Surface Ferromagnetism in HfO₂ 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 HfO₂ 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 2p spin exchange energy. Our finding provides a novel pathway to d⁰ 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 HfO₂.

Background

(1) Room-temperature ferromagnetism is important both in its potential spintronics application and scientific research.
(2) Lots of controversial of d⁰ ferromagnetism in HfO₂

Simulation Method

Density functional theory calculations with plane wave bases
Code: VASP
Eₚ: PAW GGA-PBE
Eₚ: 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.

Surface energies

Stoichiometric m:-111-90 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

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

The moment is localized on surface O atoms, which have sharp DOS peaks near Fermi level.
=> O 2p orbital large N(Eₚ).

Hole doping (O rich) is much easier to make HfO₂ polarized.

Spin exchange energy

Spin exchange energy:
Hf 5d orbital: ~1.04 eV
O 2p orbital: ~3.03 eV
Orbital radial distribution:
O 2p < Hf 5d

large U

Stoner model of ferromagnetism

(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.

Conclusion