Journal of the Nigerian Association of Mathematical Physics
Volume 53 **(November *2019 Issue*), pp197 – 200**

FIRST PRINCIPLES INVESTIGATION OF THE STRUCTURAL AND ELECTRONIC PROPERTIES OF $11\bar{2}0$ SURFACE OF WURTZITE COS

Timothy Chibuike Chibueze

Department of Physics and Astronomy, University of Nigeria, Nsukka Enugu State.

Abstract

We have investigated the structural and electronic properties of $11\bar{2}0$ surface of wurtzite cobalt monosulphide (w-CoS) using ordinary generalized gradient approximation (GGA) and addition of coloumb interaction term U to the GGA (GGA+U) within the framework of density functional theory (DFT). The surface energy was studied as a function of the number of layers using GGA and GGA+U for various values of U. A slab of six layers which gave a good convergence for the surface energy was used in the calculation. Ordinary GGA give a metallic property while GGA+U give a direct band gap. Our results are in agreement with the experimental and suggest that $11\bar{2}0$ surface of w-CoS is a potential catalyst and that w-CoS thin film is a good candidate for application as solar absorber in solar cells.

Keywords: Cobalt sulphide; $11\bar{2}0$ surface; Hubbard correction; band gap

1. Introduction

Transition metal chalcogenides (TMCs) have attracted a lot of attention in the last decadeand the interests in them are yet increasing by the day in various applications. W-CoS with space group P63mc (space group number 186) has been shown to demonstrate exceptional properties and promise a lot of applications. It has shown to be a strong catalyst for hydrogen evolution [1,2] and oxygen reduction reaction [3]. It has also been shown by experimental reports to have a potential application as solar absorber in solar cells [4-8]. To the best of our knowledge there is no clear understanding on the surface reactivity of w-CoS and there is no theoretical understanding of the surface structure. It has four low index surfaces which include $11\bar{2}0$, $10\bar{1}0$, 0001 and $000\bar{1}$ surfaces. In the present contribution, we investigate the structural and electronic properties of $11\bar{2}0$ surface of w-CoS. We employ Kohn-Sham equation within the framework of Density Functional Theory (DFT) in our calculations.

2. Theoretical Details

We performed ab-initio DFT spin polarized calculations in the GGA of Perdew, Burke and Ernzerhof (PBE) [9]. For these calculations, plane-wave self-consistent field(PWSCF) method, as implemented in the Quantum-Espresso program package [10] was used. Plane wave basis sets were used to represent wave functions and density of valence electrons with kinetic energy and augmented density cutoff of 40 Ry and 400 Ry respectively. At this cutoff, the total energy is converged to within 1 mRy/atom. Scalar relativistic ultrasoft pseudo-potentials [11] were used to describe the interaction between ions and valence electrons. Co 4s, 3d and S 3s, 3p are treated as valence orbitals. Brillouinzone integration was done over 9 x 9 x 6 k-point grid and 6x6x1 k-points grid sampled by Monkhorst-Packscheme [12] for bulk and slab models respectively. The Brillouin zone integration for the SCF calculation was carried out using the Marzari-Vanderbilt cold smearing scheme with a smearing parameter of 0.005Ry that converges the total energy to about 1 mRy/atom. The optimization criteria forthe ionic geometry relaxation was 0.0001 Ry for total energy and 0.001Ry/au for the Hellmann-Feynman forces. The lattice parameters for the w-CoS is obtained from Ref.4 as a=3.440 angstrom and c=5.790 angstrom. Using the optimized geometric structure, we examined the 11-20 surface. We used a slab of six layers containing a total of 24 atoms, four atoms in each layer. We used a symmetric slab in which the two middle layers were fixed to the bulk position while the rest were fully relaxed. We also performed PBE calculations incorporating on-site coulomb repulsion term Uwhere the on-site parameter was applied only on the Co-3d states. The coulomb repulsion term was added to the ordinary PBE functional

Corresponding Author**:** Timothy C.C., Email: dchibueze@unn.edu.ng, Tel: +2348068002470

using rotationally invariant approach proposed by Dudarev et al [13] in which the coulomb U and exchange J parameters are combined into a single parameter U_{eff}=U-J. From this time onwards, in order to be concise, we will use U in place of U_{eff} . We first obtained U using the linear response approach proposed by Cococcioni et al [14] in which converged value of U=4.8 [8] was obtained for super cells with 16 atoms and thereafter used a U value of 7 eV. We used a vacuum size of 12 Å, 6 Å on each side, in our calculation.

