Density functional study of adsorptions of CO$_2$, NO$_2$ and SO$_2$ molecules on Zn(0002) surfaces

Nugraha$^{1,2}$, A G Saputro$^{1,2}$, M K Agusta$^{1,2}$, B Yuliarto$^{1,2}$, H K Dipojono$^{1,2}$ and R Maezono$^3$

1 Engineering Physics Research Group, Faculty of Industrial Technology, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia
2 Research Center for Nanosciences and Nanotechnology, Institut Teknologi Bandung, Jl. Ganesha 10, Bandung 40132, Indonesia
3 School of Information Science, Japan Advanced Institute of Science and Technology, Asahidai 1-1, Nomi, Ishikawa 923-1292, Japan

Abstract. We report on a theoretical study of adsorptions of CO$_2$, NO$_2$ and SO$_2$ molecules on ZnO(0002) surfaces using density functional theory-based (DFT-based) calculations. These adsorptions are done on perfect and defective ZnO(0002) surfaces. We find that all of these molecules are chemically adsorbed on the perfect ZnO(0002) surface. In the presence of Zn vacancy, we find that the surface is only active toward SO$_2$ molecule. On the hydroxylated ZnO(0002) surfaces, CO$_2$ and SO$_2$ molecules can react with the pre-adsorbed OH molecule to form various adsorbates such as: carboxyl (COOH), bicarbonate (CO$_3$H), sulfonyl hydroxide (SO$_3$H), SO$_3$ and water. However, NO$_2$ molecule cannot react with the pre-adsorbed OH molecule and only physically adsorbed on the surface.

1. Introduction
The emission of carbon dioxide (CO$_2$), nitrogen oxides (NO$_x$) and sulfur dioxide (SO$_2$) gases to the environment is one of the main source of air pollution that could lead to various health problems such as infectious diseases and respiratory illness [1-4]. As a precaution to such threats, the concentration of these gases in the air should be regularly monitored and maintained. The availability of gas sensor with good sensitivity and selectivity is very crucial in order to carefully monitor the presence of these gases in the air. The sensing material of this gas sensor should be able to interact chemically with these specific gases in such a way that it responds in a specific measurable way.

Wide band gap semiconductor oxide is a class of material that usually used as the sensing part of a gas sensor. Zinc oxide (ZnO) is a semiconductor oxide that has been successfully employed as sensor for various type of gases[5-7]. However, the way to tune the selectivity of ZnO toward specific molecule is still a major problem. This is mainly due to the lack of fundamental knowledge on the interaction of ZnO surface with various gases at atomic level. With this knowledge, one could...
engineer the ZnO surface so that it can have good selectivity toward specific molecules.

It is speculated that the sensing mechanism of ZnO surface relies on the oxidation of the adsorbate by surface pre-adsorbed ionized oxygen species through catalytic interaction with the surface [8-13]. It means that in this proposed mechanism the dissociation of oxygen molecule on the surface is required in order to form the ionized oxygen species before the surface can sense some gases. A theoretical study report that O₂ dissociation is only viable on ZnO surface which has oxygen vacancies [14] while defect-free ZnO surface is found to be a very poor catalyst for this dissociation process. However, the formation energy of oxygen vacancy on ZnO surface is known to be very high [15,16]. This raise a fundamental problem in the reliability of the proposed sensing mechanism which relies on the presence of surface pre-adsorbed ionized oxygen species. Thus, it is relevant to say that the sensing mechanism on ZnO surface is still unclear.

In this work, we report on a theoretical study of CO₂, NO₂ and SO₂ molecules on ZnO(0002) surfaces using density functional theory-based (DFT-based) calculations. We focus on the role of surface defects in the selectivity of ZnO surface toward CO₂, NO₂ and SO₂ molecules in the absence of surface pre-adsorbed ionized oxygen species. We choose the polar (0002) facet of ZnO over the non-polar surfaces since previous experiment shows that ZnO thin film with polar surface has relatively better sensing performance [17].

2. Computational Details
In this work, we investigate the adsorption system of CO₂, NO₂ and SO₂ molecules on ZnO (0002) surfaces using density functional theory (DFT) calculations [18, 19]. Spin-polarized density functional theory calculations were performed using Quantum-Espresso package [20]. Exchange and correlation effects were incorporated within the generalized gradient approximation, using the Perdew-Burke-Ernzerhof (PBE) functional [21]. Kohn-Sham eigenfunctions were expanded on plane-waves basis sets where the interaction between the valence electrons and ion cores are described by ultrasoft pseudopotentials [22]. Hubbard-U correction is added by amount of 12 eV for Zn 3d states and 6 eV on O 2p states, following ref [23]. Converged results have been achieved by using cutoff energies of 28 Ry on the plane wave and of 280 Ry on the electronic density. The integration in Brillouin-zone is done on 4x4x1 k-points grid sampled by Monkhorst-Pack scheme [24]. The effect of van der Waals interactions is described using the semi-empirical correction scheme of Grimme, DFT-D2 [25]. Calculation for isolated molecule is done at the gamma point in a 30x30x30 Å³ cubic cell.

