Electronic Band Structures of Zirconium and Hafnium Oxides

Tomoyuki Hamada\textsuperscript{1,3} and Takahisa Ohno\textsuperscript{2,3}

\textsuperscript{1}Advanced Research Laboratory, Hitachi Ltd.
1-280, Higashi-koigakubo, Kokubunji, Tokyo 185-8601, Japan
Phone: +81-42-323-1111 E-mail: tomoyuki.hamada.tk@hitachi.com
\textsuperscript{2}National Institute of Materials Research
1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
\textsuperscript{3}Institute of Industrial Science, University of Tokyo
4-6-1 Komaba, Meguro, Tokyo 153-8505, Japan

1. Introduction

Zirconium oxides (ZrO\textsubscript{2}s) and hafnium oxides (HfO\textsubscript{2}s) have attracted much attention during the last decade because of their potential as high-k gate dielectric oxides for Si transistors. Their large band gap and high dielectric constant as well as their chemical stability on the Si substrate have made these oxides extremely attractive high-k materials, and considerable efforts have been devoted in theoretical studies to understanding their electronic structure, using the density functional (DFT) method in most cases. However, a well-known defect of the DFT method is that it cannot give correct band gaps for insulating materials including high-k materials, due to the unphysical self-interaction of electrons present in the DFT Hamiltonian. In this study, we calculated electronic band structures of ZrO\textsubscript{2} and HfO\textsubscript{2} crystal polymorphs by using a first principles DFT+U method partially correcting the self-interaction. The calculations provided correct band gaps for these oxides and clarified the difference in band gaps between the polymorphs.

2. Calculation Details

Electronic band structures of ZrO\textsubscript{2} and HfO\textsubscript{2} crystals in the cubic, monoclinic, and tetragonal phases (Figure 1) were calculated by using the generalized gradient approximation (GGA) DFT method and the DFT+U method. Experimental crystal structures were used for the calculations except for the case of tetragonal HfO\textsubscript{2}, for which no experimental geometry was available. In the tetragonal case, a GGA optimized crystal structure for the HfO\textsubscript{2} was used instead. In the DFT calculations, all electrons were treated as Kohn-Sham (KS) pseudo-electrons with self-interactions. In the DFT+U calculations, localized \textit{d} electrons on Zr and Hf atom sites were treated as (self-interaction free) real electrons by the approximate Hartree-Fock (HF) method taking the on-site interactions between the electrons into consideration. The interaction parameters, \textit{U}_{\textit{eff}}, were calculated from first principles by using a newly developed approximate constrained DFT approach and were used for DFT+U calculations. This first principles DFT+U approach eliminated the ambiguity in the \textit{U}_{\textit{eff}} determination in the DFT+U calculation and was contrary to the conventional approach that uses empirical \textit{U}_{\textit{eff}}s, which is determined to reproduce experimental band gaps. The calculations were carried out by using the pseudopotential (PP) method using plane wave basis sets with norm conserving (NC) PPs for Zr and Hf atoms and an ultra-soft(US) PP for O atoms. The calculations were done by using the PHASE ver. 7.01 electronic structure calculation program.[1]

