Adsorption of the H and H₂O on SnO₂ Surfaces in an O₂ Environment: Density Functional Theory Study

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Abstract. Hydrogen, oxygen and water have huge impact on gas sensing mechanisms in the environment. This research related to the H and H_2O adsorption on the SnO_2 – (110), (100), (101), (001) surfaces under different O_2 conditions. A lot of experimental and theoretical study was done previously to explain SnO_2 gas sensors behavior in the environment, but atomic size processes remain unclear. Density functional theory is usedto investigate adsorption on all possible surfaces and reconstructions in the different O_2 conditions. Environment conditions were simulated using atomistic thermodynamics. Calculations in this studyconfirm that water tends to dissociate on all surfaces in an oxygen reach surface, but not on reduced one.

1. Introduction

Chemical sensors are in great demand for many applications in industry, environment monitoring and health care. There are many kinds of materials used for gas sensing chemical sensors, but the most commonly used are semiconductors, in particular *SnO₂* [1].The pure tin dioxide is wide band gap semiconductor. It is very sensitive to defects and dopants, which induce charge carriers and increase conductance of the bulk material or the surface [2,3]. Other advantages are that conduction band has minimum on Γ point, and mobility of carriers is high, which is very important for gas sensors' sensitivity [4-8].

Tin dioxide based sensors are used to detect common and toxic gases like *H₂, H₂O, CH₄, CH₃OH, NO₂, CO, CO₂* [9-14]. Hydrogen and water are the most abounded in human environment and has huge impact on sensor parameters. Thus, in any gas sensing application the impactof these gases should be considered. Many experimental and theoretical researches were done to explain processes going on sensors' surfaces [15-17]. From experiments, it was known that water tend to dissociate on SnO₂ surfaces and desorbed at about 250ºC, and fully dehydrogenated at about 600ºC [18-21]. To explain this behavior of the surfaces, the atomic size processes should be considered.

Using density functional theory, it is possible to understand and explain gas atomic size effects. To explain adsorption and sensing mechanism it is important to define surface structure, adsorption sites of gas molecules on that surface, charge transfer amount between molecule and surface, adsorption and desorption temperatures and impact of other gases on sensitivity to particular gas [22,23]. Despite the huge amount of previous researches not all possible surface structures were calculated, thus in this research all possible surfaces and reconstructions will be considered. Using ab-initio thermodynamics, it is possible to simulate oxygen environment, find stable structures and their stability range [24-26]. Temperature and pressure will be estimated by this theory too. So, the purpose of the article is to describe atomic scale processes of *H, H₂O* adsorption on *SnO₂* in an oxygen environment, find stable adsorption structures and compare those results with previous experimental works.

2. Computational methods and theory

Density functional theory [27,28] calculations were done using Vienna Ab initio Simulation Package(VASP) [29-31]. DFT relaxations was done within (GGA) generalized gradient approximation (Perdew-Burke-Ernzerhof)[32,33]. The cutoff energy was chosen as 700 eV. Surface structures were relaxed until maximum net force of atoms becomes less than 0.01 eV/Å. The Monkhorst-Pack scheme [34] was used to sample the Brillouin zone, using 6x6x1 k-points mesh.

In the beginning of the calculations the structural relaxation of bulk SnO_2 was done to prepare appropriate surfaces. Bulk SnO_2 has rutile, tetragonal structure, with P42/mnm space group. The lattice parameters of SnO_2,from reference data[6], are a = 4.82 Å, c = 3.23 Å and u = 0.607. In our calculations each of (110), (100), (101), (001) surfaces consists of 6 tin atoms and 12 oxygen atoms and relative stability has the following sequence (110), (100), (101), (001) (Fig. 1)[35]. Stability of each surface, reconstruction and adsorption structure can be calculated and compered using surface free energy equation:

