

Density functional study of Pd adsorbates at $\text{SnO}_2(1\ 1\ 0)$ surfaces

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Abstract

Palladium adatoms adsorbed on various $\text{SnO}_2(1\ 1\ 0)$ surfaces with sub-monolayer coverages is studied theoretically by using the density functional method. At low coverages, the binding is found to occur essentially between Pd, surface Sn atoms. Twofold coordinated bridging oxygens of stoichiometric $(1\ 1\ 0)$, $(1\ 0\ 0)$, $(1\ 0\ 1)\text{SnO}_2$ surfaces also bind to Pd, but the threefold coordinated in-plane oxygens are inert. At low Pd coverages, the stability of Pd adsorbates is slightly increased due to interaction between Pd atoms which occupy neighboring $\text{SnO}_2(1\ 1\ 0)$ surface unit cells. This can lead to alignment of Pd adatoms on the $(1\ 1\ 0)$ surface along $[0\ 0\ 1]$ direction. Among the different sites that Pd may occupy and be adsorbed at, the in-plane oxygen vacancies at reduced $\text{SnO}_2(1\ 1\ 0)$ are predicted to be preferred. Substitution of tin atoms by palladium is energetically most favorable in the cases of least coordinated surface tin atoms of oxygen deficient surface. Main features of the evaluated electronic structures and charge distributions of the Pd/ $\text{SnO}_2(1\ 1\ 0)$ surfaces are considered.

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1. Introduction

Small catalytically active metal particles dispersed on metal oxide support such as Pd on SnO_2 surfaces have raised interest due to their increasing use in thin film gas sensors, and other applications [1–6]. Sophisticated preparation procedures with additional dopants are being developed in order to enhance and optimize sensor performance [7–11].

It is obvious that, theoretical approaches become increasingly important in attempts to gather relevant information concerning associated fundamental questions.

Earlier, tin oxide bulk and surfaces have been studied by using density functional methods with good reliability in predicting geometries, energetics and electronic structure [12–18]. An agreement with experimental results is found, although all predicted surface reconstructions are not confirmed experimentally. Considerable amount of literature exists about related $\text{TiO}_2(1\ 1\ 0)$ surfaces. Titanium oxide, which belongs to a class of early transition metal compounds with valence d-orbitals, is relatively complicated to model accurately.

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Many stable surface structures of $\text{TiO}_2(110)$ are however revealed, by using similar density functional methods, in good agreement with scanning tunneling microscopy images and other measurements [19–26]. While these surfaces are found to be surprisingly complicated, determination of their approximative surface structure is relatively straightforward [27,28]. It needs to be emphasised, that even in the case of carefully prepared metal oxide surfaces, considerable non-homogeneity, dependencies of bulk defect chemistry (e.g. oxygen vacancies and tin interstitials) and even metastability (e.g. coexistence of different components and strains) may appear. Here, in order to partly circumvent these difficulties, different possible (110) surfaces are considered with Pd occupying various adsorption sites and also substitutional sites in the surface layer. The present consideration provides different cases of $\text{Pd}/\text{SnO}_2(110)$ surface systems with high surface symmetry. Also, the cases of stoichiometric (101) and (100) surfaces are briefly considered.

Adsorption of palladium adatoms on tin oxide surface is not a well known phenomenon. Experimentally, nucleation and growth of Pd deposited onto lightly reduced $\text{SnO}_2(110)$ surfaces, as well as in a related case of $\text{TiO}_2(110)$ surface, is characterized to occur mainly by clustering (Volmer–Weber growth) [2,29]. At room temperature in vacuum, three dimensional isolated palladium clusters form [2,30], which is preceded by a formation of layered clusters of thickness less than three monolayers in the case of TiO_2 support [31,32]. Our calculations show that, in the limiting case of bulk crystalline palladium, the binding energy between Pd atoms exceeds interaction of palladium adatoms with perfect SnO_2 surfaces. This partly explains the tendency of Pd adatoms to concentrate in clusters above critical coverage and temperature [32]. The present consideration focuses mainly on the surface Pd density which is much lower resulting in an atomistic model of the associated phenomena. At these coverages, the interaction between nearby palladium atoms cause palladium atoms to align along $[001]$ direction on (110) surface. This observation is in agreement with experimental investigations of Pd adatoms with low density on TiO_2 support, where clusters

elongated along $[001]$ direction are observed [31]. On the other hand, the attractive interaction between adsorbate and supporting surface tend to increase their common interfacial area by deforming the supporting surface [33]. In the case of $\text{Pd}/\text{SnO}_2(110)$ the attractive interaction is mainly between palladium atoms and surface tin atoms, as well as between palladium and partially coordinated oxygens. As a result, Pd adsorbates are found to be able to substitute atoms of tin oxide surface.

