Structural, Electronic & Magnetic Properties of Pristine and Defected ZnO Monolayer: First-Principles Study

H. K. Neupane, A. Rijal and N. P. Adhikari

Journal of Nepal Physical Society

Volume 9, Issue 1, June 2023

ISSN: 2392-473X (Print), 2738-9537 (Online)

JNPS, **9** (1): 38-44 (2023)

DOI: https://doi.org/10.3126/jnphyssoc.v9i1.57552

Published by:

Nepal Physical Society
P.O. Box: 2934
Tri-Chandra Campus
Kathmandu, Nepal
Email: nps.editor@gmail.com

JNPS 9 (1): 38-44 (2023)
ISSN: 2392-473X (Print), 2738-9537 (Online)
Research Article *© Nepal Physical Society*
DOI: https://doi.org/10.3126/jnphyssoc.v9i1.57552

Structural, Electronic & Magnetic Properties of Pristine and Defected ZnO Monolayer: First-Principles Study

H. K. Neupane[1, *], A. Rijal[2], and N. P. Adhikari[3]
[1]Amrit Campus, Institute of Science and Technology Tribhuvan University, Nepal
[2]Patan Multiple Campus, Institute of Science & Technology Tribhuvan University, Nepal
[3]Central Department of Physics, Institute of Science & Technology Tribhuvan University, Nepal
[*]Corresponding Email: hari.neupane@ac.tu.edu.np

Received: *24th April, 2023;* ***Revised:*** *9th May, 2023;* ***Accepted:*** *18th June, 2023*

HIGHLIGHTS

- Structural, electronic and magnetic properties of hexagonal wurtzite crystalline structure ZnO and oxygen atom vacancy defected ZnO (ZnO_O) are studied by first-principles calculations through Quantum ESPRESSO as a computational tool and XCrySDen as a structure visualization.
- From the calculations of ground state energy, pristine and vacancy defected ZnO are found to be stable materials. Compactness of ZnO decreases in the presence of vacancy defect.
- From band structure and DOS calculations, it is found that ZnO is a n-type and ZnO_O is a p-type semiconducting materials.
- By the analysis of DOS and PDOS calculations, both the materials have non-magnetic properties.

ABSTRACT

Electronic and magnetic properties of materials are appealing properties and have budding applications in the devices. In this work, we have investigated the structural, electronic and magnetic properties of pristine Zinc-Oxide (ZnO) and Oxygen-defected Zinc-Oxide (ZnO_O) materials by spin-polarized density functional theory (DFT) method. Structural properties are studied by calculating their total ground state energy, and found that both are stable 2D materials. It is also found that ZnO have higher stability than of ZnO_O material. Electronic properties of considered materials are examined by analyzing of their band structure, density of states (DOS) calculations and found that ZnO is a direct band gap, n-type semiconductor material in its pristine form and an indirect band gap, p-type semiconductor material in its Oxygen-defected form (ZnO_O). Magnetic properties of pristine and defected ZnO are investigated by analyzing their density of states (DOS) and partial density of states (PDOS) calculations, they revealed that ZnO and ZnO_O have non-magnetic properties.

Keywords: Bands, DFT, Defects, Stability.

1. INTRODUCTION

ZnO is a II^b-VI compound and a wide gap semiconductor with a band gap of (3.44 ± 0.003) eV at 0 K and (3.37 ± 0.005) eV at 300 K. It has a hexagonal wurtzite crystalline structure. In comparison with other II^b-VI and III-V compounds, ZnO has been found to exhibit a stronger polar binding and a larger exciton binding energy. It has a density of 5.6 gcm^{-3} with 4.2×10^{22} molecules/cm^3 [1]. ZnO is a promising material with regards to its optoelectronic property. ZnO research has been heavily driven by the hope of its use in LEDs and LDs in wide spectral ranges [2]. Although GaN is mostly found to be the material of choice when it comes to the manufacturing of UV light emitters (due to

viable p-type technology), ZnO shows great promise for its replacement as it holds many advantages of its own, namely the availability of large area substrates, excess electrons and holes forming tightly-bound excitons, the possibility of low-temperature epitaxial growth, superior radiation harness etc. [2, 3].

