

ADSORPTION OF CO GAS MOLECULES ON SnO₂ SURFACE***V.M. Aroutiounian, H.A. Zakaryan**Yerevan State University
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This research is devoted to the investigation of the toxic CO gas adsorption mechanism on the tin dioxide (SnO₂) semiconductor. We used density functional theory (DFT) to describe adsorption processes, and we found out that the Mars-van Krevelen (MvK) adsorption mechanism is not responsible for adsorption on (101) and (001) surface orientations of SnO₂, unlike (110) and (100), where CO₂ molecule forms and desorbs from the surfaces. After adsorption on (101) and (001) surface orientations, CO molecule bound to the surfaces and transfer electrons to it. The charge transfer was calculated using Bader charge analysis, which showed the amount of charge transferred to the (101) and (001) surfaces is larger than to the (110) and (100) surfaces. In the case of (001) surface orientation, we considered half and full surface coverage. It was shown that during full surface coverage only one molecule can be adsorbed and transfer 2e charge. Electronic density of states (eDoS) calculation was done to explain the increase of surface conductance.

Key words: gas sensors; density functional theory (DFT); carbon monoxide (CO); adsorption; Mars-van Krevelen mechanism (MvK); electronic density of states (eDoS).

АДСОРБЦИЯ МОЛЕКУЛ УГАРНОГО ГАЗА НА ПОВЕРХНОСТИ SnO₂**В.М. Арутюнян, А.А. Закарян**Ереванский государственный университет
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Исследован механизм адсорбции угарного газа на полупроводнике – диоксиде олова (SnO₂). Для объяснения процесса адсорбции использовалась теория функционала плотности (ТФП). Показано, что адсорбция не подчиняется механизму Марс-ван Крелелена для (101) и (001) ориентаций поверхности, в отличие от (110) и (001) ориентаций, где сначала образуется, а затем десорбируется молекула CO₂. После адсорбции на (101) и (001) поверхностях, CO связывалась с поверхностью и передавала этой поверхности электроны. Перенос электронов рассчитывался с помощью анализа зарядов (расчет заряда отдельных атомов в молекулах и кристаллах с использованием метода Бейдера), из которого следует, что количество электронов, переданных (101) и (001) поверхностям, больше количества электронов, переданных (110) и (100) поверхностям. При (001) ориентации рассматривались случаи полного и пятидесятипроцентного покрытия поверхности. Показано, что при полном покрытии, только одна молекула CO может адсорбироваться и передавать 2e заряда. Для того чтобы объяснить увеличение проводимости поверхности, была рассчитана электронная плотность состояний.

Ключевые слова: газовые сенсоры; теория функционала плотности (ТФП); угарный газ (CO); адсорбция; механизм Марса-ван Крелелена; электронная плотность состояний.

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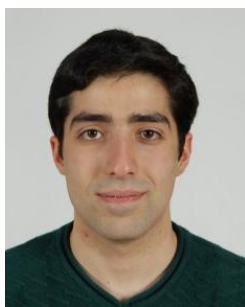
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Introduction

Carbon monoxide (CO) is tasteless and transparent substance, which is known as an “invisible killer” due to the high level of toxicity. It is extremely poisonous and can cause health effects up to a certain extent – 9 ppm, therefore, the detection of CO in the environment is quite vital. For the above reasons, chemical sensors are used to precisely monitor the concentration of the target compounds in the air. Usually, the SnO₂ semiconductor is used as a sensing material in such detectors because of high sensitivity and low response time for wide variety of molecules such as CO, H₂, CH₃OH, NO_x etc. [1–8]. In order to increase the sensitivity of the detectors, it is crucial to deeply investigate the adsorption mechanism of CO compounds.