$$E_f = \frac{1}{N}[G(T,P,N_i) - \sum N_i\mu_i(T,P)] . \qquad (1)$$

Here, $G(T,P,N_i)$ is Gibbs free energy of the slab, index i indicates molecule or atom type, N_i and $\mu_i$are number of atoms and chemical potential correspondingly. N represents unit cell number of reconstructed structure.
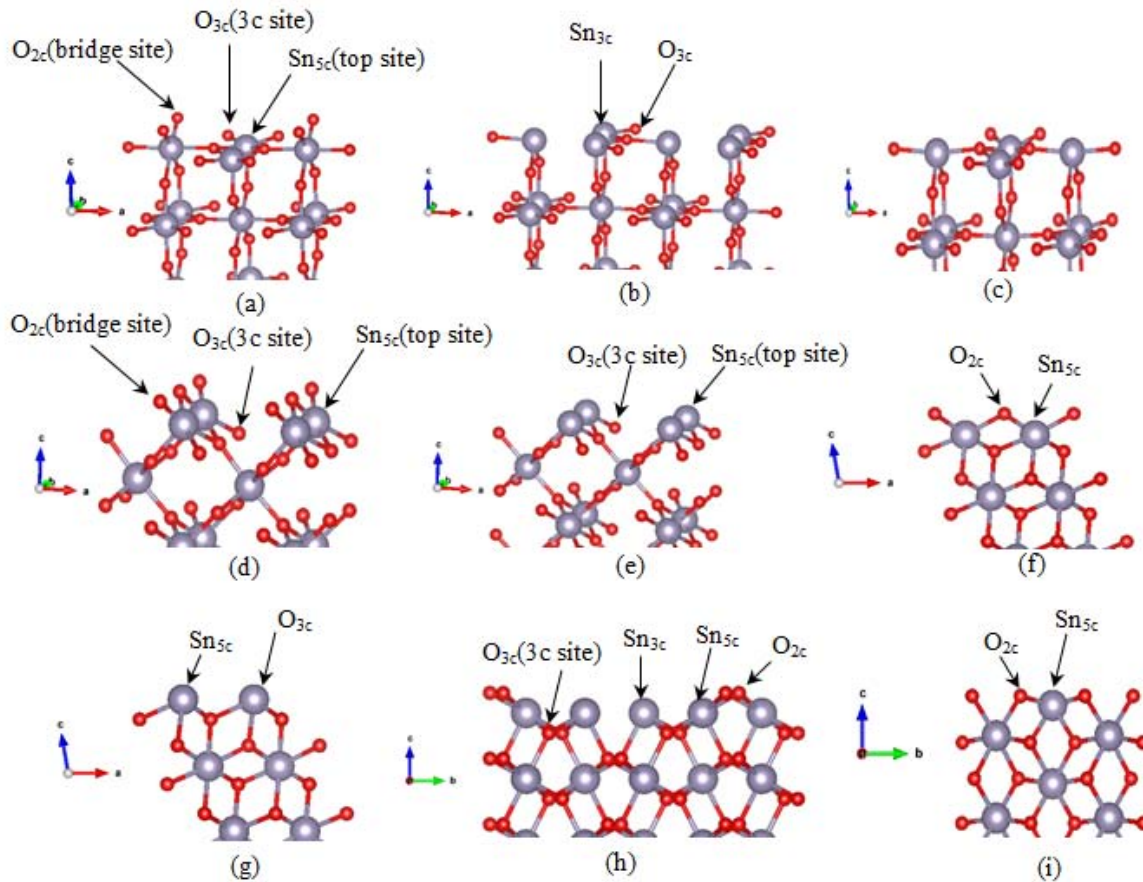

Fig.1. SnO_2 clean surfaces and possible adsorption sites. (a) (110) stoichiometric structure. (b) Stable reduced (110) surface. (c) Unstable reduced (110) surface (d) Stoichiometric (100) surface. (e) Reduced (100) surface. (f) Stoichiometric (101) surface. (g) Reduced (101). (h) (1x2) reconstruction of (101) surface, 2 oxygen reduced structure. (i) Stoichiometric (001) surface.

Gibbs free energy is equal to the total energy from the DFT calculation. Inserting type of atoms in equation (1):

$$E_f = \frac{1}{N}[G(T,P,N_i) - N_{Sn}\mu_{Sn}(T,P) - N_O\mu_O(T,P) - N_H\mu_H(T,P)] \tag{2}$$

Here, chemical potential play crucial role, because by varying itthe different environment conditions can be simulated. But, chemical potential of atoms are not independent, because gas and surface must be in thermodynamic equilibrium. In the system of our interest two gases exists, they are oxygen and hydrogen. Each of them isin equilibrium with the surface.Molecules of gases can interact with each other too and form water. In our case stability of the *SnO₂* is in such region of oxygen chemical potential that dominant gas phase component will be water molecule, if system is in full equilibrium state[26]. Taking into account this assumption equilibrium of chemical potential can be written in the following form:

$$\mu_{Sn} + \mu_O = g_{SnO2} \tag{3}$$
$$2\mu_H + \mu_O = \mu_{H2O} \tag{4}$$

Here g_{SnO2} is Gibbs free energy of bulk crystal, which equals to -18.77 eV[36]. μ_{H2O} is the water chemical potential. Inserting these equations to (2) and excluding $\mu_{Sn}$and μ_H, the following equation can be written:

$$E_f = \frac{1}{N}\left[G(T,P,N_i) - N_{Sn}g_{SnO2}(T,P) - \mu_O(T,P)\left\{N_O - 2N_{Sn} - \frac{N_H}{2}\right\} - N_H\mu_{H2O}(T,P)/2\right] \tag{5}$$

Varying chemical potential of oxygen and water we can find stable structures or reconstruction of all surfaces. But variation of chemical potential must be confined in the stability region of the surface, because if chemical potential of oxygen will be too low(oxygen poor limit or *Sn* rich limit), all oxygen in the surface will desorbed and *Sn* metallic layer will crystallized on the surface. This condition can be expressed by the following equation:

$$min(\mu_O) = \frac{1}{2}[g_{SnO2}(T,P) - g_{Sn}(T,P)] \tag{6}$$

Here g_{Sn} is Gibbs free energy of *Sn* bulk crystal. If oxygen potential is high, oxygen molecule will be formed. This condition expressed as:

$$max(\mu_O) = \frac{1}{2}E_{O2} \tag{7}$$

Here E_{O2} is the total energy of free isolated oxygen molecule, which is equal to -9.83 eV. Using equation (5), (6) and (7) borders of oxygen chemical potential can be defined as:

$$\frac{1}{2}\Delta G_f < \mu_O(T,P) - \frac{1}{2}E_{O2} < 0 \tag{8}$$

Here ΔG_f is Gibbs free energy of formation *SnO₂* bulk material. It is equal to -5.09 eV, which is in accordance with previous calculations [37]. Water chemical potential border must satisfy above mentioned condition, where only water gas molecule can exist in equilibrium. To assure this restriction chemical potential should be taken under -0.91 eV [26] with respect to total energy of *H₂O* molecule.

Equation (5) mainly used for comparison of structure surface free energies and definition of the most stable one in various environment conditions. But there is another measure to define if the adsorbed gas on particular surface site is stable. The measure is adsorption energy:

$$E_{ads} = E_{surf} - E_{clean} - E_{gas}, \tag{9}$$

where *E_{ads}* is adsorption energy, *E_{surf}* is total energy of *SnO₂* surface and adsorbed gas. *E_{clean}*is a total energy of pure surface without gas and *E_{gas}*is total energy of gas molecule. It is clear from this equation, that if *E_{ads}*is negative the configuration of adsorbed site is stable or process is exothermic. If *E_{ads}* is positive then process is endothermic and molecule will not adsorb to the surface.

