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Influence of La on electronic structure of α-Al_2O_3 high k-gate from first principles

S.M. Hosseini*, H.A. Rahnamaye Aliabad, A. Kompany

Department of Physics, Ferdowsi University of Mashad, Iran

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Abstract

The theoretical effects of La on electronic structure of Al_2O_3 high k-gate have been studied by first principles. The electronic properties of pure α-Al_2O_3 and La aluminates ($Al_{2-x}La_xO_3$, $x = 0.50$) were studied by using the density functional theory. The calculations were performed by the full potential-linearized augmented plane wave (FP-LAPW) method with the generalized gradient approximation (GGA). The calculated electronic structure and charge density yield a band gap of ~6.4 eV for pure α-Al_2O_3 (without empirical correction factor) at the Γ point in the Brillouin zone, fairly close to experimental values. The substitution of La reduces the band gap to ~3.6 eV for $Al_{1.5}La_{0.5}O_3$. The calculated density of states (DOS) of α-Al_2O_3 is in good agreement with recent experimental XPS and XES data.

Keywords: α-Al_2O_3; La; Band structure; Ab initio

1. Introduction

The electronic structure of alumina (Al_2O_3) is increasingly of interest for its variety of applications in optical, electronic and structural devices. For instance, the α-Al_2O_3 is used in electronics, the γ-phase in catalysts, and the κ-phase for cutting tools.

Alumina also is a gate dielectric replacement candidate due to its higher band gap and band offset properties similar to silica, and higher dielectric constant. There are also some efforts in determining its electronic structure from either ab initio or by experimental for pure Al_2O_3 [1–8], and by substituting Al with a transition metal as high k-gate dielectric replacement materials [9–11]. However, most of the studies carried out up to now are experimental and a few theoretical investigations so far have been done.

The aim of this study is to investigate the influence of La doping on the electronic band structure, density of state, of α-Al_2O_3.

2. Method of calculation

The corundum structure consists of hexagonal close-packed oxygen atoms with cations filling up two-third of the central octahedral sites. The hexagonal Al_2O_3 structure can be built up by placing close-packed planes of oxygen and aluminum ions, but this would give equal numbers of atoms, so one-third of the Al sites must be empty. The most convenient unit cell of α-Al_2O_3 is a rhomboheral prism comprising six such (0 0 0 1) oxygen planes separated by the associated pair of aluminum planes. The cell contains just one Al atom and three O atoms in each plane.

Although typically Al atoms are in the center of tetrahedrally and octahedrally coordinated with four and six atoms, respectively, the most widely known crystal structure α-Al_2O_3 contains all Al atoms in octahedral coordination and we chose this structure for study. The α-Al_2O_3 (corundum) structure (Fig. 1) belongs to the space group *R*-3*c* (number: 167).

The unit cell used for $Al_{1.5}La_{0.5}O_3$ is shown in Fig. 2. It consists of six oxygen layers of alumina O1, O2, O3, O4, O5, O6 with 18 oxygen atoms in total, plus nine Al layers Al1, Al2, Al3, Al4, Al5, Al6, Al7, Al8, Al9 with nine Al atoms

* Corresponding author. Tel.: +98 511 8435723.
E-mail address: sma_hosseini@yahoo.com (S.M. Hosseini).

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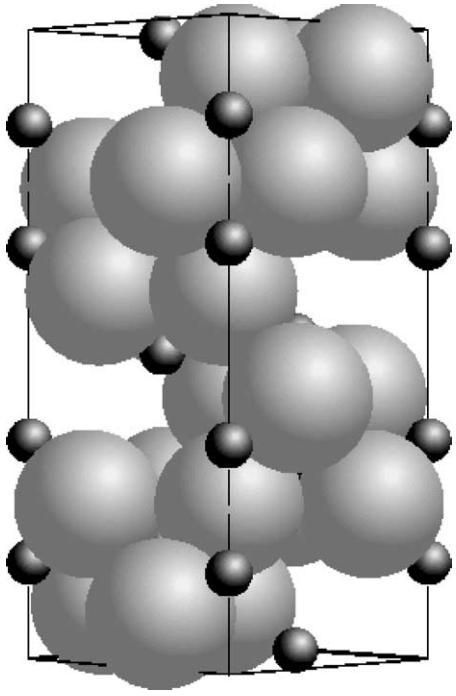

Fig. 1. The structure of α-Al_2O_3, the large circle is O atom and the smaller one is Al atom.

and three La layers La1, La2, La3 with three atoms all in octahedral positions, resulting in 30 atoms in unit cell. We suppose that substitutions of La most likely may occur at octahedral sites within the alumina structure. The lattice constant is $a = b = 8.98$ au, $c = 24.54$ au (1 au = 0.529 Å).