Important characters of doped tin oxide surfaces are surface conductivity and reactivity, for instance in the context of thin film gas sensors. These properties can be strongly influenced by the amount, distribution and chemical state of Pd dopants in addition to associated deformation of the supporting SnO_2 surface [34,35]. The electronic conductance increase associated to the sensing function is explained to be a result of adsorbates or their products acting as donors and/or causing structural changes like decrease of oxygen content of the surface, which also cause a similar effect. Decrease of the potential barriers at surfaces and contacts (Schottky barrier) are equally important in causing similar effects. Even in idealized cases, quantitative theoretical investigations of these properties is almost impossible. For instance, electronic conductivity of metal oxides is problematic because of different activated processes and scattering of charge carriers, which depend on external conditions and environment [36,37] (e.g. oxygen partial pressure and different surface coatings). We will emphasise that the electronic structure (band structure and density of states) of surface provides a starting point for such investigations providing information from which comparisons about charge carrier concentration and conduction can be derived. Band structure, and electrostatic potential provide information of reactivity indices at the early stages of chemical reactions [38].

The paper is organized as follows. In Section 2 the calculation method is described followed by the discussion of surface energetics and geometries in Section 3. The results of the optimization calculations are briefly compared at the end of Section 3. In Section 4 discussion is extended to

surface electronic structure and related properties. In Section 5 the conclusions are presented.

2. Method and SnO_2 surface slab model

The computational first-principles density functional approach used here is based on the plane wave basis set and pseudopotential concept to describe electron–ion interaction (CASTEP/CETEP code) [39]. Utilizing ultrasoft pseudopotentials [40] the plane wave basis set can be limited considerably still with good accuracy in bulk and surface geometries [12]. The plane wave cutoff used here is 400 eV. Oxygen atoms are described by 6 valence electrons, tin atoms by 4 and palladium atoms by 10 plus the corresponding pseudopotential ion cores. Electronic exchange and correlation are taken into account with the generalized-gradient approximation [41]. To sample the Brillouin zone, the number of symmetrized Monkhorst–Pack k -points [42] is 6 for the smallest unit cells. Mulliken population analysis for the structures were also performed. Mulliken charges of atoms and bond populations of pairs are calculated in terms of density matrix and overlap matrix from projections of the one-electron eigenfunctions to the atomic orbitals [43,44].

Crystalline tin dioxide is composed of sixfold coordinated tin atoms (nominally Sn^{4+}) and threefold coordinated oxygen atoms. Its (110) surface with different surface atom types is shown in Fig. 1. Stoichiometric (110) surface contains all surface bridging oxygens, and its composition corresponds to a bulk SnO_2 . It can be viewed to be a SnO_2 surface differing minimally from bulk SnO_2 . Tin dioxide surface is usually designated to be reduced if it lacks all bridging oxygens. This surface system is particularly representative as the fourfold coordinated surface tin ions appear in lower oxidation state designated as Sn^{2+} [29]. Clearly, many other oxygen deficient SnO_2 surfaces are possible [13] and some of them are here taken into account.

All surface geometries are modeled as three dimensionally periodic slab systems, with a vacuum of thickness exceeding 10 Å [12] between surfaces. Initially, most calculations were performed by

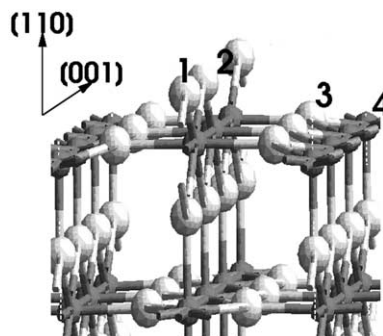


Fig. 1. $\text{SnO}_2(110)$ surface. Bridging oxygen (O_{br}) is denoted by label 1, bridging oxygen vacancy by 2, in-plane oxygen by three and fivefold coordinated surface tin (Sn_{sf}) by label 4. With all bridging oxygen atoms present the surface is called stoichiometric. If all bridging oxygens are removed, by turning the sixfold surface Sn atoms (Sn_{6f}) to fourfold (Sn_{4f}), the so called reduced surface results.

