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Theoretical studies of the effect of Ti, Zr and Hf substitutions on the electronic properties of alpha-alumina

H. A. Rahnamaye Aliabad[1], M. R. Benam[2] and H. Arabshahi[3]*

[1]Department of Physics, Tarbiat Moallem University of Sabzevar, Iran.
[2]Department of Physics, Payame-Noor University of Mashhad, Mashhad, Iran.
[3]Department of Physics, Ferdowsi University of Mashhad, Mashhad, Iran.

We have investigated the electronic properties of pure Alpha-Alumina (sapphire phase) and the aluminates α-Al2-xTxO3 where T is a transition metal and stands for Ti, Zr and Hf with x = 0.5. In this study we have employed the full potential linear augmented plane wave (FPLAPW) with Generalized Gradient Approximations (GGA) based on the Density Functional Theory (DFT) as implemented in WIEN2K code. The result shows that the electronic band structure and density of state data for pure α-Al2O3 shows that it is a nearly direct band gap insulator with E = 6.04 eV at the Γ point that is comparable with its experimental band gap. We have also shown that the aluminates transition metal substitutions introduced shallow electron states at the bottom of the conduction band edge of pure alpha-alumina which are primarily d-state in character and are originated from the transition metal impurities. The band gap of alumina is decreased for Ti and it is increased for Zr and Hf impurities.

Key words: Augmented plane wave, band gap, transition metal, density functional theory.

INTRODUCTION

The corundum or sapphire phase of alumina has a lot of applications in ceramic and semiconductor industry. It is used in particular, as an advanced substrate for ultra thin metal film deposition (Campbell, 1997). Because it's dielectric constant is about ε_R =11(Buchanan et al., 2000), that is more than the ε_R of silica, and it also exhibits a leakage current about 100 times lower than silica (Yourdshahyan et al., 1999), therefore it is a good replacement for silica in the gate of the MOSFETs transistors. In order to improve its electrical and optical properties we can dope it with other metals. But after all we need to make some predictions about the changing of its electrical properties by theoretical calculations. The best candidate of substitution atoms are transition metals (TM) because in this metals the d-bands are partially filled and will extend over the band gap and will change its size and therefore their properties will change.

Recently, it has become possible to compute with a great accuracy an important number of electronic and structural parameters of solids from first-principal calculations. The 'First Principles' method is a reliable way for predicting the properties of bulk materials. This kind of developments in computer simulations has opened up many interesting and existing possibilities in condensed matter studies.

In this paper we have studied theoretically, the effect of the substituted Ti, Zr and Hf atoms of the 4B periodic table on the electronic band structure and density of state of the pure α-Al_2O_3. It is supposed that the transition metal impurities replace in the sites of Al and will result to aluminates with α -$Al_{2-x}T_xO_3$ formula, where T is a transition metal and stands for Ti, Zr and Hf and x is selected to be 0.5.

MODEL DETAILS

In our calculations we have used Density Functional Theory (DFT) based on the work by Hohenberg and Kohn (1964) and by Kohn and Sham (1965) (French et al., 1994; French, 1990). Self-consistent electron structures were performed using the full potential linearized augmented plane wave (FP-LAPW) method as implemented in WIEN2K code (Blaha et al., 2001). We have also used the generalized gradient approximation (GGA) for the exchange-corre-

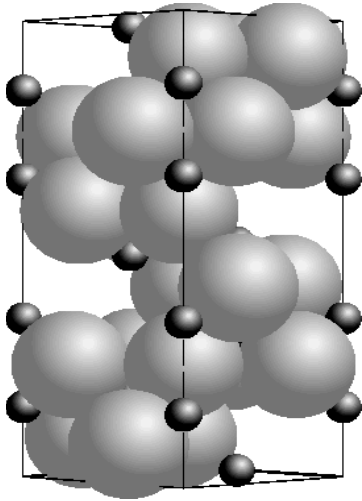*Corresponding author. E-mail: arabshahi@ferdowsi.um.ac.ir.

Figure 1 Crystal structure of α –Al₂O₃, The large circle represents the O atoms and the small one represents the Al atoms.

relation interaction (Oleinik et al., 2000). For solving the Kohn-Sham equations, the relativistic effects have been taken into account and also we have neglected the spin effects. In our calculations, we selected the parameter that determines the size of the secular matrix to be:

RMT*Kmax =7

Where the RMT is Muffin-Tin sphere radii and Kmax is the cut-off wave vector in the first Brillouin Zone.