2. Results and discussions

This section organized by discussing each of surface structures under different oxygen environment conditions, possible adsorption sites of gas molecules, phase diagrams of stable configurations at different chemical potentials of oxygen and water.

The most stable surface of tin dioxide is (110) orientation, because it has the minimum surface free energy. This surface is the most investigated both experimentally and theoretically. It was found that there are two possible reconstruction of the (110) surface, they are stoichiometric and reduced ones. These reconstructions are stable in different oxygen environment. Using equation (5) stability range was found, which is in accordance with previous calculations. Stoichiometric surface has the same atoms configuration as in bulk materials and it is the most stable configuration in $-6.79 < \mu_O < -4.93$ eV range of chemical potential. Phase diagramis given in Fig.5. The second reconstruction, which is reduced surface, two oxygen atoms are missed as in Fig. 1 (b). This reduced surface is stable in the range of $-7.47 < \mu_O < -6.79$ eV. There are other possible reconstructions described in the literature[23,37,38], which considered as not stable or metastable Fig. 1(c). So we consider only two surface structures under possible oxygen environment conditions. To describe or simulate adsorption of hydrogen or water in the $-6.79 < \mu_O < -4.93$ eVregion of oxygen chemicalpotential, the stoichiometric surface should be considered as an adsorption substrate. If chemical potential region lay in the $-7.47 < \mu_O < -6.79$ eV, reduced surface should be considered as substrate for gas adsorption. All stable structures after adsorption are given in Fig. 2.
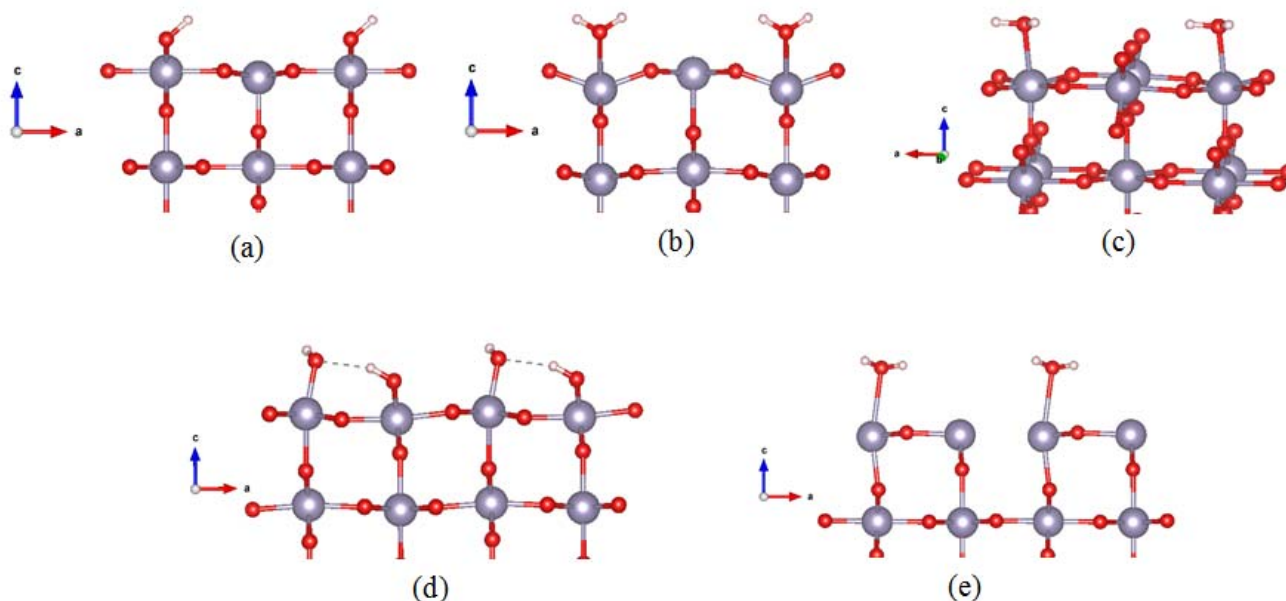

Fig. 2. Hydrogen adsorption on *SnO₂ (110)* surfaces.(a) H on bridge site. (b) Two H on bridge site. (c) *H₂O* on top site. (d) Dissociated water structure, H bonding between bridge site H and on top site OH. (c) Water adsorption on reduced (110) surface.

At first, let us consider stoichiometric (110) surface. Here adsorption sites are O_{2c} two coordinated oxygen atom (or bridge site), O_{3c} three coordinated oxygen atom (3c site) and Sn_{5c} five coordinated tin atom (top site) Fig. 1(a,b). Adsorption atoms are H, 2H and H₂O. Additional

structure of dissociated water should be considered because in experiments water tends to dissociate [17]. Calculated adsorption energies are given in the Table 1. It is clear that stable adsorption sites for hydrogen is only bridge sites. For the water both adsorbed and dissociated structures are stable but the last one has lower E_{ads}, which means that dissociation is more preferable. In dissociated structure hydrogen bond created Fig. 2(d), stabilizing and making it the most preferable configuration.

Now let us consider reduced surface. Possible adsorption sites are given in Fig. 1(b). Dissociated structure was added too. The final E_{ads} is given in the Table 2.Only stable structure is adsorbed or physisorbed water configuration. It means that in poor oxygen environment only water can adsorb. This conclusion is in accordance with experimental results [2].