The zinc-terminated (0002) surface is modeled by repeated slab approach. We consider vacuum regions of 15 Å on z direction. The slab model contains six layers of Zn-O using 2x2 supercell (The number of Zn-O layers can be seen in Fig. 1). We consider four type of surface configurations including a perfect (0002) surface and three surface defects which are known to have reasonable formation energies [15,16]:

(I) Nonhydroxilated surface [perfect (0002) surface; Fig. 1a]
(II) Hydroxilated surface (OH covered; 0.5 monolayer; Fig. 1b)
(III) Nonhydroxilated surface including single Zn vacancy/unit cell (Fig. 1c)
(IV) Hydroxilated surface with a pair of Zn-O vacancies/unit cell (Fig. 1d).
Figure 1. Models for ZnO slab with: (a) clean surface (b) OH-covered (c) surface with a Zn vacancy (d) OH-covered ZnO (0002) surface with Zn-O nearest neighbor vacancies. Zn (blue), O (red), H (light blue).

For all cases, atoms in adsorbed molecules and in topmost Zn-O layer are fully relaxed during geometry optimization with an exception on model IV, where atoms in two topmost Zn-O layers are relaxed in addition to the adsorbates. The first two Zn-O layers in model IV are relaxed to accommodate the possibility of absorption of the adsorbate due to the presence of Zn-O pair vacancies. However, our results suggest that such absorption is energetically unfavourable. To prevent the presence of artificial charge transfer from bottom O layer to top Zn layer, the bottom oxygen terminated layer is passivated by pseudo-hydrogens [15, 26]. Without this treatment, the electronic structure of the Zn-O surface will be inaccurate and of course this will affect the adsorption state of the adsorbate.

We consider the adsorption sites for CO and NO molecules on the ZnO (0002) surface at the four high symmetry sites as shown in Fig. 2. The adsorption energy of a molecule on ZnO (0002) surface is defined as:

$$E_{ad} = E_{tot} - (E_{surf} + E_{molecule}),$$

where $E_{tot}$ corresponds to the total energy of combined system, $E_{surf}$ corresponds to the total energy of clean surface and $E_{molecule}$ corresponds to the total energy of the isolated molecule. In this formulation,
negative adsorption energy refers to stable adsorption and *vice versa*. The most stable adsorption configurations for each surface model will be compared to study the selectivity of the ZnO(0002) surface.

![Figure 2. Four high symmetry adoption sites on ZnO (0002) surface.](image)

3. Results and Discussions

Optimized structures and trend of adsorption energies of the most stable CO$_2$, NO$_2$ and SO$_2$ adsorptions on ZnO surfaces are presented in Figs. 3-6.

3.1. CO$_2$ adsorption

From Fig. 3, we can see that CO$_2$ molecule is chemically adsorbed on model I, II and IV surfaces while it is only physically adsorbed on model III surface. On model I surface (perfect surface), the linearity of CO$_2$ molecule conformation is broken and the molecule is adsorbed on the fcc site with a tridendate configuration (each of its atoms bind directly to the surface) with adsorption energy of about -1.23 eV. However, in the presence of a Zn vacancy/unit cell (model III), CO$_2$ molecule goes into physisorption mode and maintain its linear O-C-O conformation with adsorption energy of about -0.49 eV.

The interaction of CO$_2$ and the surface is greatly modified when pre-adsorbed hydroxyls (*OH) are introduced on the surface (model II and IV). On model II surface, CO$_2$ molecule reacts with a pre-adsorbed *OH of and forms an adsorbed bicarbonate (*CO$_3$H) via the following reaction: CO$_2$ (g) + *OH → *CO$_3$H. The formed *CO$_3$H binds to the Zn atom of hcp site through its O-H group with adsorption energy of about -0.89 eV. On model IV surface, CO$_2$ molecule also reacts with a pre-adsorbed *OH and forms a *CO$_3$H. The formed *CO$_3$H binds to the Zn-Zn bridge (bridge site) through its O and O-H groups and forms a bidendate configuration with adsorption energy of about -0.75 eV.

