Rapid Communication

Density functional theory study of the interaction of H_2 with pure and Ti-doped WO_3 (002) surfaces*

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Density functional theory (DFT) calculations are conducted to explore the interaction of H_2 with pure and Ti-doped WO_3 (002) surfaces. Four top adsorption models of H_2 on pure and Ti-doped WO_3 (002) surfaces are investigated respectively, they are adsorption on bridging oxygen O_{1c}, absorption on plane oxygen O_{2c}, absorption on 5-fold W_{5c} (Ti), and absorption on 6-fold W_{6c}. The most stable and H_2 possible adsorption structure in the pure surface is H-end oriented to the surface plane oxygen O_{2c} site, while the favourable adsorption sites for H_2 in a Ti-doped surface is not only an O_{2c} site but also a W_{6c} site. The adsorption energy, the Fermi energy level E_F, and the electronic population are investigated and the H_2-sensing mechanism of a pure-doped WO_3 (002) surface is revealed theoretically: the theoretical results are in good accordance with our existing experimental results. By comparing the above three terms, it is found that Ti doping can obviously enhance the adsorption of H_2. It can be predicted that the method of Ti-doped into a WO_3 thin film is an effective way to improve WO_3 sensor sensitivity to H_2 gas.

Keywords: H_2 adsorption, WO_3 (002) surface, Ti-doped, density functional theory

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1. Introduction

Tungsten oxide (WO_3) is a wide band-gap n-type semiconductor that has aroused much interest recently as a promising gas sensor because of its excellent sensitivity and selectivity.[1,2] WO_3 can operate at elevated temperatures for long periods of time and can be bused to sensitively detect NO_x,[3–9] H_2S,[4,5,10] C_2H_5OH,[11,12] CO,[3,4,10] and NH_3[3,4,13] even in the presence of other gases such as CH_4[3,4,10] and H_2.[4,9–11,14–17] In order to improve gas-sensing properties, WO_3 is often modified with a small quantity of metals such as noble metals,[4,14] palladium (Pd), platinum (Pt), gold (Au) or transition metals, and titanium (Ti).[18] The gas-sensing mechanism and the experimental phenomena have already been discussed, but little theoretical work has been done. Therefore, it is necessary to understand the surface reactions at the solid–gas interface at atomic level as a complement to experimental work, which would have great significance for the relevant experimental development.

H_2 gas is a clean, portable, and potentially inexhaustible energy source, with the potential to become a panacea for a clean energy generation. However, H_2 has a wide explosion concentration range (4%–75%), low ignition energy (0.02 mJ), and large flame propagation velocity.[15,16] Owing to its ultra-small molecular size, the confinement and the containment of this gas are difficult. Safety regulations emphasize the importance of H_2 sensing to assist in risk minimization. So, the research on the atomistic understanding of interactions of H_2 with a WO_3 surface is imperative and important to the improvement of WO_3 gas sensitivity.

In previous works,[19,20] we discussed the surface energies of different WO_3 surfaces and learned that the (002) surface has a minimum energy, which is in accordance with experimental results in Refs. [21] and [22]. So, the WO_3 (002) surface was chosen as the best model to calculate gas adsorption properties. Then,

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based on density functional theory (DFT) the influence of Ti dopant on the surface property of WO_3 (002) was investigated and it was found that Ti doping can obviously enhance the adsorption of NO_2, which theoretically proved the experimental results that Ti doping can greatly increase the WO_3 gas sensor sensitivity to NO_2 gas. Never has it been discussed that Ti doping affects the sensitivity of the WO_3 (002) surface for the adsorption of H_2 gas. Therefore, in this paper, we mainly investigate the influence of a Ti dopant on the surface property of the WO_3 (002) surface and the benefits of H_2 adsorption, through comparing the interactions of H_2 with pure and Ti-doped WO_3 (002) surfaces based on the DFT.

