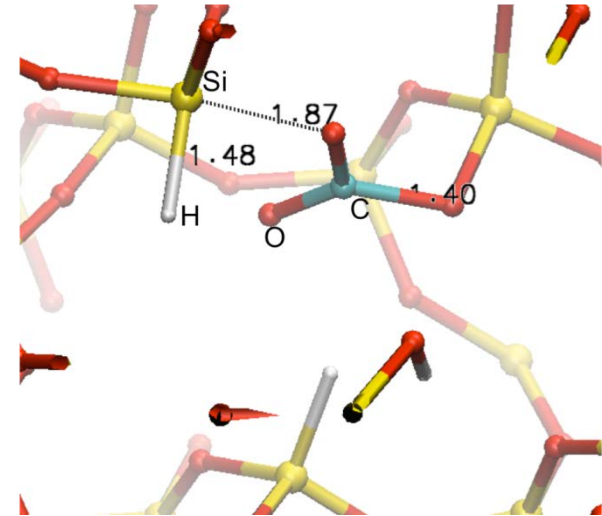
O
C
1.96
H
Si
0.97

Calculation model for bulk $SiO_2$ where a C atom and three H atoms were inserted

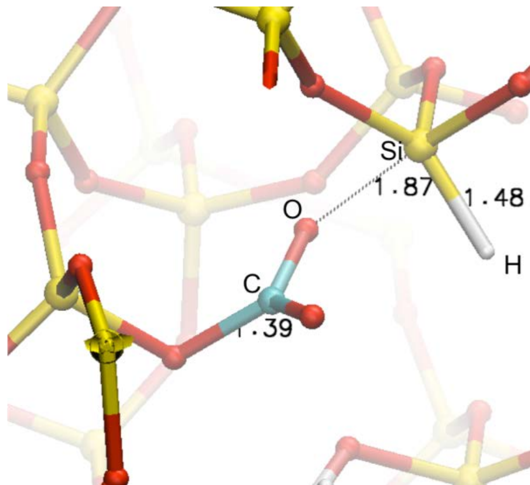
# Results: C incorporation with 3H atoms



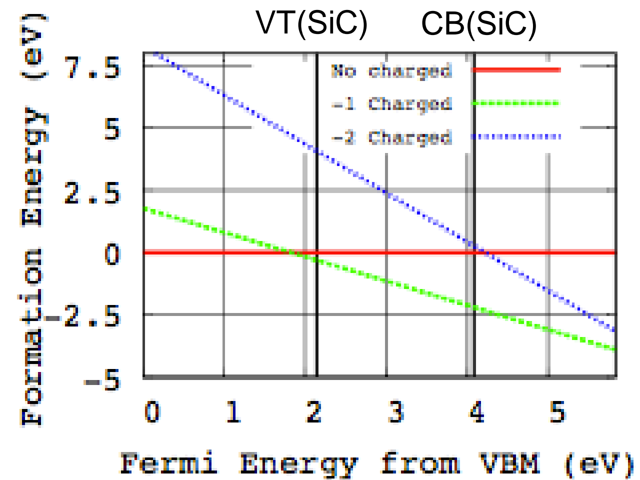

C, additional H atom inserted (0 state)




C, additional H atom inserted (-1 state)



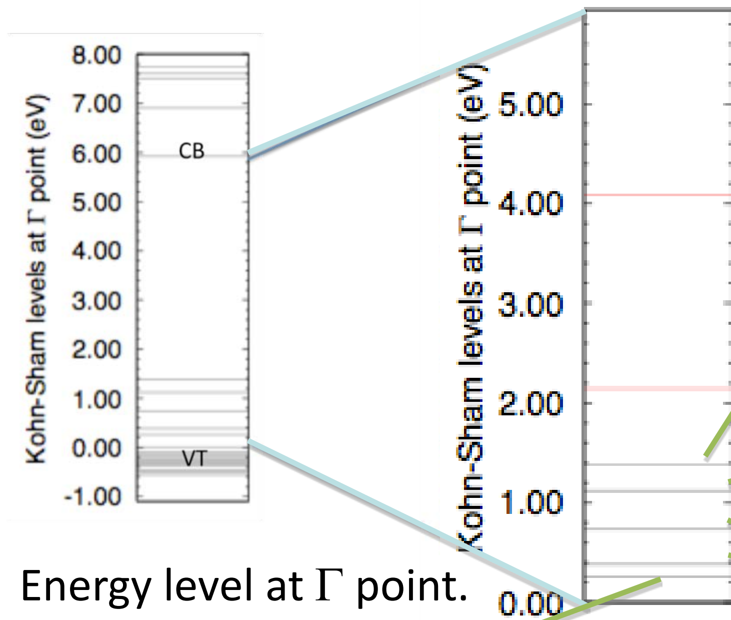

C, additional H atom inserted (-2 state)



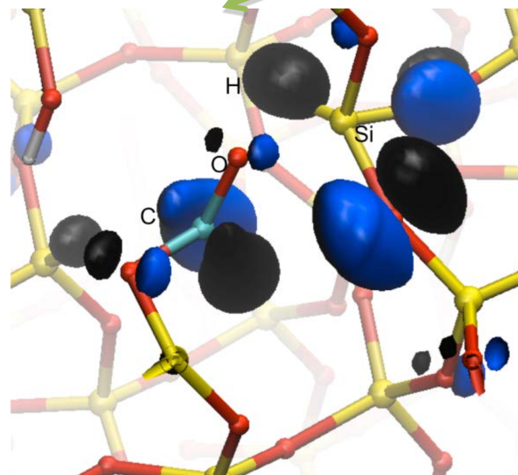

Formation energy

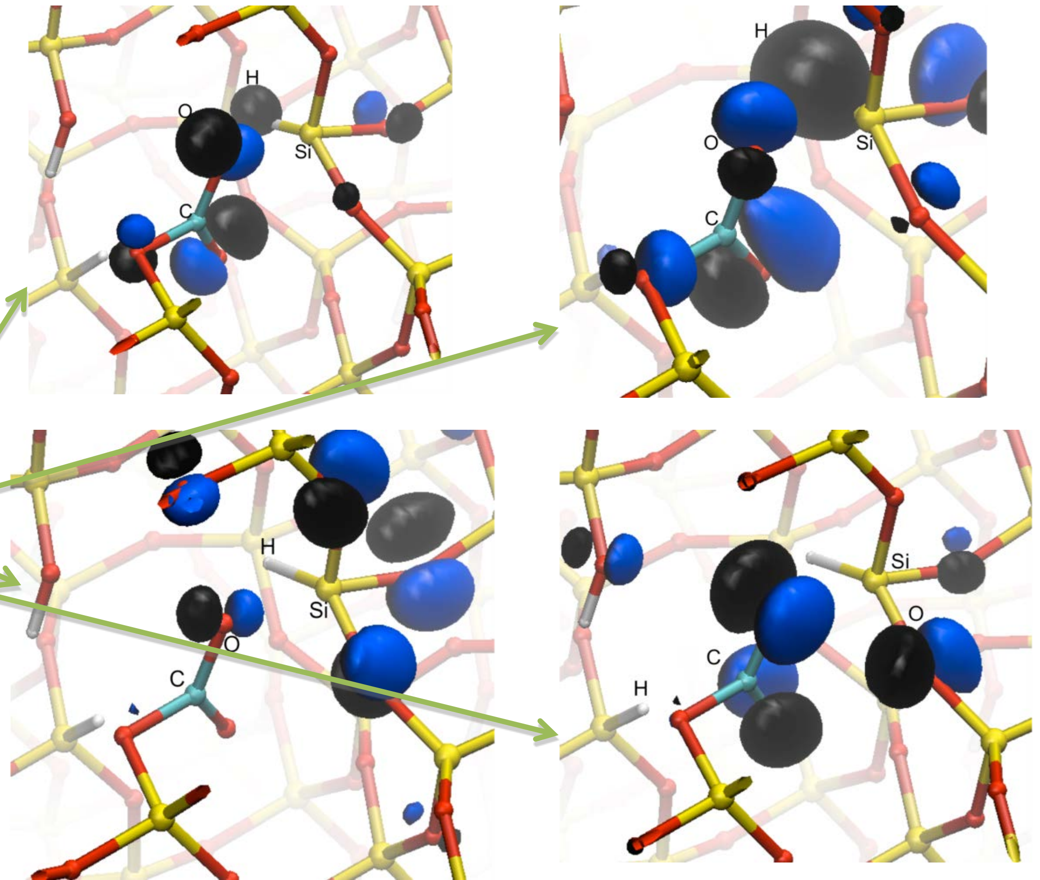
**Negatively charged pseudo carbonate ions are generated by the assist of H atoms.→ Agreement with large Vfb shift by wet oxidation (Yano et al).**

# Results: C incorporation with 3H atoms




Energy level at Γ point.
C, H atom inserted.




Wave function of $CO_3$ like

Only Energy Level composed of pseudo CO3 ions are shown.

# Summary of SiC

1. We found that C takes intrinsically preferred $sp^2$ network in $SiO_2$.
2. Especially, a carbonate-like ion is found to be formed in $SiO_2$ assisted by H.
3. These factors lead to the unexpected increase of flatband voltage shift and density of interface trap.

The present study provides a knowlege to design and to improve practical fabrication of high quality $SiC/SiO_2$ interface.

# Summary

- Computational science can predict and propose useful guiding principles of future nano-devices.
- (1) Operation mechanism of ReRAM, (2) Physical origin of negative fixed charge in SiC-MOSFET , and etc.  can really be obtained by using computational science.