3. Results and Discussion

Table I summarizes the calculated band gaps of ZrO\textsubscript{2} and HfO\textsubscript{2} crystals, and lists the experimental and previous theoretical band gaps for comparison. Theoretically calculated \textit{U}_{\textit{eff}}s for \textit{4d} orbitals of Zr atoms, \textit{U}_{\textit{eff}}(Zr\textit{4d}), and those for \textit{5d} orbitals for Hf atoms, \textit{U}_{\textit{eff}}(Hf\textit{5d}), used in the DFT+U (GGA+U) calculation are given. The results for \textit{U}_{\textit{eff}}(Zr\textit{4d}) and \textit{U}_{\textit{eff}}(Hf\textit{5d}) were 11.0 to 12.0 eV irrespective of the crystal phase. Band gaps calculated using the GGA DFT method largely underestimated the experimental band gaps for monoclinic ZrO\textsubscript{2} and HfO\textsubscript{2}, while the GGA+U method gave a band gap close to the experimental value for these monoclinic oxides. Interestingly, for these oxides, the present GGA+U calculations gave better results than more sophisticated GW calculations used in previous works,[2,3] providing band gaps closer to the experimental values than the GW band gaps. The good agreement of the calculated and experimental band gaps demonstrates the reliability of the present approach to estimate band gaps of high-k metal oxides. The GGA+U results show that ZrO\textsubscript{2} and HfO\textsubscript{2} in the same phase have a similar band gap, while those in a different phase have a different band gap. For both the ZrO\textsubscript{2} and HfO\textsubscript{2}, the GGA+U band gap increased in the order of the cubic, monoclinic, and tetragonal phases. In the HfO\textsubscript{2} case, the GGA+U band gap was smallest for cubic HfO\textsubscript{2} (4.5 eV) and was largest for tetragonal HfO\textsubscript{2} (5.3eV). The minimum band gap of cubic HfO\textsubscript{2} is at the X-point and is optically inactive. It is likely that the smaller X-point gap of cubic HfO\textsubscript{2} was missed in previous optical measurements because it is optically invisible. Figure 2 plots electronic band structures of HfO\textsubscript{2} crystals calculated using the GGA and GGA+U method. In all of the HfO\textsubscript{2} crystals, the GGA+U electronic structure differ from the GGA electronic structure in the band gap and in conduction band structures. The difference in the conduction band structure suggests that the widely used scissor operator approach,
which introduces a rigid shift of DFT conduction bands in energy to correct the band gap underestimation, is inappropriate for a study of the electronic structure of ZrO$_2$ and HfO$_2$ dielectrics.

4. Conclusion

Electronic structures of ZrO$_2$ and HfO$_2$ crystal polymorphs were investigated by using the first principles DFT+U method. This method was effective for estimating the band gap of these polymorphs.

Fig. 1 ZrO$_2$ (M=Zr) and HfO$_2$ (M=Hf) crystal polymorph structures: (a) cubic; (b) monoclinic; (c) tetragonal

Table I  Calculated band gaps of ZrO$_2$ and HfO$_2$ polymorphs. GW values from other studies and experimental values are shown for comparison. $U_{eff}$ values used in DFT+U calculations are also shown. I, X, and Γ in parentheses refer to indirect, X-point direct, and Γ-point direct gaps, respectively.

<table>
<thead>
<tr>
<th>Polymorph</th>
<th>$U_{eff}(Zr^{4d})$</th>
<th>GGA</th>
<th>GGA+U</th>
<th>GW$^a$</th>
<th>Exp.</th>
<th>$U_{eff}(Hf^{5d})$</th>
<th>GGA</th>
<th>GGA+U</th>
<th>GW$^b$</th>
<th>Exp.</th>
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<tr>
<td>cubic</td>
<td>11.80</td>
<td>3.20(I)</td>
<td>4.64(X)</td>
<td>5.55(L)</td>
<td>_____</td>
<td>11.13</td>
<td>3.77(X)</td>
<td>4.50(X)</td>
<td>5.93(I)</td>
<td>5.8$^d$</td>
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<tr>
<td></td>
<td>3.76(I)</td>
<td>5.56(Γ)</td>
<td>5.81(Γ)</td>
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<tr>
<td>monoclinic</td>
<td>11.82</td>
<td>2.78(Γ)</td>
<td>4.78(I)</td>
<td>5.42(I)</td>
<td>5.3$^b$</td>
<td>11.08</td>
<td>4.10(Γ)</td>
<td>5.18(I)</td>
<td>5.51(Γ)</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td>4.93(Γ)</td>
<td>5.46(Γ)</td>
<td>5.3$^b$</td>
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<td></td>
<td></td>
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<td></td>
<td>5.02(Γ)$^d$</td>
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<tr>
<td>tetragonal</td>
<td>11.28</td>
<td>3.90(Γ)</td>
<td>5.31(I)</td>
<td>6.40(I)</td>
<td>5.0$^b$</td>
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<td>4.55(Γ)</td>
<td>5.32(I)</td>
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$^a$Reference [2]. $^b$EELS. $^c$Reference [3]. $^d$UV.

Fig2. GGA electronic band structures of HfO$_2$ crystal polymorphs: (a) cubic; (b) monoclinic; (c) tetragonal, and GGA+U electronic band structures of the polymorphs: (a') cubic; (b') monoclinic; (c') tetragonal. The GGA+U band gap is larger than the GGA band gap for each polymorph and is close to the experimental band gap.

Acknowledgements

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References

[1] PHASE ver. 7.01, University of Tokyo (2008).