Several models, which are named as Langmuir-Hinshelwood [9, 10], Eley-Rideal [11] and the MvK [12], have been developed to describe the mechanisms that are responsible for CO adsorption on oxide semiconductors. The MvK adsorption mechanism is in a good agreement with the experiments on SnO₂–(110) surface [13, 14]. Apparently, the MvK mechanism consists of following steps; *I*) adsorbed CO molecule reacts with tin dioxide oxygen and forms CO₂ compound, leaving oxygen vacancy in the material; *II*) remaining vacancy is filled with adsorbed O₂ molecule from the environment; *III*) another CO molecule reacts with already bonded O₂ and forms CO₂, leaving material in its initial undisturbed state.

We would like to stress that there are plenty of manuscripts dedicated to the investigation of CO absorption on SnO₂ surfaces, using first principle and ab initio DFT calculations [15, 16]. Some calculations were done particularly for pristine (110) surface orientation [17], oxygen reach [18] and tainted surfaces [19]. However, very few of them are devoted to other surface orientations (100), (101) [5] and (001) [6]. In practice, the surface orientation immensely influences on sensor parameters such as sensitivity, time response etc.

Adsorption of CO on SnO₂ surface is greatly depended on O²⁻ or O⁻ existence in the environment. We consider such ions do not exist in the environment and CO molecule interacts directly with the surface in some closed volume, as it is usually made in experiments. Such cases are also considered in the [18]. In addition, it is possible to exclude oxygen ions O²⁻ or O⁻ from the environment and explore only the CO gas interaction with the surface in experiments.

In this manuscript, we explore CO adsorption on various surface orientations (110), (100), (101), (001) of SnO₂ and determine the most optimal configurations for adsorption, using ab initio DFT calculations in order to shed the light on the atomic scale processes that still remains elusive and unclear. Here, we will rise following issues: *I*) Does MvK mechanism similarly describe the adsorption processes for all surface orientations of SnO₂? *II*) What is the exact amount of charge transferred between the surface and adsorbed CO molecule? *III*) Which surface orientation is more prominent to the interaction with the CO molecule?



Список обозначений	
<u>Буквы греческого алфавита</u>	
δ	Deviations from Stoichiometry
<u>Буквы латинского алфавита</u>	
E	Energy, eV
a, c	Unit Cell Parameter, Lattice Constant, Å
u	Unit Cell Parameter, Describe Oxygen Position in Unit Cell (no metrics)
<u>Индексы нижние</u>	
ads	Adsorption
clean	Clean Surface without Gas
CO	Free Gas Molecule
g	Band gap of the material
surf	SnO ₂ Surface
2c	Two (etc.) Coordinated Atom
<u>Аббревиатуры</u>	
DFT	Density Functional Theory
eDoS	Electronic Density of States
GGA	Generalized Gradient Approximation
ML	Monolayer
MvK	Mars-van Krevelen Mechanism
PDE	Perdew-Burke-Ernzerhof
VASP	Vienna ab initio Simulation Package

Models and computational methods

Calculations were done using conventional ab initio DFT [20, 21] method implemented in VASP [22–24]. DFT relaxations were done within Perdew-Burke-Ernzerhof GGA [25]. The 500eV cutoff energy was chosen due to the total energy convergence from that value. Surface structures were relaxed until the threshold net force on atoms became less than 0.01 eV/Å. The Monkhorst-Pack scheme [26] was used to sample the Brillouin zone, using 6x6x1 k-points mesh. The ionic relaxation was done using conjugate gradient method implemented in VASP. After that relaxation, the Bader charge analysis was done to find out charge distribution around each atom [27–29]. The difference between charge distribution of the relaxed surface and pure surface was the amount of charge transferred to the surface after finishing adsorption. Stable adsorbed configurations were found using the following equation:

$$E_{\text{ads}} = E_{\text{surf}} - E_{\text{clean}} - E_{\text{CO}} \quad (1)$$

It is clear that if E_{ads} is negative, the configuration of adsorbed site is stable, in other words, the process is exothermic. In the case of positive E_{ads} , the process is endothermic: the molecule is not adsorbed onto the surface and remains in the non-interacting state.

