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Electronic Properties of α-Al_2O_3

Abdelkrim Mostefai[1,2,*]

[1] *Department of Electronics, Faculty of Electrical Engineering, University of Sidi Bel Abbes, Algeria*
[2] *Department of Electronics, Faculty of Technology, University of Saida, Algeria*

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Solid-state physics is the study of the fundamental properties of solid, crystalline or amorphous materials, energy bands (band structures or electronic band structures) of solids, it explains the range of energy levels that electrons may have inside it, and the range of energy levels that they may not have. In general, these electrons have the possibility to take that energy values within certain ranges, which are separated by forbidden energy bands (named band gaps). This approach leads to the discussion of band theory. Band theory derives these bands and band gaps by studying the authorized quantum mechanical wave functions for an electron in a large, periodic lattice of atoms or molecules. The band theory has been successfully utilized to describe many physical properties of solids and forms the basis of comprehension of all solid-state devices (transistors, diodes, solar cells, etc.). In this work, the electronic proprieties (band structures, partial and total density of states (DOS), charge density) of α-Al_2O_3 are calculated using ADF-BAND program. The calculations are based on the density functional theory (DFT), pseudopotential approximation and Slater Type Orbital (STO) as basic functions, with local density approximation (LDA) and generalized gradient approximation (GGA). α-Al_2O_3 is a high-k dielectric and has excellent properties (dielectric constant $k \approx 10$ and direct band gap $E_g \approx 8.8$ eV). Al_2O_3, HfO_2 and ZrO_2 are the promising high-k dielectric candidates to replace SiO_2 as the gate dielectric material in MOS transistors.

Keywords: DFT, α-Al_2O_3, LDA, GGA, Slater type orbital (STO), ADF-BAND, SiO_2.

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1. INTRODUCTION

For many years, SiO_2 has been used as a gate insulator in CMOS structures; this is what made possible the accelerated and advanced development of the microelectronic industry. But when it decreases its thickness below a certain value [1, 2], many problems arise [3, 4]. To overcome this problem, it is envisaged to replace the gate dielectric (SiO_2) with a higher permittivity dielectric [5]. Many materials are currently studied to replace SiO_2, the main ones are: Al_2O_3 [6-8], La_2O_3 [9], TiO_2 [10], HfO_2 [11], ZrO_2 [10], and Y_2O_3 [12].

Alumina belongs to the group of large gap metal insulating oxides. Aluminum oxide (Al_2O_3) is one of the most used ceramic materials and has excellent properties (dielectric constant $k \approx 10$, band gap $E_g \approx 8.8$ eV) for replacing SiO_2 [13]. Its excellent dielectric and thermal properties make it the material of choice for a wide range of applications (structural, electronic, and optical devices). It can also be used as an insulating barrier in Josephson diodes [14]. It exists in several crystalline α, γ, κ, λ, η, θ, and χ phases; the hexagonal α phase (α-Al_2O_3 (corundum)) is the most stable at high temperatures; γ, κ, λ, η, θ, and χ alumina are metastable or transition phases. The transition alumina appears as an intermediate phase in the transformation, which tends towards a crystallization of alumina in the α phase. Each of the polymorphs is observed in a certain temperature range. Thus, during the dehydration of aluminum hydroxides, except for the case of the α-AlO(OH) diaspore, we can see a succession of polymorphs, as shown in Fig. 1.

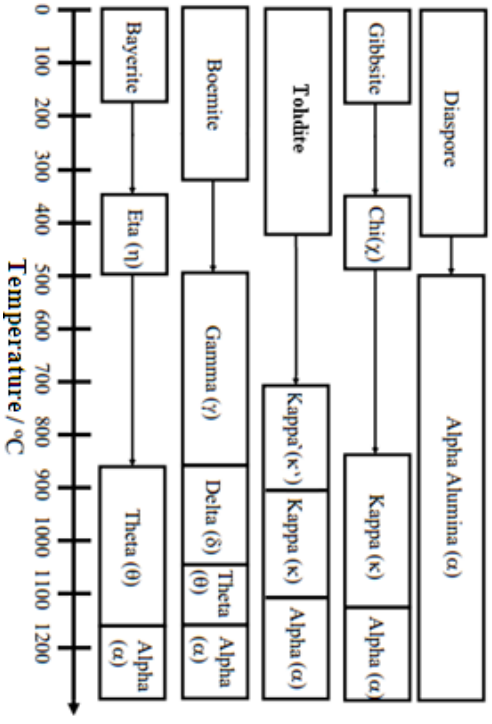

Fig. 1 – Sequence of dehydration and transformation of alumina from aluminum hydroxides