2. Modeling system and computational details

2.1. Modeling system

As studied in previous work, a WO_3 (002) surface was the optimal surface for gas adsorption. A super cell consisting of a (1×1) surface unit cell was used and a periodic slab model composed of three layers was adopted to simulate the WO_3 (002) surface. The outermost oxygen anions occupying bridging positions and coordinating cations W^{6+} are defined as O_{1c}, while in the second atomic layer, oxygen anions are in plane sites with 2-fold coordinate, marked as O_{2c}, cations W^{6+} in plane are 6-folds as W_{6c}, and unsaturated 5-fold W^{6+} as W_{5c}, and fully coordinate with plane oxygen. The third atomic layer is comprised of sub-bridging oxygen atoms. It is obviously shown that W atoms have two forms, so there are two substitution models to be considered: Ti substitutes W_{6c} and Ti substitutes W_{5c}. According to the computational results, the most stable doping structure of the Ti-doped WO_3 (002) surface is a substitution of a Ti atom for the 5-fold W atom.

Calculations of H_2 adsorption on the pure WO_3 (002) surface were conducted first, and four possible adsorption models (Fig. 1(a)) were constructed, these being adsorption on bridging O_{1c} (M_1), adsorption on plane oxygen O_{2c} (M_2), adsorption on 5-fold W_{5c} (M_3), and adsorption on 6-fold W_{6c} (M_4). That the electronic property changed the surface induced by H_2 adsorption was investigated. Then, the properties of H_2 adsorption on the Ti-doped WO_3 (002) surfaces were studied through four possible adsorptions models, they are the H_2 adsorption on bridging oxygen O_{1c} (N_1), the H_2 adsorption on plane oxygen O_{2c} (N_2), the H_2 adsorption on doped Ti (N_3), and the H_2 adsorption on 6-fold W_{6c} (N_4). The differences of adsorption energy and electronic population between the pure- and the Ti-doped surfaces were discussed.

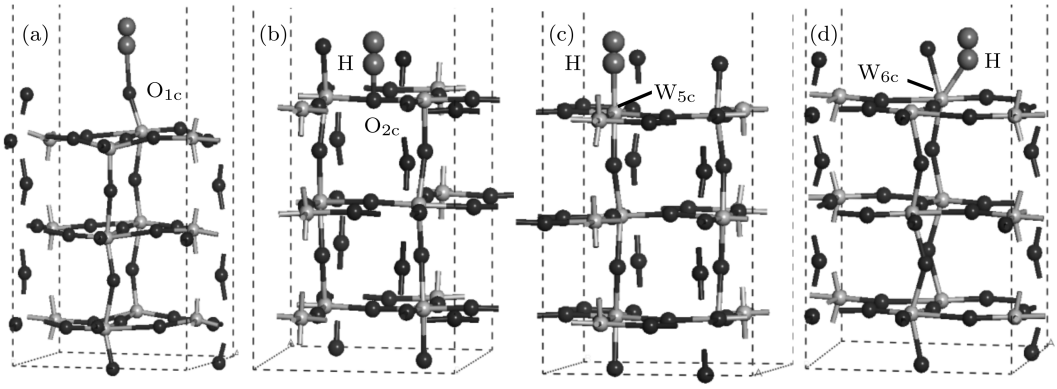


Fig. 1. H_2 adsorption models on WO_3 (002) surface: (a) M_1 model; (b) M_2 model; (c) M_3 model; (d) M_4 model.

2.2. Computational details

The periodic DFT calculations based on first principles were performed using the commercial software CASTEP in Materials Studio (Version 5.0) of Accelrys Inc,[23−25] which can provide accurate calculations of energy and the vibrational properties of adsorption.[26] Exchange and correlation effects are taken into account via local density approximation (LDA) with functional parameterized by Ceperley and Alder (CA-PZ).[27] The real-space orbital cutoff was set to be 4.0 Å (1 Å = 0.1 nm), the force threshold for optimization was 0.01 eV and the Brillouin zone k-point

sampling was performed in a 3×4×1 Monkhorst–Pack scheme. The calculations were found to be converged using an energy cut-off of 340 eV. The convergence criteria for structure optimization and energy calculation were set to be of medium quality with the tolerance for self-consistent field (SCF), energy, maximum force, and maximum displacement of 2.0×10^{-6} eV/atom, 2.0×10^{-5} eV/atom, 0.05 eV/Å and 2.0×10^{-3} Å respectively. A Fermi smearing of 0.1 eV was utilized. These values of the parameters correspond to a medium quality calculation which delivers the highest accuracy that is still computationally feasible for such large systems.