using thin slabs composed of three $\text{O}(\text{Sn}_2\text{O}_2)\text{O}$ layers to explore different possible adsorption sites, with different adsorption coverages, surface unit cell sizes and with different pseudopotentials and spin polarization. For the adsorption energy and structural calculations slabs composed of five $\text{O}(\text{Sn}_2\text{O}_2)\text{O}$ layers were used. Increasing the slab thickness to seven $\text{O}(\text{Sn}_2\text{O}_2)\text{O}$ layers influenced to energetics and surface relaxations only negligibly [12,13,15]. In all slabs the middle Sn_2O_2 layer was kept fixed in bulk geometry allowing all the other atoms to relax. In all cases the fixed layer is also a mirror plane in the slab geometry. Relatively large adsorption energies up to 4 eV/atom were found, and it can be assumed that dependence of the applied methodology is not very critical.

The main scope here is to study cases where one (or less) palladium atom is deposited at each (110) surface unit cell. In terms of palladium metal layers deposited on a substrate (density 1.4×10^{15} atoms cm^{-2}) one atom per surface unit cell corresponds to a coverage of 0.345 Pd monolayers [31].

3. Adsorption sites

Palladium may adsorb to various sites and in different oxidation states at the SnO_2 surface. Palladium oxides (PdO and PdO_2) are commonly

observed in heat treated palladium doped SnO_2 samples [7,45]. In comparison with tin (and many other metals) oxidation of palladium is energetically less favored [29,46]. This can explain the observation that the associated palladium oxide can be relatively easily reduced to palladium [7,45,47]. In our calculations positively charged Pd ions were observed, according to the Mulliken population analysis, if Pd substitutes tin site or is associated in palladium oxide. In other cases, the evaluated total charges of Pd adsorbates are close to zero or even negative. Palladium adatoms with a negative charge are indicated in the cases of other metal oxide surfaces [32] like Pd/MgO and Pd/ Al_2O_3 [48,49], for instance. Consequently, Pd atoms can be accommodated both at sites that are similar to tin and at sites that are similar to oxygen.

3.1. Pd at oxygen deficient $\text{SnO}_2(110)$ surfaces

Adsorption of palladium is strong at reduced surfaces. Fig. 2a and b shows two geometries where one Pd atom occupies a site of bridging oxygen (this geometry is labeled by $\text{Pd}_{\text{O}_{\text{br}}}/\text{R}$) at the surface unit cell of reduced surface. Considering first more coarse Pd coverages to avoid interaction between Pd adsorbates, every second of the adjacent Pd atoms are removed. The adsorption energies of these two geometries are then 3.0 eV (see Table 1). Similarly, if bridging oxygens are present on the surface and palladium occupies the bridging oxygen vacancy site, adsorption energy is almost equal (3.1 eV). The Sn–Pd bond lengths (over 2.5 Å) of these geometries significantly exceed Sn–O bond lengths (below 2.1 Å). More detailed information of the geometries, including also less stable geometries, where Pd is bound with fivefold coordinated surface tin atoms, are listed in Table 1.

By increasing Pd coverage, to correspond the case shown in Fig. 2 (one Pd atom per $(110)\text{SnO}_2$ surface unit cell), the Pd adatoms will interact attractively. This is associated to the fact that the distance between palladium atoms (3.14 Å) is of same order as the distance between Pd atoms in free Pd_2 molecule and in free periodic Pd wire (2.5 Å). As a result, adsorption energies are slightly increased with stable adsorption geometries re-

