

Charge Density and Density of States (DOS) of Monoclinic ZrO₂ Using Meta-GGA DFT Functional

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In solid-state physics and condensed matter physics, the density of states (DOS) quantifies the number of electronic states susceptible to be occupied and possessing a defined energy in the considered material. This quantity can be calculated as soon as the dispersion relation is known. DOS can be calculated for a wide variety of systems. Certain quantum systems have symmetry due to their crystal structure, which simplifies the calculation of DOS. The total DOS is a parameter that allows determining the electronic conduction properties of a material. For each atom of the crystal, we determine a sphere of radius, inside which we project the electron density onto spherical harmonics (type: *s*, *p*, *d*, or *f*). The partial DOS are used to identify the structure of chemical bonds in a crystal. A first-principles study of the charge density and DOS of monoclinic ZrO₂ (m-ZrO₂) is performed using DFT (density functional theory) with m-GGA (TPSS) functional for the exchange correlation potential, pseudopotential (PP) approximation and STO (Slater Type Orbital) as basic functions integrated in the ADF-BAND code. Zirconium oxide (ZrO₂) is a high-*k* dielectric (*k* ≈ 25 and *E_g* ≈ 6 eV). ZrO₂ is a promising high-*k* dielectric candidate to replace SiO₂ as gate oxide in CMOS because it combines excellent mechanical, thermal, chemical, and dielectric properties.

Keywords: DFT, Monoclinic ZrO₂, Meta-GGA, Slater Type Orbital (STO), ADF-BAND, SiO₂.

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1. INTRODUCTION

With the race for integration and downscaling, parasites effects appear that deteriorate the operation of the transistor and deform the model of the ideal MOS transistor. So, the Moore's law can no longer be applied, it is necessary to introduce a new theme in the work on optimizing the transistor: the integration of new materials [1, 2]. Currently, the research is focused on materials such as Al₂O₃ [3], La₂O₃ [4], TiO₂ [5], HfO₂ [6, 7], ZrO₂ [6] and Y₂O₃ [8], which are thermodynamically stable on silicon. We aim to achieve an interface quality equivalent to that of SiO₂ with these materials. High-*k* research is essentially based on the physical and electrical characterization, to better understand their physical properties (thermal stability, reactivity with the substrate, etc.) and their microstructure, in order to correlate them with their electrical properties.

Zirconium dioxide (ZrO₂) is one of the promising oxides for microelectronics, because it combines excellent mechanical, thermal, chemical, and dielectric properties [9]. Called high-*k* dielectric, it is a promising candidate to replace SiO₂ as the gate dielectric material in MOS (metal-oxide-semiconductor) transistors as the physical thickness of the SiO₂ gate oxide quickly reaches the scaling limit for CMOS (complementary MOS) technology [10, 11]. Their theoretical dielectric constant is evaluated between 20-25 [11, 12]; m-ZrO₂ is an electrical insulator with a band gap energy (the gap that separates the valence band from the conduction band) in the range of 5.1-7.8 eV [13].

ZrO₂ is found in three crystallographic phases: monoclinic (m), tetragonal (t) and cubic (c). The crystal structure of m-ZrO₂, t-ZrO₂, c-ZrO₂ and temperature-related phase transformation is presented in Fig. 1.

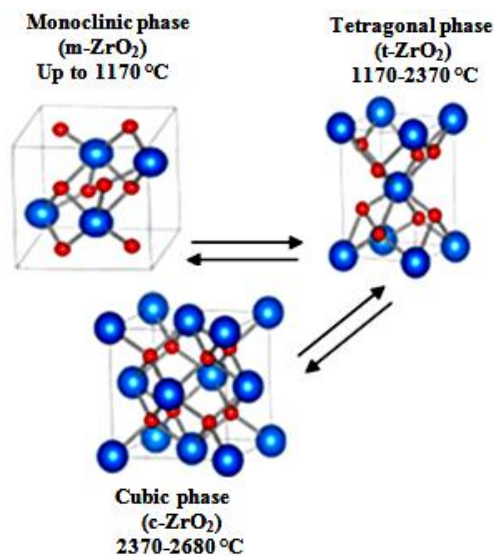


Fig. 1 – Crystallographic phases and temperature-related phase transformation of ZrO₂

The m-ZrO₂ is described by the space group P2₁/c and lattice parameters (*a* = *b* = *c*). The valence electrons for Zr are generated in the 4s²4p⁶4d²5s² configuration. The 2s²2p⁴ configuration is used for the generation of the valence electrons of oxygen. Table 1 shows the space groups and lattice parameters of the three phases of ZrO₂.

