Comparative creation of surface Schottky defects on SnO$_2$(110) and TiO$_2$(110).

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Abstract. Periodic DFT calculations have been used to study the creation of Schottky defects on MO$_2$(110) rutile surface where M=Ti or M=Sn. These defects are oxygen vacancies: a bridging oxygen atom is removed from the surface creating an F$^-$ center and readsorbed on a vicinal site. The readsorption permits to compensate a part of the energy cost required for the removal. Along this process, the stoichiometry and the atomic oxidation states remain those of the perfect surface. The energy cost for such defect is found almost 5 times weaker for TiO$_2$(110) than for SnO$_2$(110). Next, we analyze the effect of hydrogen coadsorption. We start considering the hydrogenated surface, one hydrogen atom binding to a bridging oxygen atom and reducing the metal-oxide surface. The Schottky process then becomes the displacement of a hydroxyl ion which desorbs and readsorbs on surface titanium just as basic species do. This coadsorption does not affect the energy cost in the case of TiO$_2$, while, in the case of SnO$_2$(110), it makes it weaker. This decrease in mainly due to the magnitude of the interaction between a hydroxyl group and the Sn$^{4+}$ surface atom, that is large compared with that for O.

1. Introduction

Metal-oxide surface reactivity is of primary importance for many technological applications such as coating of metals, microelectronic devices or heterogeneous catalysis. In this last case, it is supposed that point defects play an important role in the activity and selectivity of metal-oxide based catalysts. Despite recent significant advances, experimental techniques have still some difficulties for determining several characteristics and properties of these defects. Titanium dioxide in its rutile phase may be the metal oxide which has received the most attention [1]. Titanium may have several oxidation numbers according to the presence of oxygen vacancies. Hence, numerous theoretical studies have dealt with electronic and structural properties of partially reduced surfaces because of neutral oxygen vacancies (for a recent review, please see ref [2]). It is well-known that surface reactivity changes drastically upon oxygen vacancies [3,4]. SnO$_2$ may have also rutile structure. SnO$_2$ rutile is known as a gas-sensor and a catalyst. It is an interesting material as chemical resistant electrode [5] and a transparent conductor [6]. The (110) surface is the surface of lowest energy [7-12]. Sn$^{4+}$ ions as Ti$^{4+}$ are reducible cations. In the following, we will refer to the metal oxidation number (+IV) although TiO$_2$ and SnO$_2$ are semi-covalent crystal; the net charge of the metal cation is smaller and varies according to the partition technique. Sn is more electronegative than Ti and Sn-O bonds are weaker than Ti-O bonds. As a consequence, SnO$_2$ is more reducible than TiO$_2$ [13]. It is worth noticing that Ti$^{2+}$ has a high spin state [14] while Sn$^{2+}$ spin state is low [13,15]. Both TiO$_2$ and SnO$_2$ are wide band gap insulators, their bulk band gap being 3.1 and 3.6 eV, respectively [16].
Among the different properties related to defects, the formation energy of O vacancies is first to be studied. Reported values required for neutral oxygen removal may vary according to the model or technique used [2,4]. One way to reduce this energetic cost is to readsort nearby the oxygen withdrawn. Experimental conditions used to study these defects require treatments (such as Ar$^+$ ions impact) that artificially increase defect concentration and remove irremediably oxygen atoms. However, milder conditions for preparing defective surfaces or natural conditions may allow the readsorption. This is known to happen for MgO whose O vacancies induced by neutron irradiation are mostly resulting from atom displacements [17,18]. This is an experimental indication that such desorption-readsorption may occur. Such process on a surface would result in so called Schottky defects. This has already been shown theoretically on several metal-oxide surfaces to reduce the energy cost formation of oxygen removal [4]. By water or hydrogen coadsorption, Schottky process on MgO yield new structural non-neutral oxygen vacancies with similar spectroscopic properties as analogous classical defects [19,20].

The purpose of this work is to study the effect of hydrogen on the cost for Schottky defects formation. The paper is organized as follows. After a section devoted to computational details, we present the main results related to simple Schottky defect for perfect and clean surfaces. Next, we introduce hydrogen on the surface and present the energetic for an OH displacement. Finally, in order to better analyze the effect of hydrogen, we split up the Schottky defect energy in two terms: the energy cost required to remove the fragment and the energy gained upon the fragment readsorption.

2. Computational details
We performed spin polarized calculations based on density functional theory (DFT). We used the generalized gradient approximation with the PW91 exchange-functional as implemented in the VASP code [21-24] together with a plane wave basis set with a kinetic cut-off at 396 eV and ultrasoft pseudopotentials [25,26] for describing the electron-ion interaction. The calculations were performed sampling the Brillouin zone in a 5 x 5 x 1 Monkhorst-Pack set for the p(3 x 1) cell. The energies were computed within the tetrahedron method with Blöchl correction.

