Journal of Magnetism and Magnetic Materials 375 (2015) 61–64

Contents lists available at ScienceDirect

Journal of Magnetism and Magnetic Materials

journal homepage: www.elsevier.com/locate/jmmm

First-principles calculations of electronic and optical properties of F, C-codoped cubic HfO_2

Yu-Fen Zhang [a,*], Hao Ren [a], Zhi-Tao Hou [b]

[a] School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, PR China
[b] Cooperation Development Department, Shandong University, Jinan 250100, PR China

ARTICLE INFO

Article history:
Received 12 July 2014
Received in revised form
21 September 2014
Available online 23 September 2014

Keywords:
DFT
Electronic and optical properties
Codoping
Cubic HfO_2

ABSTRACT

First-principles calculations based on DFT+*U* were performed on electronic and optical properties of F, C-codoped cubic HfO_2. The calculations show that strong $2p$–$2p/5d$ admixtures result in half-metallic ferromagnetism behaviors of F, C-codoped cubic HfO_2. Both the direct $2p$–$2p$ interaction and the indirect $2p$–$5d/2p$–$2p$ coupling interactions can be expected to contribute to the long-range magnetic coupling. Meanwhile, F and C codoping induces obvious increase of refractive index and new steep absorption peaks at lower energy region ~2.8 eV, which can be used for photoabsorption applications.

1. Introduction

As a transition metal oxide, hafnium dioxide (HfO_2) is widely studied due to its excellent dielectric properties, wide band gap, high bulk modulus, high melting point and good thermal stability [1–3]. At ambient pressure, HfO_2 exists in three polymorphs: monoclinic ($P2_1/c$) at low temperature, tetragonal ($P4_2/nmc$) at around 2000 K, and cubic fluorite ($Fm3m$) at about 2900 K [4]. However, at lower temperatures the cubic phase of HfO_2 can be stabilized by element doping. Thus, this phase is in fact the stable structure and can be used in many industrial applications [5–7]. With the addition of small amounts of impurities, various structures of HfO_2 has been used as the high-*k* dielectric films [8], optical and protective coatings [9]. More recently, the resistive switching phenomena were observed in the HfO_2 thin film [10] and the doped HfO_2 films [11].

Compared to traditional charge-based semiconductor devices, spintronics devices have attracted great interest due to their unique advantages such as being more powerful, endurable and efficient. For use in applications, materials that can both generate and manipulate electronic spin at room temperature (RT) or above are essential. Recently, unexpected ferromagnetism called d° ferromagnetism (FM) has been successively observed in undoped HfO_2 and ZrO_2 [12] , TiO_2 [13] . Meanwhile, C (or N) substitution has also received much attention as potential ways to realize ferromagnetism in ZrO_2 and TiO_2 [14–16] , which challenge the traditional understanding for the origin of ferromagnetism. However, substitutional C (or N) dopants generate oxygen vacancies, and induce band gap narrowing [14,17]. It was repoted that F has a large beneficial effect on charge trapping, and can fill up oxygen vacancies by creating a shallow donor state [17]. So it can be speculated that codoping of low concentrations of F and C impurities in cubic HfO_2 could induce a different electronic structure and physical properties that may lead to new applications. It is therefore timely to investigate the electronic structures of these systems. To date, few works have been focused on the electronic and optical properties of F, C-codoped HfO_2.

For recent years, HfO_2 based materials have attracted many experimental and theoretical investigations, in which, the method of density functional theory (DFT) has been successfully used in predicting crystal structures and properties of undoped and doped cubic HfO_2 [2,17–19]. In this paper, we carried out first-principles calculations based on DFT to investigate the electronic structures of the F, C-doped cubic HfO_2 (denoted *c*-HfO_2:F, C) and to find out the probable relations between electronic structures and optical properties.