Calculation of electronic structure, of α-Al_2O_3 and $Al_{2-x}La_xO_3$ has been made with the self-consistent scheme by solving the Kohn-Sham equation using a full potential-linearized augmented plane wave (FP-LAPW) method in the framework of the DFT with the generalized gradient approximation (GGA) method [12,13] by WIEN2k package [14].

In the FP-LAPW method, space is divided into two regions, a spherical ''muffin-tins'' around the nuclei in which the radial solutions of Schroedinger equation and their energy derivatives are used as basis functions, and an ''interstitial'' region between the muffin-tins in which the basis set consists of plane waves. There is no pseudopotential approximation and core states are calculated self-consistently in the crystal potential.

Core states are treated fully relativistically, semi-core and valence states are treated semi-relativistically (i.e. ignoring the spin–orbit coupling). The energy cut-off in which defines the separation of core and both semi-core and valance states −6 Ry was chosen.

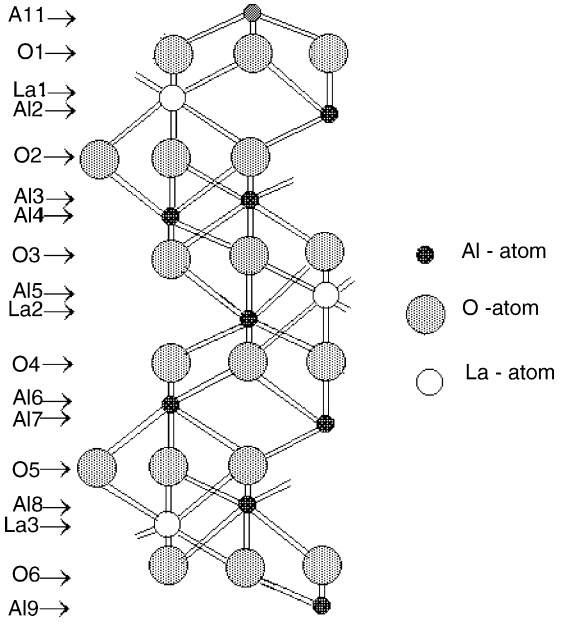

Fig. 2. The unit cell of α-$Al_{2-x}La_xO_3$ (where $x = 0.5$) used in this study.

3. Results and discussion

The pure α-alumina was first studied and calculation is performed with 400 k-points and $Rk_{max} = 7$ for the convergence parameter for which the calculations stabilize and convergence in terms of the energy are achieved. This gives well-converged basis sets consisting of approximately 2470 plane waves. Under this condition, the values of the other parameters are $G_{max} = 14$, R_{MT} (Al) = 1.7 au, R_{MT} (La) = 1.8 au, R_{MT} (O) = 1.7 au. The iteration halted when the total charge was less than 0.0001 between steps as convergence criterion.

The calculated electronic band structure of α-Al_2O_3 is shown in Fig. 3. The zero of the energy was set at the top of

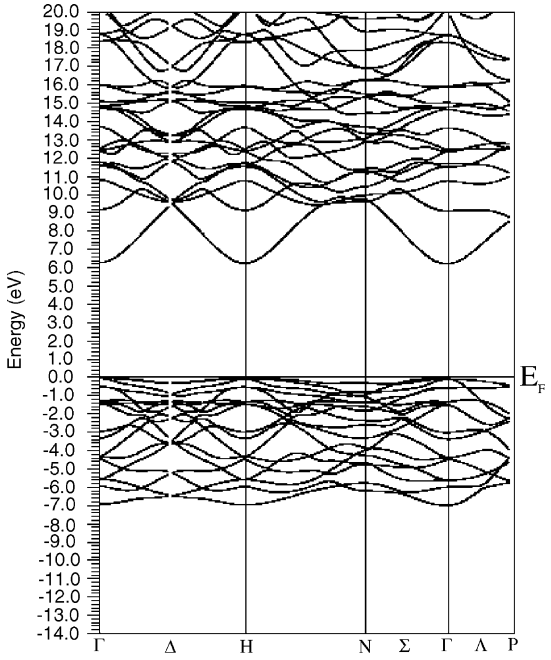

Fig. 3. The calculated electronic band structure of the α-Al_2O_3. The zero of the energy was set at the top of the valance band.