2. COMPUTATIONAL METHOD

In this paper, calculations of the electronic properties of α-Al_2O_3 are based on a self-consistent cyclic solution of the Kohn-Sham equations in the framework of the density functional theory (DFT), pseudopotential

* mostakrimo@yahoo.fr

approximation and Slater Type Orbital (STO) as basic functions, with different exchange-correlation potentials: the local density approximation (LDA) and the generalized gradient approximation (GGA), integrated in the ADF-BAND code. The α-Al_2O_3 unit cell can be determined as hexagonal or rhombohedral (two molecular units), i.e., the number of O and Al atoms in the lattice is six and four (10 atoms), respectively. It can be more easily described with a trigonal unit cell, i.e., a hexagonal crystal system, composed of thirty atoms (six molecular units) (Fig. 2). The trigonal crystal system is described by the space group R-3c, lattice parameters ($a = b$, c) and two internal parameters x_O and z_{Al} relating to the position of oxygen and aluminum.

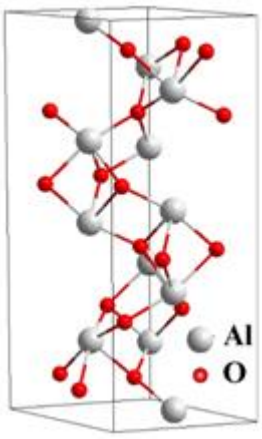

Fig. 2 – Structure of α-Al_2O_3

The solution of the Kohn and Sham equations in the ADF-BAND code is executed in two steps.

- Initialization and the self-consistent cycle. Initialization is a series of programs that generate input files for the purpose of defining a starting density, which is used in the self-consistent cycle to determine the potential and thus to solve the Schrödinger equation which gives the proper values and proper functions.
- This cycle is repeated until convergence is reached.

3. RESULTS AND DISCUSSION

The energy bands give the possible energies of an electron according to the wave vector. These bands are thus represented in reciprocal space, and for simplicity, only the directions of higher symmetries in the first Brillouin zone are treated. Fig. 3 shows the coordinates of high-symmetry points in the Brillouin zone of α-Al_2O_3.

Fig. 4 and Fig. 5 show the band structures of α-Al_2O_3 for LDA and GGA, respectively. The energy level at 0 eV indicates the Fermi level (top of the valence band).

The top of the valence band and the bottom of the conduction band are located at Γ (direct gap). The direct band gaps calculated by GGA and LDA for α-Al_2O_3 are 7 eV and 6.8 eV, respectively. Our calculated value is very close to the experimental one (8.8 eV) [15]. The top of the valence band is very flat, indicating a very large effective hole mass. The conduction bands present a large curvature at the Γ point, indicating a good

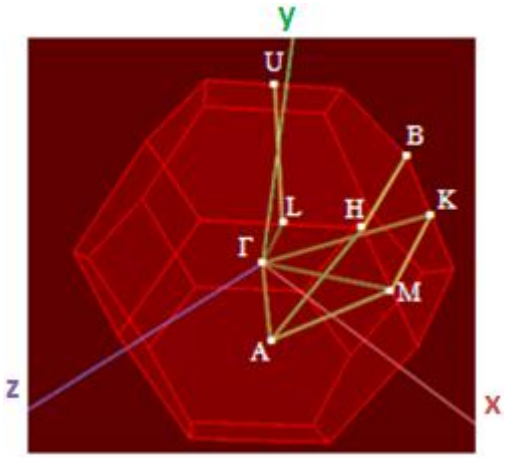

Fig. 3 – Brillouin zones of α-Al_2O_3. Coordinates of high-symmetry points in the Brillouin zone are: Γ (0, 0, 0), A (0.5, 0.5, 0.5), M (0.63, 0.63, 0.23), U (– 0.37, 0.23, – 0.37), L (0.37, 0.77, 0.37), K (0.37, 0.37, – 0.23), H (0.5, 0.77, 0.23), B (0.23, 0.5, – 0.23)