For the n-type semiconductor, band gap E_g is defined as $E_g = E_c - E_v$, where E_c and E_v represent the lowest unoccupied and the highest occupied levels, respectively. As E_F varies between E_c and (1/2) $(E_c + E_v)$ for n-type semiconductors, E_F is considered to be at a LDA mid-gap in this paper. The adsorption energy E_{ads} of H_2 is calculated as follows:

$$E_{ads} = E_{adsorbate+surf} - E_{surf} - E_{adsorbate}, \quad (1)$$

where $E_{adsorbate+surf}$ is the total energy of the adsorbate of H_2 interacting with the surface slab; E_{surf} is the total energy of the optimized surface slab; $E_{adsorbate}$ is the energy of a free H_2 molecule in a vacuum. A negative E_{ads} value indicates the adsorption is energetically favourable.

3. Computing results and discussion

When the WO_3 (002) surface is exposed to a gas atmosphere, we distinguish two sensing mechanisms: (i) adsorption induces reconstruction of the WO_3 surface and the band structure changes correspondingly with the adsorbate type and E_b; (ii) a phenomenon of charge transfer appears, owing to the relation between electron affinity of adsorbate and the work function of the WO_3 surface.

These two mechanisms both contribute to the charge redistribution of the WO_3 surface and the change of E_g correspondingly. Due to the fact that the intrinsic conductivity is controlled mainly by $\exp(-E_g/K_BT)$ under a certain temperature, a change of electronic conductance can be observed in experiment. In the following, we discuss H_2 molecule adsorption on the WO_3 (002) surface.

3.1. Adsorption energies of H_2 on a pure and Ti-doped WO_3 (002) surface

In this study, a H_2 molecule was calculated by locating an H_2 molecule in a periodically repeated box of length 10 Å and energy –30.908 eV. In the free molecule the calculated H–H distance is 0.750 Å.

The whole systems of H_2 on a pure and Ti-doped WO_3 (002) surface were optimized to calculate their physical properties. The adsorption energy and the contribution from charge transfer were gained by comparing the whole systems with a reconstructed WO_3 (002) surface or doped surface. Table 1 shows the adsorption energies of the four possible calculated models (M_1–M_4) for H_2 adsorption on the WO_3 (002) surface and four corresponding models (N_1–N_4) for H_2 on the Ti-doped WO_3 (002) surface. It can be found that all adsorption energies are negative, which means that H_2 molecules were adsorbed in all sites spontaneously without any extra energy, which is the same as a H atom on the WO_3 (001) surface in Ref. [28].

All the adsorption models were built by H-end oriented to the atoms on the surface of WO_3 or Ti-doped WO_3. The calculated results of adsorption energies for H_2 on the pure- and Ti-doped WO_3 (002) surfaces are summarized in Table 1. It can be found that for the H_2 adsorption on pure WO_3 systems (models M_1–M_4), H_2 adsorption with the H-end oriented to the surface plane oxygen (M_2 model) with the largest adsorption energy is the most stable and possible adsorption, which is different from adsorptions of the solutions of NH_3 and NO_2 in previous studies,[19,20] in that the most possible adsorptions are both N-end to O_{1c} on the surface of WO_3. However, the adsorption energy of H-end to O_{1c} (M_1 model) is the smallest among all models seen from Table 1, which indicates that the adsorption effect of H_2 on the pure WO_3 (002) surface is not strong. This phenomenon is caused mainly by different adsorption atoms. As is well known, H atoms tend to lose electrons while N atoms are more likely to obtain electrons. Therefore, the difference between the capability of gaining electrons and that of losing electrons causes the different optimum adsorption sites and adsorption geometries. Thus, the following study of adsorption properties on a pure surface are all based on the system of H_2 on an O_{2c} adsorption site (M_2 model).