Although difficult to realize in the lab, p-type ZnO are found to exist nonetheless [2]. The current situation with ZnO parallels that of GaN many years ago when the workable methods for p-type doping of GaN was not yet realized. Manufacturing proper p-ZnO is the only way to obtain high-quality homojunction ZnO LEDs. Experimental homojunction ZnO LEDs that have been demonstrated so far do not offer the commercial goals required for them to be efficient, reliable, durable and feasible. However, although slow, the progress is continually being made in this field [4-7]. It is very likely that in the coming years, a breakthrough discovery in p-type doping of ZnO will make its appearance and an entirely novel device emitting blue and UV light will be realized [4].

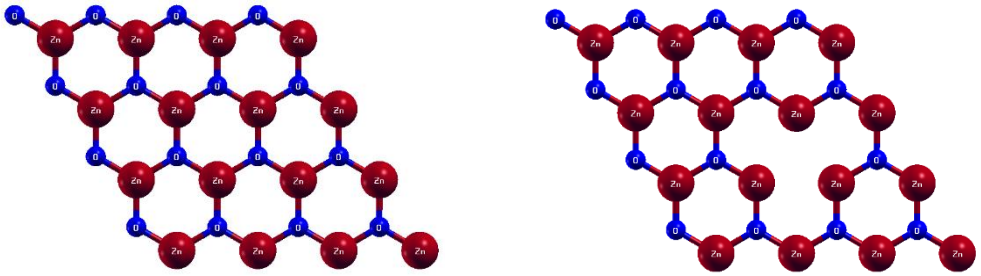
Other aspects that are driving ZnO research include development of nano lasers through nano rods, application in the development of solar cells, application in the development of gas sensors etc. [8]. Single vacancy defect is one of the simplest possible point defects in a crystal, in which, a single atom is removed from the lattice site [9]. Vacancy defect is an inherent property of any crystal above 0 K temperature. The number of such defects increase exponentially with the increase in temperature [10]. Many novel properties can be induced by such point defects, which can lead to the defective materials having properties useful for technological applications; for example, an otherwise nonmagnetic material, graphene is found to exhibit magnetic moment of (1.12 to1.53) μ_B per vacancy defect, depending on the defect concentration [11]. So, studying the effects of such defects is very valuable in the case of ZnO as well.

In this paper, we discuss the structural, electronic and magnetic properties of two-dimensional (2D) pristine ZnO crystal and an Oxygen atom vacancy defected ZnO (ZnO_O) crystal through the analysis of band structure, density of states (DOS) and partial density of states (PDOS) calculations. We have performed this study using spin-polarized density functional theory (DFT) method of calculations through computational package Quantum ESPRESSO (QE) codes and structure visualization tool XCrySDen.

2. METHODS AND MATERIALS

Implemented in the computational package Quantum ESPRESSO (QE) [12], using the spin-polarized density functional theory (DFT) method [13, 14], the calculations of structural, electronic and magnetic properties of pristine and defected ZnO have been performed. All electrons in the systems are treated by the Generalized Gradient Approximation (GGA) using Perdew-Burke-Ernzerhof (PBE) exchange-correlation (XC) functional [15]. Rappe-Rabe-Kaxiraas-Joannopoulos (RRKJ) model of plane-wave ultra-soft pseudopotential [16] has been chosen. The optimized and relaxed, stable ZnO structure is shown in Fig.1(a). Broyden-Fletcher-Goldfarb-Shanno (BFGS) scheme [17] is implemented for the structure optimization and self-consistent field (SCF) calculations, where, the atoms are fully relaxed unless the change in the total energy is below 10^{-4} Ry in between two successive SCF steps and each component of the acting force is below 10^{-3} Ry/Bohrs.

We determined a k-mesh of (16×16×1) from the convergence test, for calculating the self-consistent total energy. Also, for the expansion of ground state electronic wave function, we used kinetic energy cut-off value of 40 Ry and charge density cut-off value of 400 Ry. Furthermore, the Marzari-Vanderbilt (MV) method [18] of "smearing" with a width of 0.001 Ry is used. We used the meshes of (16×16×1) k-points for electronic band structure, and (16×16×1) k-points for density of states (DOS) and partial density of state (PDOS) calculations, where 256 k-points are used along the high symmetric points connecting the reciprocal space for band structure calculations. The (4×4) supercell structure of ZnO monolayer is constructed by extending the unit cell of ZnO along x and y-directions. For Oxygen atom (O) vacancy defected ZnO material, we have removed one O atom from (4×4) supercell monolayer structure of ZnO, and then relax by using BFGS scheme [17] which is shown in Fig.1(b). Findings are obtained from band structure, DOS and PDOS calculations of pristine and vacancy defected materials are described in results and discussion section.