We selected the muffin-tin radii for Ti, Zr, Hf and O to be nearly: 1.7, 1.72, 1.73, 1.8 and 1.7 a.u., respectively. The iteration process was stopped after the calculated total energy converged to less than 0.0001 Ryd. A total of 12 iterations were necessary to achieve self-consistency in our calculations.

The crystal structure of α–Al₂O₃ is hcp (Figure 1) and consists of close-packed planes of Oxygen and Aluminum. Its space group is R-3c (number 167). The used unit cell of α–Al₂O₃ consist of 12, Al and 18, O atoms (30 atoms in unit cell).The doped transition atoms supposed to substitute in the Al sites (Hosseini et al., 2005). If we choose $x = 0.5$ in aluminates α-Al$_{2-x}$T$_x$O₃, the number of TM atoms in unit cell will be 3 atoms.

RESULTS

The calculated band structure and density of state (DOS) for pure α–Al₂O₃ has been shown in Figure 2. It is evident that it is an insulator with direct band gap at the Γ point. The obtained band gap for α–Al₂O₃ is 6.04 eV (without empirical correction factor).

The total density of state of α-Al₂O₃ between -20 eV and 15 eV is shown in Figure 2(b). The partial DOS of O atom and Al atom are shown in Figure 2(c and d). There are a large number of relatively localized states at the top of the valance band originating mainly from the O 2p atom. The valence band edges near the Fermi energy for O atom are quite sharp, while the conduction band edges near the Fermi energy are not. The valance band, which
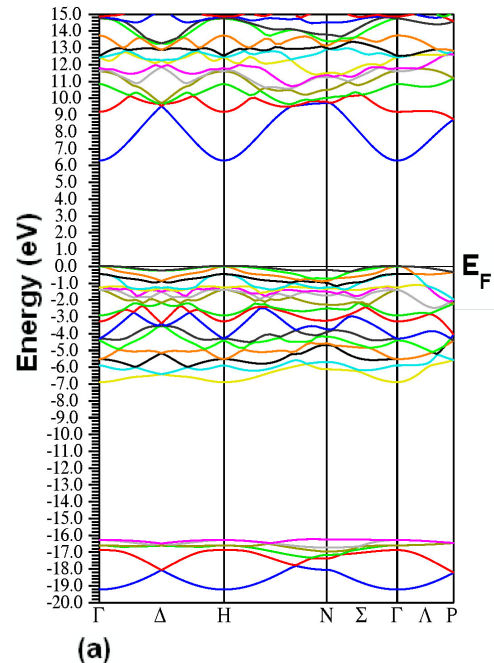

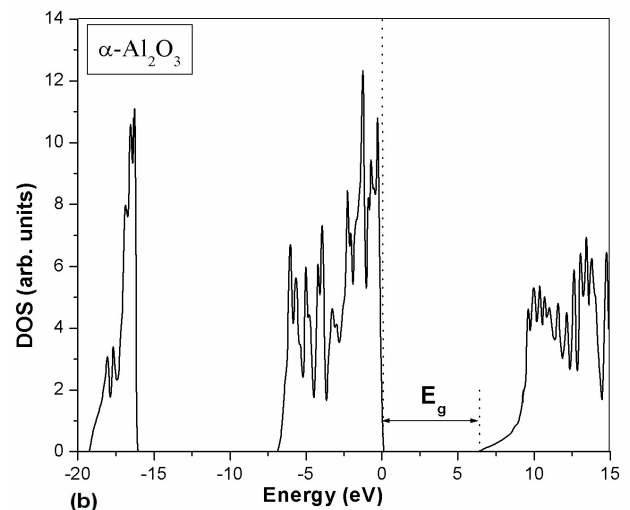**Figure 2**(a)**.** The calculated band structure for α–Al₂O₃.

