Surface Ferromagnetism in HfO_2 Induced by Excess Oxygen Atoms

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Abstract

First principles simulations based on density functional theory are performed to study surface magnetic properties of low index cubic, tetragonal, and monoclinic HfO_2 surfaces with different terminations. Our systematic calculations reveal that i) stoichiometric surfaces as well as Hf rich non-stoichiometric surfaces are non magnetic, and ii) O rich non-stoichiometric surfaces are ferromagnetic and often half metallic. The ferromagnetism found here is attributed to O surface electronic states with large O 2*p* spin exchange energy. Our finding provides a novel pathway to d^0 ferromagnetism for simple oxides with no magnetic ions involved. We further calculate the surface energy to discuss a possible reason for recent controversial observations of ferromagnetism in HfO_2.

Background

(1) Room-temperature ferromagnetism is important both in its potential spintronics application and scientific research.

(2) Lots of controversial of d^0 ferromagnetism in HfO_2

Simulation Method

Density functional theory calculations with plane wave bases

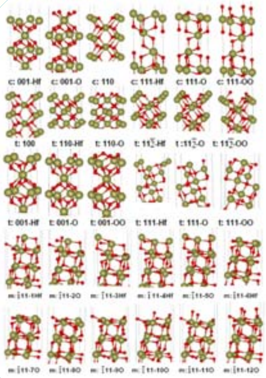
Code: VASP

E_{xc}: PAW GGA-PBE — E_{cut}: 500 eV

k-mesh: Monkhorst-Pack — Surface: symmetrical slab

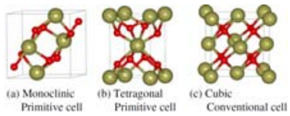
Spin polarized calculation

Systems



Systems: low index cubic, tetragonal and monoclinic surfaces with different terminations

Halves of the symmetrical surfaces are given in the left figure.



(1)For Hf rich and stoichiometric surfaces, their ground state are non-magnetic.

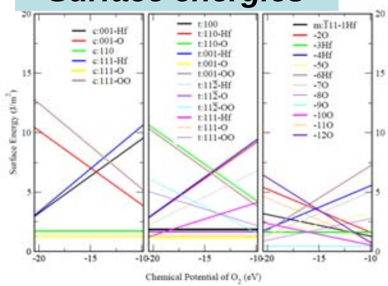
(2)Oxygen rich surfaces are magnetic.

For c:111-OO

ΔE_{FM-AM} = -0.11 eV

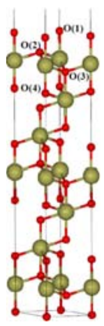
➢ The ground state is ferromagnetic.

Surface energies

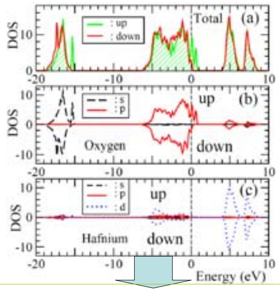


Stoichiometric m:-111-9O is the most stable. The non-stoichiometric surfaces could be stable under some chemical condition.

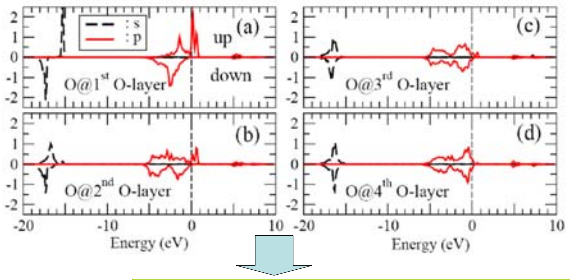
Density of States — layer by layer: spin-polarized — non-spin-polarized



c:111-OO

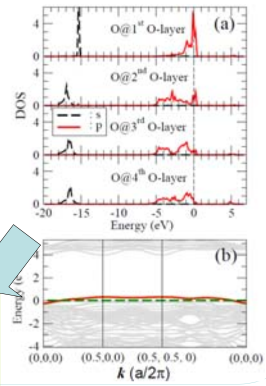


The surface is ferromagnetic, half metallic; Hole states are introduced near VBM, which are polarized O 2*p* orbitals.

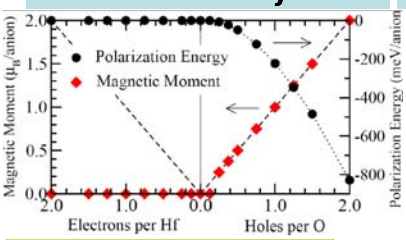


The moment is localized on surface O atoms, which have sharp DOS peaks near Fermi level.

=> O 2*p* orbital **large N(E_F)**.



Electron/Hole injection



Hole doping (O rich) is much easier to make HfO_2 polarized.

Spin exchange energy

Spin exchange energy :

Hf 5*d* orbital: ~1.04 eV

O 2*p* orbital: ~3.03 eV

Orbital radial distribution:

O 2p < Hf 5d

large U

$\frac{1}{2}UN(E_F) > 1$

Stoner model of ferromagnetism

Conclusion

(1) The O rich surfaces could be stable under some chemical condition.

(2) O rich surfaces can be ferromagnetic.

(3) The ferromagnetism is attributed to the large surface O electronic states with large O 2p exchange energy.