(a) **(b)**

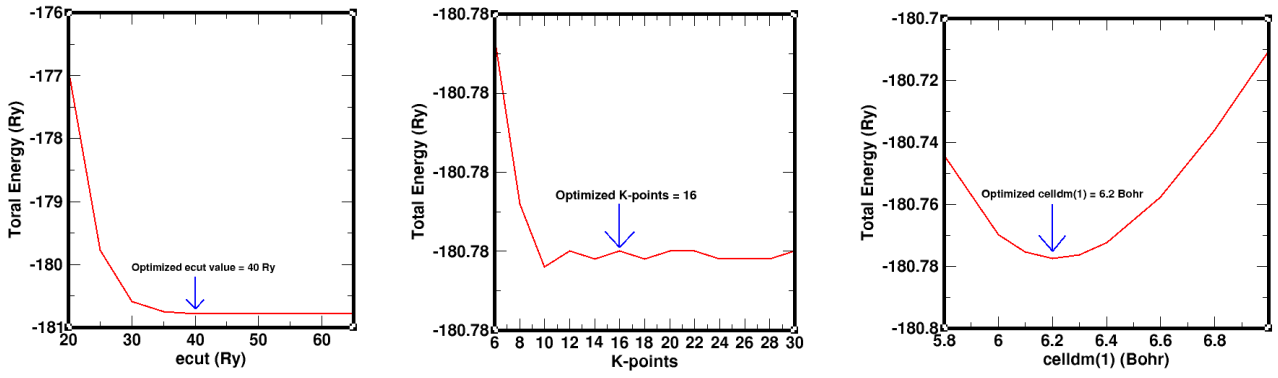
Fig. 1: (Colour online) Optimized and relax stable structures of pristine and vacancy defected ZnO: (a) (4×4) supercell structure of ZnO monolayer material, (b) (4×4) supercell structure of Oxygen atom vacancy defected ZnO monolayer (ZnO_O) material.

3. RESULTS AND DISCUSSION

In this section, we have presented the analysis of structural, electronic and magnetic properties of pristine ZnO and Oxygen atom vacancy defected ZnO materials, and then compared our findings parameters with the reported values available in the literatures.

3.1. Structural Properties

Primitive unit cell of ZnO is extended along x and y-directions in order to obtain its 2D, (4×4) supercell structure. The lattice parameters of ZnO (wurtzite phase) are found to be: a = 3.28 *Å* (or 6.20 Bohr) and c/a = 1.62, which matched closely with the experimentally reported values a ~ 3.25*Å* and c/a ~ 1.60 [1]. These are found out by optimizing the lattice parameters. Along with optimizing the lattice parameters, we also have to optimize the cut-off energy value (or ecut) and number of k-points. The values of optimized parameters such as ecut, k-points and lattice parameter are found to be 40 Ry, 16 and 6.20 Bohr (or 3.28 *Å*) respectively, through the plots of energy versus ecut, k-point and lattice parameters are shown in Fig. 2 (a-c) respectively. Optimized parameters are used in the input file of ZnO, and then performed relax calculations by employing BFGS scheme. The optimized and relaxed stable structure of pristine ZnO monolayer is prepared is shown in Fig.1(a).



(a) **(b)** **(c)**

Fig. 2: (Colour online) Determination of optimized parameters: (a) optimized value of energy cut-off (ecut), (b) optimized value of number of k-points, and (c) optimized value of lattice parameter (celldm1).

The Oxygen atom vacancy defected structure (ZnO_O) is prepared by removing one Oxygen (O) atom from the pristine ZnO material. The prepared ZnO_O structure is relaxed by using the BFGS method and found that it is stable to carry out further calculations. Stability of material is predicted by calculating the total ground state energy of the system, which are given in Table -1. The optimized and relaxed stable structure of ZnO_O is shown in Fig.1(b). The total energy of the system is evaluated by the sum of one-electron contributions, Hartree contribution, exchange-correlation contribution, Ewald contribution and smearing contribution. We obtained these values from self-consistent field (SCF) calculations. Lower value of total energy indicated that the system is more stable [19-21].