Figure 2(b). The calculated total density of state for α–Al₂O₃.
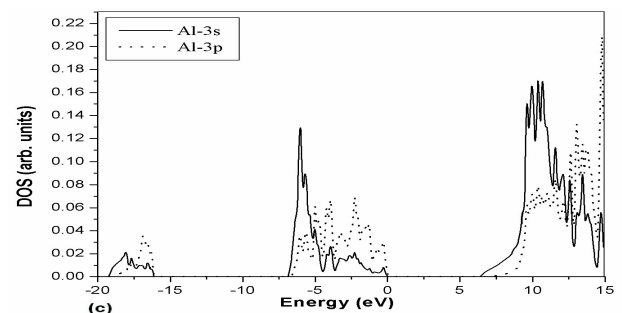
Figure 2(c). The calculated Al-3s, Al-3p for α–Al₂O₃.

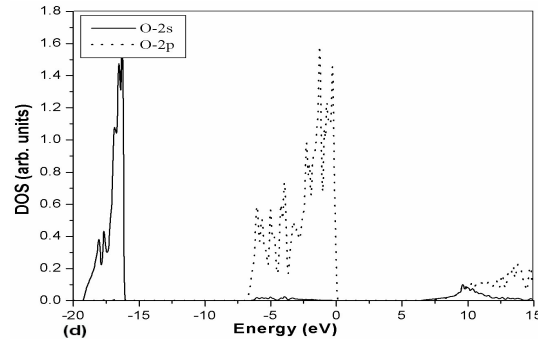**Figure 2(d).** The calculated O-2s, O-2p for α-Al₂O₃.
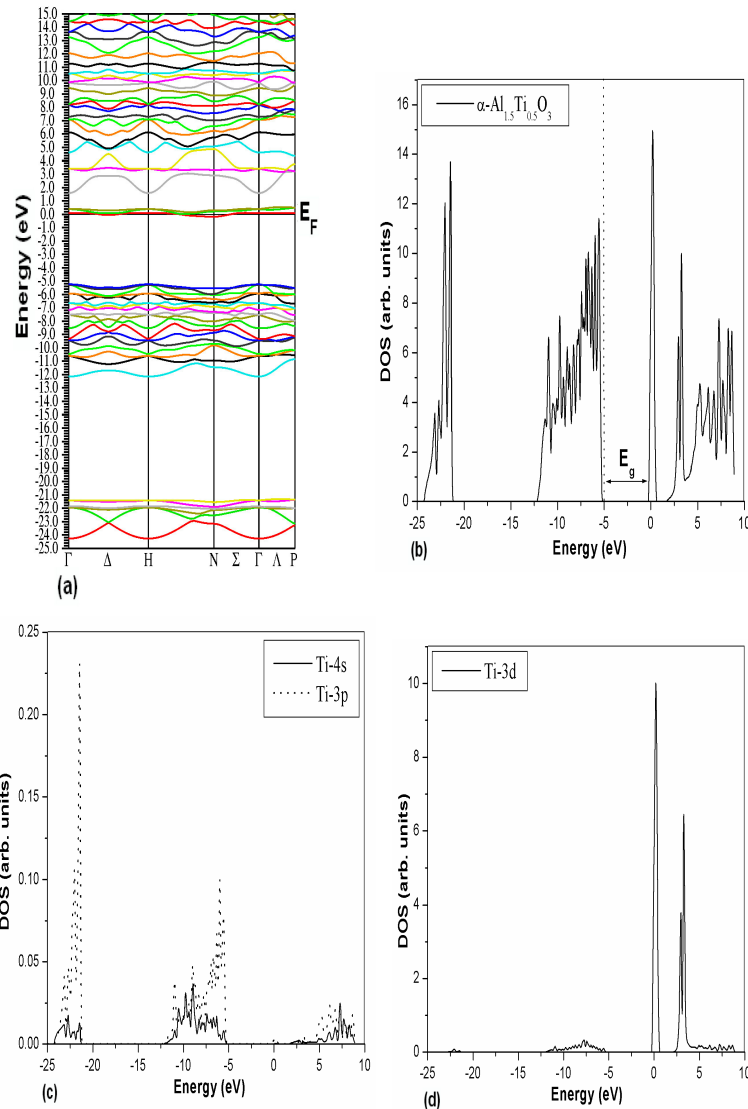
Figure 3. The calculated (a) Band structure, (b) Total density of state, (c) Ti-4s,Ti-3p and (d) Ti-3d for α -Al₁.₅Ti ₀.₅O₃.