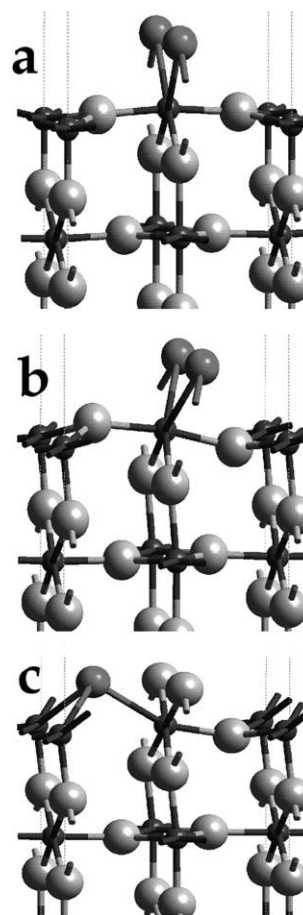


Fig. 2. The geometries of Pd adsorbed at reduced surface. The geometries in a and b are labeled by $\text{Pd}_{\text{O}_{\text{br}}}/\text{R}$ and by $\text{Pd}_{\text{O}_{\text{vpi}}}/\text{R}$ in c. The angles of the Sn–Pd–Sn bonds shown are 77° . The geometries are similar in the case of lower Pd density. Note that the stoichiometry is the same in all cases.

maining similar. Adsorption energies of 3.3 eV were obtained, in the cases of Fig. 2a and b. Thus, a formation of continuous row of Pd adatoms along $[001]$ direction can occur. This may be followed by attachment of Pd adsorbates to such rows. Such adsorption events, with Pd bound with the Pd row and fivefold coordinated surface tin atoms, were found to have almost same (3.1–3.3 eV/atom) adsorption energies. The palladium row formation and agglomeration can be enhanced by relatively small diffusion barriers. For diffusion of palladium above the path joining fourfold coordinated tin atoms (along $[001]$ direction) and for

Table 1

Surface adsorption energies (E_{ads} , in eV) with respect to free Pd atom, and distances between nearest atoms (in Å)

Coverage	Site	E_{ads}	Symm.	Pd–Sn _c	Pd–Sn _{sf}	Pd–O _{bri}	Pd–Pd
<i>Pd at reduced (R) surface</i>							
0.35	Pd _{O_{bri}} /R (Fig. 2a)	3.3	1×1	2.52			3.14
0.17	Pd _{O_{bri}} /R	3.0	1×2	2.50			6.3
0.35	Pd _{O_{bri}} /R (Fig. 2b)	3.3	1×1	2.54	3.32		3.14
0.17	Pd _{O_{bri}} /S ^a	3.1	1×2	2.50			6.3
0.17	Pd on Sn _{sf}	1.4	1×2		2.50		6.3
<i>Pd at position of in-plane oxygen with all bridging oxygens present</i>							
0.35	Pd _{O_{impl}} /S (Fig. 2c)	3.5 ^b	1×1	2.55	2.53		3.14
0.17	Pd _{O_{impl}} /S	4.0 ^c	1×2	2.50	2.49		6.3
<i>Pd at position of in-plane oxygen with bridging oxygens removed^d</i>							
0.17	Pd _{O_{impl}} /R	4.3	1×4	2.45	2.52		6.6
<i>Pd at stoichiometric (S) surface</i>							
0.35	Pd/S (Fig. 3a) ^e	2.6	1×1		2.58	2.12	3.14
0.17	Pd/S	2.3	1×2		2.55	2.10	6.3
0.35	Pd on Sn _{sf}	1.8	1×1		2.52	3.5	3.14
0.35	Pd betw. Sn _{sf}	1.8	1×1		2.74	3.8	3.14
0.35	Pd rows (Fig. 3b)	2.6	2×1		2.74	2.24	2.52
<i>Pd at stoichiometric (100) and (101) surfaces (shown in Fig. 4)</i>							
0.12	Pd/S(100)	2.5	2×2		2.70	2.2 ^f	6.3
0.49	Pd/S(100)	2.6	1×1		2.75	2.19	3.14
0.27	Pd/S(101)	2.7	1×1		2.53	2.14	4.7

Also Pd coverages (cover: 0.35 and 0.17 correspond to one and half Pd/unit cell) and surface symmetries are listed. The atom Sn_c corresponds to a tin atom (four or sixfold coordinated) at the center of the surface unit cell and Sn_{sf} at the corner.

^a One bridging oxygen of stoichiometric surface is replaced by Pd. Results are the same if also one bridging oxygen alongside Pd is removed (1×3 symmetry).

^b E_{ads} evaluated with respect to reduced surface.

^c E_{ads} with respect to stoichiometric surface with a bridging oxygen vacancy.

^d The in-plane oxygen vacancy distribution, with respect to which E_{ads} is evaluated, has 1×4 symmetry [13].