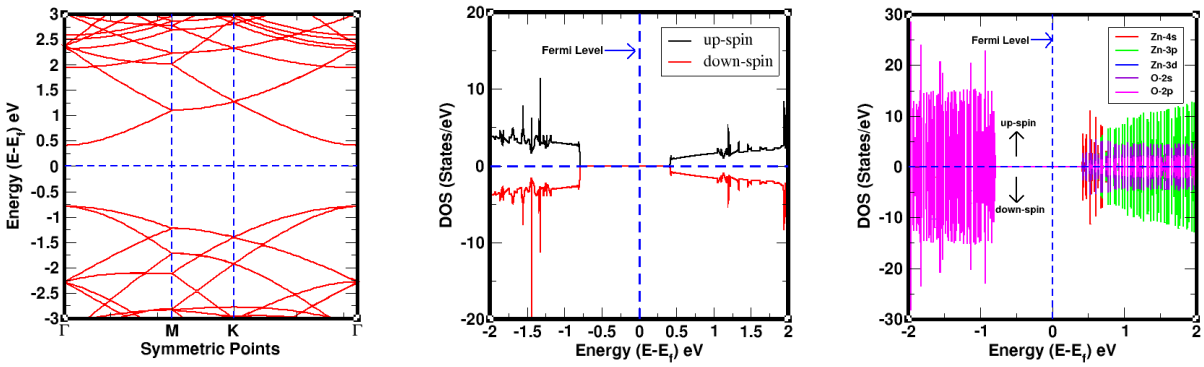
Hence, Pristine ZnO is found to be more stable than O atom vacancy defected ZnO. In addition, we have estimated the average bond lengths around vacancy site in crystal structure of ZnO_O and corresponding bond lengths in crystal structure of ZnO materials are given in Table-1. We found that Zn atoms in ZnO have come closer in ZnO material compared to the corresponding Zn atoms around the O-vacancy site in ZnO_O material. Furthermore, the Zn-O bond lengths of those Zn atoms in ZnO_O material have increased. Both of these results agree with each other in indicating that the material has become less compact upon introducing the defect. Hence, pristine structure of ZnO is more compact and stable material than Oxygen atom vacancy defected ZnO material.

Table-1: Fermi energy (E_f), Fermi energy shift (E_s), bandgap energy (E_g) and total energy (E_t), average bond lengths around vacancy site in ZnO_O and corresponding bond lengths in ZnO of pristine ZnO and vacancy defected ZnO materials.

Materials	(E_f) eV	(E_s) eV	(E_g) eV	(E_t) Ry	Zn-Zn (Å)	Zn-O (Å)
ZnO	-1.53	-	1.20	-2890.18	3.26	1.89
ZnO_O	1.65	3.17	1.37	-2859.92	3.29	1.90

3.2. Electronic and Magnetic Properties

Materials are promising candidate in electronic, spintronic and optoelectronic devices on the basis of their electronic, magnetic and transport properties. Thus, electronic, magnetic and transport properties of material have blossoming application in the fields of devices [20, 22, 23]. Defects (vacancy and impurity) in materials are used to develop the desire properties, they generate attracting properties in the crystalline materials [10, 24, 25]. In the present work, we have investigated the electronic and magnetic properties of considered materials by the analysis of their band–DOS and DOS-PDOS plots respectively. In Fig. 3(a-b) and Fig. 4(a-b), we have shown the band structures and DOS plots of ZnO and ZnO_O materials respectively. Γ-M-K-Γ are chosen as high symmetric points in the irreducible Brillouin zone (BZ) for band structure plots taking 100 k-points along the direction. In the band structure plots, the x-axis represents the high symmetric points in the primary Brillouin zone (BZ) and y-axis represents the corresponding energy values. The horizontal dotted line represents the Fermi level. In the DOS plots, x-axis represents the energy level and the corresponding density of electron states is represented in the y-axis. The dotted vertical line marks Fermi energy level and the horizontal dotted line marks the axis that separates the up-spin states of electron from the down-spin states of electron in the orbitals of all atoms in material samples. The electronic configuration of Zn and O in ZnO are: [Ar] $3d^{10}$ $4s^2$ and [He] $2s^2$ $2p^4$, respectively. Thus, Zn does not have any unpaired electrons in its sub-orbitals, while O has a paired $2p_x$ sub-orbital with two unpaired $2p_y$ and $2p_z$ sub-orbitals. Before investigating about the electronic and magnetic properties of vacancy defected ZnO materials, we need to first study the electronic and magnetic properties of pristine ZnO material.