Table 1. Adsorption energies of (110) stoichiometric surface.

Adsorbtion sites	Values of E_{ads} for (110) stoichiometric surface	
	$E_{ads}(eV)$	*Gas*
Bridge	-0.08	*2H*
Bridge	-1.07	*H*
3c	0.34	*H*
top	1.73	*H*
Bridge, top, 3c	1.30	*3H*
top	-1.10	*H₂O*
Top, bridge	-1.68	*H₂O, dissociated*

Table 2. Adsorption energies of (110) reduced surface.

Adsorbtion sites	Values of E_{ads} for (110) reduced surface	
	$E_{ads}(eV)$	*Gas*
top	1.27	*H*
3c	0.56	*H*
top	-0.14	*H₂O*
top	0.44	*H₂O, dissociated*

So, we found all possible structures, now using equation (5) phase diagram can be constructedfor all structures in all possible environment conditions of oxygen and water. Varying μ_O and μ_{H2O} phase diagram plotted in the Fig.6(a). In the plot each color indicates the particular structure, which has the minimum in that region. For (110) surface, only three structures are possible, they are clean stoichiometric(grey color on Fig. 6(a)), reduced(black colored region), and dissociated water configuration(white colored region). The stability regions are in accordance with experimental results obtained by other researchers[37]. Using chemical potential values from phase diagram, it is possible to estimate stability regions of pressure and temperature.

The following stable surface after (110) is (100). (110) surface has two possible surface structures: stoichiometric and reduced. Possible adsorption sites are O_{2c}(bridge) on the top of surface, O_{3c} which is inside the layer(3c site) and Sn_{5c}(top).DFT calculation results are presented in Table 3 and 4. Here, stable sites are bridge and 3c (Fig. 3). From the tables, it is clear, that water tends to dissociate. For reduced surface, only water adsorption or physisorption is preferable. Phase diagram is shown in Fig. 6(b).
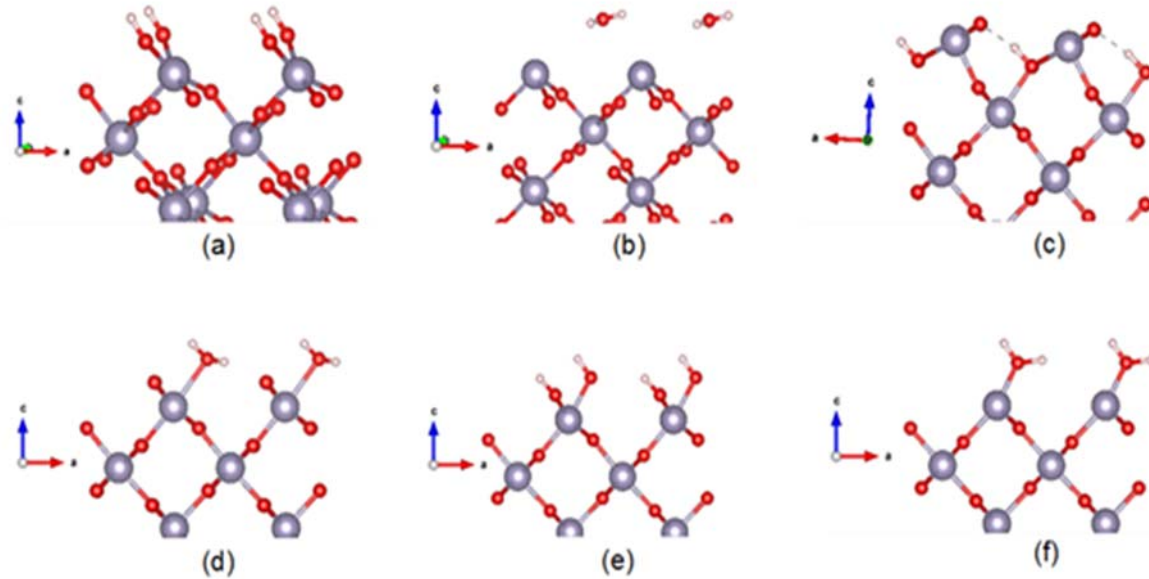
Fig. 3.Hydrogen and water adsorption on the (100) surfaces. (a) *H* adsorption on O_{2c}site. (b) Desorbed water after adsorption two hydrogen atoms on O_{2c}site. (c) *H* adsorption and *H* bonding formation on O_{3c}site. (d) Water adsorption on the Sn_{5c}site. (e) Dissociated on the stoichiometric (100) surface. (f) Water adsorption on the reduced (100) surface.

Table 3. Adsorption energies of (100) stoichiometric surface.

Adsorbtion sites	Values of E_{ads} for (100) stoichiometric surface	
	$E_{ads}(eV)$	*Gas*
bridge	-0.32	*H*
bridge	-1.20	*2H*
3c	-0.13	*H*
top	2.13	*H*
top	-0.87	*H₂O*
top	-1.21	*H₂O, dissociated*

Table 4. Adsorption energies of (100) reduced surface.