^e If the positions of Pd and bridging oxygen are exchanged E_{ads} is 1.7 eV.

^f Pd is bound with two bridging oxygens as shown in Fig. 4.

the path joining in-plane oxygens (along [001] direction) the barriers are of order 1.0 eV. To ensure that the found structures will not tend to dimerize or reconstruct, optimization runs with larger surface unit cells up to 1×4 symmetry were also performed. The geometries introduced above can be attributed to initial states of Pd adsorbed on reduced SnO₂(110) surface. As will be next described, these geometries do not, however, correspond to total energy minima.

Palladium adatoms were noticed to be likely to substitute or occupy in-plane oxygen sites. Related surface models have recently been considered also in the case of sulphur adsorbed at titanium oxide (110) surface [50]. We first concentrate on the case of Fig. 2c (labeled here by Pd_{O_{impl}}/S) where Pd

adsorbate is relaxed towards the vacuum, while the opposite surface in-plane oxygen is displaced inwards. Immediate comparisons of total energies to above reduced models are possible due to same stoichiometry. An exchange of in-plane oxygen with palladium at the position of bridging oxygen (Fig. 2c), amounts to the total energy decrease of 0.2 eV per Pd atom, at the coverage of one Pd per surface unit cell. Thus, the geometry of Fig. 2c is more stable than the corresponding geometries of Fig. 2a and b. Similarly, in the case of the half coverage, the energy is decreased 0.9 eV per Pd atom (see Table 1). The total energy increases if Pd is exchanged with other oxygen atoms below surface layer, which is expected since Sn–Pd bond length tends to be longer than Sn–O bond.

With increasing oxygen deficiency there is a possibility that some in-plane oxygens and bridging oxygen sites are vacant. If initially no bridging oxygens on (110) surface are present and vacant in-plane oxygen site becomes occupied by Pd, a geometry with the largest adsorption energy (4.3 eV) were found (labeled by Pd_{O_{impl}}/R). In this case, a coarse distribution of surface in-plane oxygen vacancies is considered with every fourth in-plane oxygen along [001] removed in a distribution, which is known as 1×4 in-plane oxygen vacancy model [13]. Corresponding alignment of the Pd adatoms along [001] direction was not found to decrease the total energy significantly.

3.2. Pd at stoichiometric (110), (100) and (101) surfaces

Adsorption energies of Pd on different stoichiometric surfaces were found to be significantly lower than in the cases of oxygen deficient surfaces. Attractive interactions of Pd with twofold coordinated bridging oxygen atoms and with fivefold coordinated surface tin atoms are weaker.

For a single Pd atom on stoichiometric (110) surface (Pd/S), adsorption energy of 2.3 eV was obtained, when Pd is bound with both bridging oxygen and with fivefold coordinated surface tin atoms. The geometry is similar to that shown in Fig. 3a, which corresponds to a higher coverage (one Pd per unit cell). In both cases, the angle between Sn–Pd–O bonds is almost 90°, and therefore *sd* or *sd*² hybridization can be present [51]. The interaction between Pd atoms increases adsorption energy of the geometry of Fig. 3a to a value of 2.6 eV. Thus, rows of Pd atoms along [001] can be formed. Another possibility at higher coverages is a formation of a double row along [001], as shown in Fig. 3b. Other possible adsorption geometries, with lower adsorption energies are indicated in Table 1.

The proposed geometries of the Pd on (100) and (101)SnO₂ surfaces are shown in Fig. 4 and quantitative information is given in Table 1. In the case of (100) surface, almost equal value of the adsorption energy (2.6 eV) with respect to (110) surface is obtained, when Pd adatoms on surface interact attractively. At lower Pd coverage, ad-

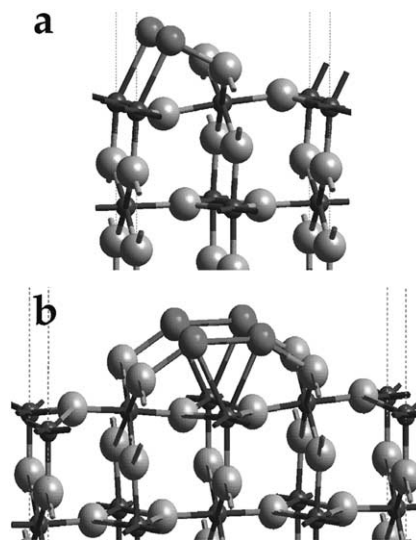


Fig. 3. The geometries of Pd adsorbed on stoichiometric (110) surface unit cell (Pd/S). The angles of the O–Pd–Sn bonds shown are 89.7° in a and 87.4° in b. The stoichiometry is the same in both cases.