Next, we discuss the adsorption energies for H_2 on the Ti-doped WO_3 (002) surfaces. The results

in Table 1 show that H_2 adsorption with the H-end oriented to the surface 2-fold plane oxygen (N_2 model) is the energy favoured adsorption geometry, and the adsorption energy of 4.442 eV is much larger than the value 0.889 eV calculated in the pure surface. According to the definition of adsorption energy

Table 1. Adsorption energies of different models of pure and Ti-doped WO_3 (002) surfaces.

Calculated mode	Energy/eV	Adsorption energy/eV	Calculated mode	Energy/eV	Adsorption energy/eV
H_2	–30.908				
WO_3 (002)	–38991.492		Ti-WO_3 (002)	–38659.988	
H_2 on O_{1C} (M_1)	–39022.724	–0.076	H_2 on O_{1C} (N_1)	–38690.864	–0.032
H_2 on O_{2C} (M_2)	–39023.804	–1.404	H_2 on O_{1C} (N_2)	–38695.338	–4.442
H_2 on W_{5C} (M_3)	-39022.937	–0.537	H_2 on Ti (N_3)	–39691.028	–0.122
H_2 on W_{6C} (M_4)	–39022.759	–0.359	H_2 on W_{6C} (N_4)	–38694.844	–3.948

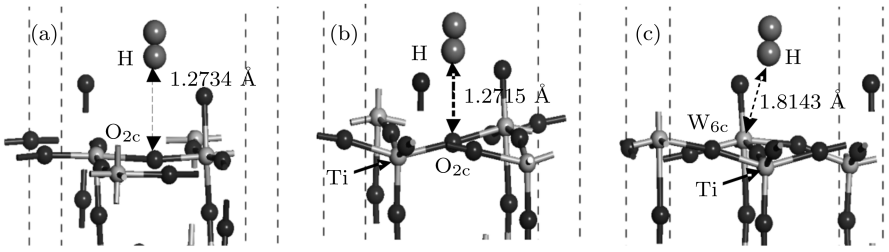


Fig. 2. The bond lengths of H_2 adsorption at (a) O_{2c} site of pure WO_3 surface (M_2 model), (b) O_{2c} site of Ti doped WO_3 surface, and (c) W_{6c} site of Ti-doped WO_3 surface.

in Eq. (1), the large adsorption energy means that the energy of the whole system has a greater reduction after adsorption; therefore, the possibility of H_2 self-adsorption on the WO_3 (002) surface is increased. The main reason for that is that doped Ti reduces the surface energy and makes H_2 adsorption easier. Another favourable adsorption structure is H_2 attached by the W_{6c} atom (model N_4), with an adsorption energy of 3.948 eV. The results indicate that doped Ti has a significant influence on the adsorption energy of the model to some extent. It can be seen that doped Ti can reduce surface energy, meanwhile increase adsorption active centre sites, making more H_2 molecules adsorbed easily and improving the sensor activity.

3.2. Binding energies of H-atoms to the pure and Ti-doped WO_3 (002) surfaces

When H_2 molecules were adsorbed to the surfaces of pure and Ti-doped WO3 (002) surfaces, the binding energies were calculated. While three models were considered, which are H_2 absorption on an O_{2c} site of the WO_3 surface (M_2 model), H_2 absorption on an O_{2c} site of the Ti-doped WO_3 surface, and H_2 absorption on a W_{6c} site of the Ti-doped WO_3 surface as shown in Figs. 2(a), 2(b), and 2(c). The bond length of H–O_{2c} of M_2 model is 1.2734 Å, which is a little longer than that of H–O_{2c} of the N_2 model (1.2715 Å). As for the N_4 model, when a H^+ ion tends to combine with a W_{6c} ion, it is easily bound to an O ion on the top of a W_{6c} ion, thus changing the angle of binding, besides increasing the bond length. So, the bond length of H–W_{6c} is 1.8143 Å, which is the longest of the three models. The geometries of these surfaces after H_2 adsorption were also studied and it was found that the H atom "pulls" the O atom when it is attached to the O atom, resulting in an elongation of the respective bond of the O atom with Ti or W in these surfaces.