3.2. NO$_2$ adsorption

Figure 4 shows that NO$_2$ molecule is chemically adsorbed on model I surface, while it is only physically adsorbed on the other surfaces. NO$_2$ molecule is adsorbed on the fcc site of model I surface with a tridendate configuration as in CO$_2$ adsorption case, but with much stronger adsorption energy (-3.14 eV). Similar with CO$_2$ case, NO$_2$ molecule only physically adsorbed on model II surface with
adsorption energy of about -0.47 eV. We find interesting results for the hydroxilated surfaces (model II and IV). On these surfaces, NO₂ molecule is only physically adsorbed on the surface while maintaining its molecular form, instead of reacting with the pre-adsorbed hydroxyls as in CO₂ case.

![Figure 3. Adsorption energy trend for CO₂ adsorption on ZnO (0002) surfaces.](image3)

![Figure 4. Adsorption energy trend for NO₂ adsorption on ZnO (0002) surfaces.](image4)

3.3. SO₂ adsorption

Unlike CO₂ and NO₂ cases, SO₂ molecule is chemically adsorbed on all of model surfaces. We find that SO₂ molecule adsorbed on hcp site of model I surface with a tridendate configuration and with
adsorption energy of about -3.00 eV.

On model III surface, S atom of SO₂ molecule binds to the O atom of the surface that is located next to the Zn vacancy. This interaction results in a SO₂-like configuration. This situation is very different with the CO₂ and NO₂ cases in which the molecules are only physically adsorbed on the surface.

Similar with the CO₂ case, SO₂ molecule also react with the hydroxyl of hydroxylated surfaces (model II and IV). On model II surface, SO₂ molecule reacts with two pre-adsorbed *OH molecules and forms an adsorbed SO₃ and an H₂O via the following reaction: \( \text{SO}_2 (g) + 2*\text{OH} \rightarrow *\text{SO}_3 + \text{H}_2\text{O} \). The formed SO₃ is adsorbed on fcc site with a tridendate configuration. On model IV surface, SO₂ molecule reacts with a pre-adsorbed *OH and forms an adsorbed sulfonyl hydroxide (*SO₃H) via the following reaction: \( \text{SO}_2 (g) + *\text{OH} \rightarrow *\text{SO}_3\text{H} \). The formed SO₃H is adsorbed on fcc site with a tridendate configuration.

![Figure 5. Adsorption energy trend for SO₂ adsorption on ZnO(0002) surfaces.](image)

3.4. Selectivity of ZnO(0002) surfaces toward CO₂, NO₂ and SO₂ molecules

The strength of chemisorption energy of a molecule on a surface can be used as an indicator for the selectivity of the surface since the detection of the molecule requires strong chemisorption. Figure 6 shows that SO₂ molecule has the strongest chemisorption strength on most of the ZnO(0002) surfaces. This might imply that these surfaces are in general more selective toward SO₂ molecule, especially in model III surface since this surface is only active toward SO₂ molecule. In model I surface, the chemisorption strengths of NO₂ and SO₂ are almost comparable while the chemisorption strength of CO₂ molecule is the weakest. Therefore, on a perfect ZnO(0002) surface, it might be easier to distinguish between NO₂/SO₂ and CO₂ as compared to NO₂ and SO₂. The presence of pre-adsorbed hydroxyls (model II and IV) makes the surfaces become less sensitive toward NO₂ molecule due to the weak NO₂-surface interaction. Therefore, the hydroxylated surfaces are only selective toward CO₂ and SO₂ molecules.
4. Summary

We report on a theoretical study of CO₂, NO₂ and SO₂ molecules on ZnO(0002) surfaces in the absence of surface-adsorbed ionized oxygen species using density functional theory-based (DFT-based) calculations. These adsorptions are done on perfect and defective ZnO(0002) surfaces.

We find that all of these molecules are chemically adsorbed on perfect ZnO(0002) surface (model I). The chemisorption strengths of NO₂ and SO₂ on this surface are almost comparable while the chemisorption strength of CO₂ molecule is the weakest. Therefore, on this surface, it might be easier to distinguish between NO₂/SO₂ and CO₂ as compared to NO₂ and SO₂. In the presence of Zn vacancy (model III), we find that the surface is only active toward SO₂ molecule. On the hydroxylated surfaces (model II and IV), we find that CO₂ and SO₂ molecules can react with the pre-adsorbed OH molecule to form various adsorbates such as: carboxyl (COOH), bicarbonate (CO₃H), sulfonyl hydroxide (SO₃H), SO₃ and water. However, NO₂ molecule cannot react with the pre-adsorbed OH molecule and only physically adsorbed on the surface.

All of this data suggest that even in the absence of surface-adsorbed ionized oxygen species, the ZnO(0002) surfaces have selectivity toward CO₂, NO₂ and SO₂ molecules.

