Effects of Y dopant on structural stability and defect properties of cubic HfO_2

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Abstract

First-principles calculations have been performed to study the structural and electronic properties of pure and Y-doped cubic HfO_2. It is found that Y dopant in cubic HfO_2 can increase the stability relative to the monoclinic phase by decreasing the energy difference and the phase transition pressure. These findings could help to understand the stabilization of cubic phase of HfO_2 with the addition of Y observed in the experiments. The calculated formation energies of the oxygen vacancies (V_O) indicate that V_O^+ is more stable than neutral V_O and charged V_O^{++} in cubic structure of Y-doped HfO_2. Due to Y having one *d*-electron less than Hf and Y substitution for Hf making oxygen *p*-band no longer fully occupied, Y dopant can lower the highest occupied defect states induced by V_O^+ into the valence bands rather than lying in the energy gap, which explains experimental observation that gap states related to oxygen vacancy defects become non-detectable in Y-doped HfO_2 films.

Background

1. SiO2 should be replaced by high κ dielectrics to ensure large driving current and low leakage current of CMOS devices.

2. **HfO_2 attracts more attention due to: high κ (~25); thermal stable with Si; large band gap … …**

Computation

All calculations here are performed on VASP, details as follows:

Systems: 1) primitive cell of m-HfO_2, c-HfO_2;

2) Y:m-HfO_2, Y:c-HfO_2 **2×2×2 atom supercell**

3) V_O : c-HfO_2 – a 3×3×3 supercell

E_{xc}: GGA

Energy cutoff: 495eV

Potential: ultrasoft Vanderbilt pp

K points: Monkhorst- Pack scheme

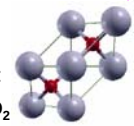
Relaxation: H-F force < 0.01 eV/Å per atom

Energy convergency: 10meV

Defect formation energy and Ionic energy are :

$$E_f(V_O^q) = E_{def}(V_O^q) + \mu_O - E_{per} + q(E_V + \Delta V + \varepsilon_F)$$

$$I_p(D^q) = E_{per}^- + E_{def}^{q+1} - E_{per}^0 - E_{def}^q + \kappa$$



C-HfO_2

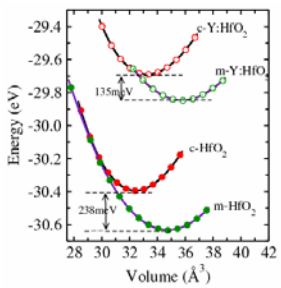
Results

I. Calculated bulk parameters of monoclinc and cubic HfO_2

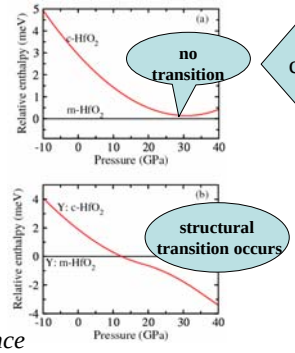
Data agree well with exp.

	Our work	Exp.
Cubic		
V_0 (Å^3)	32.43	32.77
a (Å)	5.06	5.08
B_0 (GPa)	261	

1. EOS



2. H-P: tangent E-V

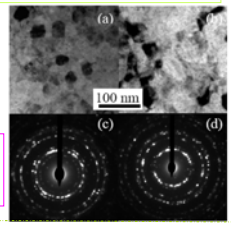


calculation

c-HfO_2 can be stabilized by Y dopant.

show light on exp.

3. Upper: TEM images Lower: diffraction patterns



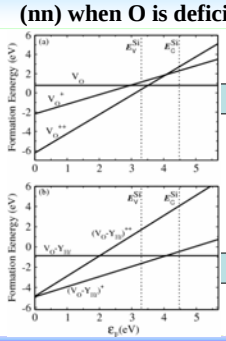
(a) (c) : HfO_2 , →m phase with possible t.

(b) (d) : Y incorporated HfO_2 , →cubic

➢After doping Y, *the energy difference between two phases decreased.*

➢Transition pressure for m→c reduces greatly.

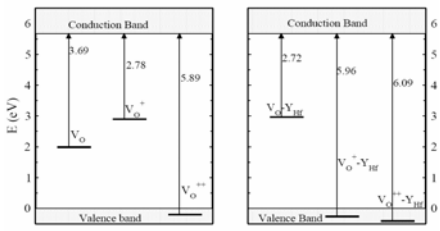
4. Calculated formation energies of oxygen vacancies (nn) when O is deficient.



V_O^+ is favorable in c-HfO_2 with Y.

V_O^{++} and V_O is favorable in c-HfO_2 without Y.

5. Ionization energies for oxygen vacancies in c-HfO_2 and Y: c-HfO_2



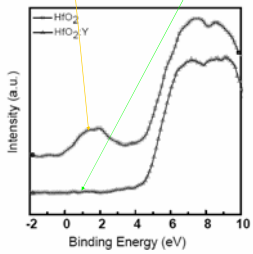
Left: stable V_O^{++} and V_O are gap states.

Right: stable V_O^+ no gap states.

6. Experiment: XPS

defect DOS peak between ε_F and VBM in pure HfO_2

peak undetectable upon Y incorporation



Defect state peaked at ~2.5 eV below the ε_F can be attributed to the O vacancy related defects, commonly reported in HfO_2 [APL 88. 182903, 2006].

Y dopant in HfO_2 makes c-HfO_2 stabilized. As Y and Hf are not isovalent, Y_{Hf} introduces an acceptor level near the VBM , contributing to the passivation of oxygen states, which are gap states, in c-HfO_2.

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Summary: **C-HfO_2 can be stabilized by Y dopant. Doped Y in c-HfO_2 moves gap states away.**

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