

Density functional theory based investigation of hydrogen adsorption on ZnO (10 $\bar{1}$ 0) surface

Manuel M. Balmeo¹, John Symon C. Dizon¹, Erick John Carlo D. Solibet², Melvin John F. Empizo³, Arnel A. Salvador², Hiroshi Nakanishi⁴, Nobuhiko Sarukura³, and Allan Abraham B. Padama¹

¹ Institute of Mathematical Sciences and Physics, College of Arts and Sciences, University of the Philippines Los Baños, College, Los Baños, 4031, Philippines

² National Institute of Physics, University of the Philippines Diliman, Diliman, Quezon City 1101, Philippines

³ Institute of Laser Engineering, Osaka University, 2-6 Yamadaoka, Suita, Osaka 565-0871, Japan

⁴ National Institute of Technology, Akashi College, 679-3 Nishioka, Uozumi, Akashi, Hyogo 674-8501, Japan

INTRODUCTION

The increasing demands for functional materials and the current trends in device miniaturization have led to intensive research focused on improving material efficiency and durability for various applications. For example, the stability of zinc oxide (ZnO) crystal in radiation environments is the subject of previous works in relation to its application as a scintillator material. Bulk ZnO single crystal is an excellent scintillator because its emission lifetimes are similar regardless of the sample temperature. In a radiation environment, however, energetic particles can generate defects, damage, and/or penetrate the material which could alter its electronic and optical properties. For instance, it was found that hydrogen-ion (H-ion) irradiation of a bulk ZnO crystal on its (10 $\bar{1}$ 0) surface has led to the decrease in the visible transparencies, red shifting of the emission peaks, shortening of the ultraviolet (UV) emission lifetimes, and suppression of the visible emission bands. These observations were then attributed to the generation of defects during irradiation and to the possible interaction of H-ions with the surface. These experimental results provide evidence that H-ions can modify the electronic properties of ZnO. Probing this phenomenon in the atomic scale will unravel the origin of the changes in the electronic properties and will establish mechanisms that will be useful in materials design. The interaction of hydrogen with ZnO surfaces has been investigated in the past using first-principles calculations. Previous investigations focused mainly on the catalytic performance of ZnO, its potential use as a gas sensor, and the modification of the properties of the material (induced metallicity). These reports did not examine the possible difference between the interactions

of hydrogen with ZnO and the impact of the species on the optical properties of the material.

In this regard, we investigate hydrogen (H) adsorption on ZnO (10 $\bar{1}$ 0) surface by performing density functional theory (DFT) based calculations [1]. Specifically, we aim to provide comprehensive details on the adsorption of hydrogen on ZnO (10 $\bar{1}$ 0) surface with information on its geometric structures and the analysis of the interactions between hydrogen and the surface atoms. The results are expected to provide more accurate prediction and new insights on how H modify the geometry and the electronic properties of ZnO for a much-needed understanding of ZnO's potential applications.

COMPUTATIONAL DETAILS

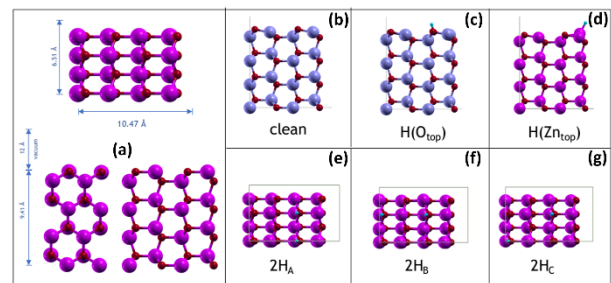


Fig.1. (a) Initial clean ZnO (10 $\bar{1}$ 0) surface with the lattice parameters and schematic diagram of the (a) clean ZnO surface compared with (b) single H on top of O [H(O_{top})], (c) single H on top of Zn [H(Zn_{top})], and two H atoms on top of O atoms on different sites designated as (e) 2H_a, (f) 2H_b, and (g) 2H_c. Magenta, red, and cyan spheres represent Zn, O, and H, respectively.

We performed first-principles calculations based on DFT implemented in the open-source Quantum

ESPRESSO package. Vanderbilt pseudopotentials were used under the generalized gradient approximation (GGA) scheme using Perdew-Burke-Ernzerhof (PBE) as the exchange-correlation functional. A 2×2 supercell of four bilayers of ZnO (10 $\bar{1}$ 0) was constructed to model the surface. Note that the bilayer consists of one layer of Zn atoms stacked with one layer of O atoms. A vacuum of 12 Å is added to replicate the surface. The calculated parameters of the clean surface such as the interlayer spacings and the Zn-O interatomic distances are in good agreement with previous works. Single and multiple H atoms are then simulated to be adsorbed on different geometric sites, as indicated in Fig. 1. Electronic band structures and density of states (DOS) were systematically obtained and plotted for each system.