Adsorbtion sites	Values of E_{ads} for (100) reduced surface	
	$E_{ads}(eV)$	*Gas*
3c	0.85	*H*
top	1.42	*H*
top	-0.26	*H₂O*
top	0.42	*H₂O, dissociated*

The next surface orientation is (101). Depending on oxygen environment, it has three possible reconstructions [37]. First is stoichiometric configuration, which is like bulk material Fig. 1(g). There are two possible adsorption sites, which are Sn_{2c} and Sn_{5c}. As in previous case *H, 2H, H₂O* and dissociated water will be considered as adsorbents. In addition, one mono layer (ML = 1) of hydrogen coverage also considered, because there are two equivalent O_{2c} and Sn_{5c} sites. In this case, the only preferable site for hydrogen is bridge site and for water-dissociated configuration (Tables 5 and 6).One monolayer coverage has lower surface free energy, which means that adsorbed molecules do not prevent other molecules to adsorb. Reduced (101) surface two oxygen atoms are missed. As in previous case, here only water adsorption is preferable and full covered structure has the minimum surface energy.
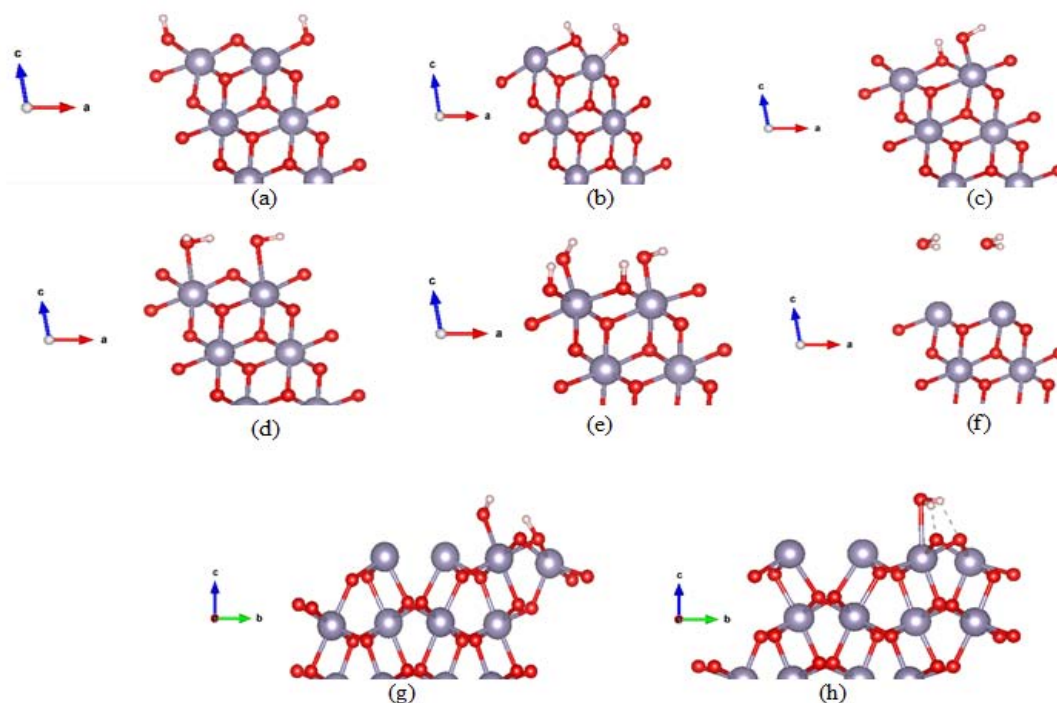
Fig. 4. H and H_2O adsorption on (101) surfaces. (a) H on (101) bridge site. (b) (101) surface covered by one monolayer of H adsorption. (c) Dissociated water on stoichiometric (101). (d) Water on the top site, fully covered surface. (e) One monolayer covered and dissociated water structures. (f) Desorbed water on reduced (101) surface. (g) Dissociated water on (1x2) reconstruction. (h) Adsorbed water on (1x2) reconstruction.

The third possible structure is (1x2) reconstruction, which means that unit cell is doubled and N = 2. Here, 4 possible adsorption sites exist, they are O_{3c}, O_{2c}, Sn_{3c} and Sn_{5c}. The most stable structures configurations are given in Fig. 4(g) and (h). Phase diagram is plotted in the Fig. 6(c).

Table 5. Adsorption energies of (101) stoichiometric surface.

Ads. sites	Values of E_{ads} for (101) stoichiometric surface	
	$E_{ads}(eV)$	Gas
Bridge site	-1.02	H
Br. Site, ML =1	-1.89	H
Top	1.62	H
Top	-0.78	H_2O
Top	-0.80	H_2O, dissociated
Top, ML = 1	-1.58	H_2O
Top, ML=1	-2.5	H_2O, dissociated

Table 6. Adsorption energies of (101) reduced surface.

Ads. sites	Values of E_{ads} for (101) reduced surface	
	$E_{ads}(eV)$	Gas
O_{3c}	0.78	H
Top	1.59	H
Top	-0.01	H_2O
Top	1.25	H_2O, dissociated
Top, ML = 1	-0.35	H_2O

The stable structures are stoichiometric, which is in blue, in gray region (1x2) reconstruction is the most stable, reduced structure is in black region. Yellow region is one dissociated water molecule, and white region is completely covered surface (ML = 1) with dissociated H_2O. In red, water dissociated on (1x2) reconstruction is the dominated one. The adsorption energies for

all possible adsorption structures are given in Table 7. It is worth to note, that all adsorption configurations are stable, because adsorption energies are negative. Thus, (1x2) reconstructed (101) surface will be very sensitive to hydrogen and water. This information may be very useful for gas sensor applications.