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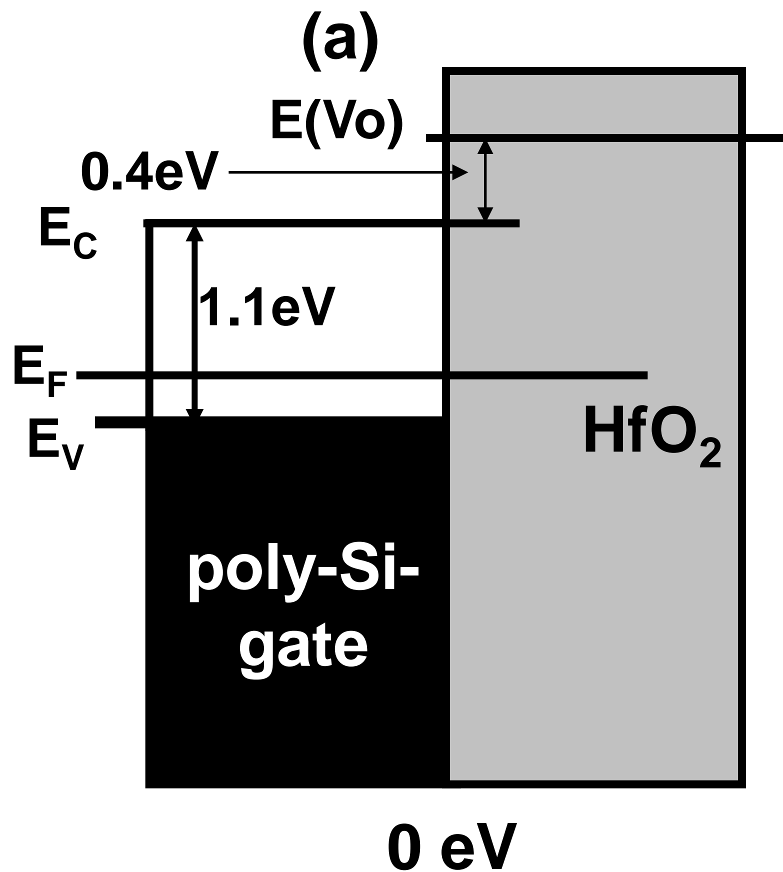
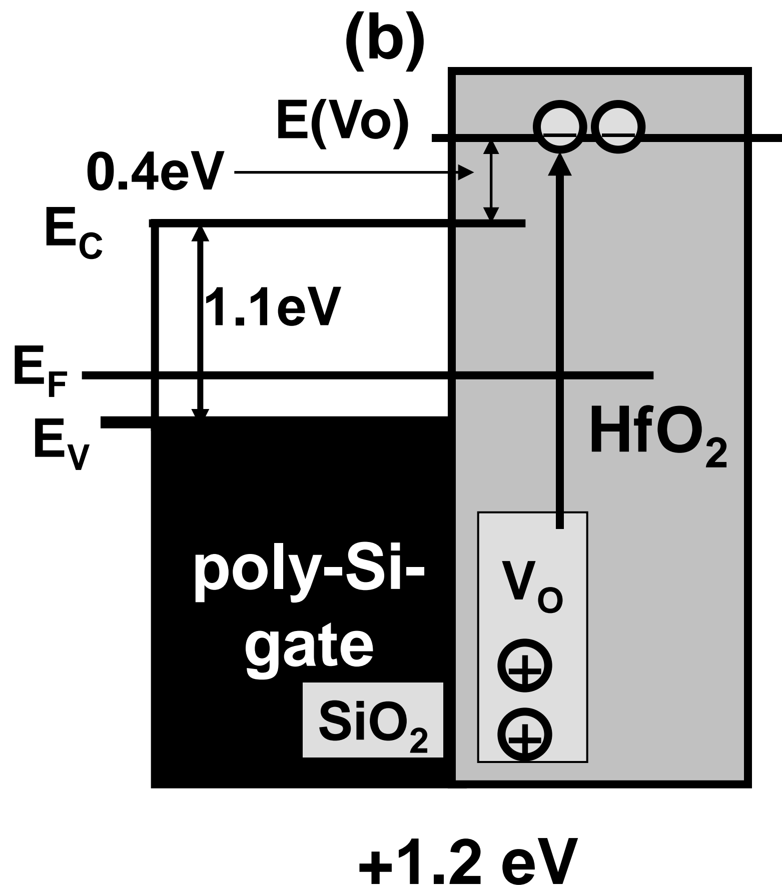
# 5. Interface physics in high-k gate stacks

## Energy gain (loss) when $HfO_2$ is in contact with Si




**0 eV**

**+1.2 eV**

Energy loss obtained by computational science

Hf-O bond is much stronger than Si-O bond->Si cannot reduces HfO2

Formation enthalpy: 11.6eV(HfO2), 9.4eV(SiO2)

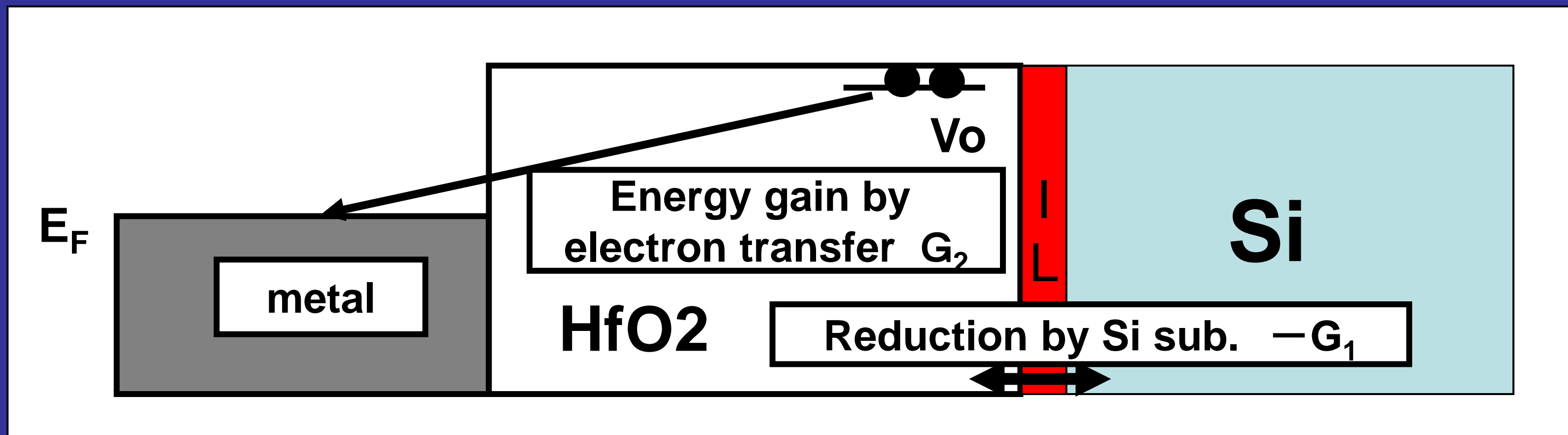
When electrons occupy Vo level and Vo is neutral (same as bulk)

# Change in O ion form induces unexpected flat-band shift

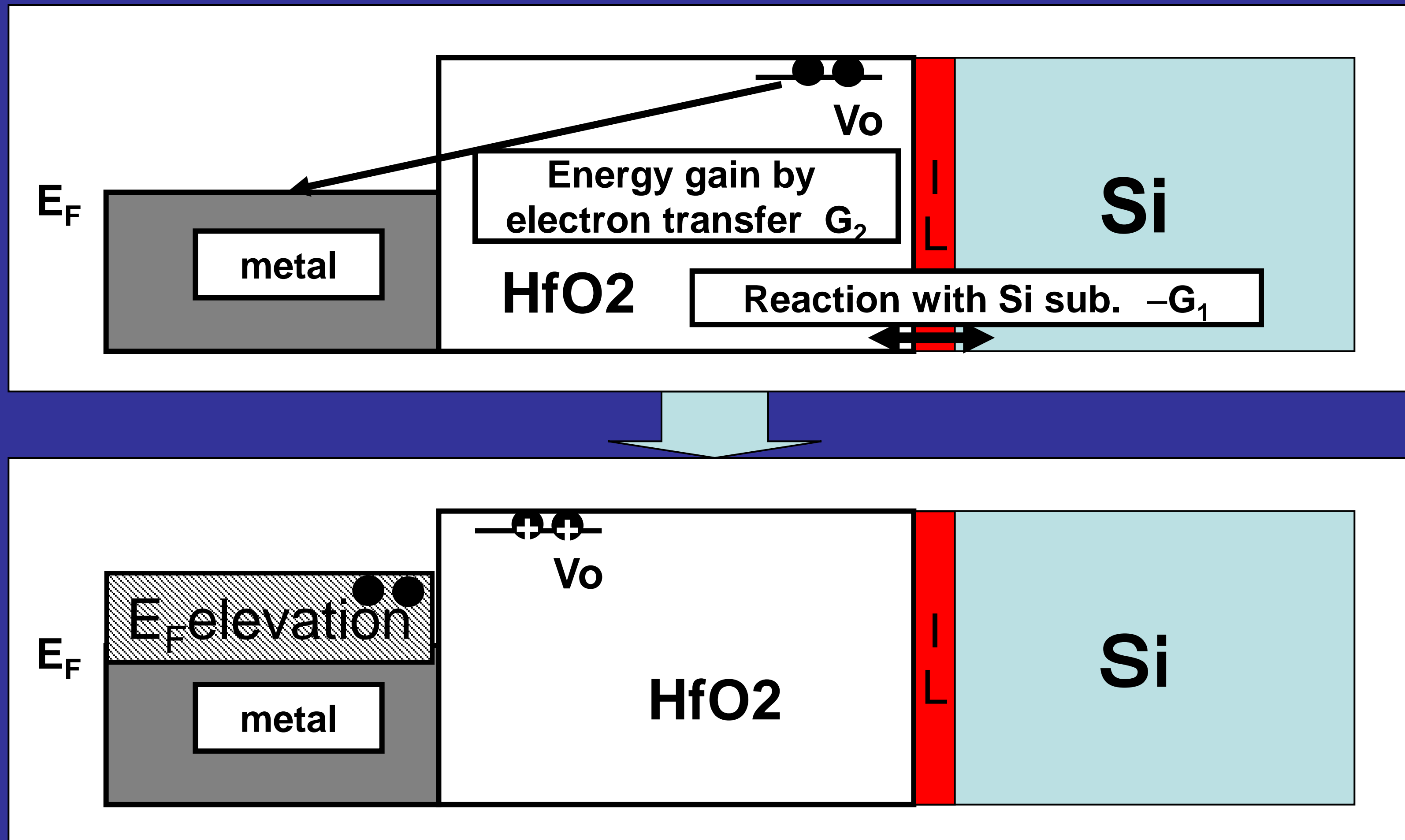
Y. Akasaka et al. Jpn. J. Appl. Phys. 2006

J. Robertson, O. Sharia, and A. A. Demkov,APL 2007
(including image charge)

P.Broqvist et al. APL 2008 (Including amorphous effect)



