

Half-Metallicity in Fe doped HfO₂

Chandra Kumar Dixit, Ramesh Sharma, and K. C. Bhamu

Citation: [AIP Conference Proceedings](#) **1832**, 120002 (2017); doi: 10.1063/1.4980687

View online: <http://dx.doi.org/10.1063/1.4980687>

View Table of Contents: <http://aip.scitation.org/toc/apc/1832/1>

Published by the [American Institute of Physics](#)

Half-Metallicity in Fe Doped HfO₂

Chandra Kumar Dixit^{1*}, Ramesh Sharma² and K.C Bhamu³

¹*Dept. of Physics, Dr. Shakuntala Misra National Rehabilitation University, Lucknow-226017 (India)*

²*Dept. of Physics, Feroze Gandhi Institute of Engineering and Technology, Raebareli-229001 (India)*

³*Dept. of Physics, Goa University, Goa -403206 (India)*

*Corresponding Author: ckparadise@gmail.com

Abstract. This paper presents structural, electronic, optical and magnetic properties of pure and Fe doped cubic Hafnia (HfO₂). We used mBJ potential within FP-LAPW approximation to compute these properties. The calculated values of band gap from relaxed atomic positions and lattice parameter is in good agreement with experimental band gap. The calculation indicates that the Fe doped compound is direct transition semiconductors with half-metallic property. With the increase of Fe-doping concentration, the Fermi level shifts towards valence band. The impurity may change the property of the bond formation to some extent, and make it to have metallic bond characteristic. The total magnetic moment is mainly due to 3d states of Fe atoms and small induced magnetic moment exists due to other nonmagnetic atom, with a magnetic moment of about 4.0 μ_B per Fe-dopant. We have also computed and interpreted the absorption spectrum corresponding to the imaginary part of dielectric function in the range 0-40 eV. The peaks are related to the transition of electrons, which indicates internal relationship between the electronic structures and optical properties. The absorption of visible light can be enhanced after Fe doping.

Keywords: Spintronics, Electronic structure, DFT, magnetism, optical properties.

PACS: 71.15.Mb, 73.20.at, 71.20.Gj,

INTRODUCTION

Hafnium oxide (HfO₂) is a dielectric material with several potential applications. It is a nice substitute for silicon dioxide (SiO₂) which is extensively used as gate dielectric material in metal-oxide-semiconductor. Among these, the binary metal oxide-based receives a great deal of attention due to its multifaceted advantages, such as the simple metal-insulator-metal (MIM) sandwich configuration, high density storage high speed to read and write, low power consumption compatible with CMOS and the small size of device for the resistance switching (RS) phenomenon which is just localized to one or a few conducting channel parts. High temperature ferromagnetism have been obtained for 3d transition metal binary oxide materials such as ZnO [1], TiO₂ [2], SnO₂ [3], ZrO₂ [4]. Hong et al. measured the ferromagnetism in Fe doped HfO₂ thin-films and showed that the ferromagnetism is caused by O vacancy [5]. Ran et al. measured the PL-spectra and ferromagnetism in Co doped HfO₂ [6]. Rao et al. studied the structural and magnetic properties of Fe and Co (5% each) doped HfO₂ thin films by PLD technique [7].

Till now monoclinic phase of Hafnia has been studied extensively as compared to other phases. We

have investigated in detail electronic, optical and magnetic properties of Fe doped cubic HfO₂.

METHODOLOGY

The calculations reported in this work are computed using generalized gradient approximation (GGA) as given by PBEsol [14] and TB-mBJ potential given by [15,16] as implemented in WIEN2K computer code [17] which is based on FP-LAPW scheme.

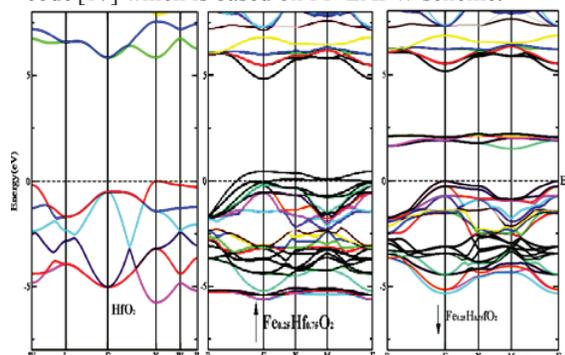


FIGURE 1. High symmetry direction of Energy bands of pure and Fe doped c-HfO₂ (Spin Up and Spin Down).

The behavior of wave function inside the MT sphere is controlled by keeping spherical harmonic function $l_{max}=10$. The convergence criteria is controlled by keeping the cut-off parameter $R_{MT} \times K_{max} = 7$, where R_{MT} is the radius of the smallest atom and K_{max} is the magnitude of the largest wave vector in the unit cell. For the integral over the irreducible Brillouin zone we used 165 and 864 k-points for pure and Fe doped c-HfO₂, respectively. The MT sphere radii (R_{MT}) for each atom are tabulated in Table1. HfO₂ exist the cubic fluorite type structure (space group Fm3m) at high temperature. The atomic positions of Hf and O atoms are (0, 0, 0) and (0.25, 0.25, 0.25), in order.