2. COMPUTATIONAL METHODOLOGY

A meta-GGA functional in its original form includes the Laplacian (the second derivative) of the electron density. This is a natural development after the gene-

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Table 1 – Crystallographic phases of zirconium oxide at atmospheric pressure

	Cubic phase (c-ZrO ₂)	Tetragonal phase (t-ZrO ₂)	Monoclinic phase (m-ZrO ₂)
Space group	Fm3m	P4 ₂ /nmc	P2 ₁ /c
Lattice parameters (Å)	$a = b = c = 5.085$	$a = b = 3.6$ $c = 5.179$	$a = 5.150$ $b = 5.211$ $c = 5.317$ $\beta = 99.23^\circ$

ralized gradient approximation (GGA). That includes only the density and its first derivative in the exchange-correlation potential. Actually, a meta-GGA functional is referred more typically to one that includes a dependence on the kinetic energy density (τ) [14], instead of the Laplacian because it is numerically more stable. Available functionals of this type are TPSS, tHCTH, VSXC and M06L. In this paper, calculations are based on DFT, pseudopotential (PP) approximation and STO (Slater Type Orbital) as basic functions, m-GGA (TPSS) is applied for the exchange-correlation potential integrated in the ADF-BAND code.

In this context, this paper describes the charge density and the density of state (DOS) of monoclinic ZrO₂ using meta-GGA DFT functional.

3. RESULTS AND DISCUSSION

The distribution of the valence charge density in a crystal is an essential element of the electronic structure because it explains the character of chemical bonds in the crystal. Ionicity which is associated with the nature of chemical bonds in the crystal provides a method to describe the properties of solids. The ionic nature depends largely on the total valence charge density. In general, the importance of the electronic charge density and density of states (DOS) of a material lies in the fact that they allow us to analyze and understand the nature of the bonds that are formed between the different elements of this material.

The total DOS (density of states) and orbital projected DOS (partial DOS) for m-ZrO₂ are shown in Fig. 2-Fig. 6. The Brillouin band of ZrO₂ (dominated by O 2s orbitals) is from -18.3164 to -15.8592 eV. The valence band of ZrO₂ (dominated by O 2p and Zr 4d orbitals) is from -5.34779 to 0 eV. The conduction band of ZrO₂ (dominated by Zr 4d orbitals) is higher than 3.11 eV. The band gap of m-ZrO₂ is 3.11 eV for m-GGA functional. It is smaller than the experimental