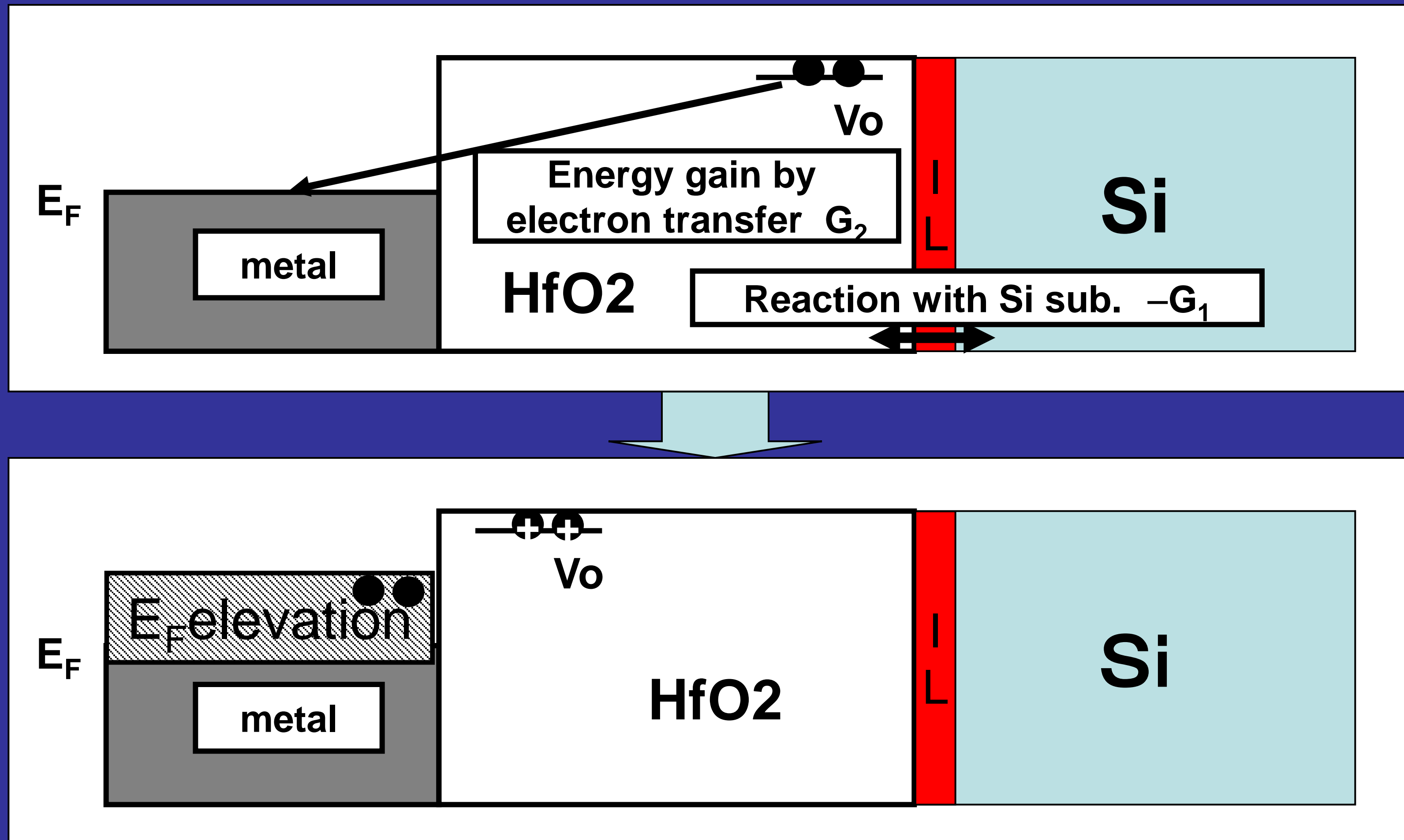
# Change in O ion form induces unexpected flat-band shift




**Pinning position of a metal gate is defined by G1-G2=0:**

**The reaction at Si/HfO2 interface governs the work function of a metal under thermal equilibrium (Not metal/HfO2 interface. Gate first processes).**

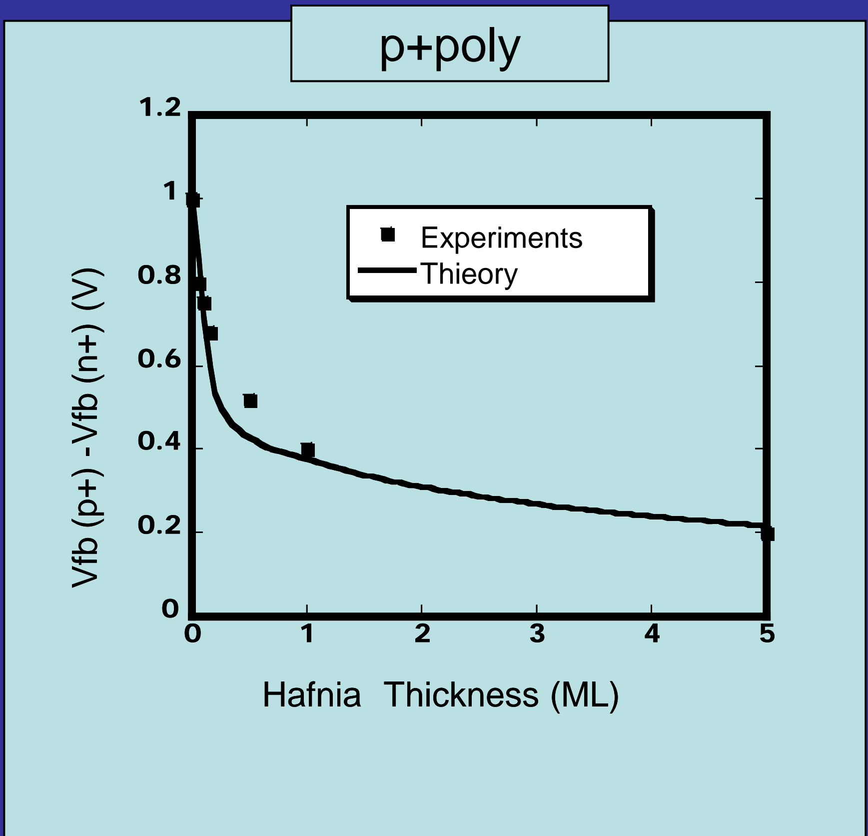
# Change in O ion form induces unexpected flat-band shift