To model the MO$_2$(110) surface, we used a p(3 x 1) unit cell and a three-layer slab which we believe to be thick enough for our purpose. The calculations are periodic in three dimensions and we imposed between successive slabs a distance large enough of at least 10 Å to prevent any noticeable interaction. The adsorbates and the first layer (three atomic layers) were fully relaxed whereas the two bottom layers were kept at bulk position.

The formation energy of a defect and the readsorption energies were calculated as the absolute value of the following expression:

$$E = E_{\text{ref}} + E_{\text{frag}} - E_{\text{system}}$$

$E_{\text{ref}}$ is the energy of the reference system. $E_{\text{frag}}$ is the energy of the fragment involved in the Schottky defect, namely the oxygen atom or the hydroxyl group. $E_{\text{frag}}$ has been determined for O with respect to the energy of an O($^3$P) atom computed at the spin polarized level using an asymmetric box of 10 x 11 x 12 Å$^3$. Similarly, the reference used for the calculation of the energy involving the hydroxyl group contains the energy of HO$^-$ radical calculated in a large box at the spin polarized level taking into account one unpaired electron. With our conventions, the larger $E_{\text{ads}}$, the more exothermic process and the larger $E_{\text{removal}}$, the more expensive the removal. Let us consider an example with the hydroxyl migration. The total energy cost for this migration, called here the Schottky defect energy, is the energy difference between the initial system before the migration (H stands on the perfect surface) and the system after migration (OH on pentacoordinated Ti of a surface with an oxygen vacancy). This migration is split in two terms. The first one is the removal of HO$^-$ radical from the hydrogenated surface. The cost for removing HO is the difference between on the one hand the sum of the energy of the HO$^-$ radical and of the surface with an oxygen vacancy and on the other hand the hydrogenated perfect surface. Finally, the second term is the readsorption of HO$^-$ radical on a pentacoordinated Ti from the surface with an oxygen vacancy. The corresponding adsorption energy is the difference between the energy of the surface before and after this migration.
between on the one hand the energy of the surface with oxygen vacancy plus the energy of a hydroxyl radical in gas phase and on the other hand the energy of the system where OH adsorbs on a pentacoordinated Ti of the surface with an oxygen vacancy. It is important to notice that every system considered in each term of formulas is neutral. We will refer to charged moities, like peroxy or hydroxyl ions, only analyzing species when interacting with the surface.

3. Results and discussion

3.1. Schottky defect associated with the oxygen displacement.

The main results of the energy cost for a Schottky process has already been studied elsewhere [4]. We remind here and we summarize the main results focussing on the comparison of TiO$_2$ with SnO$_2$. We have removed an oxygen atom, forming a vacancy and we have readsorbed it on the surface. The first step only corresponds to a reduction of the surface. We have considered two possibilities for the second step, oxygen readsorption. In the first one, the oxygen adatom forms with a protuberant bridging surface oxygen a peroxy group which is oriented perpendicularly to the direction of the bridging oxygen row (figure 1). This occurs when the oxygen吸附s on the perfect surface without vacancy. The two oxygen atoms forming the peroxy group have oxidation number $+1$. The oxidation numbers of all other atoms are those of the reduced surface generated by the first step. The second possibility for the second step is an O adsorption on a Ti site, the closest 5-fold coordinated surface Ti ion. Then, the oxidation states are those of the clean surface. Formally, the first case corresponds to an atomic migration of O while the second one has to be associated with a migration of an ion, O$^{2-}$.

![Figure 1](image1.png)  

Figure 1. Top view of the MO$_2$(110) surface with Schottky defect associated with a ionic migration (left hand side) and to an atomic migration (right hand side). The dotted lines show the p(3 x 1) cell.
used. The arrows show the oxygen atom displacement from the perfect surface site to the site of lowest energy. For sake of clarity, only the two metal-oxide upper layers are shown.

It is worth noticing that all the systems are closed shell except the case of TiO$_2$ for the peroxo mode resulting from an atomic migration on O. The case of an anion migration is obvious. That of an atomic migration necessitates considering the reduction of the metal ions. For the O defective surface (our intermediate state after the first step), the two electrons of reduction are not paired for TiO$_2$ while they are paired for SnO$_2$ [13]. After O adsorption on TiO$_2$ surface, the total number of unpaired electrons per cell remains equal to two. An O$^{2-}$ ion is replaced by a peroxo group O$_2^{2-}$ in the final state and this substitution maintains all the oxidation numbers – formally a redox process takes place between the two O atoms from the peroxo- : the case of TiO$_2$ remains open shell and that of SnO$_2$ closed shell.

The energy cost for creating a Schottky defect is larger for SnO$_2$ than TiO$_2$, 2.7 eV versus 0.59 eV, respectively.