Acknowledgements
This work is funded by the Directorate of Higher Education, Ministry of Education and Culture, Republic of Indonesia through the Decentralization Project Grant. R.M. is grateful for financial support from MEXT-KAKENHI grants 26287063, 25600156 and that from the Asahi glass Foundation. Calculations were performed using High Performance Computer facility in Insitut Teknologi Bandung and in Center for Information Science of JAIST.

References
[1] K. Shahzad, M. Saleem, M. Ghauri, J. Akhtar, N. Ali and N. A. Akhtar, *Combustion Science and
Technology, 2015, 187, 1079–1092.
[2] W.-S. Yang, H. Zhao, X. Wang, Q. Deng, W.-Y. Fan and L. Wang, European Journal of Cancer Prevention, March 9, 2015.
[3] J. Borken, H. Steller, T. MerĂł'iei and F. Vanhove, Transportation Research Record: Journal of the Transportation Research Board, 2007, 2011, 127–136.
[4] D. Streets and S. Waldhoff, Atmospheric Environment, 2000, 34, 363 – 374.
[5] M. H. Huang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo and P. Yang, Science, 2001, 292, 1897–1899.
[6] Q. Wan, Q. H. Li, Y. J. Chen, T. H. Wang, X. L. He, J. P. Li and C. L. Lin, Applied Physics Letters, 2004, 84, 3654–3656.
[7] L. Liao, H. B. Lu, J. C. Li, H. He, D. F. Wang, D. J. Fu, C. Liu and W. F. Zhang, The Journal of Physical Chemistry C, 2007, 111, 1900–1903.
[8] J. Xu, Q. Pan, Y. Shun and Z. Tian, Sensors and Actuators B: Chemical, 2000, 66, 277 – 279.
[9] P. Feng, X. Xue, Y. Liu, Q. Wan and T. Wang, Applied physics letters, 2006, 89, 112114–112114.
[10] A. Chatterjee, P. Mitra and A. Mukhopadhyay, Journal of MaterialsScience,1999,34, 4225–4231.
[11] B.Rao, Materials Chemistry and Physics, 2000, 64,62–65.
[12] M.Chen, Z.Wang, D.Han, F.Gu and G.Guo, The Journal of Physical Chemistry C, 2011,115,12763–12773.
[13] T.T.Trinh, N.H.Tu, H.H.Le, K.Y.Ryu, K.B.Le, K.Pillai and J.Yi, Sensors and Actuators B:Chemical, 2011,152,73–81.
[14] Y.Li, L.K.Schirra, J.Shim, H.Cheun, B.Kippelen, O.L.A.Monti and J. L.Bredas, Chemistry of Materials,2012,24, 3044–3055.
[15] G.Kresse, O.Dulub and U.Diebold, Phys. Rev. B,2003,68,245409.
[16] S.Tian, F.Yang, D.Zeng and C.Xie, The Journal of Physical Chemistry C,2012,116,10586–10591.
[17] P.Hohenberg and W.Kohn, Phys. Rev.,1964,136,B864–B871.
[18] W.Kohn and L.J.Sham, Phys. Rev.,1965,140,A1133–A1138.
[19] P.Gianozzi, S.Baroni, N.Bonini, M.Calandra, R.Car, C.Cavazzoni, D.Ceresoli, G.L.Chiarotti, M.Cococcioni, I.Dabo, A. D. Corso, S. de Gironcoli, S. Fabris, G. Fratesi, R. Gebauer, U. Gerstmann, C. Gougoussis, A. Kokalj, M. Lazzeri,L. Martin-Samos, N. Marzari, F. Mauri, R. Mazzarello, S. Paolini, A. Pasquarello, L. Paulatto, C. Sbraccia, S. Scandolo, G. Scuauzer, A. P. Seitsonen, A. Smogunov, P. Umari and R. M. Wentzcovitch, J. Phys.: Condens. Matter, 2009, 21, 395502.
[20] J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett.,1996,77,3865–3868.
[21] D.Vanderbilt, Phys. Rev. B,1990,41,7892–7895.
[22] F.Fabbri, M.Villani, A.Catellani, A.Calzolari, G.Cicero, D.Calestani, G.Calestani, A.Zappettini, B.Dierie, T.Sekiguchi and G. Salviati, Sci. Rep., 2014, 4, year.
[23] H.J.Monkhorst and J.D.Pack, Phys. Rev. B,1976,13,5188–5192.
[24] S.Grimme, J. Comput. Chem., 2006,27,1787–1799.
[25] O.Dulub, U.Diebold and G.Kresse, Phys. Rev. Lett., 2003,90,016102.