Table 1
α-Al_2O_3 band gap calculated by various methods

Methods	Band gap (eV)
Experimental	
α-Alumina [3]	∼10.8
α-Alumina [7]	∼8.8
Amorphous alumina [15]	∼8.7
Theory (LDA)	
κ-Alumina [4]	∼5.3
α-Alumina [11]	∼6.2
FP-LAPW (GGA) α-alumina (this work)	∼6.4

the valance band. The energy scale is in eV and the origin of energy was arbitrarily set to be at the maximum valance band. Fig. 3 shows a large dispersion of the bands near the top of valance band and the FP-LAPW method yield a band gap ∼6.4 eV (without empirical correction factor) at Γ point, fairly close to experimental values from ∼8.3 eV to 9 eV [4,15].

The calculated band gap and those of other methods are summarized in Table 1. This value is smaller than the experimental band gap 8.8 eV for α-Al_2O_3, but is higher than any theoretical values calculated and published so far.

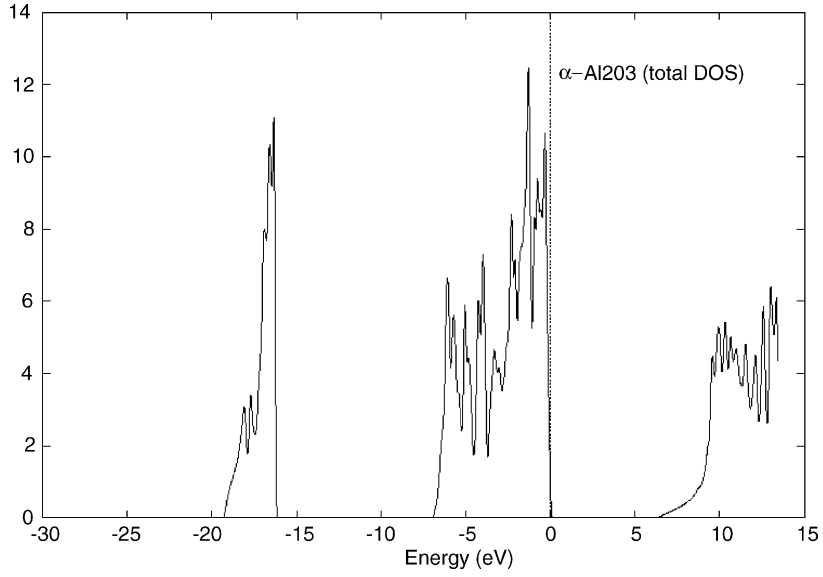

Fig. 4. The total density of states (DOS) for α-Al_2O_3.

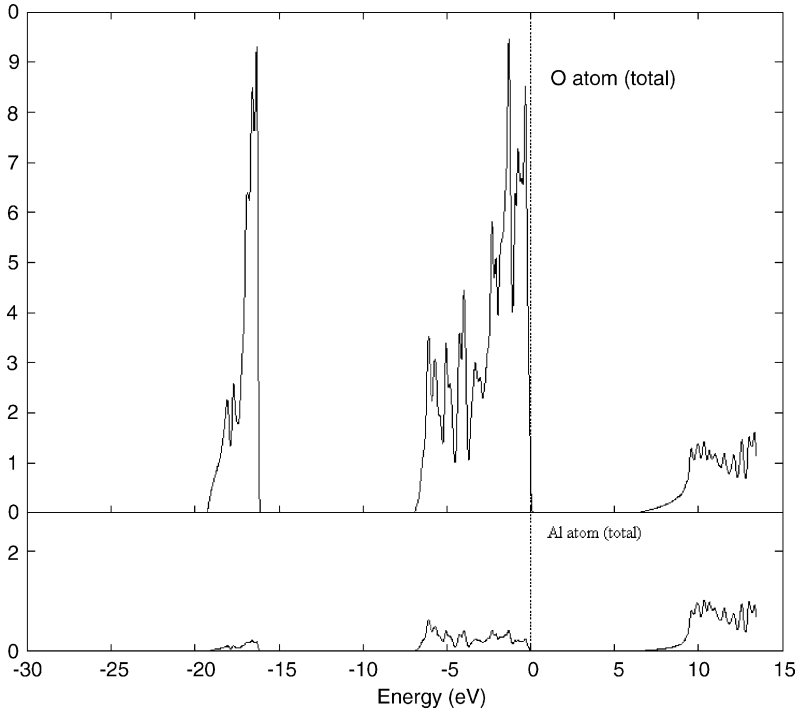

Fig. 5. The total density of state for O and Al atom.