Bulk SnO₂ has rutile, tetragonal structure, corresponding to the P42/mnm space group. The lattice parameters of SnO₂ from [30–32] are $a = 4.82 \text{ \AA}$, $c = 3.23 \text{ \AA}$ and $u = 0.307$. In our calculations (see Fig. 1), each (110), (100), (101), (001) surface consists of 4 layers and relative stability has the following sequence (110), (100), (101), (001) [6]. Here, a number of layers

was tuned to check the convergence of surface energy. However, after getting all results, we double checked the obtained data by recalculating stable structures with a big substrate of 12 atoms of tin and 24 atoms of oxygen, and we made sure that the results were reliable. For all calculations, we chose vacuum thickness of 15 Å, which was greater than substrate thickness. For each surface, the electronic density of states (eDoS) was calculated and established that the gap between valence and conduction bands was underestimated because of the self-consistency of DFT calculations. From the experiments, it was known that value of band gap was 3.6 eV, but we got 1 eV, which was in accordance with the previous DFT calculations [33].

Despite the gap underestimation, it does not influence on the value of the adsorption energies and bond lengths of the calculation. Even if the gap is narrower than it is in experiment, the trend of band gap change after gas molecule adsorption will be the same because the charge transfer or charge density calculated by PBE has minimal error between known functionals. It is worth mentioning that there are some experimental works where white-colour clean SnO₂ is dielectric having the band gap 3.6 eV. Mainly, SnO₂ changes to non-stoichiometric SnO_{2- δ} with a lot of intrinsic defects during the manufacture of different devices made of it. Deviations from stoichiometry were investigated, in particular, by P. Kofstad [34]. The energy of activation for SnO_{2- δ} was equal to 1.44 eV [34]. Creation of many vacancies in the SnO₂ oxygen sub-lattice and inter-lattice fin leads to dramatically high decrease in the conductivity on several orders of magnitude and realization of n-type conductivity. This situation is typical for sensors made of SnO_{2- δ} . Realization of p-type SnO_{2- δ} is possible in the case of large quantity of self-vacancies of tin.