RESULTS AND DISCUSSIONS

We have modeled a supercell consisting of $1 \times 1 \times 1$ HfO₂ unit-cell, in which one Hf atom is replaced by Fe atom which corresponds to concentrations of 0.25%. After doping, structures and all atomic positions are relaxed during SCF calculations until the atomic forces are reached less than 0.0001Ryd.

The equilibrium values of optimized lattice parameter for pure c-HfO₂ was found to be 5.12Å which is in good agreement to the experiment value 5.08Å [11]. The band structures, shown in Fig.1, in first Brillouin zone are obtained along with the high symmetric directions W-L-Γ-X-W-K and R-Γ-X-M-Γ for pure and Fe doped c-HfO₂, respectively. From Fig.1 it can be observed that c-HfO₂ is a direct band gap insulator as the top valence and the bottom conduction are found at the same Γ point. The calculated band gap of pure c-HfO₂ is 5.81 eV, which is in reasonable agreement with earlier experimental

[8, 9]. It is found that for Fe doped c-HfO₂ the minority channel is metallic in nature whereas majority channel is insulating with an indirect energy gap 6.70 eV shown in Fig.1

The total density of states (DOS) for c-HfO₂ is shown in Fig. 2(a). The totally DOS shows the nonmagnetic character. From the DOS curve, it is clear that valence band is dominated by O-2p states. Hf 5d states contribute a little to valence band, whereas the conduction band of Hafnia is mainly composed of Hf 5d state. The DOS curves for Fe-doped c-Hafnia are shown in Fig. 2(b). From Fig. 2, we can say that Fe-doped c-Hafnia is half-metallic material with the spin-up states for Fe crossing the Fermi level. From the DOS curve, it is clear that the Fermi level passes through the minority-spin component, i.e., shows the metallic character for minority-spin component, whereas band gap exists for majority-spin component, which indicates that the system is half-metallic. From the partial density of states (PDOS) curve, it is clear that the substitution of dopant-induced impurity level contains a large contribution of the Fe 3d states and O 2p states. Also, not only Fe- 3d states are available at the Fermi level, but O p states are also present at the Fermi level which results in p-d coupling. This p-d coupling may result in parallel alignment of magnetic moments of the Fe and its neighboring O atom. In case of Fe-doped oxides, there exist ferromagnetic coupling between Fe and Hf atoms. On decreasing the concentration, the nature of coupling should be changed, and there exist a ferromagnetic coupling between Fe and O atoms, whereas anti-ferromagnetic coupling between Fe and Hf atom.

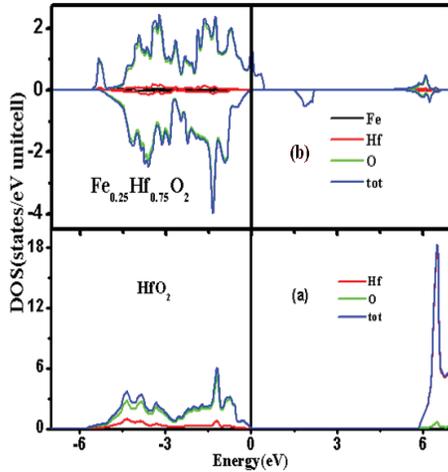


FIGURE 2. Total DOS of pure and Fe doped HfO₂

Table 1: Input parameters

	HfO ₂	Fe _{0.25} Hf _{0.75} O ₂
a(Å)	5.12	5.243
E _g (eV)		
PBE-sol	3.70	No gap↑ 0.50
mBJ	5.81	No gap↑ 1.81↓
Exp.	5.80[8,9]	-----
α(hν)(Å)	6.34	7.34
Exp.	5.68[10]	-----
R _{MT} (Å)	Hf=2.20 O=1.91	Fe=2.00 Hf=2.00 O=1.71
Tot.	-30476.7	-94269.88
Energy (Ryd.)		
m _{Fe} (μB)		4.00
m _{Hf} (μB)		0.05061
m _O (μB)		-0.6526
m _{tot} (μB)		4.15

The optical properties can be calculated by the complex dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$, where $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are the real and imaginary parts of the dielectric function, respectively. The imaginary part of the dielectric function $\epsilon_2(\omega)$ of the pure c-HfO₂, and Fe doped HfO₂ is shown in Fig. 3(a) with energy up to 40 eV. For pure HfO₂, there are five main peaks located at 10.77, 12.60, 16.7 eV, 20.0 and 34.85 due to the electronic transition from the *s* states of O to the *d* states of Hf while the imaginary parts $\epsilon_2(\omega)$ of Fe-doped c-HfO₂ have peaks in low energy region, which are originated mainly from the transitions between Fe-*4s* and O-*p* states and Hf-*s* states in the conduction band. On the other hand, compared with other peaks of pure HfO₂, the corresponding peaks for Fe doped c-HfO₂ shift downward in higher region because an optical band gap with Fe doped increases and an excitonic peak is observed in the low energy region. The calculated $\epsilon_2(\omega)$ of pure HfO₂ shows good agreement in the lower energy range with the experimental data measured by Lim et al. [12] and Edwards [13]. The absorption coefficients of pure and Fe doped c-HfO₂ are plotted in Fig.3 (b). The calculated optical band gap for pure c-HfO₂ is in tune with the experimental value 5.68 eV [10]. In UV region, the absorption coefficient decreases for Fe doping, while in near IR region, the absorption coefficient increases. We have observed the absorption spectra mostly prominent in the UV region. We identify the same interband transitions below the plasmon energy are mainly due to O-2*p*-Hf-4*d* at 7–8 eV with mBJ approximation.