lies between 0 eV (Fermi energy) to -7 e V, is composed of the O 2p orbital hybridized w orbital. The lower valance is formed predominantly by O 2s atom and extends from -16 eV to -19.5 eV. The band structure and density of state of α–Al1.5Ti0.5O3 aluminates has been shown in Figure 3. By comparing Figures 2 and 3, it can be seen that the substitution of Ti for Al in α-Al2O3 results in reducing the band gap to 4.73 eV. Substituting
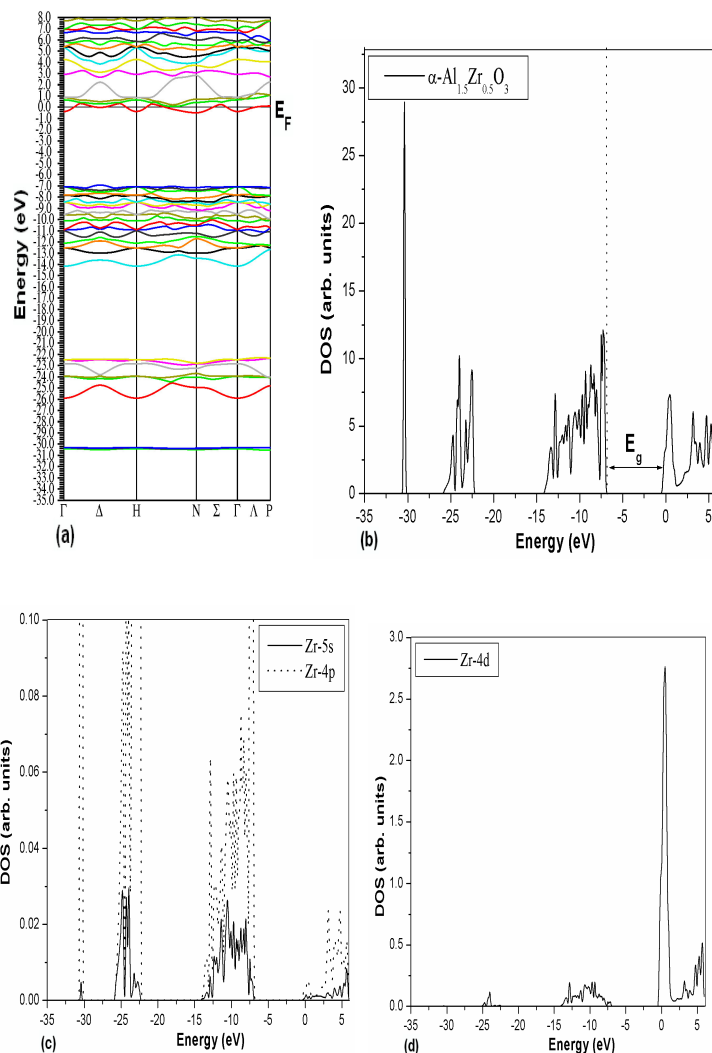
Figure 4. The calculated (a) Band structure, (b) Total density of state, (c) Zr-5s, Zr-4p and (d) Zr-4d for α -Al$_{1.5}$Zr$_{0.5}$O$_3$.

Table 1. Calculated band gaps values for pure α-Al$_2$O$_3$ and doped with Ti, Zr and Hf.

Methods	Band gap (eV)
This work: (FL-LAPW method GGA)	
Pure α-Al$_2$O$_3$	6.04
α –Al$_{1.5}$Ti$_{0.5}$O$_3$	4.73
α –Al$_{1.5}$Zr$_{0.5}$O$_3$	6.15
α –Al$_{1.5}$Hf$_{0.5}$O$_3$	. 6.26
Theory	
Pure α-Al$_2$O$_3$[9]	6.2
Pure κ-Al$_2$O$_3$[10]	5.3
α –Al$_{1.5}$La$_{0.5}$O$_3$[11]	3.6
Experimental	
Pure α-Al$_2$O$_3$[12]	10.8
Pure α-Al$_2$O$_3$[13]	8.8
α-Al$_2$O$_3$(Amorphous)[14]	8.7

by Ti, shifts the number of localized states at the top of the valance band (O - 2p) from 0-(-7 eV) eV to (-5)-(-12) eV. The band gap decreases mainly due to the number of state originating from Ti-d state in the conduction band.