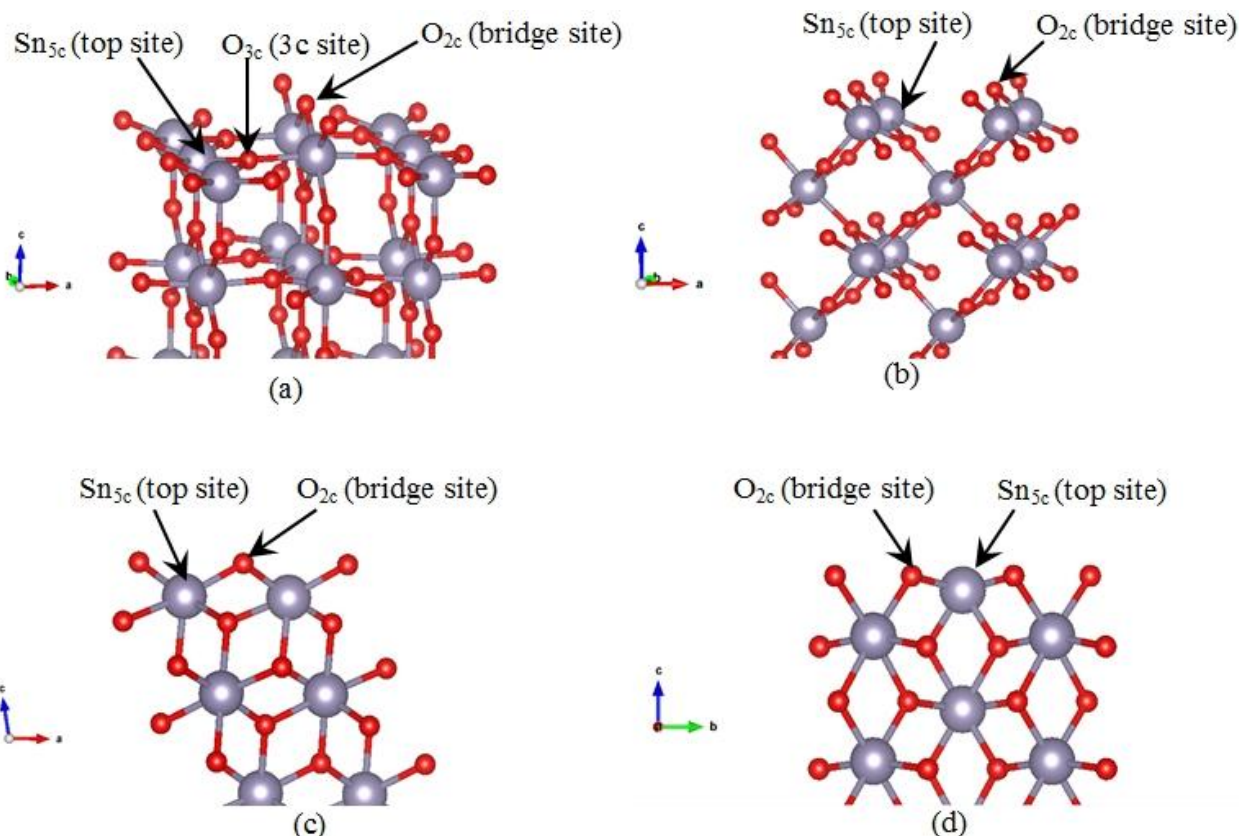


Fig. 1 – Different surfaces of SnO₂ and possible adsorption sites on it: a) (110) b) (100) c) (101) d) (001)

We detected the same situation in process of the semiconductor photoelectrodes constructing for photo electrochemical conversion of solar energy made from ZnO_{2-δ} and TiO_{2-δ} [7]. Therefore, band gap E_g for intrinsic clean SnO₂, TiO₂ is always higher than values of band gap in SnO_{2-δ}, TiO_{2-δ}.

Results and Discussion

In this section, each surface orientation would be described separately. Moreover, Bader charge analysis, eDoS and stable structures would be presented.

SnO₂ (110) surface

This surface orientation consists of 4 layers, each of them comprises of 3 subsequent layers. The top sublayer

represents oxygen where each atom (O_{2c}) is connected to 2 Sn atoms by the covalent bond. The second sublayer has 2 Sn atoms and 2 oxygen atoms. The third one is similar to the first layer. So, together these 3 sublayers can be treated as one layer which is continually repeated 4 times (see Fig1 a). There are 3 possible adsorption sites: top site (t), bridge site (br), three-coordinated oxygen site (3c). For each site, we consider 2 configurations: I) C atom in a CO molecule is closer to the surface (C down configuration) and II) the vice versa configuration (O down configuration). Thus, we end up with 6 possible configurations for (110) surface.

For each separate configuration, calculated adsorption energies are given in Table 1. As we can clearly see, the O down configuration for all surfaces is completely unstable.

Table 1

Adsorption energies, distances and Bader charge analysis of (110) surface

Ads. sites and configurations	Values of E _{ads} , distance and bader charge analysis		
	E _{ads} (eV)	CO distanced surface(Å)	Charge transferred to surface(e)
br	-0.48	3.1	1.7
br(O down)	0.31	2.58	0.0
top	-0.16	2.465	0.0
top(O down)	0.01	2.69	0.0
3c	-0.03	2.61	0.0
3c(O down)	0.5	2.62	0.0

In the case of C down configuration, (110) surface has 3 stable sites. However, there is only the one that transfers the charge from molecule to the surface, and it corresponds to the case when molecule approaches to br-site, reacts with oxygen and takes it away forming a CO₂ molecule and leaves oxygen vacancy on the surface. Here, vacancy could be an adsorption site for O₂ or CO molecule, as described in [15, 18]. The eDoS of surface reveals that conductivity of the surface increases by decreasing of the band gap. The Bader charge analysis shows charge transport to the surface of 1.7e. Such processes were examined in a number of experimental and theoretical studies [13, 15, 18]. It is important to note that, for this particular configuration and surface orientation, the first step of MvK mechanism is

preserved and the distance between CO₂ molecule and surface is 3.1 Å.