2. Computational method and details

The first-principles electronic structure calculations based on DFT [20] within CASTEP code [21] were carried out to determine the stability and electronic structures of undoped and F,

---

[*] Corresponding author.
E-mail address: chm_zhangyf1@ujn.edu.cn (Y.-F. Zhang).

http://dx.doi.org/10.1016/j.jmmm.2014.09.043
0304-8853/

C-codoped cubic HfO_2. In the calculations, the electron–ionic core interaction is represented by the Vanderbilt ultrasoft pseudopotential [22]. The Hf (5*d*, 6*s*), O (2*s*, 2*p*), F (2*s*, 2*p*) and C (2*s*, 2*p*) levels are treated as valence states. To treat electron exchange and correlation, we chose the Perdew–Burke–Ernzerhof formulation of the generalized gradient approximation (GGA-PBE) [23] taking into account the on-site Coulomb repulsive interaction. A cutoff energy of 550 eV for undoped and F, C-codoped cubic HfO_2 in the plane wave expansion was employed in the calculations. A $2\times2\times2$ (or $5\times5\times5$) Monkhorst–Pack grid [24] was used for integration over the irreducible part of the Brillouin zone of the F, C-codoped cubic HfO_2 (or undoped system). Good convergence was achieved with the cutoff energy and number of *k* points. The default convergence criteria of CASTEP was applied within energy tolerance 5.0e−6 eV/atom, max force tolerance 0.03 eV/Å, max displacement tolerance 5.0e−4 Å and max stress tolerance 0.02 GPa. To explore the electronic and optical properties of these solid solutions, we employed a 96-atoms supercell (containing $2\times2\times2$ full cubic cells) with the starting configuration of cubic HfO_2 suggested in Ref. [18]. We substituted O atoms by C and F atoms to model substitutional C and F impurities in cubic HfO_2, the resulting supercell is $Hf_{32}F_4C_4O_{56}$.

For the F, C-codoped system, the C concentration is 6.25%, which results from evenly substituting four O atoms with four C atoms in a 96-atoms supercell. There is only one anion site in cubic HfO_2, so subsitituting O atom with C does not need to consider the site preference. In this system, the F concentration is also 6.25%, which results from evenly substituting four O atoms with four F atoms in the 96-atoms C-doped supercell. There are sereval O sites in C-doped cubic HfO_2, so subsitituting O atom with F needs to consider the site preference. We modeled two structures of F, C-codoped cubic HfO_2, including structure (I) (F and C share a Hf atom at a distance of ~4.59 Å) and structure (II) (F and C share no Hf atom at a distance of ~5.30 Å). Meanwhile, the calculations show that the structure (I) energetically favors over the structure (II) by 182 meV per F/C. This implies that the admixture of F and C atoms will obviously stablize the F, C-codoped cubic HfO_2.

Within the Broyden–Fletcher–Goldfarb–Shanno (BFGS) scheme [25], geometry optimization was performed allowing both cell parameter and internal coordinates relaxation. In the optical property calculation, the underestimation of the band gap (inherent in DFT calculations) was corrected by introducing a "scissors operator" (2.64 eV), by which the conduction bands positions were raised in energy prior to the interband transition strength calculation to match the general features of the measured imaginary part of dielectric function [19].

The standard DFT formulation usually fails to describe strongly correlated electrons behavior. This limitation can be corrected using the DFT+*U* method, which introduces a Hubbard parameter "*U*" for the description of the on-site interactions of those electrons [26]. Considering that the strength of the effective on-site Coulomb repulsion interaction between Hf 5*d* electrons is comparable with the valence bandwidth and the screening of Hf 6*s* electrons, we used the DFT+*U* methodology with an *U* value of 2.0 eV to describe the interactions of Hf 5*d* electrons [27,28].