Table 7. Adsorption energies of (1x2) reconstructed (101) surface

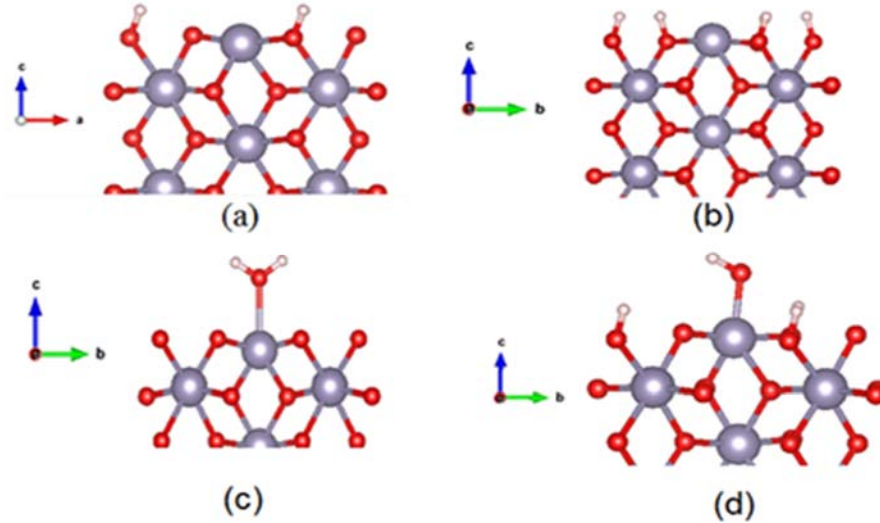| Ads. sites	Values of E_{ads} for (1x2) reconstructed (101) surface	
	$E_{ads}(eV)$	Gas
O_{2c}	-0.49	2H
O_{2c}	-0.57	H
O_{2c}, ML=1	-1.34	2H
O_{3c}	-0.07	H
Sn_{3c}	-0.48	H_2O
Sn_{3c}	-0.44	H_2O, dissociated
Sn_{5c}	-0.68	H_2O
Sn_{3c}	-1.20	H_2O, dissociated
Sn_{3c}, Sn_{5c}, ML=1	-1.81	4(H_2O)

Fig. 5. Hydrogen and water adsorption configurations on (001) surface. (a) Hydrogen on O_{2c} site. (b) One monolayer covered (001) surface. (c) Water on Sn_{5c} site. (d) Dissociated water on (001) surface.

The last surface is (001). In some experiments [37], the surface was not observed, but its existence is very high due to theoretical calculations [35,39]. This surface has only one known configuration Fig. 1(i). The possible structures are O_{2c} and Sn_{5c} (top). As for other surfaces, H atom does not bind tin atoms, but only two coordinated oxygen. Water tends to dissociate forming OH bonds Fig. 5. Adsorption energies are given in the Table 8. Phase diagram is given in Fig. 6(d). In black region, stable structure is stoichiometric one, white is dissociated water, in blue region structure H on O_{2c} site (Fig. 5(a)) is the most stable. In grey region, the structure completely covered by H is the most favorable.

Table 8. Adsorption energies of (001)
stoichiometric surface.

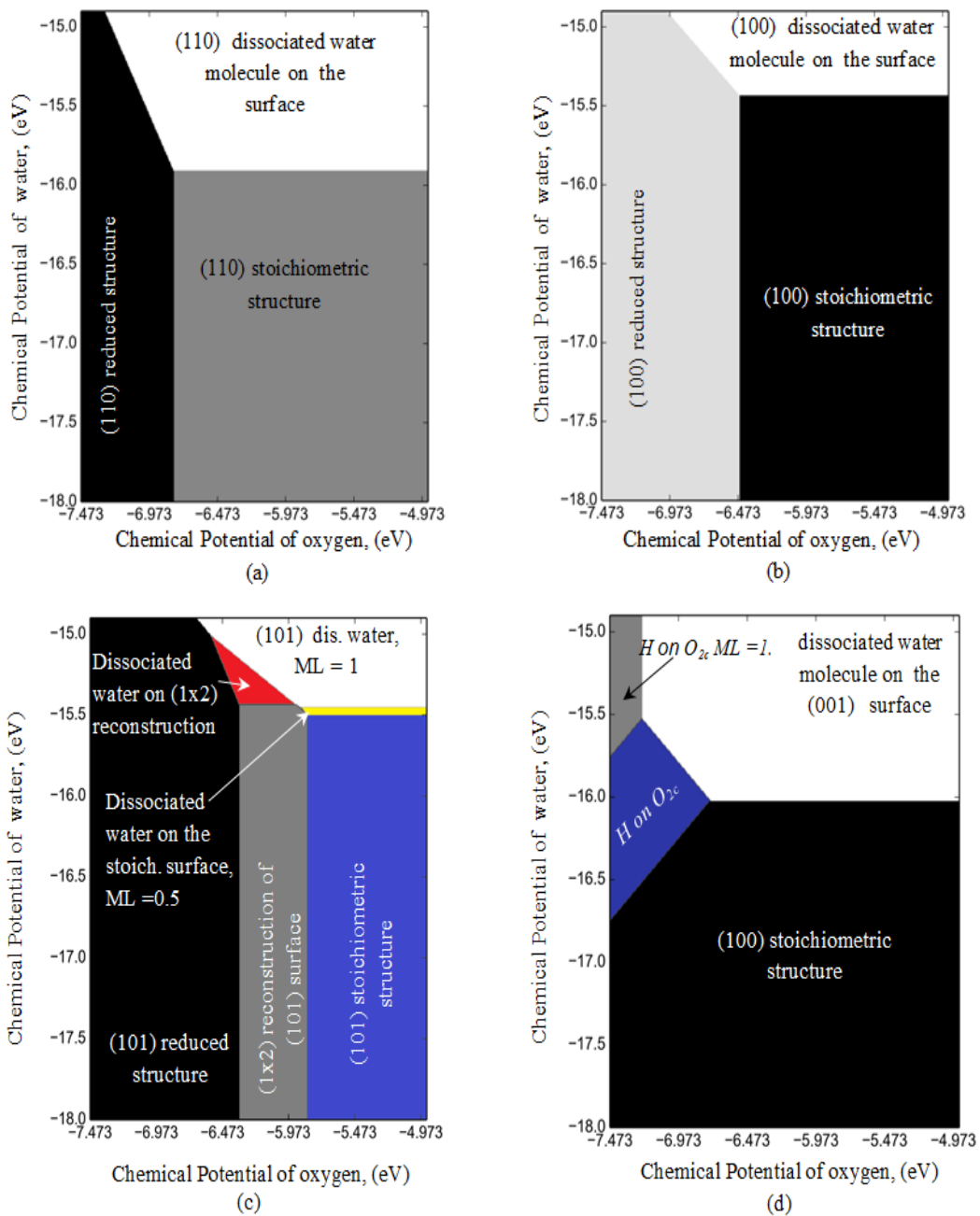| Ads. sites	Values of E_{ads} for (001) stoichiometric surface	
	$E_{ads}(eV)$	*Gas*
O_{2c}	-1.25	*H*
O_{2c}, ML =1	-2.01	*H*
top	1.30	*H*
top	-0.48	*H₂O*
top	-1.79	*H₂O, dissociated*