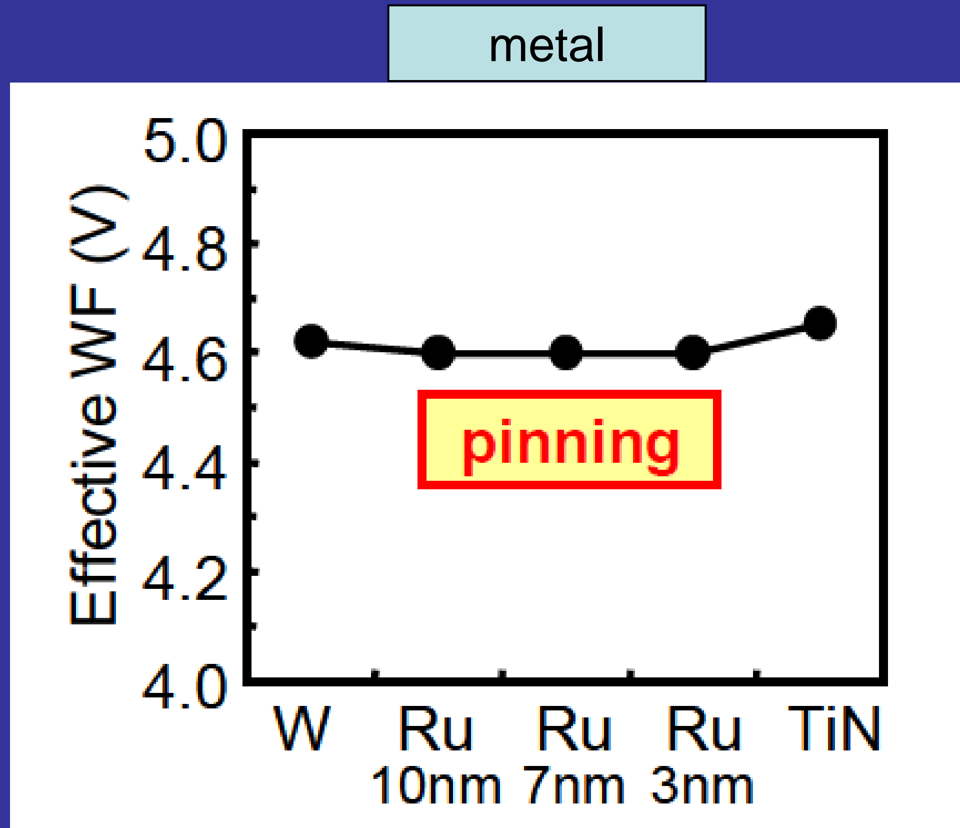



**Thermodynamics of interface reaction governs the FLP position**

**$HfO2 + ½ Si \rightarrow (HfO2 + Vo^{2+} + 2e) + ½ SiO2$**

# Famous FLP occurs, and a metal WF is independent of metal species nor metal thickness



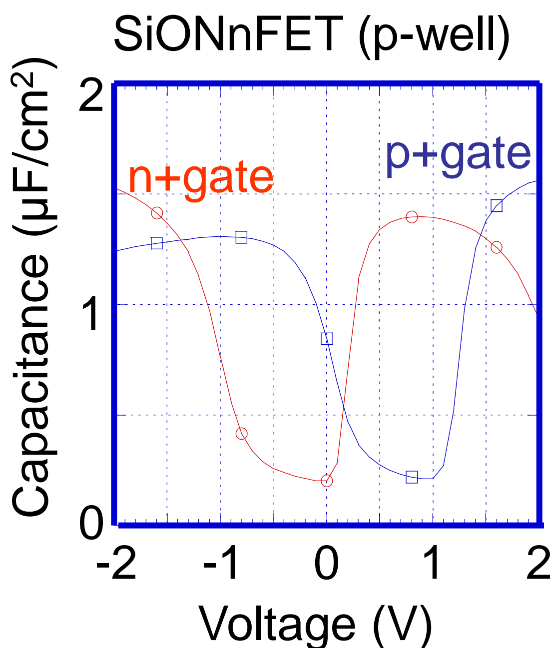

C. Hobbs et al. VLSI 2003
(Theory, K. Shiraishi et al VLSI 2004)

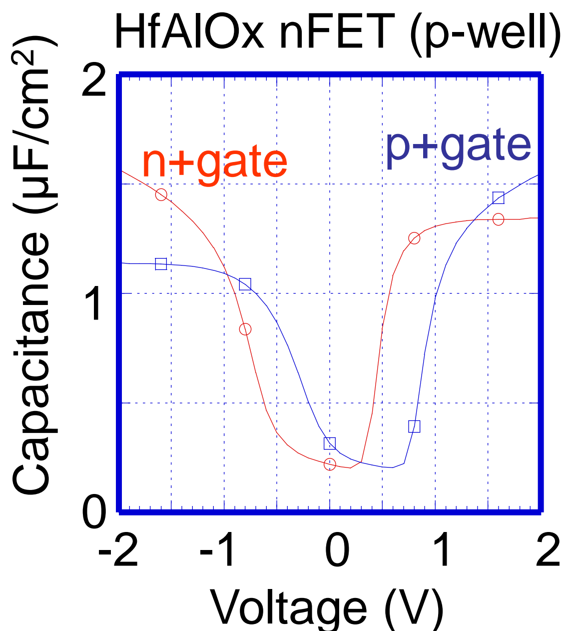
M. Kadoshima et al. VLSI 2007

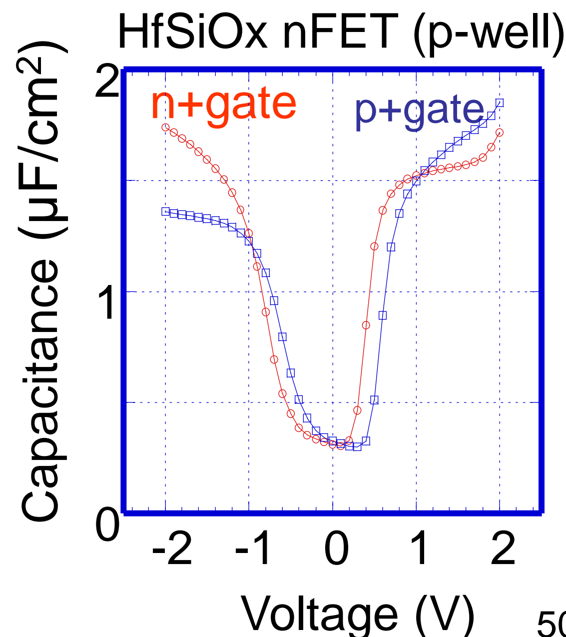
## Summary of mechanism of Fermi level pinning of poly-Si gate

**Vo formation in ionic $HfO_2$ and subsequent electron transfer across the gate/dielectric interface generate large interface dipole. This is the basic origin of large flat band shift (Fermi level pinning).**

**Development of metal gates is necessary.**



# Differences between poly-Si gates and metal gates when IL is thin.

e⁻ transfer O transfer

Poly-Si

occur occur
$Vo^{2+}$
occur very small
$p^+$ poly−Si 2 $HfO_2$ Si sub.

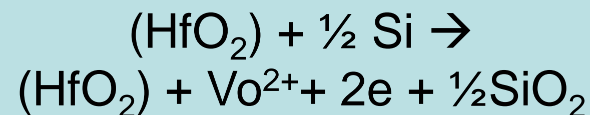
Poly-Si with cap layer

not occur occur
$Vo^{2+}$
occur very small
$p^+$ poly barrier $HfO_2$ Si sub.

p-metal

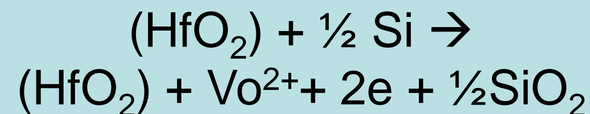
not occur occur
$Vo^{2+}$
occur very small
p−metal $HfO_2$ Si sub.

Substrate reaction

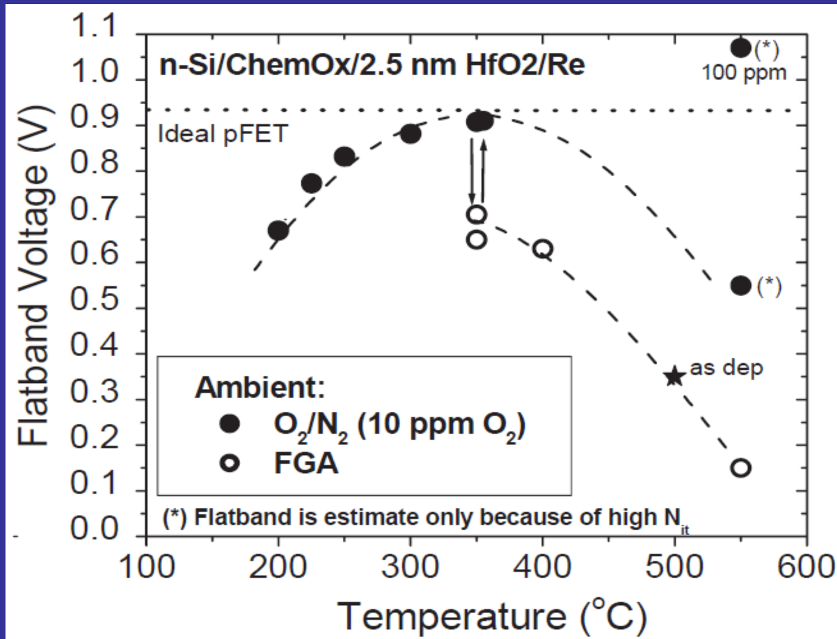



occurs in every case.

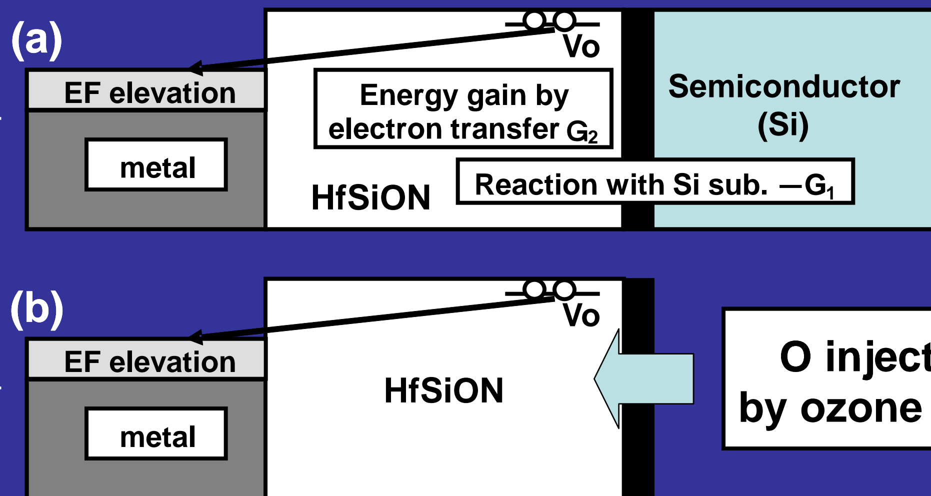
This reaction is the same as poly-Si gate reaction.



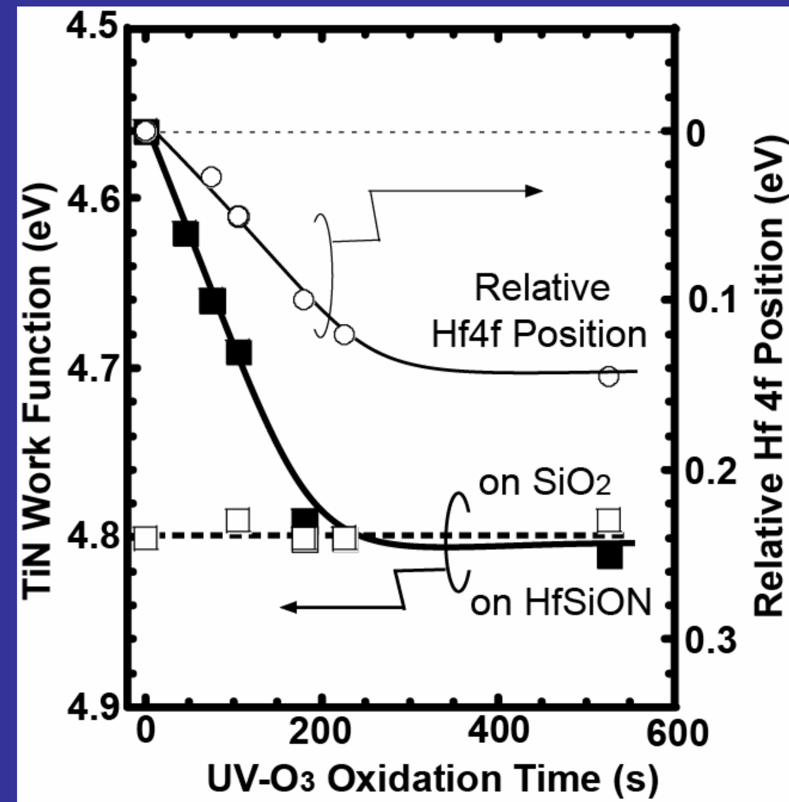
# FLP recovery by O injection



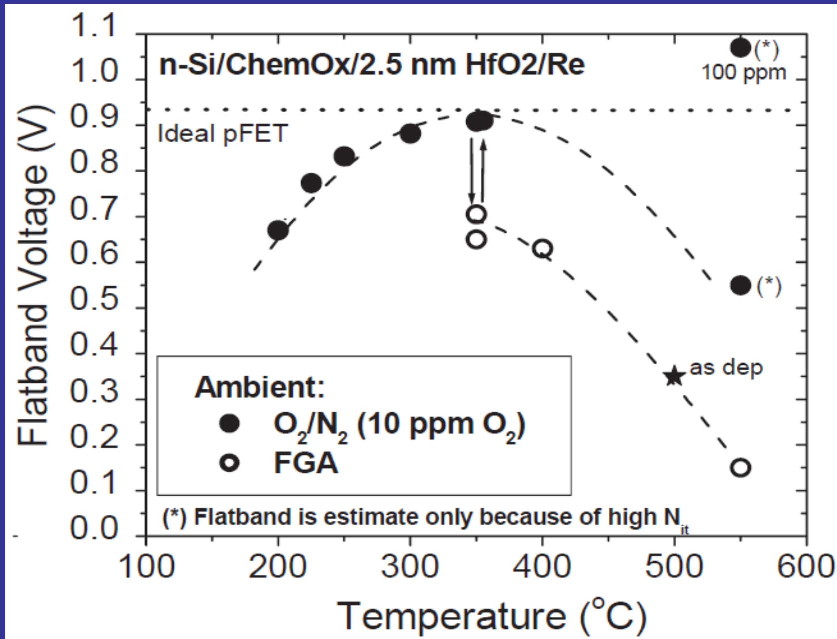

It is known that O injection can recover FLP
(E. Cartier,VLSI 2005)