3. Results and discussions

3.1. Structural stability and population analysis

The calculated equilibrium structural parameters and the results of population analysis of undoped and F, C-codoped cubic HfO_2 structures are summarized in Table 1. The calculated equilibrium structural parameter *a* for cubic HfO_2 is 5.274 Å, which is in agreement with the experimental value of 5.08 Å [29]. This can demonstrate the applicability of our theoretical model in geometry optimization for HfO_2. For F, C-codoped cubic HfO_2, the equilibrium structural parameter *a* is about 0.4–0.5% larger than cubic HfO_2, which can be explained by the larger radius and lower electronegativity of C compared with O atoms. From the results of population analysis, it is clearly found that substitutional codoping of F and C will greatly decrease the Mulliken charge of C atoms, slightly increase the charge of O atoms, and obviously decrease the charge of Zr atoms. This implies that F and C codoping will obviously enhance the covalent character of Zr–C bond.

Table 1
Calculated equilibrium structural parameters and the results of population analysis of undoped and F, C-codoped cubic HfO_2 structures.

Structure	*a* (Å)	Charge (e)/μ_B	Bond order (bond length, Å)
c-HfO_2	5.274	O: $-0.76/0$ Hf: $1.52/0$	Hf–O: 0.32 (2.284) In total: 10.24
c-HfO_2: F, C (I)	5.297	C: $-0.80/0.56$ F: $-0.51/0.02$ O_{1NN}: $-0.74/0.04$ O_{2NN}: $-0.77/0$ O_{3NN}: $-0.77/0$ O_{4NN}: $-0.74/0.04$ Hf_I: $1.47–1.48/\pm0.04$ Hf_{II}: $1.49–1.50/0$	Hf–O: 0.28–0.32 (2.261–2.319) Hf–C: 0.43–0.44 (2.183–2.212) Hf–F: 0.10–0.12 (2.376–2.404) In total: 9.49
hc-HfO_2: F, C (II)	5.299	C: $-0.83/0.64$ F: $-0.50/0$ O_{1NN}: $-0.75/0.02–0.04$ O_{2NN}: $-0.76/0$ O_{3NN-1}: $-0.74/0.14$ O_{3NN-2}: $-0.74/0$ Hf_I: $1.48/0\sim-0.02$ Hf_{II}: $1.49/0$	Hf–O: 0.24–0.34 (2.226–2.373) Hf–C: 0.46–0.48 (2.254–2.281) Hf–F: 0.11 (2.361–2.368) In total: 9.54

Spin-polarized calculations reveal the nonmagnetic character of the undoped cubic HfO_2. By F and C codoping, a total magnetic moment of ~1.0 μ_B per F/C is mostly contributed by the C dopant (~0.60 μ_B) with some contributions from its first nearest-neighboring (NN) O atoms (~0.2 μ_B). Meanwhile, the calculations show that the magnetic solutions energetically favor over the nonmagnetic solutions by 49–57 meV per F/C, which are even larger than that of Cu-doped ZnO (42 meV), which is known to be RTFM [30]. Therefore, RTFM in F, C-codoped cubic HfO_2 is possible. In both F, C-codoped structures, there are two kinds of Hf atoms, the C-connected Hf (Hf_I) and the C-unconnected Hf (Hf_{II}). In structure (I), the neighboring O atoms of C dopant can be numbered based on their distances from C dopant, including the first-NN to the fourth-NN O atoms (denoted O_{1NN}, O_{2NN}, O_{3NN} and O_{4NN}) at distances of about 2.69, 3.75, 4.59 and 5.30 Å, respectively. It is found that both O_{1NN} and O_{2NN} share Hf with C dopant, while O_{3NN} and O_{4NN} share no Hf with C dopant. In structure (II), the neighboring O atoms of C dopant can be numbered based on their distances from C dopant, including the O_{1NN}, O_{2NN}, O_{3NN} ($O_{3NN\text{-}1}$ and $O_{3NN\text{-}2}$) at distances of about 2.77, 3.75 and 4.59 Å, respectively. It is found that O_{1NN}, O_{2NN} and $O_{3NN\text{-}1}$ share Hf with C dopant, while $O_{3NN\text{-}2}$ does not share Hf with C dopant.

From the calculations, it is found that the obvious magnetic moments of the O_{1NN} in both F, C-codoped structures suggest that the wave function of the C dopant extends to its O_{1NN}, which are polarized in the same direction with that of the C dopant, hinting