3.3. Density of state and electronic structure

A comparison of the density of states (DOSs) of WO_3 (002) surfaces before and after H_2 adsorption of model M_2 is shown in Fig. 3(a), in which the Fermi level is shifted to energy zero so as to superpose the two DOSs at the same Fermi level, it can be observed that the H_2 adsorption has only a little effect on the DOS of the whole surface, that is, all states shift a little toward the left after adsorption. The adsorption of H_2 molecules does not inject electronic states into the band gap E_g of the surface but reduces the band gap of the WO_3 (002) surface from 1.638 eV to

1.529 eV. Meanwhile, the Fermi level E_F makes a little shift of 0.123 eV towards the high-energy direction from –3.70 eV for the WO_3 (002) surface and –2.28 eV for the H_2 adsorbed WO_3 (002) surface. Therefore, the heightening of Fermi level E_F and the change of the electronic states of surface are the main reasons for the sensible changes of the electrical properties of the surface.

Figure 3(b) shows the DOSs of the Ti–WO_3 (002) surfaces before and after H_2 adsorption of models N_2 and N_4. It can be found clearly that for both adsorption models of N_2 and N_4 compared with the DOS of the WO_3 (002) surface, the peak heights of waves drop off and there are small electronic states of 9.98 eV injected in a range of –35 eV∼30 eV, which is caused

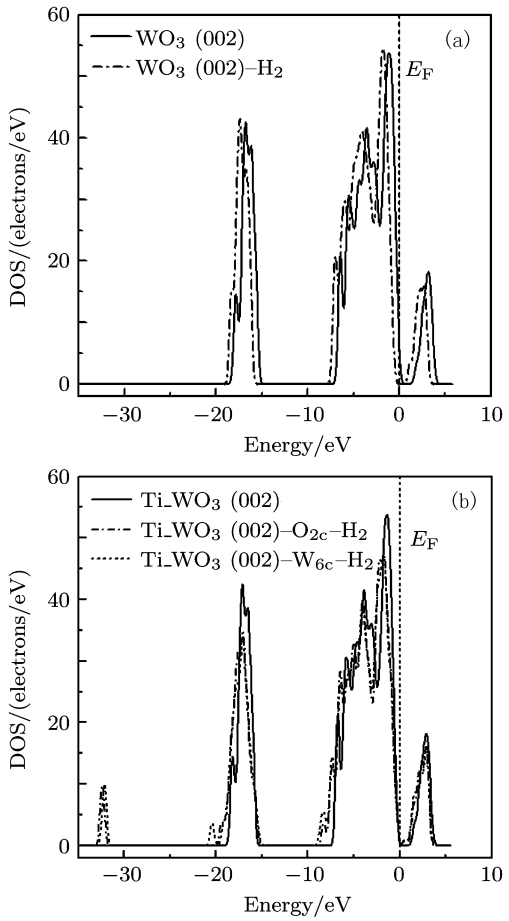


Fig. 3. (a) DOSs of the WO_3 (002) surface before and after H_2 adsorption; (b) DOSs of Ti-doped WO_3 (002) surface before and after H_2 adsorption.

by Ti doping according to the previous study of the contribution of Ti doped to the WO_3 (002) surface. After adsorption the values of band gap E_g of the two systems (N_2 is 0.584 eV and N_4 is 0.536 eV) narrow down more than that of H_2 adsorption to the pure WO_3 (002) surface (M_2 is 1.529 eV). Also the values of Fermi level E_F are moved up from –3.70 eV to –3.07 eV for the N_2 model and –2.95 eV for the N_4 model. The narrower band gap and the higher Fermi level devoted by Ti doping make great contributions to the improvement of the WO_3 sensor sensitivity to H_2 gas.

