Computational Science Studies toward Future Nano-Devices

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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

Interfaces with various materials are inevitable

Computational material design becomes a crucial tool
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2. Key Interface physics between Ionic and covalent materials

Difference in O forms in ionic HfO2 and covalent SiO2

HfO2

O^{2-} form in HfO2. 

SiO2

O^0 form in SiO2.

K. Shiraishi et al. VLSI 2004
Computational Science Knowledge for O Vacancies in HfO$_2$
-First Principles results-

Vo wave function is composed of Hf 5d.

Occupied 1.1~1.2 eV
Conduction Band (Hf5d) 0.3 eV
Valence Band (O2p)

Unoccupied

$V_O^0$, $V_O^{2+}$
What is the crucial difference between covalent SiO₂ and ionic HfO₂ from microscopic viewpoint: (Energy level position of Vo) Relatively higher energy level position is the origin of the large Vfb shift of HfO₂ dielectrics as well as the easy formation of Vo.

In HfO₂, Vo energy level is located much higher position compared to Vo energy level of SiO₂. (additional electron generation is difficult in SiO₂)


A. Oshiyama: JJAP 37, L232 (1998) :

Si-Si bond formation lowers the energy level position

Isolated Vo in an ionic materials tends to become 2+.
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 HfO$_2$ (La$_2$O$_3$)/SiO$_2$ interfaces.
Coexistence of Covalency and Ionicity $\rightarrow$ new interface physics

HfO$_2$(ionic) | SiO$_2$(covalent)

O$^2-$
Coexistence of Covalency and Ionicity $\rightarrow$ new interface physics

<table>
<thead>
<tr>
<th>HfO$_2$(ionic)</th>
<th>SiO$_2$(covalent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$O^{2-}$</td>
<td></td>
</tr>
</tbody>
</table>
Coexistence of Covalency and Ionicity → new interface physics

HfO2(ionic)  SiO2(covalent)

O^{2-}
Coexistence of Covalency and Ionicity → new interface physics

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<tr>
<th>HfO$_2$(ionic)</th>
<th>SiO$_2$(covalent)</th>
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<tbody>
<tr>
<td>Vo+2e</td>
<td>O$^0$</td>
</tr>
</tbody>
</table>
When $O^{2-}$ ion moves from ionic HfO$_2$ into covalent SiO$_2$, two surplus electrons are generated. These two electrons tends to transfer into gate metals, leading to formation of Vo(2+).

TiO$_2$ and ZrO$_2$ also have above tendency.
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RRAM types

Set | Reset
Unipolar (filamentary) | Bipolar (filamentary) | Bipolar/analog (interface)

From D. Ilemini Lecture
Conventional Model of ReRAM Operation

**Dopant = oxygen vacancy \( V_0^{2+} \)**

- Insulating \( TiO_2 + \) low-resistivity \( TiO_{2-x} \)

- \( V_0^{2+} \) drift toward the cathode: \( TiO_2 \) reduction lowers resistance (n doping by \( V_0^{2+} \)) 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 \( TiO_2-TiO_{2-x} \) model?

From D. Ilemini Lecture
Question

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

Purpose

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

- We propose new ReRAM operation model by investigating TiO2 based ReRAM by LDA+U method.
Message:
Carrier injection/removal induces Cohesion-Isolation transition
We investigated isolated Vo and Vo chain by first principles calculations.
Isolated Vo and Vo chains are calculated in a 108 atom supercell, LDA+U, 4Vo in supercell.

**Isolated Vo**

**Vo chain**

**Vo chain with 1 Vo disruption**

**Vo chain with 2 Vo disruption**
Favorable charge state difference between isolated Vo and a Vo chain (filament).

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

(a) Insulating
(b) Metallic
(c) Semi-insulating
(d) Insulating

Isolated Vo
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.

\[ E_c(q) = E(V_0^q - \text{chain}) + 3 \times E(\text{bulk}) - 4 \times E(\text{isolated} - V_0^q), \]

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)
- Carriers are injected from both electrodes and filaments
- Electron injection from electrode 1 → Filament growth
- Hole injection from electrode 1 → Filament disruption

(b) Bipolar (Reset)
- Electron injection from filament → Filament growth

(c) Unipolar (Set)
- Carriers are injected only from filaments

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.