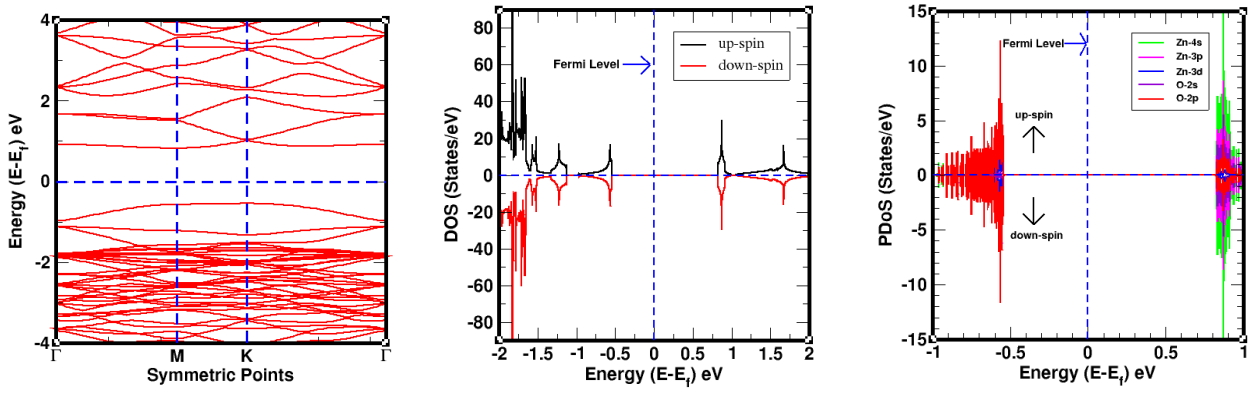
(a) (b) (c)

Fig. 3: (Colour online) Band structure, DOS and PDOS plots of pristine ZnO monolayer: (a) Band structure of ZnO, (b) DOS plot of ZnO and, (c) PDOS plot of ZnO.

From Fig.3(a), we can see that the conduction band edge is at k = 0, the Γ-point, which is also the k-value of the valence band edge for ZnO. Hence, ZnO is a direct band gap semiconductor since the valence and conduction band edges occur at the same k-values. We know that the bandgap is given by, $E_g = E_c + E_v$, where, E_c is the band energy gap in between the lower most conduction band to the Fermi energy and E_v is the energy gap between the uppermost valence band and Fermi energy. From the band structure in Fig. 3(a), we found that E_c = 0.41 eV and E_v = -0.79 eV. Hence, the direct bandgap of ZnO is 1.20 eV, which is sightly differs from the experimental observed value of 3.44 eV [1] because of using DFT with PBE through the GGA approximation.

In addition to the band structure calculations, we have also performed density of states (DOS) calculations. The DOS plot from that calculation is shown in Fig. 3(b), where we can see that the unoccupied up and down spin states of electrons are available 0.79 eV below the Fermi level (in the valence band) and 0.41 eV above the Fermi level (in the conduction band). The band gap being 1.20 eV, which gives a confirmation to the data from the band structure analysis as well. We can easily see here that since the conduction band edge lies much closer to the Fermi energy level, it is an n-type semiconductor. Furthermore, we have investigated the electronic properties of ZnO_O material through electronic band structure and DOS plots as shown in Fig.4. In Fig. 4(a), we can see that the conduction band edge is at k = 0.58, the M-point, which differs from the k-value of the valence band edge for ZnO_O, which is at k = 0.91, the K-point. Hence, ZnO_O is an indirect band gap semiconductor, since the valence and conduction band edges do not occur at the same k-values. From the band structure in Fig. 4(a), we found that E_c = 0.82 eV (at M-point) and E_v = -0.54 eV (at K-point), hence, the direct bandgap energy of ZnO_O is 1.37 eV. Moreover, the band structure calculations, we have also performed DOS calculations is shown in Fig. 4(b). We can see that the unoccupied up and down spin states of electrons are available 0.54 eV below the Fermi level (in the valence band) and 0.82 eV above the Fermi level (in the conduction band). The bandgap being 1.37 eV. This gives a confirmation to the data from the band structure analysis as well. We can easily see here that since the valence band edge lies much closer to the Fermi energy level. So, it is a p-type semiconductor material.