A. Ohta et al., IWDTF 2006



# FLP recovery by O injection

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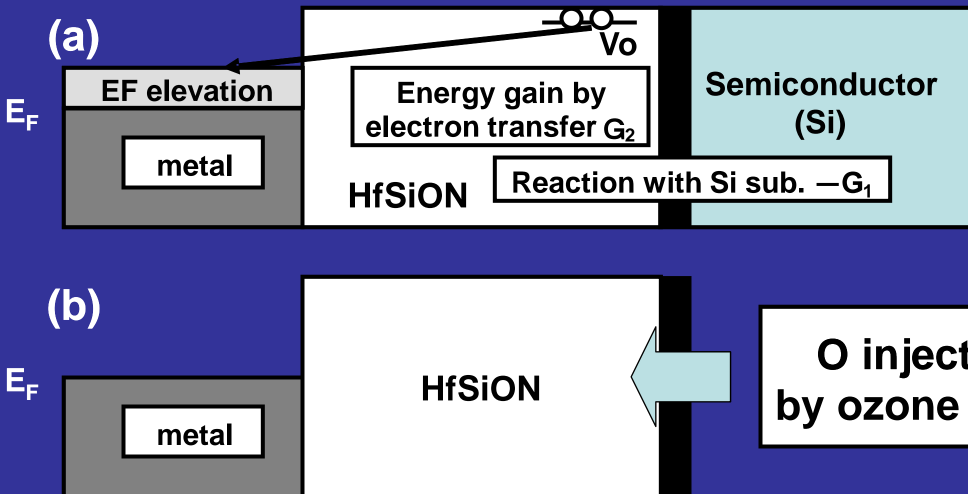
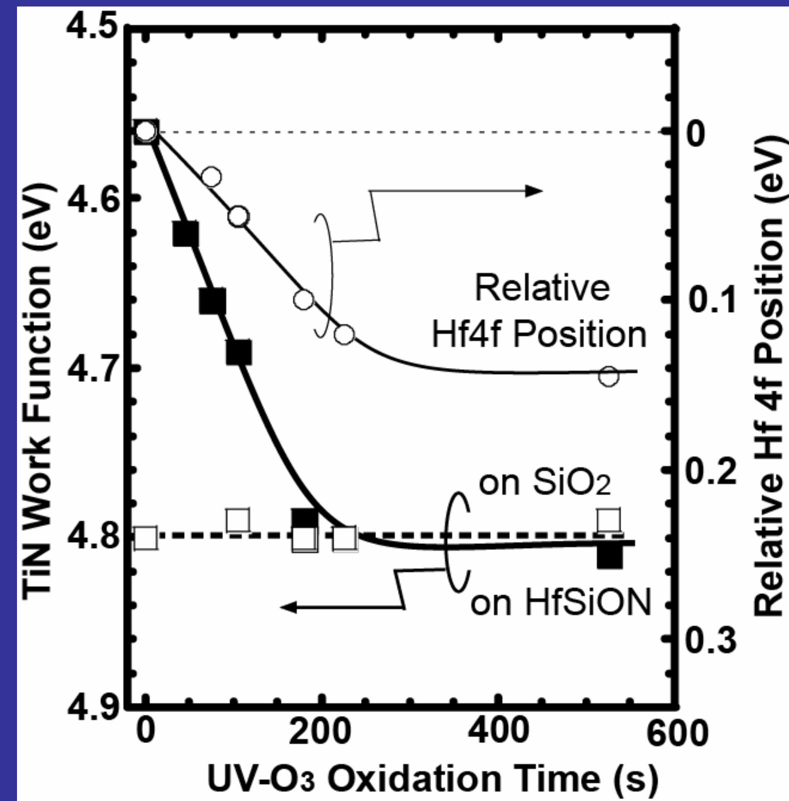



A. Ohta et al., IWDTF 2006



# Summary

- Computational science can predict and propose useful guiding principles of future nano-devices.
- (1) Operation mechanism of ReRAM, (2) Physical origin of negative fixed charge in SiC-MOSFET , and etc. can really be obtained by using computational science.

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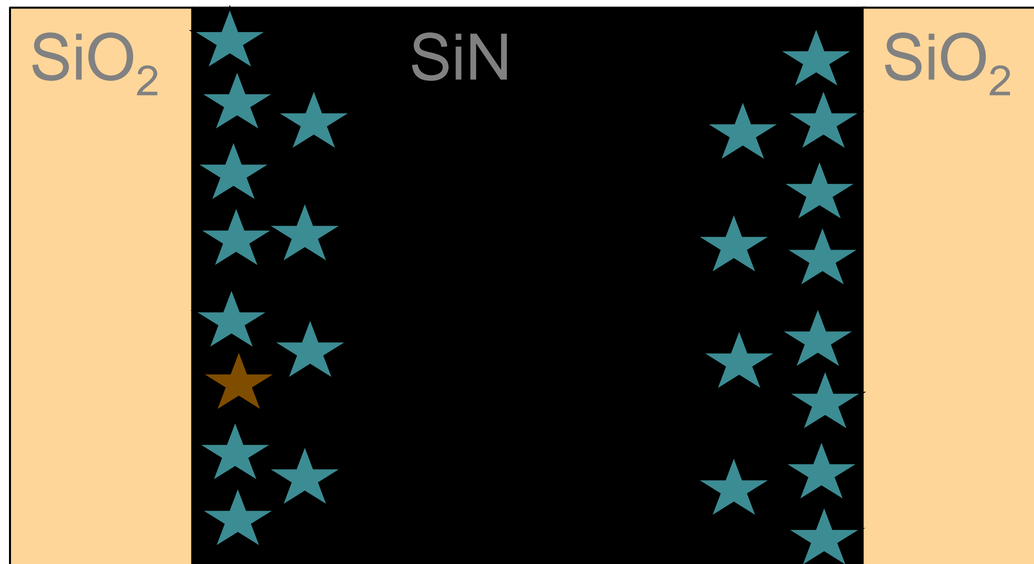
6. Guiding Principles toward high quality MONOS.
7. Summary

# Basic MONOS structures O-incorporation into SiN layers is experimentally reported



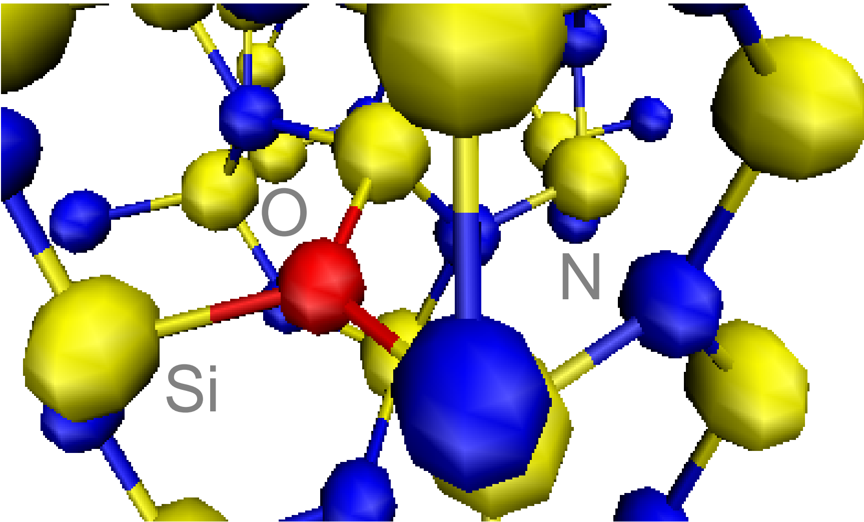

M. Miura, et al., IEICE Technical Report SDM2007-34

There are lots of O atoms in $SiO_2$/SiN interfaces.

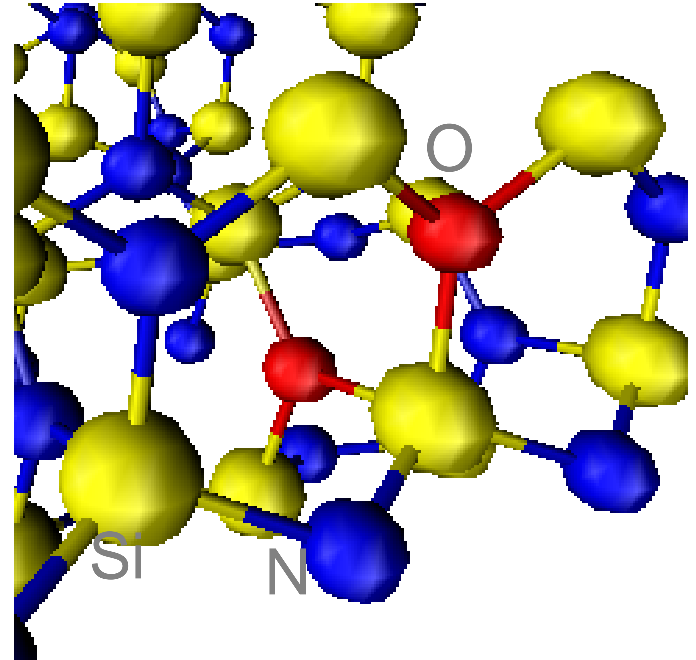
Effects of O- incorporation should be investigated for realization of high quality MONOS.