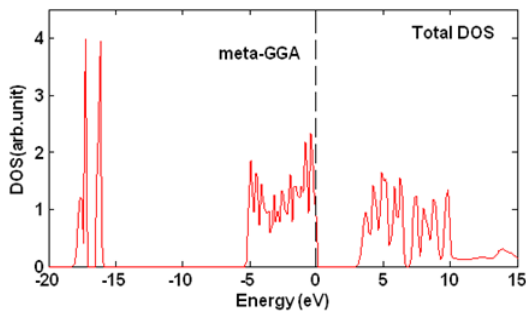


Fig. 2 – Total DOS

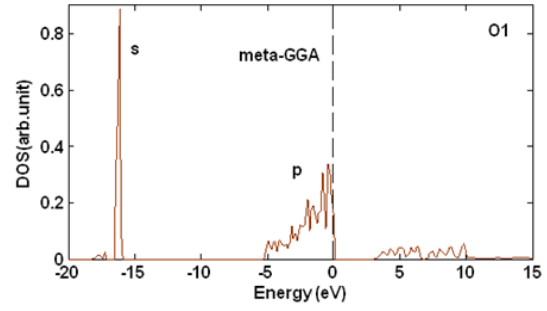


Fig. 3 – Partial DOS for O1

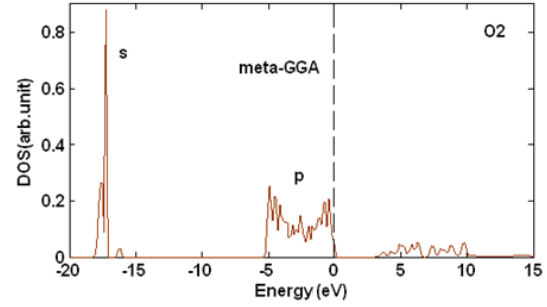


Fig. 4 – Partial DOS for O2

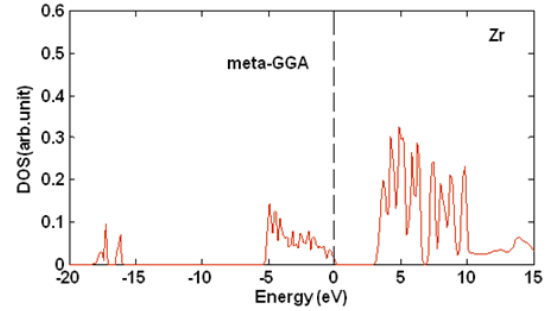


Fig. 5 – Partial DOS for Zr

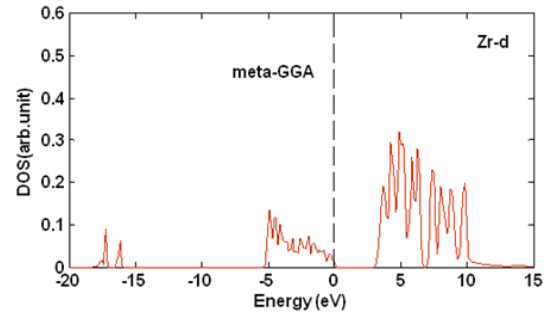


Fig. 6 – Partial DOS for Zr-d

value of 5.42 eV [13, 15].

The valence charge density for various plane positions is shown in Fig. 7 (unit cell: 4 atoms of Zr and 8 atoms of O). The valence charge density is analyzed by eliminating the core states. On the one hand, charge density exists in the outer regions of Zr and O atoms, and on the other hand, it is absent in the interstitial regions. This variation is a characteristic of metallic bonds.

The results of this work are in good agreement with previous results calculated using different approximations [16-20].