For other sites (top and 3c), the CO molecule does not exchange electrons, that serves as a confirmation that we have physisorption process onto the surface. In these cases, band gap does not change and distances from carbon to tin atoms are 2.46, 2.61 Å respectively.

SnO₂ (100) surface

For (100) surface orientation the unit cell also consists of the same 4 layers, where each layer can be divided into 3 sublayers: O-Sn-O layers. The top atom of the surface is 2-coordinated oxygen as in (110) surface (see Fig. 1 b). Adsorption energies for possible two site configurations are given in Table 2.

Adsorption energies, distances and Bader charge analysis of (100) surface

Table 2

Ads. sites	Values of E _{ads} , distance and bader charge		
	E _{ads} (eV)	CO distanced surface(Å)	Charge transferred to surface(e)
br	-0.48	3.25	1.6
top	-0.16	2.65	0.0

According to the calculations, interaction of CO with the O_{2c} site of oxygen leads to the formation of CO₂ molecule and also leaves a vacancy on the surface (Fig. 2 a).

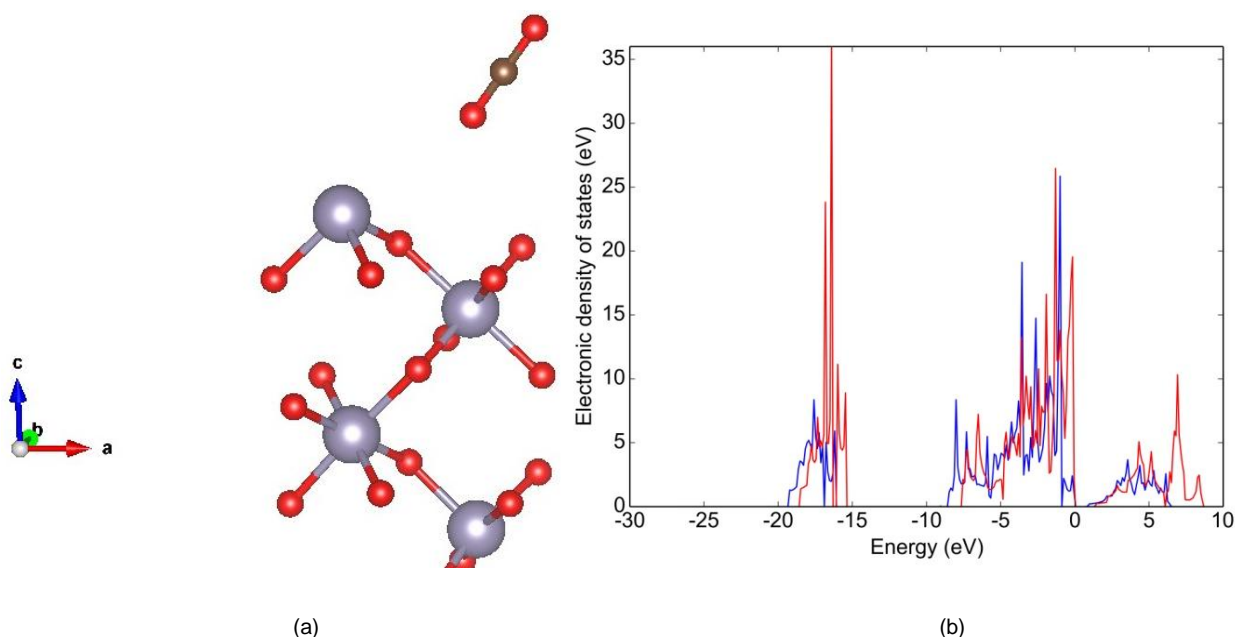


Fig. 2 – Structure and eDoS of (100) surface: a) desorbed CO₂ molecule from (100) surface (red circle is oxygen, grey is Sn, brown is C atoms); b) eDoS of substrate before adsorption (red line), and after CO₂ desorption (blue line)