# Calculation model

One substitutional O atom at N site

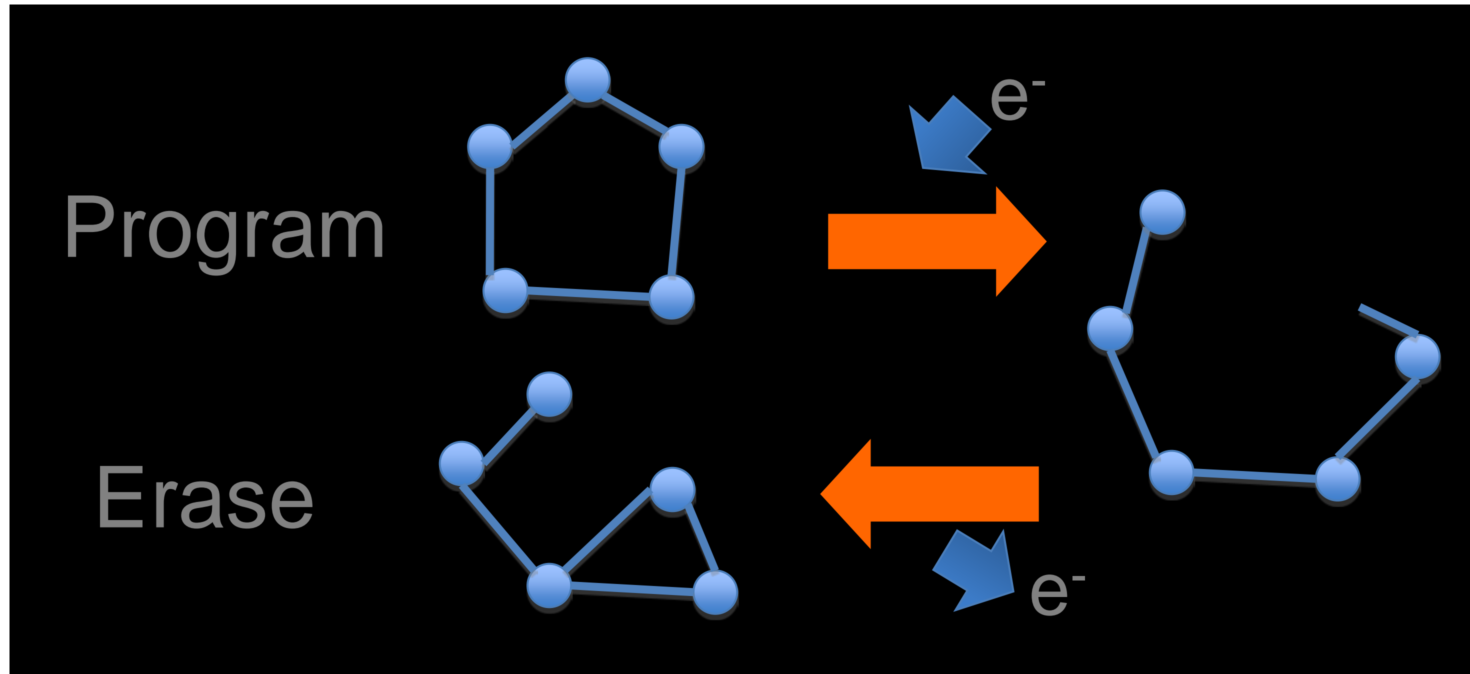



Two substitutional O atoms at N sites nearest to the Si atom




Taking into account the O- incorporation, we investigated two types of O-incorporated defect.

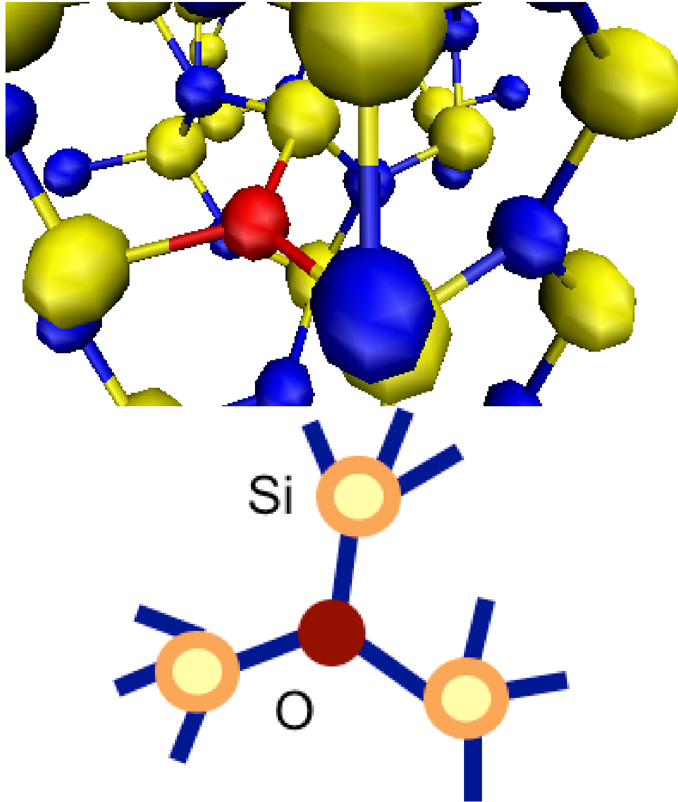
The calculation of P/E operation




We investigated atomic and electronic structural changes during Program/Erase operations (carrier injection & removal).

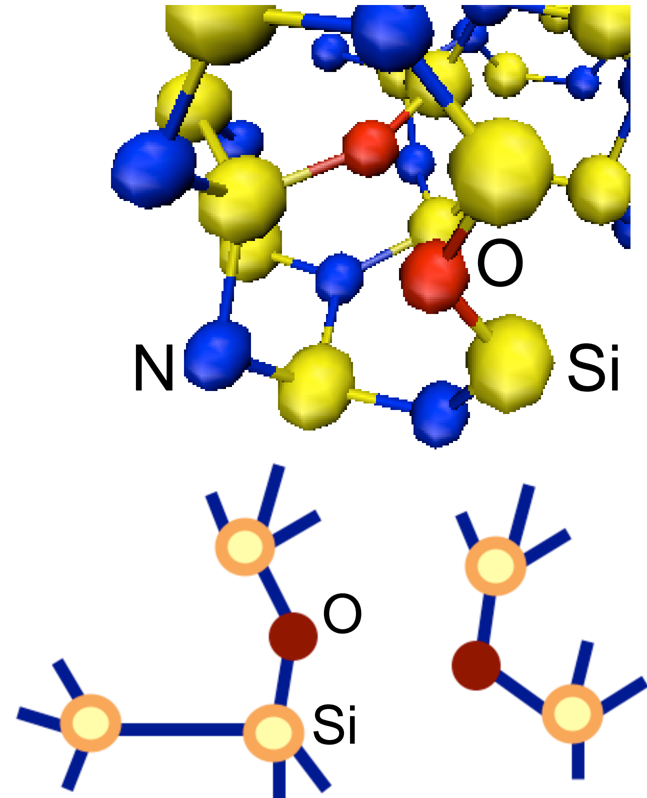
# Most stable structure of each defect

One substitutional O atom



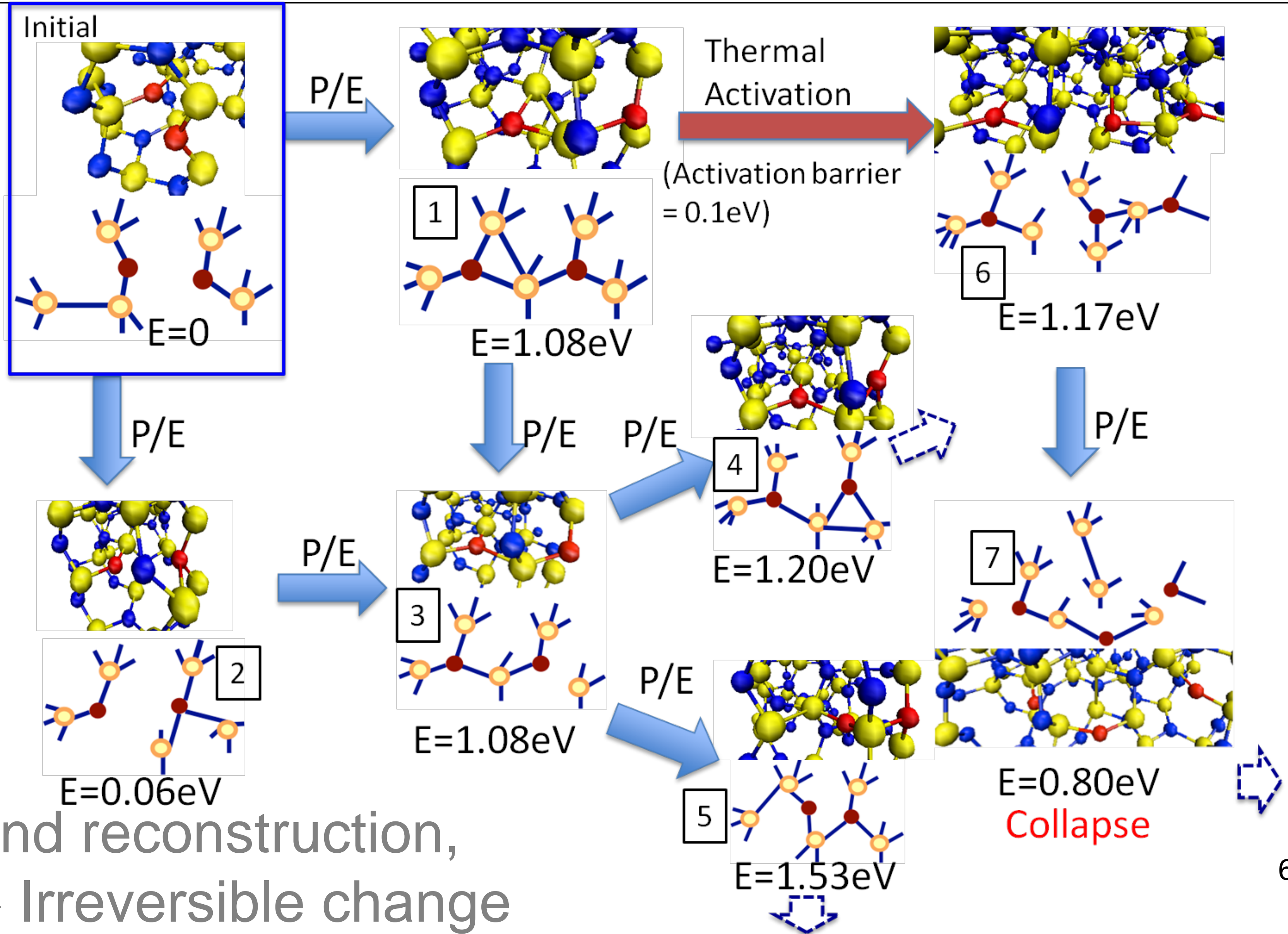

- Si atoms →four-fold
- O atom → three-fold

Two substitutional O atoms




- Si atoms → four-fold
- O atoms → two-fold

# Many meta-stable states appear by P/E & thermal activation (investigating 2 O model)




Bond reconstruction,
→ Irreversible change

# Many meta-stable states appear by P/E & thermal activation

Initial

E=0

P/E

1

E=1.08eV

Thermal Activation

(Activation barrier = 0.1eV)