The magnetic properties of ZnO and ZnO_O materials are investigated by the analysis of their density of states (DOS) and partial density of states (PDOS) calculations are shown in Fig. 3(b-c) and Fig. 4(b-c) respectively. From DOS plots (in Fig. 3(b) and Fig.4(b)), we found that up-spin and down-spin states are symmetrically distributed around the fermi energy level, which gives zero value of magnetic moment. Hence, both materials have non-magnetic properties. In addition to the DOS calculations, we also performed the PDOS calculations of ZnO material. The PDOS plot clearly shows that the contribution in the net magnetic moment by the up and down spin states of electrons in 4s-Zn, 3p-Zn, 3d-Zn, O-2s and O-2p orbitals are all zero. Hence, monolayer pristine ZnO is a non-magnetic, n-type direct band gap semiconductor.



(a) (b) (c)

Fig. 4: (Colour online) Band structure, DOS and PDOS plots of Oxygen atom vacancy defected ZnO (ZnO_O) monolayer: (a) band structure of ZnO_O, (b) DOS plot of ZnO_O and, (c) PDOS plot of ZnO_O material.

Similarly, we have analyzed the PDOS plots of ZnO_O material and found that up-spin states of electrons are symmetrically balanced by down-spin states of electrons at all energy values. It shows that ZnO_O is a non-magnetic material. Also, PDOS plot clearly shows that the contribution in the net magnetic moment by up and down spin states of electrons in 4s-Zn, 3p-Zn, 3d-Zn, O-2s and O-2p orbitals are all zero. Hence, ZnO_O is a non-magnetic, p-type, indirect band gap semiconductor.

4. CONCLUSIONS

In the present work, we have investigated the structural, electronic and magnetic properties of hexagonal wurtzite crystalline structure ZnO and oxygen atom vacancy defected ZnO (i.e., ZnO_O) materials using spin-polarized density functional theory (DFT) method. The structures visualization and computational work are carried out respectively through XCrySDden and Quantum ESPRESSO software packages. We found that both materials (ZnO & ZnO_O) are found to be stable material. Compactness of material are decreased in the defected structure than pristine form of ZnO which is due to the unpaired arrangement of spin states of electrons in the orbital of atoms. Electronic properties of these materials are examined by the analysis of their band structure and density of states (DOS) calculations. It is found that ZnO is a direct band gap, n-type semiconductor with a band gap energy 1.20 eV, while ZnO_O is an indirect band gap, p-type semiconducting material. The band gap energy of ZnO_O is found to be 1.37 eV, which is slightly greater than the band gap energy of pristine ZnO. Thus, n-type semiconducting ZnO material changes to p-type semiconducting ZnO_O material due to the presence of O vacancy defect. For the investigation of magnetic properties, we have analyzed density of states (DOS) and partial density of states (PDOS) calculations of ZnO and ZnO_O materials. In these calculations, it is found that up and down spin states of electrons are symmetrically distributed around the Fermi energy level and hence, both materials have zero value of magnetic moment. These calculations revealed that ZnO and ZnO_O materials have non-magnetic properties.

ACKNOWLEDGEMENTS

Authors acknowledge the network project NT-14 of ICTP/OEA, and University Grants Commission (UGC) Nepal, Grants CRG 073/74 -S&T -01.

Author contributions

HKN conceived the idea, HKN and AR carried out all the calculations. Both the authors have written the manuscript. All the authors analyzed the results and read the manuscript.

Declarations conflict of interest

The authors declare no competing interests.

Data Availability

In case reproduction of the figures/tables used in this paper is desired, all the data can be accessed via the corresponding author.

REFERENCES

[1] Madelung, O.; Rössler, U. and Schulz, M. (Eds.). (n.d.). *General Introduction: Datasheet from Landolt-Börnstein - Group III Condensed Matter. Volume 41B: ``II-VI and I-VII Compounds; Semimagnetic Compounds'' in SpringerMaterials.* doi:10.1007/10681719_259 to 0.1007/10681719_313

[2] Look, D. C.; Claflin, B.' Alivov, Y. I. & Park, S. J. *The future of ZnO light emitters. Physica Status Solidi (a),* **201** (10): 2203–2212 (2004).

[3] Look, D. C. Recent advances in ZnO materials and devices. *Materials Science and Engineering: B,* **80** (1): 383–387 (2001).