3.2. Schottky defect with the hydroxyl displacement.

Let us now add a hydrogen atom per unit cell. This hydrogen is located on top of a bridging oxygen atom and reduces the metal-oxide surface [27]. Adsorption energies of 3.05 eV and 2.64 eV have been reported at coverage ½ on rutile SnO$_2$(110) and TiO$_2$(110) respectively [13] with O-H bond lengths of ~0.97 Å. We have then displaced the hydroxyl group to the closest surface acidic site, a 5-fold coordinated titanium atom. The O-H axis bents by 30° relative to the direction normal to the surface. For all systems, TiO$_2$ included, there is only one unpaired electron per unit cell. This means that upon readsorption of the hydroxyl group, one of the two unpaired electrons of the defective surface reduces OH and yields OH$^-$ for which all the electrons are paired; one electron remaining in the surface makes the system an open shell one.

The energetic results for a Schottky defect are presented in Table I.

|          | Clean surface | Surface covered with H | ΔE     |
|----------|---------------|------------------------|--------|
| TiO$_2$  | 0.59          | 0.64                   | 0.04   |
| SnO$_2$  | 2.75          | 1.38                   | -1.37  |

Table 1. Energy (eV) required for on each metal-oxide surface without and with hydrogen. The last column is the magnitude of the energy change for the formation of a Schottky defect upon hydrogen introduction. A negative value stands for a decrease.

It turns out that, in the case of SnO$_2$, adding hydrogen decreases by a large amount the energy cost for the creation of a Schottky defect (a reduction by one half). On the contrary, in the case of TiO$_2$, the cost remains roughly constant (increases by 0.04 eV). Despite this trend, the cost remains weaker for TiO$_2$.

In order to investigate further the origin of the difference for the two metal-oxides, we have decomposed the energy of Schottky defect in two terms. The first one is the removal from the surface of oxygen (or of hydroxyl) and the second one is its readsorption on the defective surface. Then, the total energy cost for a Schottky formation appears as the cost required for the mobile group removal (cost for removal) minus the energy gain obtained for its readsorption on a terrace ($E_{ad}$. The results are presented in Table 2.

|          | Schottky defect | Schottky defect with H |
|----------|-----------------|------------------------|
|          | cost for removal | $E_{ad}$ | cost for removal | $E_{ad}$ |
| TiO$_2$  | 5.56            | 4.97        | 4.40            | 3.76    |
| SnO$_2$  | 5.19            | 2.44        | 4.34            | 2.96    |

Table 2. Energetic (eV) for a Schottky process which is splitted in two terms: desorption and adsorption on a terrace. With the sign convention, the total cost for the Schottky process is the difference of the two terms. For TiO$_2$, the total energy cost remains almost the same upon hydrogen
introduction because these two terms compensate. On the contrary, in the case of SnO₂, when H is present, there is a noticeable increase of the gain for adsorption and the total energy for the Schottky process decreases.

The very first conclusion which arises from the table is that the reason for the small cost in the case of TiO₂ originates from a balance between the two terms. The second conclusion on the hydrogenated systems is that the difference between SnO₂ and TiO₂ arises mainly from differences in readsorption. For TiO₂, the defective surface is much more effective towards OH adsorption than SnO₂ does by 0.8 eV. For TiO₂, E_{ads} is large and decreases with the introduction of hydrogen. For SnO₂, E_{ads} is weak and increases with the introduction of hydrogen.

4. Conclusion
Periodic DFT surface calculations have been carried out on two metal-oxide surfaces TiO₂(110) and SnO₂(110) whose structures are rutile. We have evaluated the effect of hydrogen on the energetic of surface Schottky defects. Two kinds of Schottky defects are generated. In the simple case, one surface bridging oxygen is removed and readsorbs on a surface Ti^{IV}. The readsorption permits to partially compensate the cost required for oxygen removal. Oxygen adsorbs on Ti^{IV} rather than forms a peroxo group with surface oxygen as it does on the perfect surface. This demonstrates that the reactivity is different on a perfect surface than on a reduced surface, controlled by electron counting. It appears that the energy cost for Schottky defects is lower for TiO₂ than for SnO₂ due to a larger oxygen readsorption on terraces. The energy compensation upon readsorption is larger for TiO₂. For a hydrogenated surface, the Schottky defect is the displacement of a hydroxyl group. Again, the energy cost remains still larger on SnO₂. However, relative costs comparing the clean and the hydrogenated surfaces show a factor 2. For TiO₂, hydrogen does not change the energy cost because the decrease of the fragment removal energy cost is almost equal to the decrease of the fragment readsorption energy gain. On the contrary, for SnO₂ the cost for removal does not change while the energy gain upon readsorption increases.

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