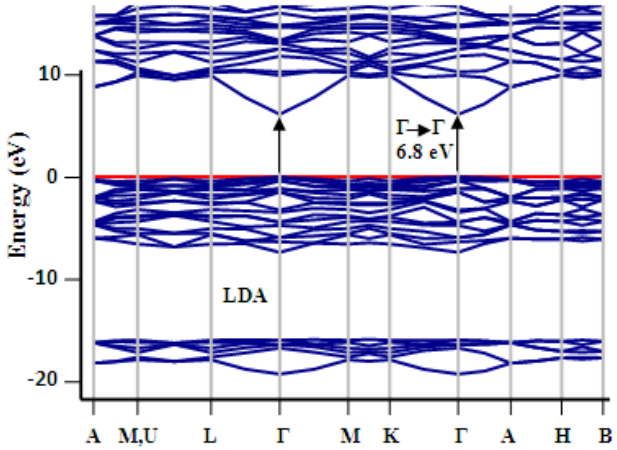

Fig. 4 – Band structure obtained by LDA

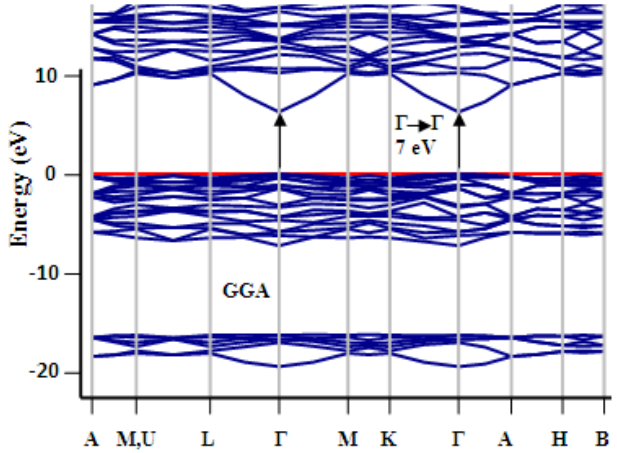

Fig. 5 – Band structure obtained by GGA

mobility of electrons if they only could be excited across the wide band gap.

Fig. 6 and Fig. 7 show the total density of states (DOS) of α-Al_2O_3 for LDA and GGA, respectively. The top of the valence band includes 2p orbitals of oxygen

and 2*p* orbitals of aluminum. The bottom of the conduction band includes 2*p* orbitals of oxygen, 3*s* and 3*p* orbitals of aluminum. The 2*s* orbitals of oxygen and 2*s* orbitals of aluminum make the core states.

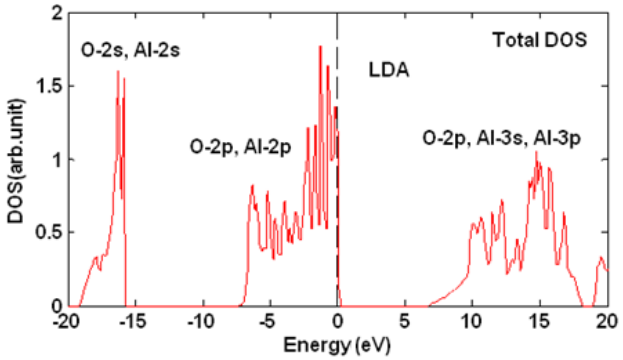

Fig. 6 – Total DOS obtained by LDA

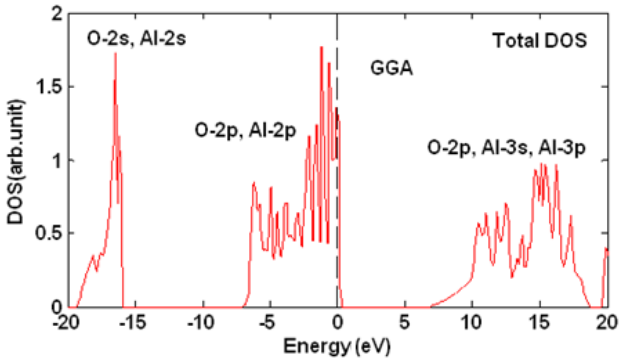

Fig. 7 – Total DOS obtained by GGA

Fig. 8 shows the charge density of α-Al_2O_3 for LDA and GGA, respectively. The valence charge density is treated by neglecting the core states. It is described as having O^{2-} anions arranged in a compact hexagonal manner with Al^{3+} cations, in order to have the highest possible density.

The results in this paper are in good agreement with other theoretically calculated values [16-20].