RESULTS

Figures 2 and 3 show the electronic band structures and DOS of the clean ZnO (10 $\bar{1}$ 0) and the H(O_{top}) system, respectively. Our results show an underestimation of the band gap for the clean ZnO surface – a limitation of standard DFT calculations. Nevertheless, the band features are identical to previous DFT investigations. On the other hand, the system becomes metallic when an H atom is adsorbed on the ZnO surface as revealed by the crossing of the minimum valence band crossing below the Fermi level.

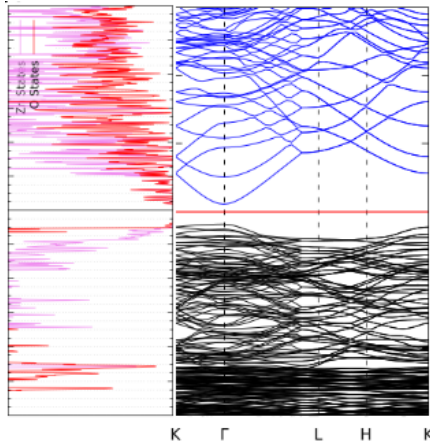


Fig. 2. Electronic band structure and DOS of a clean ZnO (10 $\bar{1}$ 0) surface.

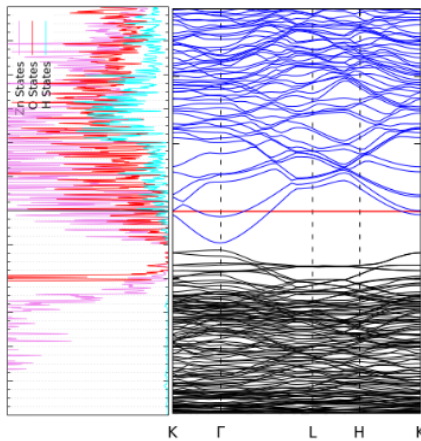


Fig. 3. Electronic band structure and DOS of H(O_{top})

system.

The adsorption energies for each structure were then calculated using the equation:

$$E_{ads,H} = \frac{E_{tot} - n \times E_H - E_{clean}}{n} \quad (1)$$

where E_{tot} is the total energy of the system, E_H is the total energy of one H atom, E_{clean} is the total energy of the clean ZnO (100) surface, and n is the number of H atoms present in the system. A summary of the results is shown in **Table 1**.

Table 1. Adsorption energies of H in each system where H atom(s) is/are adsorbed on specific geometric sites of the ZnO (100) surface.

System	Adsorption Energy (eV)
H(O _{top})	-2.50
H(Zn _{top})	-0.679
2H ₁ (O _{top})	-2.18
2H ₂ (O _{top})	-2.30
2H ₃ (O _{top})	-2.31
4H (O _{top})	-2.13
8H (O _{top} , Zn _{top})	-2.50

SUMMARY AND FUTURE WORK

We have analyzed the changes in the electronic properties of the ZnO (10 $\bar{1}$ 0) surface in the presence of hydrogen. We found that a low concentration of H adsorbed at on top site of O atom of ZnO will result in the shifting of the conduction band below the Fermi energy level. This phenomenon is attributed to the ionic bonding between H and O, in which, the O atom receives charge from the adsorbed H atom. The conduction band which is dominated by the O atom, thus, shifts below the Fermi energy level. For H that is adsorbed at the on-top site of Zn, the interaction is characterized by covalent bonding. Derived states, with contributions from O, Zn, and H, are formed near the Fermi level. The involvement of O in the adsorption of H explains the retained forbidden region in the band structure of the system. We note that such overlapping of states between Zn and O likewise occurs in the valence band of the clean ZnO (100) surface. In the future, we will extend the analysis for systems with higher H coverage and implement corrections to obtain more accurate band gap measurements of the systems.

ACKNOWLEDGMENT

This work was supported by the Osaka University Institute of Laser Engineering through the Collaborative Research for the Laser Energetics Program Grant No. 2019B1-PADAMA.

REFERENCE

- [1] M. M. Balmeo et al., manuscript in preparation.