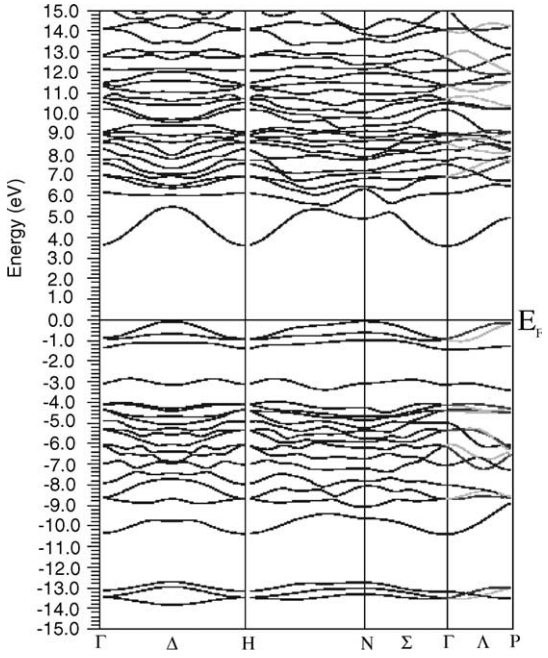

Fig. 6. The calculated electronic band structure for α-$Al_{2-x}La_xO_3$ (where $x = 0.5$). The zero of the energy was set at top of the valence band.

The electron distribution in an energy spectrum is described by the density of states (DOS) and can be measured in photoemission experiments. The total DOS spectrum of α-Al_2O_3 between −30 eV and 15 eV is shown in Fig. 4.

The total DOS of O atom and Al atom are shown in Fig. 5. 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 lies between 0 eV (Fermi energy) to −7 eV, is composed of the O 2p orbital hybridized with the Al 3s, 3p and 3d orbitals. The lower valance is formed predominantly by O 2s atom and extends from −16 eV to −19.5 eV. The contribution of Al 3d and Al 3p in the valance band are rather small (see Fig. 5). The total DOS of Al atom has no distinct peak and its distribution extends over the conduction band.

The calculated electronic band structure of α-$Al_{1.5}La_{0.5}O_3$ is shown in Fig. 6. By comparing Figs. 3 and 6, it can be seen that the substitution of La for Al in α-Al_2O_3 results in reducing the band gap to ∼3.6 eV.

The total density of states of α-$Al_{1.5}La_{0.5}O_3$ is shown in Fig. 7. Substituting by La decreases the number of localized states at the top of the valance band but extends it to −10 eV in this band. The band gap decreases mainly due to the number of state originating from La-d state in the conduction band.

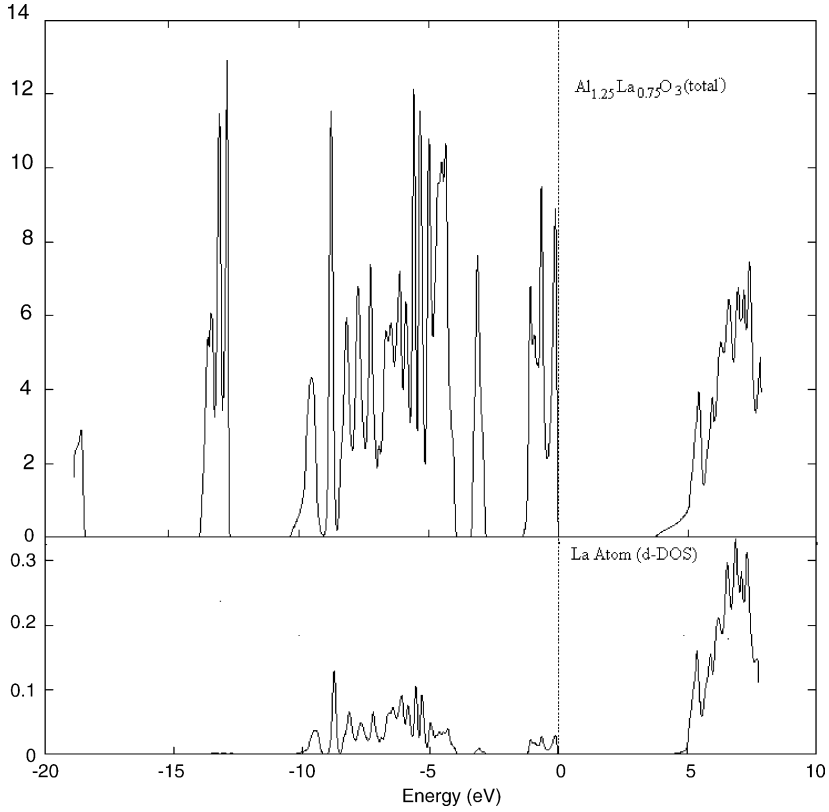

Fig. 7. The total density of states for $Al_{1.5}La_{0.5}O_3$ and partial density of state of La-d orbital.

