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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 Aliabad¹, M. R. Benam² and H. Arabshahi³*

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

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We have investigated the electronic properties of pure Alpha-Alumina (sapphire phase) and the aluminates $\alpha$-$\text{Al}_{2-x}\text{T}_x\text{O}_3$ 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 $\alpha$-$\text{Al}_2\text{O}_3$ shows that it is a nearly direct band gap insulator with $E = 6.04$ eV at the $\Gamma$ 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 $\varepsilon_r = 11$ (Buchanan et al., 2000), that is more than the $\varepsilon_r$ 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 $\alpha$-$\text{Al}_2\text{O}_3$. It is supposed that the transition metal impurities replace in the sites of Al and will result to aluminates with $\alpha$-$\text{Al}_{2-x}\text{T}_x\text{O}_3$ 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-
The crystal structure of \( \alpha - Al_2O_3 \) 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 \( \alpha - Al_2O_3 \) 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 \( \alpha - Al_{2-x}T_xO_3 \), the number of TM atoms in unit cell will be 3 atoms.

**RESULTS**

The calculated band structure and density of state (DOS) for pure \( \alpha - Al_2O_3 \) has been shown in Figure 2. It is evident that it is an insulator with direct band gap at the \( \Gamma \) point. The obtained band gap for \( \alpha - Al_2O_3 \) is 6.04 eV (without empirical correction factor).

The total density of state of \( \alpha - Al_2O_3 \) 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 valance 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
lies between 0 eV (Fermi energy) to -7 eV, is composed of the O 2p orbital hybridized with 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
Table 1. Calculated band gaps values for pure $\alpha$-Al$_2$O$_3$ and doped with Ti, Zr and Hf.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Band gap (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>This work: (FL-LAPW method GGA)</strong></td>
<td></td>
</tr>
<tr>
<td>Pure $\alpha$-Al$_2$O$_3$</td>
<td>6.04</td>
</tr>
<tr>
<td>$\alpha$-Al$<em>{1.5}$Ti$</em>{0.5}$O$_3$</td>
<td>4.73</td>
</tr>
<tr>
<td>$\alpha$-Al$<em>{1.5}$Zr$</em>{0.5}$O$_3$</td>
<td>6.15</td>
</tr>
<tr>
<td>$\alpha$-Al$<em>{1.5}$Hf$</em>{0.5}$O$_3$</td>
<td>6.26</td>
</tr>
<tr>
<td><strong>Theory</strong></td>
<td></td>
</tr>
<tr>
<td>Pure $\alpha$-Al$_2$O$_3$[9]</td>
<td>6.2</td>
</tr>
<tr>
<td>Pure $\kappa$-Al$_2$O$_3$[10]</td>
<td>5.3</td>
</tr>
<tr>
<td>$\alpha$-Al$<em>{1.5}$La$</em>{0.5}$O$_3$[11]</td>
<td>3.6</td>
</tr>
<tr>
<td><strong>Experimental</strong></td>
<td></td>
</tr>
<tr>
<td>Pure $\alpha$-Al$_2$O$_3$[12]</td>
<td>10.8</td>
</tr>
<tr>
<td>Pure $\alpha$-Al$_2$O$_3$[13]</td>
<td>8.8</td>
</tr>
<tr>
<td>$\alpha$-Al$_2$O$_3$(Amorphous)[14]</td>
<td>8.7</td>
</tr>
</tbody>
</table>

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 $\alpha$-Al$_{1.5}$Zr$_{0.5}$O$_3$ and $\alpha$-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 summarized in Table 1. The value of band gap for $\alpha$-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 electro-nical properties with doping pure alumina with these im-
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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on the electronic and optical properties of Pb (Zr0.5Ti 0.5)O3, Ceramics International. pp. 31-671.