Fig. 6. Phase diagram of SnO₂ surfaces in an O2 and H₂O environment. (a) (110). (b) (100). (c) (101). (d) (001).

4. Conclusions

Thus, in this research we found all possible structures and sites of *H, 2H* and water adsorptions. It was shown that water tends to dissociate on oxygen reach surface and physisorb on reduced ones. Different oxygen and water environment conditions were considered using ab-initio thermodynamics. Stability range was calculated and phase diagrams were presented. The phase diagrams describe all stable structures and environment conditions of their stability. These results can be used as a guide at the fabrication of gas sensors worked in hydrogen, oxygen and water environments.

References

[1] V. Aroutiounian, "Metal oxide hydrogen, oxygen, and carbon monoxide sensors for hydrogen setups and cells," *Int. J. Hydrog. Energy*, vol. 32, no. 9, pp. 1145–1158, Jun. 2007.

[2] A. Z. Adamyan, Z. N. Adamyan, and V. M. Aroutiounian, "Study of sensitivity and response kinetics changes for SnO2 thin-film hydrogen sensors," *Int. J. Hydrog. Energy*, vol. 34, no. 19, pp. 8438–8443, Oct. 2009.

[3] S. Gong, J. Liu, J. Xia, L. Quan, H. Liu, and D. Zhou, "Gas sensing characteristics of SnO2 thin films and analyses of sensor response by the gas diffusion theory," *Mater. Sci. Eng. B*, vol. 164, no. 2, pp. 85–90, Aug. 2009.

[4] C. C. Yang and S. Li, "Cohesive Energy: The Intrinsic Dominant of Thermal Stability and Structural Evolution in Sn from Size Scales of Bulk to Dimer," *J. Phys. Chem. C*, vol. 113, no. 32, pp. 14207–14212, Aug. 2009.

[5] F. Bassani and L. Liu, "Electronic Band Structure of Gray Tin," *Phys. Rev.*, vol. 132, no. 5, pp. 2047–2050, Dec. 1963.

[6] K. C. Mishra, K. H. Johnson, and P. C. Schmidt, "Electronic structure of antimony-doped tin oxide," *Phys. Rev. B*, vol. 51, no. 20, p. 13972, 1995.

[7] F. Trani, M. Causà, D. Ninno, G. Cantele, and V. Barone, "Density functional study of oxygen vacancies at the SnO 2 surface and subsurface sites," *Phys. Rev. B*, vol. 77, no. 24, p. 245410, 2008.

[8] T. T. Rantala, T. S. Rantala, and V. Lantto, "Electronic structure of SnO2 (110) surface," *Mater. Sci. Semicond. Process.*, vol. 3, no. 1–2, pp. 103–107, Mar. 2000.

[9] J. D. Prades, A. Cirera, and J. R. Morante, "First-Principles Study of NO x and SO2 Adsorption onto SnO2 (110)," *J. Electrochem. Soc.*, vol. 154, no. 8, pp. H675–H680, Aug. 2007.

[10] K. R. Hahn, A. Tricoli, G. Santarossa, A. Vargas, and A. Baiker, "First Principles Analysis of H2O Adsorption on the (110) Surfaces of SnO2, TiO2 and Their Solid Solutions," *Langmuir*, vol. 28, no. 2, pp. 1646–1656, Jan. 2012.

[11] V. M. Aroutiounian *et al.*, "Study of the surface-ruthenated SnO2/MWCNTs nanocomposite thick-film gas sensors," *Sens. Actuators B Chem.*, vol. 177, pp. 308–315, Feb. 2013.

[12] V. M. Aroutiounian *et al.*, "Manufacturing and investigations of i-butane sensor made of SnO2/multiwall-carbon-nanotube nanocomposite," *Sens. Actuators B Chem.*, vol. 173, pp. 890–896, Oct. 2012.

[13] V. M. Aroutiounian, "Metal oxide gas sensors decorated with carbon nanotubes," *Lith. J. Phys.*, vol. 55, no. 4, Jan. 2016.

[14] J. Yu, D. Zhao, X. Xu, X. Wang, and N. Zhang, "Study on RuO2/SnO2: Novel and Active Catalysts for CO and CH4 Oxidation," *ChemCatChem*, vol. 4, no. 8, pp. 1122–1132, Aug. 2012.

[15] M. Melle-Franco and G. Pacchioni, "CO adsorption on SnO2(110): cluster and periodic ab initio calculations," *Surf. Sci.*, vol. 461, no. 1–3, pp. 54–66, Aug. 2000.