sorption energy decreases to 2.5 eV. The Pd/SnO₂(101) adsorption geometry, with low Pd coverage, is associated with a slightly larger stability with adsorption energy of value 2.7 eV. This result is interesting since in the case of TiO₂ there is experimental evidence for increased adsorption on (101) surfaces [52].

3.3. Palladium substituting surface tin atom

It is possible that surface tin atom can be substituted by palladium atom, or that surface cation vacancies can be produced otherwise [31], and occupied by Pd adatom. These are suggested also by the fact that ionic radius of positively charged Pd²⁺ (0.8 Å) ion is between ionic radii of Sn⁴⁺ (0.7 Å) and Sn²⁺ (0.9 Å) ions [53]. Furthermore, the valence orbitals of free Pd atom are higher in energy with respect to the valence band of stoichiometric SnO₂(110) surface, which suggests that Pd is able to donate charge to SnO₂ in adsorption process [32].

The surface tin atoms that were initially replaced by Pd in geometry optimizations were those of reduced and stoichiometric surfaces and fivefold coordinated tin atom associated with bridging

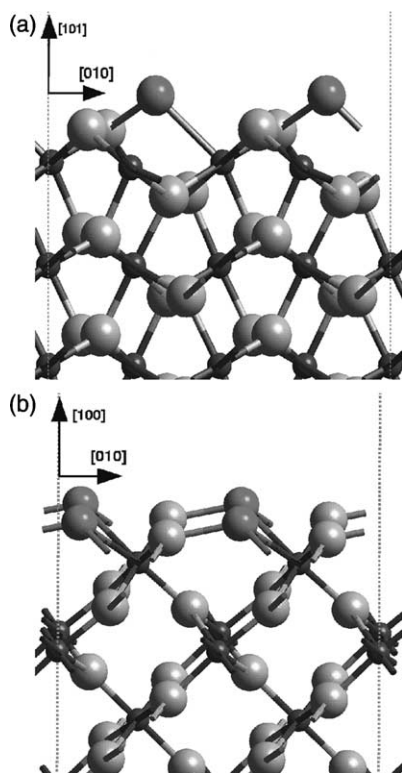


Fig. 4. The geometries of a Pd adsorbate on stoichiometric (a) (1 0 1), (b) (1 0 0) surfaces (labeled by Pd/S(1 0 1) Pd/S(1 0 0)).

oxygen vacancy (see Fig. 1). Of these surface tin atoms, the fourfold coordinated tin atom (Sn^{2+}) was found to be the most preferred. The corresponding geometry ($\text{Pd}_{\text{Sn4f}}/\text{R}$) is shown in Fig. 5a. Mulliken charges indicate that the Pd ion is now positively charged by about 0.2 e. In what follows this ion will be designated here as Pd^+ , distinct from the above considered neutral or negative Pd atoms which are designated as Pd^0 . Palladium Pd^+ ions interact also attractively favoring positions where Pd atoms are next to each other (rather than between two surface Sn^{2+} ions), which was noticed in optimizations with larger surface unit cell.

The above results suggest that especially at oxygen deficient surfaces tin may be replaced by palladium. One may thus question, if threefold coordinated surface tin atoms of more oxygen deficient $\text{SnO}_2(1\ 1\ 0)$ surface [13,54] can be substituted by Pd. In this case, it was noticed that Pd adsorption cause surface to deform drastically to

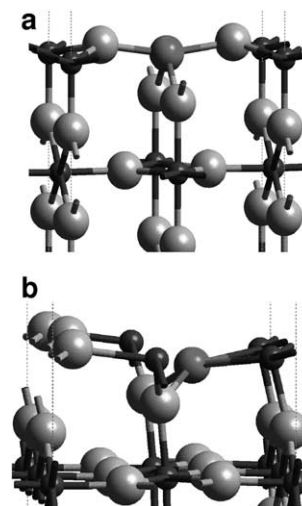


Fig. 5. The geometries of Pd substituting surface tin atoms: (a) Pd substitutes a fourfold coordinated surface tin atom ($\text{Pd}_{\text{Sn4f}}/\text{R}$); (b) Pd substitutes a threefold coordinated surface tin atom after which the surface layer is considerably deformed.

