Structural Properties and Electronic Structures of Amorphous HfO_2/Si(001) interface

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Abstract

Using the projector augmented wave method within the generalized gradient approximation, we have performed *ab-initio* molecular dynamics simulations to generate an atomic structure model of amorphous hafnium dioxide (*a*-HfO_2) by a melt-and-quench scheme, and have investigated the structural and electronic properties of *a*-HfO_2 /Si(001)-*c*(2×2) interface. The structure of *a*-HfO_2 sample is analyzed via the atomic coordination number and partial pair-radius distribution functions. Our results show the average Hf-O nearest-neighbor distance is 2.06 Å, which is comparable with the Hf-O bond lengths (in the range from 2.04Å ~ to 2.25Å) in monoclinic HfO_2 crystalline, and also indicate the generated sample essentially reflects the experimentally measured structural characteristics of *a*-HfO_2. Most importantly, it is found that the valence band offset of *a*-HfO_2/Si interface is about 2.97eV, and our results suggest that the coordination of Si atoms at interface would significantly affect the electronic properties of interface.

Simulation Methods

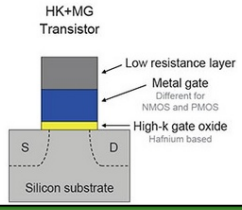
VASP: Projected Augmented Wave method

E_{xc}: GGA-PW91; E_{cut} : 500eV ; *k*-mesh: 3*3*1

Relaxation criteria: force < 0.025 eV/atom

MD: Canonical Ensemble – Nose thermostat

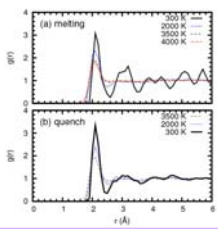
Background

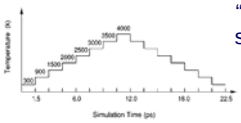


1. **SiO_2 in CMOS has been replaced by Hf-based high κ material in Intel's 45nm technology.**
2. **HfO_2 attracts attention due to: high κ (~25); thermal stable with Si; large band gap … …**

Results

a-HfO_2: Melt-and-quench



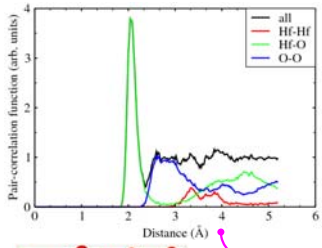


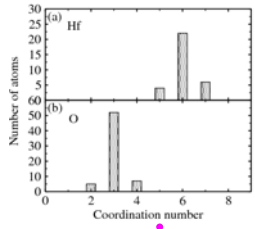
"melt-and-quench" simulation scheme

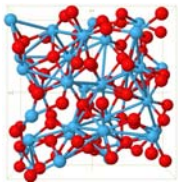
T is increased from 300 to 4000 K in steps of 1.5 ps, then decreased in a reversed sequence, for a total simulation time of 22.5 ps

96 atoms in a cubic cell

The structure was relaxed after quench







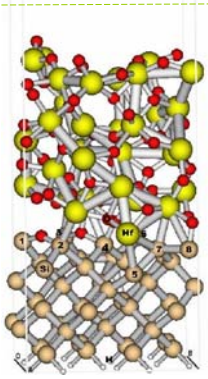
First peak: ~2.06 A Hf-O

Comparable to that in crystal and the exp.

Coordination number < that in crystal HfO_2

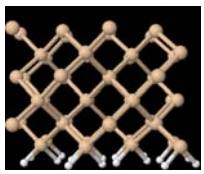
Resonable amorphous HfO_2 was obtained.

Structure Analysis



Si(#)	N_{Si-Hf}	N_{Si-O}	d_{Si-Hf}/Å	d_{Si-O}/Å
Si(1)	0	2	-	1.67, 1.67
Si(2)	1	1	2.72	1.70
Si(3)	2	1	2.78, 3.40	1.80
Si(4)	1	2	3.07	1.71, 1.74
Si(5)	1	0	2.87	-
Si(6)	2	0	2.91, 3.38	-
Si(7)	2	0	2.83, 2.97	-
Si(8)	1	1	3.16	1.76

Coordination number of the Si atom at the interface is smaller than that in the bulk.



a : 0.5468nm (cal.)

0.5340nm(exp.)

Si: $(001)_{2*2}$

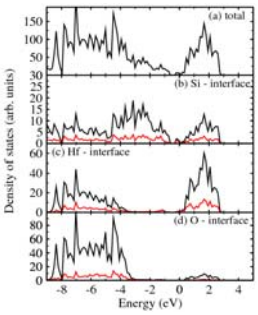
6 layers (48 atoms)

a*b*c=10.936*10.936*c

no surface reconstruction

H saturated (16 H atoms)

(H relaxed with 5 layers fixed)

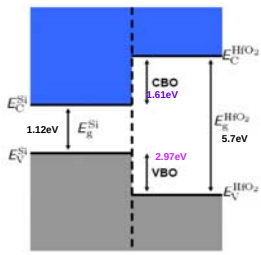


Density of States

a) A peak appears at about -0.2eV below the fermi level.

b) The peak is dominated by the interface Si atoms.

=>The electronic properties of the interface are greatly affected by the bond states of the interface Si atoms.



Band Offset

Eg^{Si} :	0.77eV (cal.)
	1.12eV (exp.)
$Eg^{a\text{-}Hfo2}$:	3.39eV (cal.)
	5.7eV (exp.[a])

CBO = $E_g^{a\text{-}Hfo2} - E_g^{Si}$ - VBO

VBO = $VBM_{HfO2(0)} - VBM_{Si(0)} + \{\Delta core_{mix} - \Delta core_{sept}\}$

2.97eV and 1.61eV inhibit the Schotty emission of electrons or holes.

(1) Reasonable amorphous HfO_2 sample has been obtained via the *ab-initio* molecular dynamics.

(2) The electronic properties of the Interface are greatly affected by the coordination of the interface Si atoms.

(3) The VBO(2.97eV) and CBO (1.61eV) inhibit the Schottky emission of electrons or holes.

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