In this case, the first step of MvK mechanism is also conserved and it leads to charge transfer of 1.6e to the surface. Therefore, the surface conductance is increasing because of transferred charge leading to the band gap

reduction by 0.1eV in comparison to the uncharged surface, see Fig. 2 b. Here, the blue lines represent the eDoS after desorption that correspond to 3.25 Å distance from CO molecule to the surface.

The second possible adsorption site is top(t) on Sn atom. Here as for (110), the CO is physisorbed and no charge transfer has been observed. Due to physisorption, the distance from a carbon atom of CO molecule to the oxygen atom of the surface is 2.65 Å.

SnO₂ (101) surface

In the case of (101) surface orientation, each of 4 layers consists of 3 subsequent layers of 2O, 2Sn, 2O. There are 3 possible sites of adsorptions O_{2c}, Sn atom and 3-coordinated O, which is located in third sublayer as it is shown in Fig. 1 (c). Here, only one configuration has negative adsorption energy and it is O_{2c} (Table 3).

Table 3

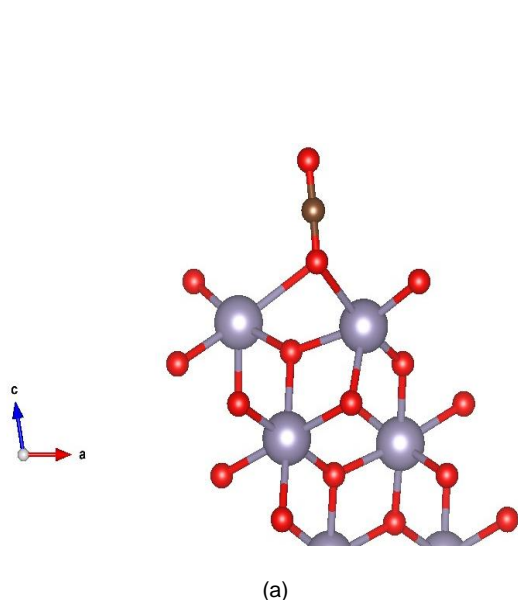
Adsorption energies, distances and Bader charge analysis of (101) surface

Ads. sites	Values of E _{ads} , distance and bader charge		
	E _{ads} (eV)	CO distanced surface(Å)	Charge transferred to
O _{2c}	-0.47	1.18	1.9

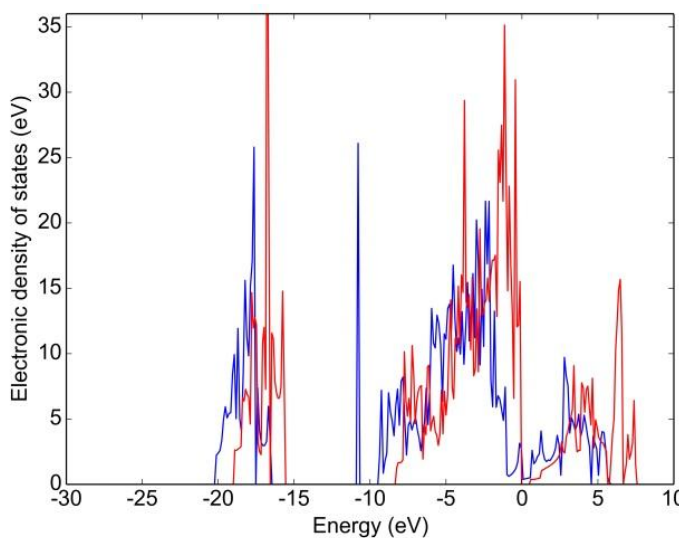
The CO molecule is adsorbed on the surface and connected to it in O_{2c} site with a distance of 1.18 Å (see Fig. 3). During that process, the distance between O_{2c} oxygen and Sn atom increases up to 2.5 Å.