4. Conclusions

We have calculated the electronic structure and DOS of pure α-Al_2O_3 and La aluminate ($Al_{2-x}La_xO_3$, $x = 0.5$) by using the full potential-linearized augmented plane wave method with the generalized gradient approximation (GGA). The calculations show a band gap of ∼6.4 eV at the Γ point for pure alumina. There are also a large number of relatively localized states at the top of the valance band originating mainly from O 2p atom. The contributions of Al 3d and Al 3p in the valance band are rather small. The total DOS of Al atom has no distinct peak and its distribution extends over the conduction band.

Substituting La for Al reduces the band gap to ∼3.6 eV, mainly due to number of states originating from the La-d state in the conduction band. It also decreases the number of localized states at the top of the valance band but extends it to −10 eV.

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References

[1] R.A. Evarestor, A.N. Ermoshkin, V.A. Lovchikov, Band structure of corundum, Phys. Stat. Sol. 99 (1980) 387–396.
[2] I. Batra, Electronic structure of α-Al_2O_3, J. Phys. C: Solid State Phys. 15 (26) (1982) 5399–5410.
[3] W. Tews, R. Gundler, α-Al_2O_3 and γ-Al_2O_3 energy loss data, Phys. Stat. Sol. 109 (1982) 255–264.
[4] Y. Yourdshahyan, C. Ruberto, M. Halvarsson, L. Bengtsson, V. Langer, B. Lundqvist, Theoretical structure determination of complex material: kappa-Al_2O_3, J. Am. Ceram. Soc. 82 (6) (1999) 1365–1445.
[5] R. Vali, S.M. Hosseini, First-principles study of structural, dynamical, and dielectric properties of κ-Al_2O_3, Comput. Mater. Sci. 29 (2) (2004) 138–144.
[6] R. Ahuja, J.M. Osorio-Guillen, J. Souza de Almeida, B. Holm, W.Y. Ching, B. Johansson, Electronic and optical properties of γ-Al_2O_3 from ab-initio theory, J. Phys.: Condens. Matter 16 (2004) 2891–2900.
[7] R.H. French, D.J. Jones, S. Loughin, Interband electronic structure of α-Al_2O_3 up to 2167 K, J. Am. Ceram. Soc. 77 (1994) 412–422.
[8] M.L. Bortz, R.H. French, D.J. Jones, R.V. Kasowski, F.S. Ohuchi, Temperature dependence of the electronic structure of Al_2O_3, $MgAl_2O_4$ and MgO, Phys. Scripta 41 (4) (1990) 537–541.
[9] M. Haverty, A. Kawamoto, G. Jun, K. Cho, R. Dutton, Preliminary first principle study of Hf and Zr aluminates as replacement high-k dielectric, in: Proceedings of the MRS 2001 Spring Meeting, 2001, pp. 1–10.
[10] M. Haverty, A. Kawamoto, K. Cho, R. Dutton, First-principle study of transition-metal aluminates as high-k gate dielectrics, Appl. Phys. Lett. 80 (15) (2002) 2669–2671.
[11] I.I. Oleinik, E. Yu Tsymbal, D.G. Pettifor, Structural and electronic properties of Co/Al_2O_3/Co magnetic tunnel junction from first principles, Phys. Rev. B 62 (6) (2000) 3952–3959.
[12] J.P. Perdew, J.A. Chevary, S.H. Vosko, K.A. Jackson, M.R. Pederson, D.J. Singh, C. Fiolhais, Atoms, molecules, solids, and surfaces: applications of the generalized gradient approximation for exchange and correlation, Phys. Rev. B46 (1992) 6671–6687.
[13] M. Peterson, F. Wanger, L. Hufnagel, M. Scheffler, P. Blaha, K. Schwarz, Improving the efficiency of FP-LAPW calculations, Comput. Phys. Commun. 126 (2000) 294–309.
[14] P. Blaha, K. Schwarz, WIEN2k, Vienna University of Technology Austria, 2002.
[15] R.H. French, Electronic structure of α-Al_2O_3, with comparison to AlON and AlN, J. Am. Ceram. Soc. 73 (3) (1990) 477–489.