3. Result and Discussion

(a) (b)

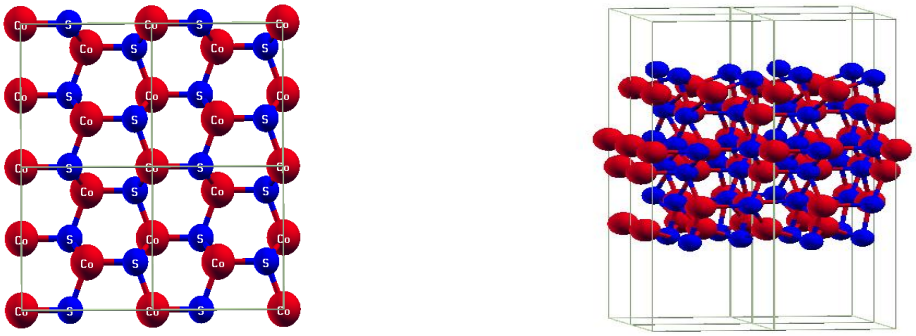


Figure 1: w-CoS $11\bar{2}0$ non polar surface. The blue atoms are the sulphur atoms while the red atoms are the Cobalt atoms. On the left (a) is the surface structure while on the right (b) is the full slab model.

For our slab shown in Figure 1, we calculated the surface energy of the six layer slab using equation (1)

$$\alpha = \frac{1}{2A}[E_S - nE_b] \quad (1)$$

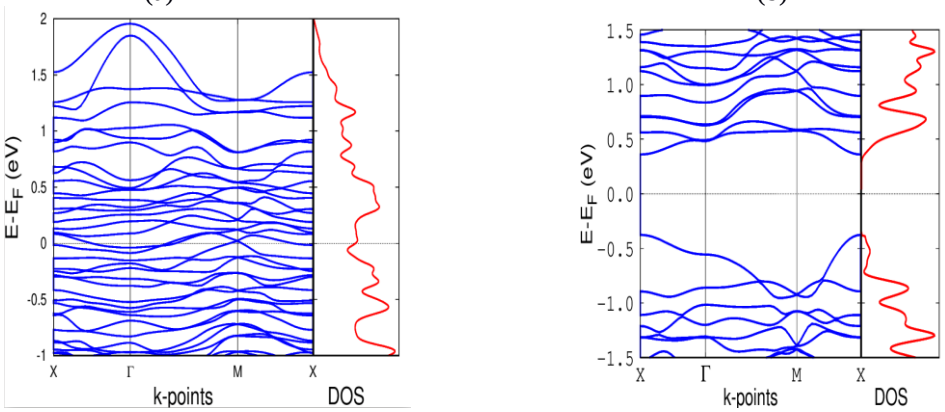
where A is the surface area of the slab and the factor two is to capture both the top and bottom surface of the slab, E_s is the total energy of the slab,E_b is the total energy per formula unit of the bulk and n is the total number of formula units in the slab.

We obtained a value of 0.12 J/m^2 for the surface energy which suggests that the $11\bar{2}0$ surface is good for catalytic applications.

Relaxation of the surface showed some degree of surface reconstruction mainly on the first layer and slightly on the second layer.

We calculated the density of states (DOS) for U values of 0 eV, 4.8 eV and 7.0eV and obtained aband gap of 0, 0.90 eV, 1.59eV respectively. This means that U=0 eV returns a metallic state for the wurtziteCoS while that for U=4.8 eV and 7.0 eV returns a semiconductor. From the DOS, it observed that the states around the top of the valence band are low while that around the bottom of the conduction band are high. From the electronic band structure, we observe that the band gap is directat the symmetry k-point X as shown in Figure 2. Our result for U=7 eV agrees with the experimental results of Kamble [4] and Govindasamy [5] while that of U=4.8 agrees with the result of Basu et al [6]. We suggest that the U value of 4.8 eV obtained from the linear response approach of Cococcioni et al [14] does not accurately explain the electronic properties of wurtziteCoS and so requires a little modification. We therefore recommend a U value of 7.0 eV which gives a much desired band gap value of 1.5 eV (obtained using some advanced experimental procedure) required for optimum performance of wurtziteCoS thin film as an absorption window in solar cells.