3.4. Population analysis

The population analysis of H_2 molecules before and after adsorption on pure- or Ti-doped WO_3 (002) surfaces is reported in Table 2. As for a H atom, only the s orbital has an electron and participates in electronic transfer in the process of H_2 adsorption on the pure- or Ti-doped WO_3 (002) surface. The results show that in the system of H-end to O_{2c} of the pure WO_3 (002) surface (M_2 model) the s orbital electron number of H_1 atoms is increased from 1.0 to 1.08, while the number of H_2 molecules is reduced from 1.16 to 1. In other terms, the bond length can be varied with electron population. From the calculated results of bond length it follows that the H–H bond length decreases slightly compared to that of free H_2: the H–H bond length decreases from 0.78762 Å to 0.76850 Å. The free H_2 molecules before adsorption are in electric neutrality, while after adsorption, the H_1 atom obtains $0.08e$ but the H_2 atom loses $0.16e$, which means that the whole H_2 molecule loses $0.08e$. The lost electrons are transferred to the WO_3 surface, which can reduce the height of the barrier in the depletion region and increase the conductance of the surface. Sensitivity varies with conductance, so WO_3 is widely used for gas detection such as H_2, NO_2, NH_3.

From the results of these calculations of the electron population of H_2 molecules adsorbed on the Ti-doped WO_3 surface listed in Table 2, it is known that for an H atom, two models have the same tendency: the s orbital electron is reduced. However, the numbers of transfer electrons are slightly different: for the N_2 model (H-end to O_{2c}),the H_1 atom obtains $0.38e$ and H_2 gains $0.52e$, so, the H_2 molecule loses a total of $0.9e$; for the N_4 model (H-end to W_{6c}), the H_1 atom obtains $0.47e$, H_2 gains $0.53e$, and the H_2 molecule loses a total of $1e$. From the analysis above it follows that the lost electrons of both N_2 and N_4 models are much larger than the value $0.08e$ of

Table 2. Electron populations of H_2 molecules before and after adsorptions on the pure WO_3 (002) surface (M_2 model) and the Ti-doped WO_3 (002) surface (N_1 and N_4 models).

Atom	Before adsorption/e	After adsorption/e		After adsorption/e			
		M_2 model		N_2 model		N_4 model	
	s	s	trans[a]	s	trans	s	trans
H_1	1.0	1.08	+0.08	0.62	–0.38	0.53	–0.47
H_2	1.0	0.84	-0.16	0.48	–0.52	0.47	–0.53

[a]Trans: Transfer electrons.

the electron transfer on the pure surface. The larger calculated results of the electron population prove that Ti doping can greatly increase WO_3 sensor sensitivity to H_2 gas, so can do the NO_2. This is consistent with the experimental results in Ref. [29].

3.5. Comparison with existing experiments

WO_3 thin film gas sensors were prepared by DC reactive magnetron sputtering on an unpolished alumina substrate and annealed in dry air. The sensing elements were fabricated as follows. First, interdigital Pt electrodes were deposited on the clean Al_2O_3 ceramic substrates (0.9 cm $\times$ 2.4 cm) by RF magnetron sputtering. Then, a WO_3 nano-thin film was deposited on the top surface of the Pt film. In the whole sputtering process, we used a DPS-III ultrahigh vacuum facing target magnetron sputtering system. The thickness of the WO_3 thin film was 100 nm. The sensors were annealed in the dry air of a high-temperature heating furnace (at 400 °C and 600 °C) for 4 h.

In order to measure the sensitivity of the WO_3 thin film to H_2 gas, a sealed test box was used. A sample was located in the test box and the test gas was precisely pumped by an injector. The sensors were connected to the outside electronics to monitor their resistance change independently. The sensitivity S is defined as $S = R_a/R_g$, where R_a is the resistance in ambient air and R_g is the resistance in the hydrogen and air-mixed gas. When sensing elements were exposed to a volume fraction of 3×10^{-4} hydrogen, the sensitivity of the WO_3 thin film was measured as a function of working temperature as shown in Fig. 4. From it, we know that under 400 °C of annealing temperature and 270 °C of operating temperature, the hydrogen sensitivity of the thin film can reach a maximum of 77. With the above mentioned features, WO_3 film can be treated as an ideal hydrogen gas sensing material.