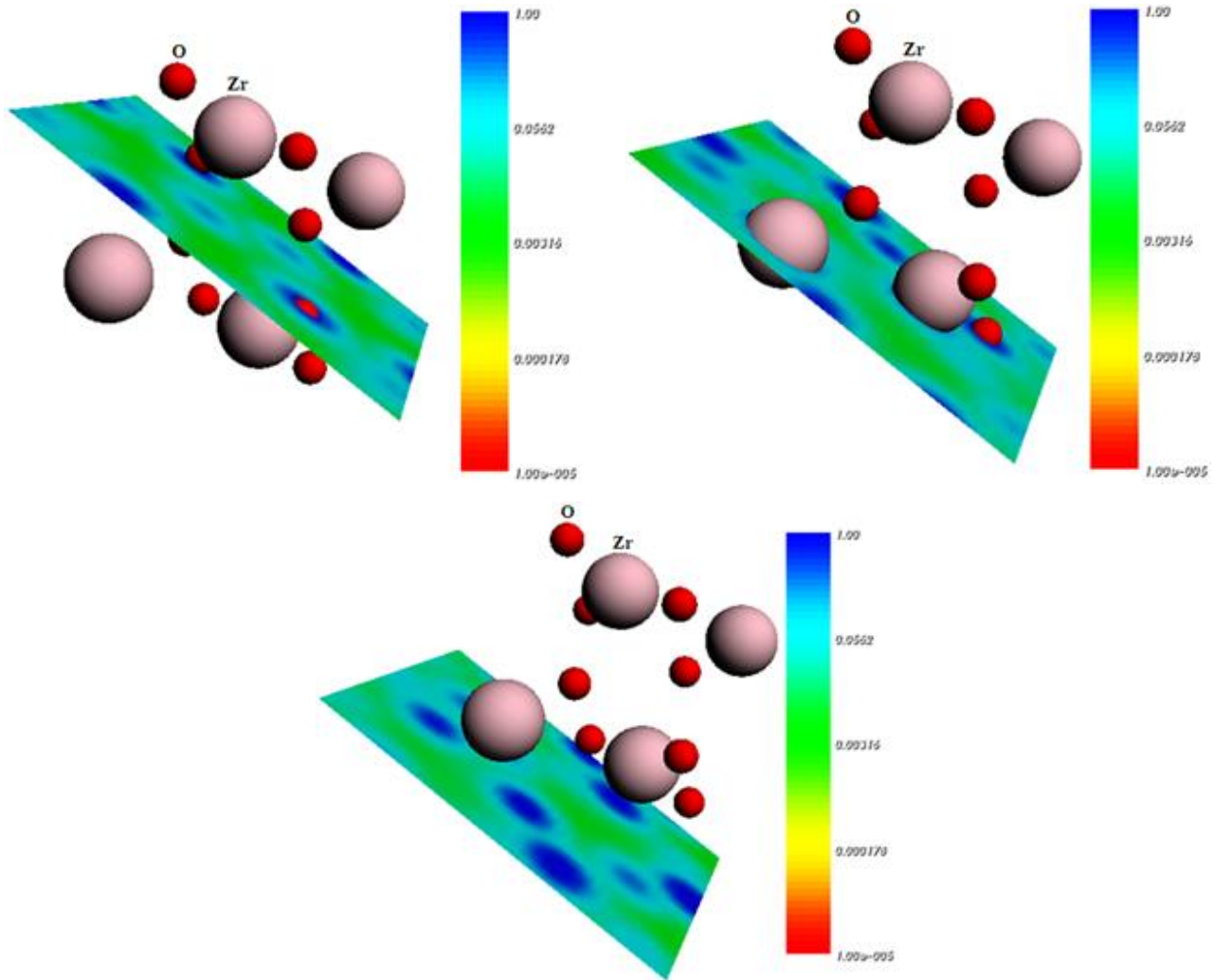


Fig. 7 – Charge density (in $e/\text{\AA}^3$) for various plane positions

4. CONCLUSIONS

Zirconium oxide (ZrO_2) is an important compound in modern technology and materials science. There are different methods and approximations to analyze and treat the electronic properties of ZrO_2 . In this paper, charge density and density of states (DOS) for monoclinic ZrO_2 have been treated with first-principles density functional theory (DFT) using m-GGA (TPSS)

functional for the exchange-correlation potential, Slater Type Orbital (STO) and pseudopotential (PP) approximation. We have found that the calculated properties are in good agreement with previous results. Finally, our future objective is to deepen this study in order to understand and master different theoretical methods and approximations.