[4] Rahman, F. Zinc oxide light-emitting diodes: A review. *Optical Engineering*, **58** (1): (2019).

[5] Hwang, D. K.; Oh, M. S.; Lim, J. H. & Park, S. J. ZnO thin films and light-emitting diodes. *Journal of Physics D: Applied Physics*, **40** (R387) (2007).

[6] Choi, Y. S.; Kang, J. W.; Hwang, D. K. & Park, S. J. Recent Advances in ZnO-Based Light-Emitting Diodes. *Electron Devices, IEEE Transactions On*, **57**: 26–41 (2010).

[7] Pearton, S. J. & Ren, F. Advances in ZnO-based materials for light emitting diodes. *Current Opinion in Chemical Engineering*, **3**: 51–55 (2014).

[8] Klingshirn, C.; Fallert, J.; Zhou, H.; Sartor, J.; Thiele, C. et al. 65 years of ZnO research – old and very recent results. *Phys. Status Solidi B.* (2010).

[9] Nordlund, K. & Averback, R. Point Defects in Metals. *Handbook of Materials Modeling*, 1855–1876 (2005).

[10] Kittel, C. & McEuen, P. Introduction to Solid State Physics. *Wiley, New York* (1996).

[11] Yazyev, O. V. & Helm, L. Defect-induced magnetism in graphene. *Phys. Rev. B*, **75:** 125408 (2007).

[12] Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R. et al. QUANTUM ESPRESSO: a modular and open-source software project for

quantum simulations of materials. *Journal of physics. Condensed matter: An Institute of Physics journal*, **21** (39): 395502 (2009).

[13] Hohenberg, P. & Kohn, W. Inhomogeneous Electron Gas. *Physical Review;* **136** (3B): (1964).

[14] Kohn, W. & Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Physical Review;* **140** (4A): (1965).

[15] Perdew, J. P.; Burke, K. & Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.*, **77**: 3865–3868 (1996).

[16] Rappe, A. M.; Rabe, K. M.; Kaxiras, E. & Joannopoulos, J. D. Optimized pseudopotentials. *Phys. Rev. B*, **41**: 1227–1230 (1990).

[17] Pfrommer, B. G.; Côté, M.; Louie, S. G. & Cohen, M. L. Relaxation of Crystals with The Quasi-Newton Method. *Journal of Computational Physics*, **131** (1): 233–240 (1997).

[18] Marzari, N.; Vanderbilt, D.; De Vita, A. & Payne, M. C. Thermal Contraction and Disordering of the Al (110) Surface. *Phys. Rev. Lett.*, **82**: 3296–3299 (1999).

[19] Neupane, H. K. & Adhikari, N. P. Effect of vacancy defects in 2D vdW graphene/h-BN heterostructure: First-principles study. *AIP Advances*, **11** (8): 085218 (2021).

[20] Neupane, H. K. & Adhikari, N. P. Structure, electronic and magnetic properties of 2D Graphene-Molybdenum diSulphide (G-MoS2) Heterostructure (HS) with vacancy defects at Mo sites. *Computational Condensed Matter*, **24**: e00489 (2020).

[21] Neupane, H. K. & Adhikari, N. P. First-principles study of structure, electronic, and magnetic properties of C sites vacancy defects in water adsorbed graphene/MoS 2 van der Waals heterostructures. *Journal of Molecular Modeling*, **27**: 1-12 (2021).

[22] Neupane, H. K.; Bhattarai, B. & Adhikari, N. P. Tuning transport properties of B and C sites vacancy defects Graphene/h-BN heterostructures: first-principles study. *EUROPEAN PHYSICAL JOURNAL B*, **95** (10): (2022).

[23] Neupane, H. K. & Adhikari, N. P. Tuning structural, electronic, and magnetic properties of C sites vacancy defects in graphene/MoS2 van der waals heterostructure materials: a first-principles study. *Advances in Condensed Matter Physics*, **2020**: 1-11 (2020).

[24] Neupane, H. K. & Adhikari, N. P. Electronic and magnetic properties of defected MoS2 monolayer. *BIBECHANA*, **18** (2): 68-79 (2021).

[25] Neupane, H. K. & Adhikari, N. P. Adsorption of water on C sites vacancy defected graphene/h-BN: First-principles study. *Journal of Molecular Modeling*, **28** (4): 107 (2022).