The sensing mechanism can be explained by the theoretical results calculated above. As an n-type semiconductor, the carriers of WO_3 are mainly electrons. When oxidizing gas H_2 was injected into the test chamber, the resistance of the sensor diminished and the number of electrons became large. In the previous calculation, on the one hand, E_F improvement after H_2 adsorption makes the carriers move into the conductive band easily, so that resistance is reduced. On the other hand, H_2 molecule injection brings some electrons to the WO_3 surface; so the increase of electron number means that the number of carriers increases.

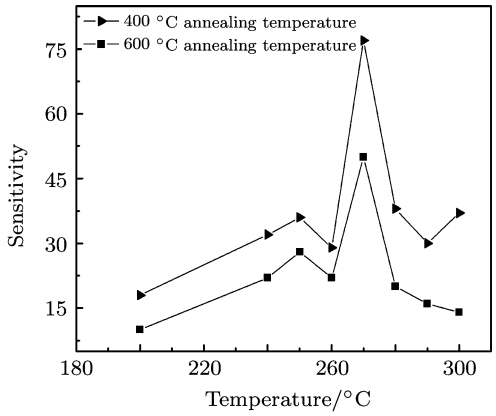


Fig. 4. Sensitivities of WO_3 thin films each as a function of working temperature.

For H_2 adsorption Ti-doped WO_3 thin film, there is no relevant experiment for the moment. From the above analysis it follows theoretically that first, Ti doping can increase adsorption active centre sites. Second, in terms of electron population analysis, H_2 molecules transfer more electrons to the surface of Ti-doped WO_3 than those to the surface of the pure WO_3, which means that Ti-doped WO_3 owns more carriers than the pure WO_3 after H_2 adsorption. And the level of E_F is higher than that of adsorption on the pure surface. And from the study of DOS and electronic structure, after adsorption the band gaps of the two systems are both narrower than those of H_2 adsorption

to the pure WO_3 (002) surface and Fermi levels become higher. So, it can be predicted that the method of Ti-doping into the WO_3 thin film is an effective way to improve the sensitivity of the WO_3 sensor to H_2 gas.

4. Conclusion

In this paper, first principles calculations based on the DFT are used to investigate the sensing mechanisms of H_2 adsorption properties of pure- and Ti-doped WO_3 (002) surfaces through four adsorption models, separately. It is found that all the adsorption energies are negative and H_2 molecules are adsorbed on the surfaces spontaneously. In the case of energy, the adsorption sites of H_2 with Ti-doped WO_3 (002) surfaces have one site more than the H-end oriented to the 2-fold plane oxygen O_{2c} sites of pure WO_3 (002) surfaces (M_2 model), that is, H_2 is attached to the W_{6c} atom (N_4 model). And the adsorption energies (4.442 eV for N_2 and 3.948 eV for N_4) of H_2 on the Ti-doped WO_3 (002) surfaces are both much larger than the value (0.889 eV) calculated in the pure surface. The results indicate that doped Ti can reduce surface energy and makes H_2 adsorption easier. This is beneficial to the increase of the sensitivity to H_2 gas. Furthermore, the electron populations of H_2 molecules adsorbed on the pure and the Ti-doped WO_3 surfaces indicate that the Ti-doped surface obtains more electrons after H_2 adsorption compared with the value $0.58e$ of electron transfer from the pure surface. Besides, the level of E_F of H_2 adsorption with Ti-doped surface is higher than that of H_2 with pure ones.

According to the above analysis, we can know that when the gas molecule is adsorbed on the surface, the electronic conductance of the gas sensor changes. These theoretical results of H_2 adsorption on the pure WO_3 (002) surface are in good accordance with our existing experimental results and the results of H_2 adsorption on the Ti-doped WO_3 (002) surface theoretically prove a prediction that Ti doping can improve the sensitivity of a gas sensor to H_2 on a WO_3 surface.

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