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(a)



(b)



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Fig. 3 – a) Adsorbed CO on the (101) surface (red circle is oxygen, grey is Sn, brown is C atoms); b) eDoS of the clean (101) surface (red line) and CO adsorbed on it (blue line)

The Bader charge analysis shows that the 1.9e charge is transferred to the surface, which makes it more conductive. Thus, adsorption mechanism on (101) surface differs from MvK because no CO₂ desorption observed. Conductivity increases and band gap decreases due to transferred charge, see Fig. 3 (b), where blue lines represent eDoS after adsorption and have more states around Fermi level (Energy = 0 in the horizontal axis).

SnO₂(001) surface

In this case, we have a completely different situation. Instead of 4 layers that consist of 3 subsequent layers,

we have got only the one that consists of one Sn atom and 2 oxygen atoms. There are two possible sites: on top of Sn (t) site and O_{2c} (2c) site Fig. 1 (d). Moreover, there are 2 equivalent 2c sites in one unit cell, thus we should take into account two possible coverages. The first is when both sites are occupied by the CO molecule and form one monolayer (ML=1). The second possible coverage is when only one site is occupied and forms half monolayer of CO (ML = 0.5). For ML = 0.5, carbon monoxide is adsorbed and stay bounded with a distance of 1.16 Å (Fig. 4) to the O_{2c} atom, transferring 2e charge to the substrate (see Table 4).