6

E=1.17eV

P/E

P/E

P/E

P/E

4

E=1.20eV

P/E

7

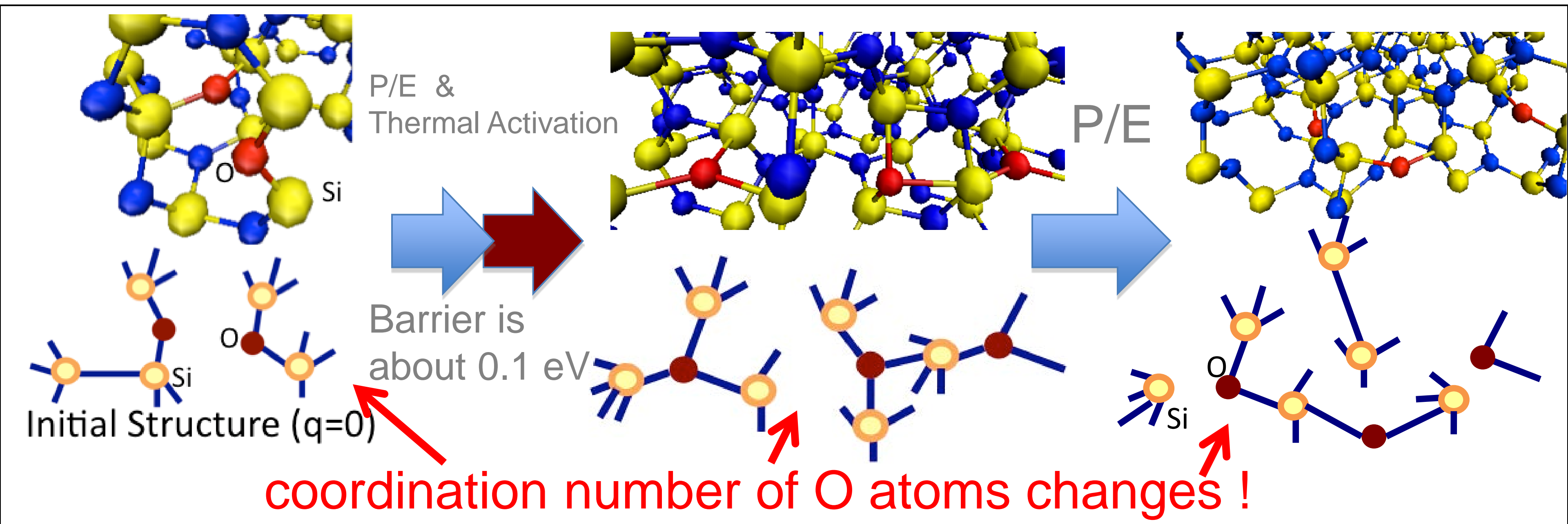
E=0.80eV

Collapse

E=1.53eV

There is a path which cause local collapse

# The collapse is caused by P/E & thermal activation with low barrier (~0.1eV)




Coordination number of O atoms is changed by P/E & thermal activation.

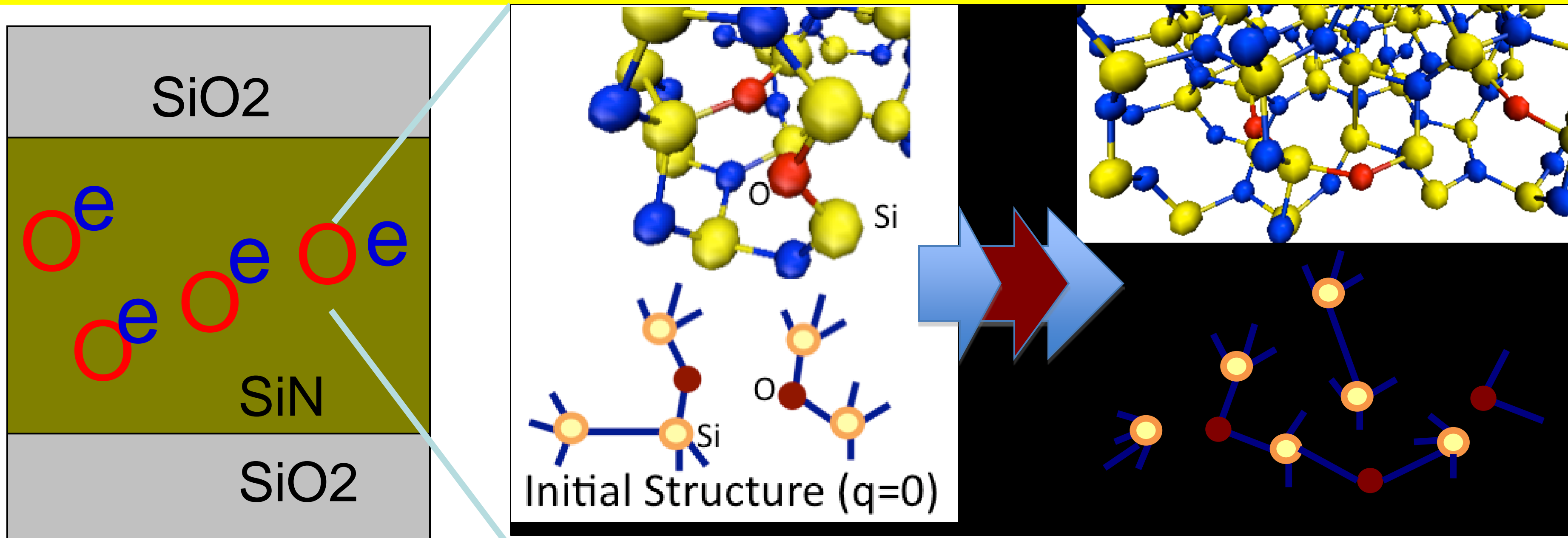
→ Long movement of O atoms

→ Local collapse of SiN layers

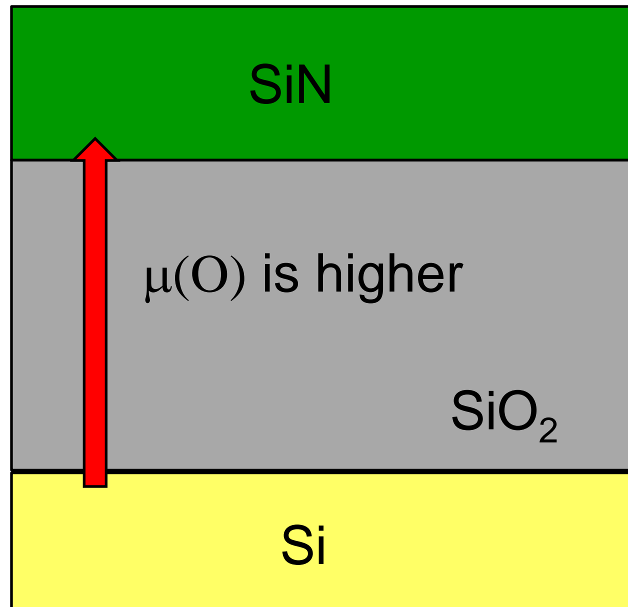
# Proposal
## The Ideal Memory Structure of MONOS

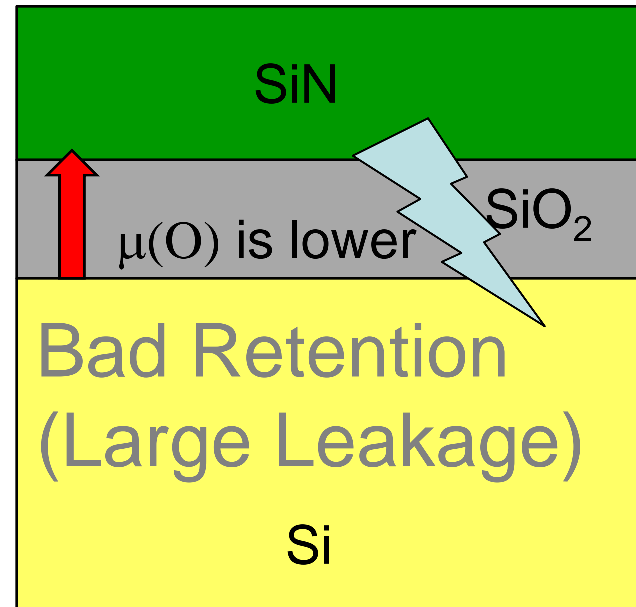
O atoms are charge traps, but irreversible!!

- O-incorporation should be suppressed
- The number of charge trap should be maintained



# For lowering $\mu_O$, our proposal is inserting a thin Si layer into $SiO_2$




Placed Si within $SiN/SiO_2$ interface can lower $\mu_O$

→ One method is decrease the $SiO_2$ thickness
A thin $SiO_2$ layer reduces the retention character of a MONOS type memory.

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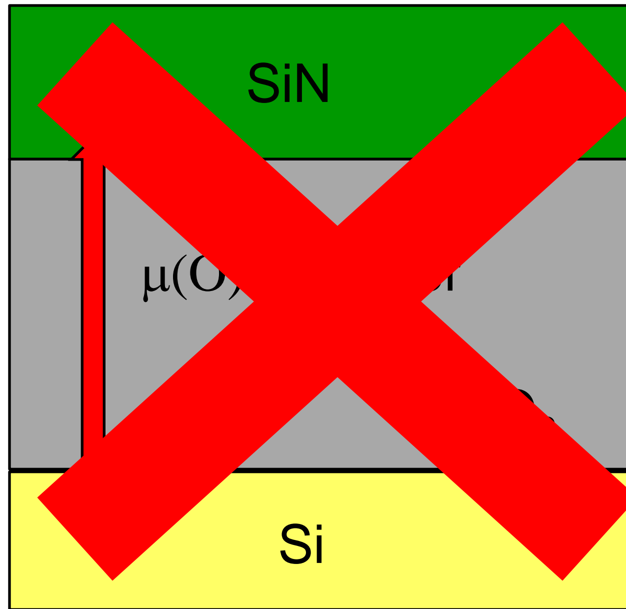