Fermi level position of electrodes should be similar to Vo energy level.
Guiding principles for TiO2 based ReRAM

<table>
<thead>
<tr>
<th>Electrode</th>
<th>$\phi$ (eV)</th>
<th>Accessibility</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>4.25</td>
<td>Good</td>
</tr>
<tr>
<td>Ag</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>4.5</td>
<td></td>
</tr>
<tr>
<td>Au</td>
<td>4.85</td>
<td></td>
</tr>
<tr>
<td>Pt</td>
<td>5.1</td>
<td>Bad</td>
</tr>
<tr>
<td>TiO$_2$ film</td>
<td>4.05</td>
<td></td>
</tr>
</tbody>
</table>

Low work function metal are suitable for TiO2 based ReRAM.
Computational science has clarified that the ON-OFF switching in TiO2-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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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.

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.


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.
A inserted Carbon atom replace a Si atom in SiO₂.
-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))

- 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\textsubscript{2}.

We found that carbonate-like anti-bonding state and O lone pare state was formed in the SiO\textsubscript{2} band gap.
Results: C incorporation with 3H atoms

Calculation model for bulk SiO$_2$ where a C atom and three H atoms were inserted
Results: C incorporation with 3H atoms

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 $\Gamma$ 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 knowledge to design and to improve practical fabrication of high quality SiC/SiO$_2$ interface.
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

Hf-O bond is much stronger than Si-O bond -> Si cannot reduce HfO$_2$

Formation enthalpy:

- $11.6\text{eV}(\text{HfO}_2)$
- $9.4\text{eV}(\text{SiO}_2)$

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

Energy loss obtained by computational science

+1.2 eV
Change in O ion form induces unexpected flat-band shift

J. Robertson, O. Sharia, and A. A. Demkov, APL 2007 (including image charge)
P. Broqvist et al. APL 2008 (Including amorphous effect)

HfO2 +1/2 Si $\rightarrow$ (HfO2+Vo$^{2+}$+2e)+1/2 SiO2
Change in O ion form induces unexpected flat-band shift

Pinning position of a metal gate is defined by $G_1 - G_2 = 0$:
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

\[ \text{HfO}_2 + \frac{1}{2} \text{Si} \rightarrow (\text{HfO}_2 + \text{Vo}^{2+} + 2\text{e}) + \frac{1}{2} \text{SiO}_2 \]
Famous FLP occurs, and a metal WF is independent of metal species nor metal thickness.


M. Kadoshima et al. VLSI 2007
Summary of mechanism of Fermi level pinning of poly-Si gate

Vo formation in ionic HfO₂ 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.

Substrate reaction

\[(\text{HfO}_2) + \frac{1}{2} \text{Si} \rightarrow (\text{HfO}_2) + \text{Vo}^{2+} + 2\text{e} + \frac{1}{2}\text{SiO}_2\]

occurs in every case.

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

\[(\text{HfO}_2) + \frac{1}{2} \text{Si} \rightarrow (\text{HfO}_2) + \text{Vo}^{2+} + 2\text{e} + \frac{1}{2}\text{SiO}_2\]
It is known that O injection can recover FLP (E. Cartier, VLSI 2005).

**Diagram:**
- **Graph:**
  - Flatband Voltage (V) vs. Temperature (°C)
  - Ambient conditions: O2/N2 (10 ppm O2), FGA
  - Flatband is estimated only because of high N2.

- **Diagram Description:**
  - (a) Reaction with Si sub.
  - Energy gain by electron transfer G2
  - Semiconductor (Si)
  - Reaction with Si sub. -G1

- **Figure:**
  - TIN Work Function (eV) vs. UV-O3 Oxidation Time (s)
  - Relative Hf 4f Position
  - O injection by ozone at RT

**References:**
- A. Ohta et al., IWDTF 2006
FLP recovery by O injection

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

A. Ohta et al., IWDTF 2006

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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

There are lots of O atoms in SiO₂/SiN interfaces.
Effects of O- incorporation should be investigated for realization of high quality MONOS.
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, $\rightarrow$ Irreversible change
Many meta-stable states appear by P/E & thermal activation.

There is a path which cause local collapse.
The collapse is caused by P/E & thermal activation with low barrier (~0.1 eV)

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.
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.
For lowering $\mu_O$, our proposal is inserting a thin Si layer into SiO$_2$.

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

Suppression of O-incorporation

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

K. Yamaguchi et al. IEDM 2010
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