The calculated band structure and density of state of α–Al$_{1.5}$Zr$_{0.5}$O$_3$ and α–Al$_{1.5}$Hf$_{0.5}$O$_3$ aluminates have been shown in Figure 4 and 5. We see that, unlike Ti impurity, doping the pure alumina with these impurities has increased band gap. Increasing of band gap is maybe due to larger ionic radius of these impurities with respect to Al.

The calculated band gaps for pure Alumina and doped Alumina and also those of other methods are summarizeed in Table 1. The value of band gap for α-Al$_2$O$_3$ is smaller than the experimental value 8.8 eV, but it's in good agreement with theoretical values calculated and published so far.

A simple explanation about becoming optimum electronical properties with doping pure alumina with these im-
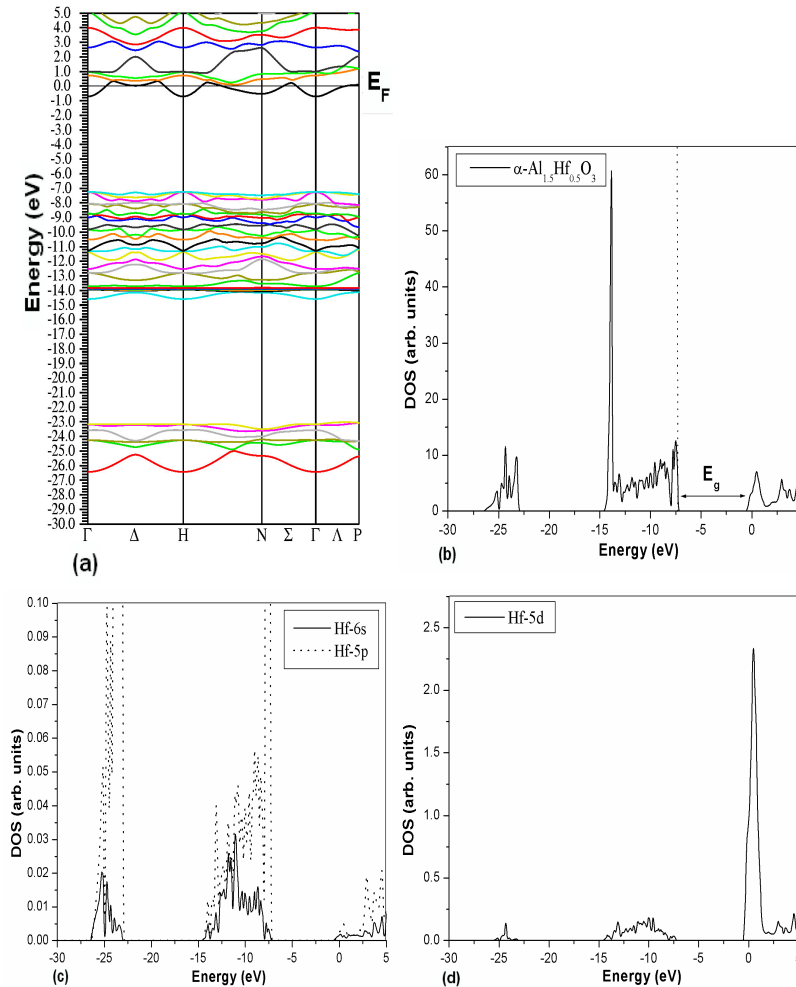
Figure 5. The calculated (a) Band structure, (b) Total density of state, (c) Hf-6s,Hf-5p and (d) Hf-5d for α -Al$_{1.5}$Hf $_{0.5}$O$_3$.

these impurities is maybe due to the mismatching of their valance electrons with aluminum valance number. Al, Ti, Zr, and Hf have the Ne $3s^2 3p^1$, $Ar3d^2 4s^2$, $Kr4d^2$ $5s^2$ and $Xe4f^{14}5d^2 4s^2$ electronic configurations, respectively. Therefore the substituted atoms will have one electron more than the Al atom in their outer shell and will act as carrier dopants by partially occupying the lowest conduction band, resulting in a good electronic structure.

Conclusion

We have calculated the band structure and density of state of Ti, Zr, and Hf aluminates from the first principle method .From these results, we showed that by introducing these impurities, band gap of alumina is decreasing for Ti and it is increasing for Zr and Hf impurities. Therefore, due to the increasing of the leakage current, we can conclude that Ti aluminates are not good candidates for high-k replacement gate dielectrics in MOSFETs but Zr and Hf aluminates are suitable.

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