4. CONCLUSIONS

In this work, the electronic properties of α-Al_2O_3 have been analyzed and examined using the density functional theory (DFT), pseudopotential and Slater Type Orbital (STO) as basic functions implemented in ADF-BAND program. For that, the band structure,

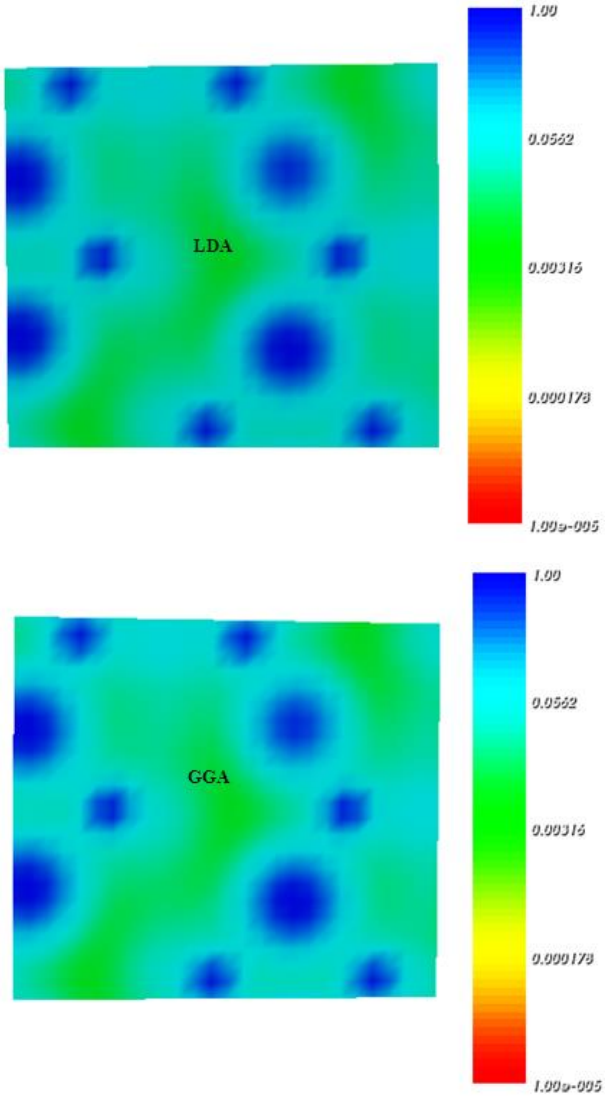

Fig. 8 – Charge density (in e/Å^3) obtained by LDA and GGA

partial and total density of states (DOS), and charge density of α-Al_2O_3 have been performed and treated with density functional theory (DFT) using LDA (local density approximation) and GGA (generalized gradient approximation) for the exchange correlation potential. α-Al_2O_3 is an electrical insulator with a measured direct band gap E_g of 8.8 eV. Our calculation of the direct band gap for α-Al_2O_3 presents good agreement with the experimental measurements.

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Електронні властивості α-Al_2O_3

Abdelkrim Mostefai[1,2]

[1] *Department of Electronics, Faculty of Electrical Engineering, University of Sidi Bel Abbes, Algeria*
[2] *Department of Electronics, Faculty of Technology, University of Saida, Algeria*

Фізика твердого тіла вивчає фундаментальні властивості твердих, кристалічних або аморфних матеріалів, енергетичних зон (зонних структур або електронних зонних структур) твердих тіл. Вона пояснює діапазон рівнів енергії, які електрони можуть мати всередині, і діапазон енергетичних рівнів, яких вони можуть не мати. Загалом, ці електрони мають можливість приймати значення енергії в певних діапазонах, які розділені забороненими енергетичними зонами. Цей підхід веде до обговорення зонної теорії. Зонна теорія отримує ці смуги і заборонені зони шляхом вивчення дозволених квантово-механічних хвильових функцій для електрона у великій періодичній решітці атомів або молекул. Зонна теорія була успішно використана для опису багатьох фізичних властивостей твердих тіл і є основою для розуміння всіх твердотільних пристроїв (транзисторів, діодів, сонячних елементів, тощо). У роботі за допомогою програми ADF-BAND розраховано електронні властивості α-Al_2O_3 (зонна структура, часткова та загальна густина станів (DOS), густина заряду). Розрахунки ґрунтуються на теорії функціоналу густини (DFT), наближенні псевдопотенціалу та орбіталі типу Слейтера (STO) як базових функціях з наближенням локальної щільності (LDA) та наближенням узагальненого градієнта (GGA). α-Al_2O_3 є high-k діелектриком і має чудові властивості (діелектрична проникність $k \approx 10$ і пряма заборонена зона $E_g \approx 8.8$ еВ). Al_2O_3, HfO_2 та ZrO_2 є багатообіцяючими high-k діелектричними кандидатами на заміну SiO_2 як матеріалу затвора в MOS-транзисторах.

Ключові слова: DFT, α-Al_2O_3, LDA, GGA, Орбіталі типу Слейтера (STO), ADF-BAND, SiO_2.