[16] P. J. Lindan, "Water chemistry at the SnO 2 (110) surface: the role of inter-molecular interactions and surface geometry," *Chem. Phys. Lett.*, vol. 328, no. 4, pp. 325–329, 2000.

[17] M. Batzill and U. Diebold, "The surface and materials science of tin oxide," *Prog. Surf. Sci.*, vol. 79, no. 2–4, pp. 47–154, 2005.

[18] T. T. Rantala, T. S. Rantala, and V. Lantto, "Surface relaxation of the (110) face of rutile SnO2," *Surf. Sci.*, vol. 420, no. 1, pp. 103–109, Jan. 1999.

[19] M. Batzill, W. Bergermayer, I. Tanaka, and U. Diebold, "Tuning the chemical functionality of a gas sensitive material: Water adsorption on SnO2(101)," *Surf. Sci.*, vol. 600, no. 4, pp. 29–32, Feb. 2006.

[20] J. Yue, X. Jiang, and A. Yu, "Adsorption of the OH Group on SnO 2 (110) Oxygen Bridges: A Molecular Dynamics and Density Functional Theory Study," *J. Phys. Chem. C*, vol. 117, no. 19, pp. 9962–9969, May 2013.

[21] R. A. Evarestov, A. V. Bandura, and E. V. Proskurov, "Plain DFT and hybrid HF-DFT LCAO calculations of SnO2 (110) and (100) bare and hydroxylated surfaces," *Phys. Status Solidi B*, vol. 243, no. 8, pp. 1823–1834, Jul. 2006.

[22] Y. Chen, X. Wang, C. Shi, L. Li, H. Qin, and J. Hu, "Sensing mechanism of SnO2(110) surface to H2: Density functional theory calculations," *Sens. Actuators B Chem.*, vol. 220, pp. 279–287, Dec. 2015.

[23] P. Ágoston and K. Albe, "Disordered reconstructions of the reduced SnO2-(110) surface," *Surf. Sci.*, vol. 605, no. 7–8, pp. 714–722, Apr. 2011.

[24] K. Reuter and M. Scheffler, "Composition, structure, and stability of RuO 2 (110) as a function of oxygen pressure," *Phys. Rev. B*, vol. 65, no. 3, Dec. 2001.

[25] K. Reuter and M. Scheffler, "Composition and structure of the RuO 2 (110) surface in an O 2 and CO environment: Implications for the catalytic formation of CO 2," *Phys. Rev. B*, vol. 68, no. 4, p. 45407, 2003.

[26] Q. Sun, K. Reuter, and M. Scheffler, "Effect of a humid environment on the surface structure of RuO 2 (110)," *Phys. Rev. B*, vol. 67, no. 20, p. 205424, 2003.

[27] P. Hohenberg and W. Kohn, "Inhomogeneous Electron Gas," *Phys. Rev.*, vol. 136, no. 3B, pp. B864–B871, Nov. 1964.

[28] W. Kohn and L. J. Sham, "Self-Consistent Equations Including Exchange and Correlation Effects," *Phys. Rev.*, vol. 140, no. 4A, pp. A1133–A1138, Nov. 1965.

[29] G. Kresse and J. Furthmüller, "Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set," *Phys. Rev. B*, vol. 54, no. 16, pp. 11169–11186, Oct. 1996.

[30] G. Kresse and J. Hafner, "Ab initio molecular-dynamics simulation of the liquid-metal–amorphous-semiconductor transition in germanium," *Phys. Rev. B*, vol. 49, no. 20, pp. 14251–14269, May 1994.

[31] G. Kresse and J. Hafner, "Ab initio molecular dynamics for liquid metals," *Phys. Rev. B*, vol. 47, no. 1, pp. 558–561, Jan. 1993.

[32] J. P. Perdew, K. Burke, and M. Ernzerhof, "Generalized Gradient Approximation Made Simple," *Phys. Rev. Lett.*, vol. 77, no. 18, pp. 3865–3868, Oct. 1996.

[33] J. P. Perdew *et al.*, "Restoring the Density-Gradient Expansion for Exchange in Solids and Surfaces," *Phys. Rev. Lett.*, vol. 100, no. 13, Apr. 2008.

[34] H. J. Monkhorst and J. D. Pack, "Special points for Brillouin-zone integrations," *Phys. Rev. B*, vol. 13, no. 12, pp. 5188–5192, Jun. 1976.

[35] C. Xu, Y. Jiang, D. Yi, S. Sun, and Z. Yu, "Environment-dependent surface structures and stabilities of SnO2 from the first principles," *J. Appl. Phys.*, vol. 111, no. 6, p. 63504, 2012.

[36] M. A. Mäki-Jaskari and T. T. Rantala, "Band structure and optical parameters of the SnO2 (110) surface," *Phys. Rev. B*, vol. 64, no. 7, p. 75407, Jul. 2001.

[37] M. Batzill, K. Katsiev, J. M. Burst, U. Diebold, A. M. Chaka, and B. Delley, "Gas-phase-dependent properties of Sn O 2 (110), (100), and (101) single-crystal surfaces: Structure, composition, and electronic properties," *Phys. Rev. B*, vol. 72, no. 16, Oct. 2005.

[38] J. Oviedo and M. . Gillan, "Energetics and structure of stoichiometric SnO2 surfaces studied by first-principles calculations," *Surf. Sci.*, vol. 463, no. 2, pp. 93–101, Sep. 2000.

[39] A. V. Bandura, J. O. Sofo, and J. D. Kubicki, "Derivation of Force Field Parameters for SnO2−H2O Surface Systems from Plane-Wave Density Functional Theory Calculations," *J. Phys. Chem. B*, vol. 110, no. 16, pp. 8386–8397, Apr. 2006.