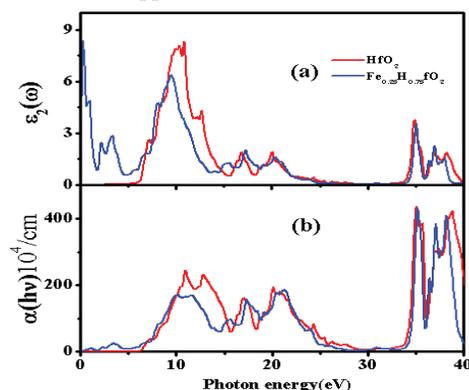


FIGURE 3. Optical properties of pure and Fe doped HfO₂

CONCLUSIONS

In conclusions, we have used Wien2k code based on FPLAPW (mBJ) method to calculate the accurate ground state electronic structure and to understand the origin of magnetism in Fe-doped c-HfO₂. With the Fe doping, Fe-3*d* bands are introduced in the host

material. It is found that Fe-doped c-HfO₂ is half-metallic and the half-metallicity remains intact on reducing the Fe concentrations. This property shows that Fe doped c-HfO₂ is suitable for spin-dependent devices. The main contribution to magnetic moment comes from Fe atom due to the presence of 3*d* states. The calculated dielectric function and absorption coefficient shows consistency with the experimental results.

ACKNOWLEDGMENTS

We are grateful to Prof. Blaha and his team for the Wien2k code. One of the authors K.C Bhamu acknowledges University Grant Commission (UGC), New Delhi for providing financial assistantship under Dr. D.S. Kothari Post-doctoral Fellowship.

REFERENCES

1. S.J. Pearton D.P. Norton M.P. Ivill, A. F. Hebard, J. M. Zavada, W. M. Chen, and I. A. Buyanova *IEEE Trans. On Electron Devices* **54**, 1040 (2007).
2. T. Umabayashi T. Yamaki, H. Itoh and K. Asai, *J. Phys. and Chem. of Solids* **63**, 1909 (2002)
3. Y. Feng, W. Ji, B.J. Huang, X. Chen, F. Li, P. Li, C. Zhang and P.J. Wang *RSC Adv.* **5**,24306 (2015).
4. M. Boujnah H.Zaari H.Labrim O. Mounkachi *J. of App. Phys.* **115**, 123909 (2014).
5. N. H. Hong, N. Poirot and J. Sakai *App. Phys. Let.*, **89**, 042503 (1993).
6. J. Ran and Z. Yan *J. Semiconductor*, **30**, 102002-1 (2009).
7. M. S. R. Rao, D.C. Kundaliya, S. Dhar, C. A. Cardoso, A. Curtin, S. J. Welz, R. Erni, N. D. Browning, S. E. Lofland, C. J. Metting, S. B. Ogale and T. Venkatesan *MRS Proc.* **830**, D6.13 (2004).
8. P. W. Peacock and J. Robertson, *J. Appl. Phys.* **92**, 4712 (2002).
9. A. A. Demkov, *Phys. Stat. Sol. (b)* **226**, 57 (2001).
10. M. Balog, M. Scheiber, M. Michman, and S. Patai, *Thin Solid Films* **41**, 247 (1977)
11. J. Wang, H. P. Li, and R. Stevens, *J. Mater. Sci.* **27**, 5397 (1992).
12. S.G. Lim, S. Kriventsov, T. N. Jackson, J. H. Haeni, D. G. Schlom, A. M. Balbashov, R. Uecker, P. Reiche, J. L. Freeouf, and G. Lucovsky, *J. Appl. Phys.* **91**, 4500 (2002).
13. N. V. Edwards, *AIP Conf. Proc.* **683** (1), 723 (2003).
14. J. P. Perdew, A. Ruzsinszky, G. I. Csonka, O. A. Vydrov, G. E. Scuseria, L. A. Constantin, X. Zhou, and K. Burke, *Phys. Rev. Let.* **100**, 136406 (2008)
15. F. Tran and P. Blaha, *Phys. Rev. Lett.* **102**, 22640 (2009).
16. A. D. Becke and E. R. Johnson, *J. Chem. Phys.* **124**, 221101 (2006).
17. P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka, J. Luitz: WIEN2k, An augmented plane wave + Local Orbitals Program for calculating Crystal Properties, Techn. Universitat Wien, Wien, Austria, 2001, ISBN 3-9501031-1-2.