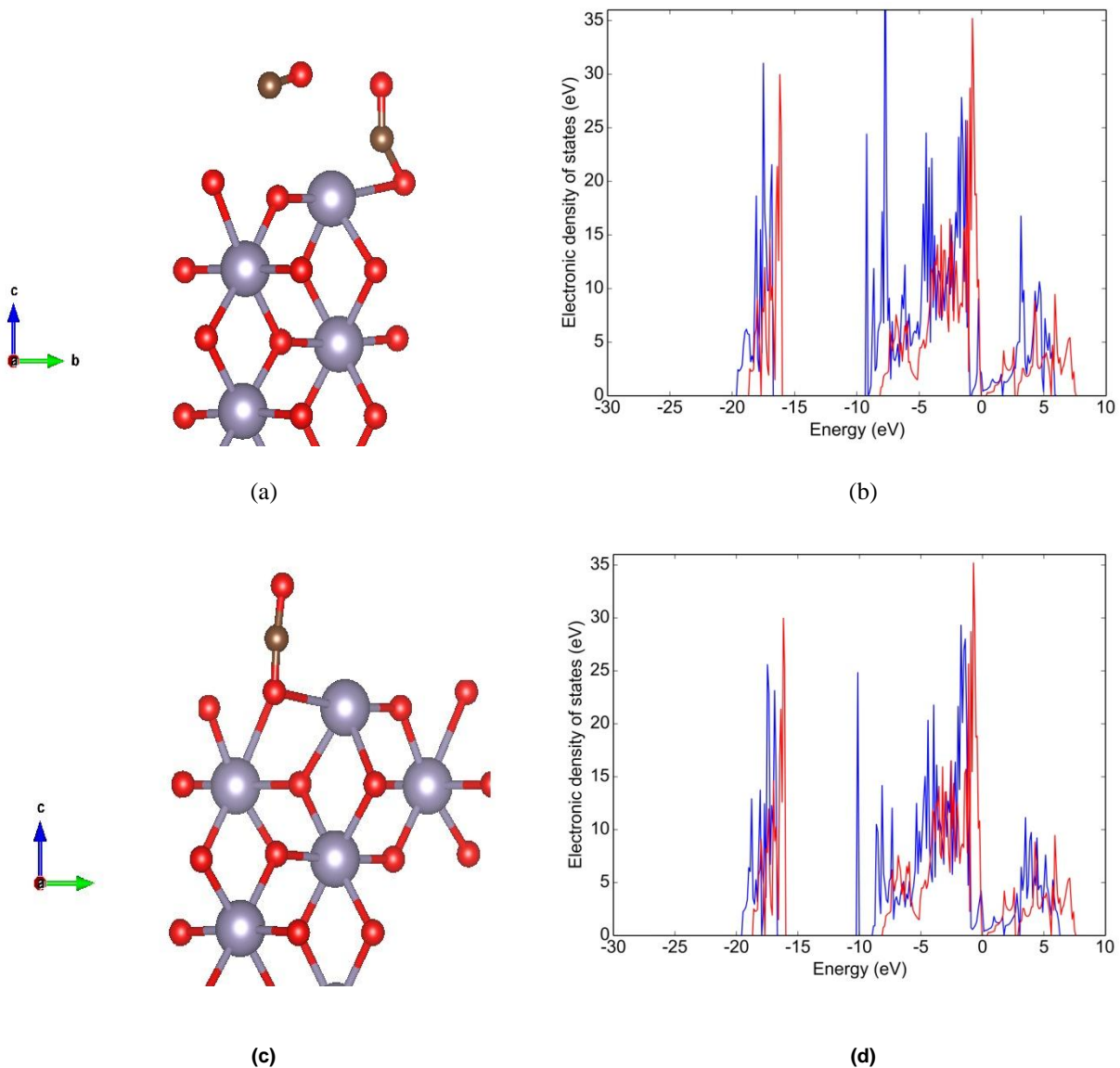


Fig. 4 – Configurations and eDoS of (001) surface (red circle is oxygen, grey is Sn, brown is C atoms): (a) adsorption when ML=1; (b) eDoS before and after adsorption, when ML = 1; (c) adsorption when ML= 0.5; (d) eDoS before and after adsorption when ML = 1

For ML = 1, one CO molecule is adsorbed and one is physisorbed in a 1.255 and 2.6 Å distances respectively. In fact, for (001) only ML=0.5 coverage can happen

because when one CO is adsorbed, the second one is physisorbed. Bader charge analysis shows that 1.83e is transferred to the surface.

Table 4
Adsorption energies, distances and Bader charge analysis of (001) surface

Adsorption sites	Values of E _{ads} , distance and bader charge		
	E _{ads} (eV)	CO distanced surface(Å)	Charge transferred to surface(e)
2c, ML = 0.5	-1.19	1.16	2.0
2c, ML = 1	-1.24	1.25	1.8
top	-0.19	2.41	0.0

In both cases, surface conduction increases and band gap decreases due to charge transfer from the CO molecule. On Fig. 4 (b)(d), the red lines represent eDoS of

undistorted surface and blue ones correspond to the eDoS after adsorption, which has more states around Fermi level

compared to undistorted surfaces eDoS. Physisorption occurs in the top site with distance 2.41 Å.

Conclusion

Previously, it was considered that adsorption on SnO₂ surfaces follows MvK mechanism; however, we have proven that CO adsorption on SnO₂(101), (001) is different. Here, the C atom of the CO molecule remains bonded to surface's O atom. Moreover, we find out that in the case of (001) surface orientation CO coverage can be only half monolayer (ML = 0.5). For (110) and (100) surfaces, we establish that adsorption obeys MvK mechanism where its first stage CO₂ molecules are forming during CO-surface interaction. For all adsorption cases, O down configuration was not stable due to positive adsorption energy.

The Bader charge analysis reveals that charge transfer to (101), (001) surfaces are 1.9e, 2e respectively and 1.7e, 1.6e for (110), (100) surfaces. The eDoS combined with Bader analysis shows that (101), (001) surface orientations gather more electrons than the rest orientations, thus, those should be considered as a better platform for the interaction of the CO molecules with SnO₂ surfaces. We believe that our findings will pave the way for the fabrication of SnO₂ based CO sensors with higher sensitivity and lower response time.

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