(a) (b)



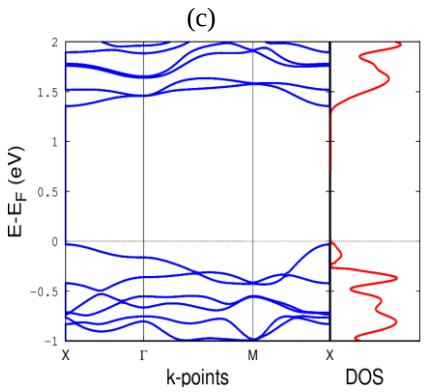


Figure 2: Electronic band structure and DOS for (a) U=0 eV (b)U=4.8 eV and (c) U=7.0 eV

4. Conclusion

We have modeled a six layer slab of the $11\bar{2}0$ surface of w-CoS. The obtained surface energy is relatively small which shows that the surface is promising for use as heterogeneous catalyst in hydrogen evolution reaction. The direct band gap obtained using DFT+U for U=7.0 eV which is in agreement with some experimental data is recommended for the electronic structure of wurtzite CoS.

Acknowledgement

We gratefully acknowledge the Centre for High Performance Computing (CHPC), Cape Town (South Africa) for providing computational resources.

Reference

[1] Y. Sun, C. Liu, D.C. Grauer, J. Yano, J.R. Long, P. Yang, C.J. Chang, Electro deposited cobalt-sulfide catalyst for electrochemical and photo electrochemical hydrogen generation from water, (2013) J. Am. Chem. Soc. 135 17699-17702.

[2] E. Aslan, I. Akin, I.H. Patir, Highly active cobalt sulfide-carbon nanotube catalyst for hydrogen evolution at soft interfaces, (2016) Chem-A. Eur. J. 22 5342-5349.

[3] H. Wang, Y. Liang, Y.Li,H. Dai, $Co_{1-x}S$-graphene hybrid: a high-performance metal chalcogenide electrocatalyst for oxygen reduction, (2011) Angewandte Chem. Int. Ed. 5010969-10972.

[4] S.S. Kamble, A. Sikora, S.T. Pawar, N.N. Maldar, L.P. Deshmukh, Cobalt sulfide thin films: chemical growth, reaction kinetics and micro structural analysis, (2015) J. Alloys and Compd. 623 466-472

[5] G. Govindasamy, P. Murugasen, S. Sagadevan, Optical and Electrical Properties of Chemical Bath Deposited Cobalt Sulphide thin films, (2017) Mater. Res. 20 62-67.

[6] P.K. Basu, P. Pramanik, Solution growth technique for the deposition of cobalt sulphidethin film, (1986) J. Mater. Sci. Lett. 5 1216-1218.

[7] M.S. Sonawane, R.S. Patil, Characterization of chemically deposited nanocrystallinecobalt sulphide thin films, (2014) Int. J. Adv. Sci. Technical Res. 3 57-64.

[8] T.C Chibueze, C.M.I Okoye, First principles study of the structural, electronic and magnetic properties of w-CoS. (2019). Physica B: Condensed Matter, 554, 165-172.

[9] J.P. Perdew, K. Burke, M. Ernzerhof, Generalized gradient approximation made simple,(1996)Phys. Rev. Lett. 77 3865-3868.

[10] Giannozzi P., Baroni S., Bonini N., Calandra M., Car R., Cavazzoni C., Ceresoli D., Chiarotti G.L., Cococcioni M., Dabo I., Corso A.D., de Gironcoli S., Fabris S.,Fratesi G., Gebauer R., Gerstmann U., Gougoussis C., Kokalj A., Lazzeri M., Martin-Samos L., Marzari N., Mauri F., Mazzarello R., Paolini S., Pasquarello A., PaulattoL., Sbraccia C., Scandolo S., Sclauzero G., Seitsonen A.P., Smogunov A., Umari P., Wentzcovitch R.M., (2009). "QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials". J. Phys.: Condens. Matter.21, 395502.

[11] D. Vanderbilt, Soft self-consistent pseudopotentials in a generalized eigenvalue formalism, (1990) Phys. Rev. B. 41 7892-7895.

[12] H.J. Monkhorst, J.D. Pack, Special points for Brillouin-zone integrations, (1976) Phys. Rev. B. 13 5188-5192.
[13] S.L. Dudarev, G.A. Botton, S.Y. Savrasov, C.J. Humphreys, A.P. Sutton, Electronenergy loss spectra and the structural stability of nickel oxide: An LSDA+ U study, (1998) Phys.Rev. B, 57 1505-1509.
[14] M. Cococcioni, S. De Gironcoli, Linear response approach to the calculation of the effective interaction parameters in the LDA+ U method,(2005) Phys. Rev. B, 71 035105-035121.