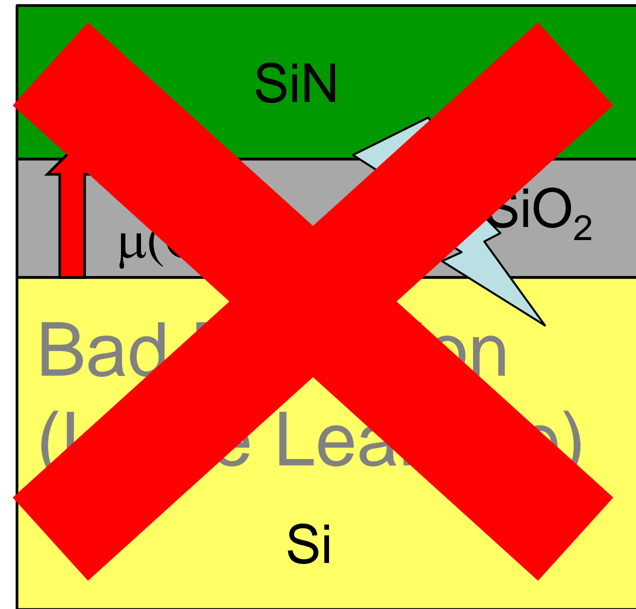


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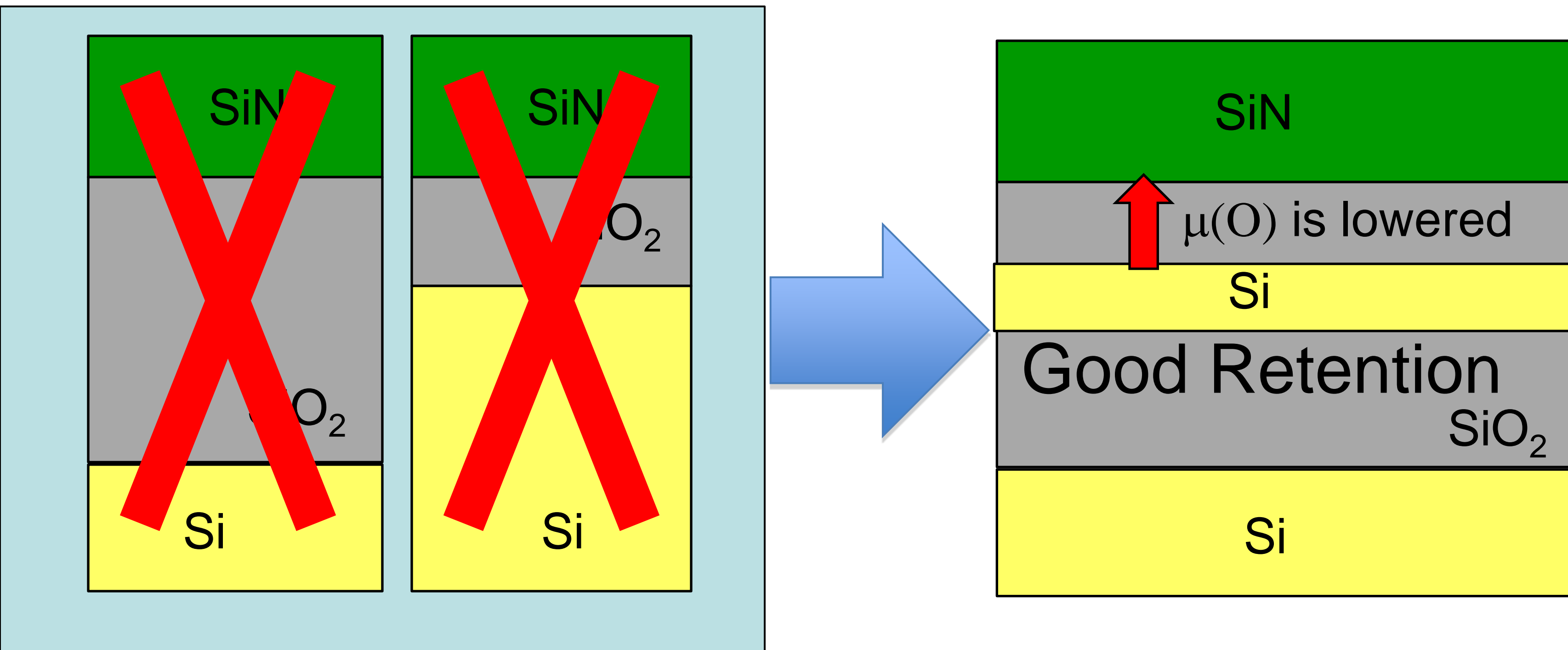
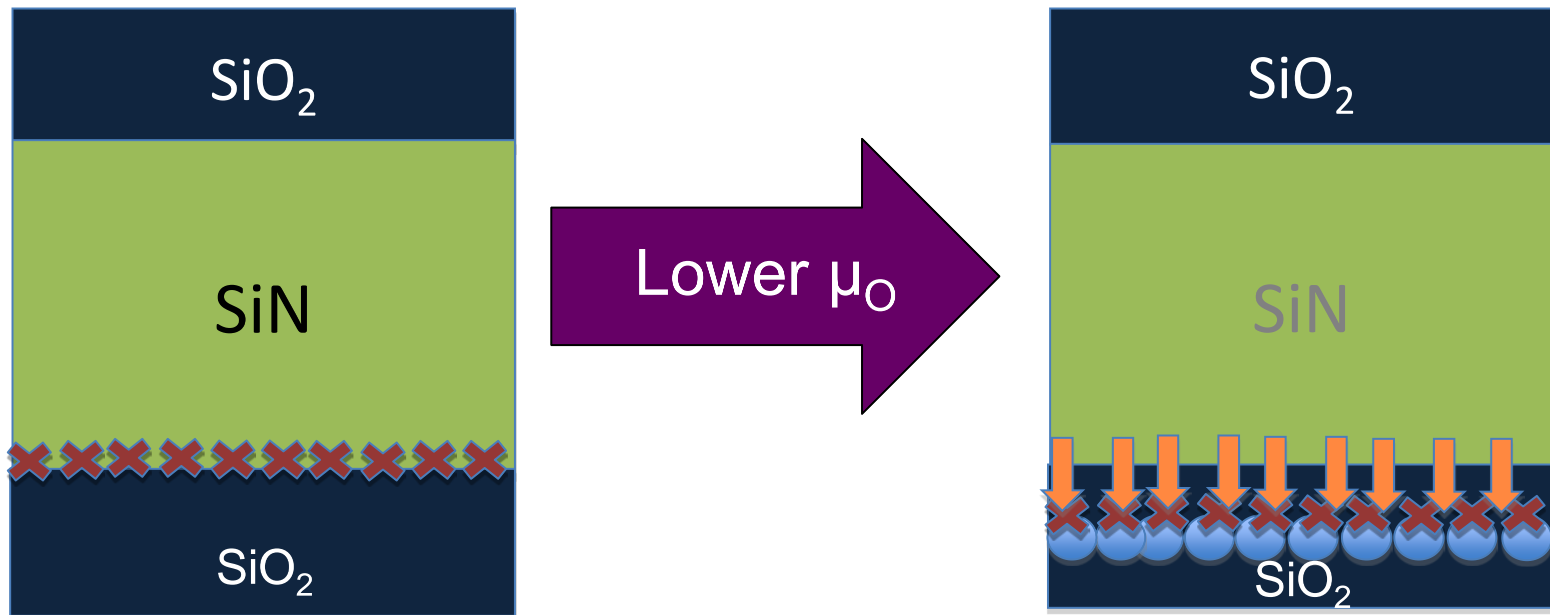



Our proposal recipe is Insertion of a thin Si layer into a $SiO_2$ layer near the $SiN/SiO_2$ .
This recipe realizes short distance between $Si/SiO_2$ and $SiO_2/SiN$ with good retention.

# Insertion of Si nano-dots or nano-wire




K. Yamaguchi et al. IEDM 2010

## Suppression of O-incorporation

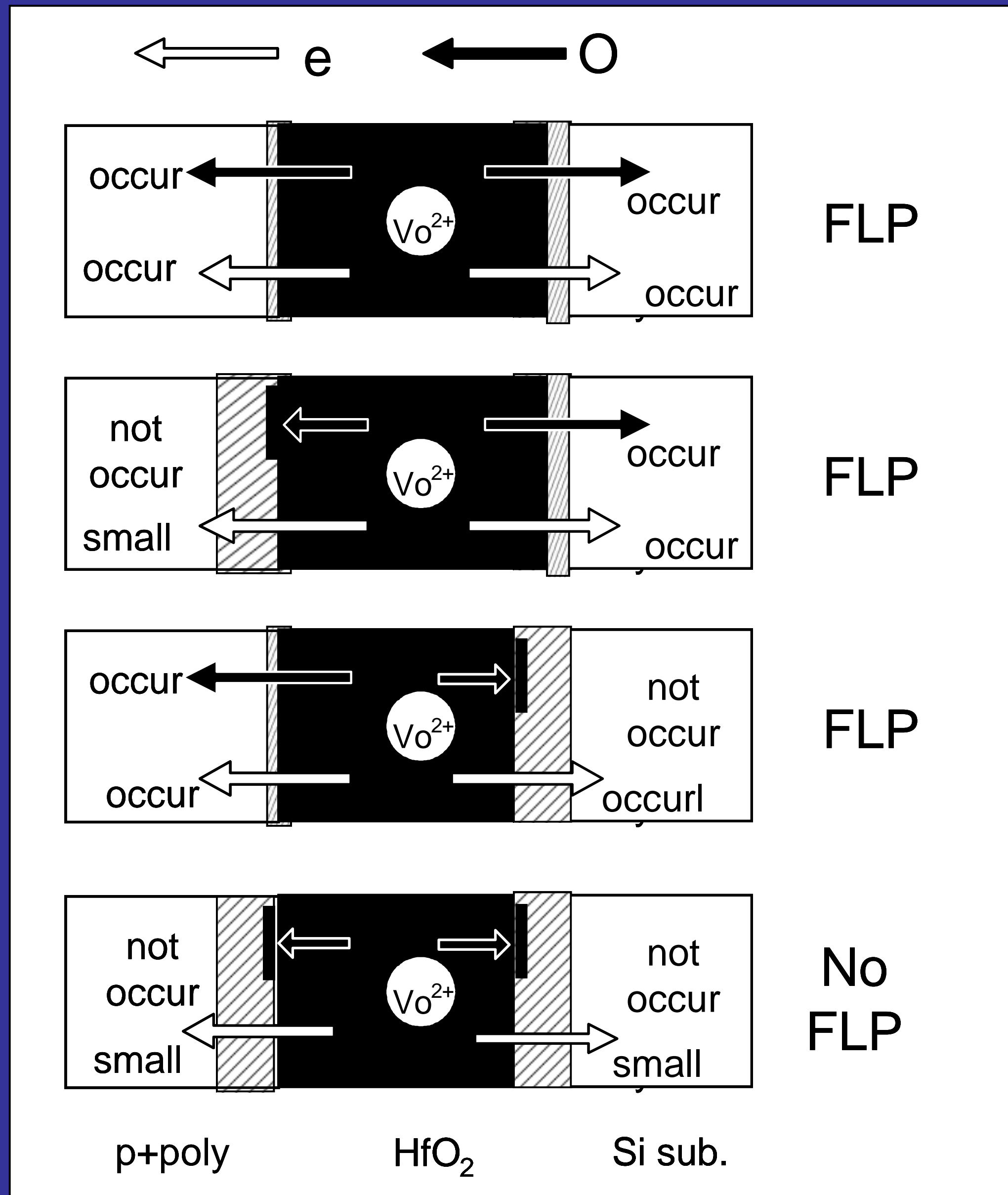
- It is a common guiding principle to synthesize the sharp and high quality oxide interfaces.

# Summary

- Computational science can predict and propose useful guiding principles of future nano-devices.
- Interface physics of high-k gate stacks, operation mechanism of ReRAM, guideline of high-endurance MONOS, etc., can really be obtained by using computational science.

# Other experiments for new interface physics concept

Y. Kamimuta et al.
SSDM 2005




Interface reaction between HfO2 and Si is crucial