REFERENCES

1. A. Mostefai, S. Berrah, H. Abid, *J. Nano- Electron. Phys.* **13**, No 6, 06004 (2021).
2. J. Robertson, *Rep. Prog. Phys.* **69**, 327 (2006).
3. J. Houska, J. Blazek, J. Rezek, S. Proksova, *Thin Solid Films* **520** No 16, 5405 (2012).
4. Y.H. Wu, M.Y. Yang, A. Chin, W.J. Chen, C.M. Kwei, *IEEE. Electron. Device Lett.* **21** No 7, 341 (2000).
5. C. Chaneliere, J.L. Autran, J.P. Reynard, J. Michailos, K. Barla, A. Hiroe, K. Shimomura, A. Kakimoto, *Mater. Res. Soc. Symp. Proc.* **592**, 75 (2000).
6. G.D. Wilk, R.M. Wallace, J.M. Anthony, *J. Appl. Phys.* **87**, 484 (2000).
7. A. Mostefai, S. Berrah, H. Abid, *J. Nano- Electron. Phys.* **10**, No 6, 06026 (2018).
8. M.E. Hunter, M.J. Reed, N.A. El-Masry, J.C. Roberts, S.M. Bedair, *Appl. Phys. Lett.* **76**, 1935 (2000).
9. J. Cizek, O. Melikhova, I. Prochazka, J. Kuriplach, R. Kuzel, G. Brauer, W. Anwand, T.E. Konstantinova, I.A. Danilenko, *Phys. Rev B* **81**, 024116 (2010).
10. M. Houssa, *High-k Gate Dielectrics* (Bristol and Philadelphia: Institute of Physics: 2004).
11. M. Copel, M. Gribelyuk, E. Gusev, *Appl. Phys. Lett.* **76**, 436 (2000).
12. R.M. Wallace, G.D. Wilk, *High-k gate dielectric materials*, *MRS Bulletin* **27**, 192 (2002).
13. M. Houssa, M. Tuominen, M. Naili, V. Afanasév, A. Stesmans, S. Haukka, M. M. Heyns, *J. Appl. Phys.* **87**, 8615 (2000).

14. C.J. Cramer, *Essentials of Computational Chemistry* (2nd Ed.) (Chichester: John Wiley & Sons: 2004).
15. B. Králík, E.K. Chang, S.G. Louie, *Phys. Rev B* **57**, 7027 (1998).
16. M.A. Taylor, R.E. Alonso, L.A. Errico, A. Lopez-Garcia, P. de la Presa, A. Svane, N.E. Christensen, *Phys. Rev B* **85**, 155202 (2012)
17. X. Zhao, D. Vanderbilt, *Mat. Res. Soc. Proc.* **745**, 283 (2011).
18. J.C. Garcia, L.M.R. Scolfaro, A.T. Lino, V.N. Freire, G.A. Farias, C.C. Silva, H.W. Leite Alves, S.C.P. Rodrigues, E.F. da Silva Jr., *J. Appl. Phys.* **100**, 104103 (2006).
19. J. Li, S. Meng, J. Niu, H. Lu, *J. Adv. Ceram.* **6** No 1, 43 (2017).
20. H. Luo, D. Tian, C. Zeng, Y. Fu, H. Wang, *Comput. Condens. Matter.* **11**, 1 (2017).

Густина заряду та густина станів (DOS) моноклінного ZrO_2 з використанням функціоналу Meta-GGA DFT

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У фізиці твердого тіла та фізиці конденсованої речовини густина станів (DOS) визначає кількість електронних станів, які можуть бути зайняті та мають певну енергію в розглянутому матеріалі. Цю величину можна обчислити, якщо відоме дисперсійне співвідношення. DOS можна розрахувати для широкого спектру систем. Деякі квантові системи мають симетрію завдяки своїй кристалічній структурі, що спрощує розрахунок DOS. Загальна DOS є параметром, який дозволяє визначити властивості електронної провідності матеріалу. Для кожного атома кристалу ми визначаємо радіус сфери, всередині якої проектуємо електронну густина на сферичні гармоніки (типи s , p , d , або f). Часткові DOS використовуються для ідентифікації структури хімічних зв'язків у кристалі. Дослідження з перших принципів густини заряду та DOS моноклінного ZrO_2 (m - ZrO_2) виконано за допомогою DFT (теорії функціоналу густини) з функціоналом m -GGA (TPSS) для обмінно-кореляційного потенціалу, наближення псевдопотенціалу (PP) та STO (орбіталі типу Слейтера) як основних функцій, інтегрованих в код ADF-BAND. Оксид цирконію (ZrO_2) є $high-k$ діелектриком ($k \approx 25$ і $E_g \approx 6$ eV). ZrO_2 є багатообіцяючим $high-k$ діелектричним кандидатом на заміну SiO_2 як оксиду затвора в CMOS, оскільки він поєднує чудові механічні, термічні, хімічні та діелектричні властивості.

Ключові слова: DFT, Моноклінний ZrO_2 , Meta-GGA, Орбіталі типу Слейтера (STO), ADF-BAND, SiO_2 .