a geometry shown in Fig. 5b. The comparison of the total energies indicates that this replacement of surface tin by palladium is the most preferred, which can of course be influenced also by the low stability of the initial $\text{SnO}_2(1\ 1\ 0)$ surface. Thus, Pd is predicted to have a tendency to substitute least coordinated surface tin atoms of the (1 1 0) surface. It is noticeable that in the structure of Fig. 5b tin atoms are outermost. This is similar to what has been suggested in experimental investigations with oxygen deficient Pd/ SnO_2 surfaces, where tin alloy is formed on reduced surface [55].

3.4. Comparison of different surfaces

The ordering of the adsorption energies of palladium is concluded to decrease in the following order

$$\text{Pd}_{\text{Oimpl}} > \text{Pd}_{\text{FCC}} > \text{Pd}_{\text{Obrl}}/\text{R} > \text{Pd}/\text{S} > \text{Pd on Sn}_{5\text{f}} \\ > \text{Pd on O}_{\text{brl}}$$

The symbols correspond to those used in figures and in Table 1, added with a bulk binding energy of face-centered cubic structure palladium (Pd_{FCC}), for which a value 3.9 eV was calculated (experimental value 3.9 eV [56]). The symbol Pd_{Oimpl}

represents adsorption energies of Pd adsorbed at in-plane oxygen vacancy site in the cases of reduced surface and surface with in-plane oxygen vacancy with no bridging oxygens.

The ordering indicates that occupation of in-plane oxygen vacancy sites by palladium atoms is most favorable. This may provide seeds for cluster formation and have an influence on the overall clustering process [32,48]. Initially, the mutual cohesion energy of Pd adatoms is quite modest for a few atoms, but increases with increasing number of palladium neighbors, explaining the formation of crystalline palladium clusters [2]. In the case of strongly reduced surfaces, such clustering is expected to be hindered, which can be concluded from the ordering.

Palladium, which does not oxidize easily, can stabilize reduced surfaces with respect to stoichiometric surface. In terms of total energy, less energy is needed for release of oxygen from Pd/S surface (creating Pd/R) than what is needed without Pd adatoms (from stoichiometric to reduced). This energy difference exceeds 0.7 eV/atom for the surface of Fig. 2c. There are also experimental observations of similar unstability of oxygen in the case of Pd/SnO₂ material [45,47].

4. Electronic structure of Pd/SnO₂(110)

According to the above discussion, the most representative selection of low coverage Pd adsorption geometries is assumed to include the geometries shown in Figs. 2a,c, 3a and 5a, corresponding to exchange of in-plane oxygen by Pd, Pd on reduced and on stoichiometric (110) surfaces, in addition to the case of Pd replacing a fourfold coordinated surface tin atom. The electronic structures of these surfaces, including also lower Pd coverages (when continuous Pd row is not formed), are considered next.

All surfaces are non-metallic and have differing band gaps. These are illustrated in Fig. 6, including the so called scissor correction, of value 2.25 eV. It corrects the underestimation of the GGA method by shifting conduction band to match the experimental bulk band gap (3.6 eV [12]). It is observed in Fig. 6, that the band gap decreases to

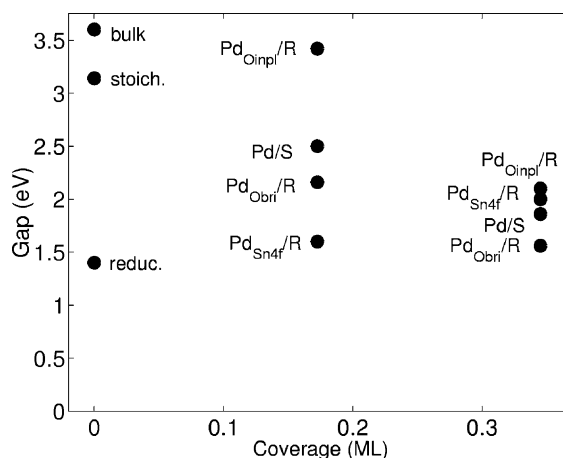


Fig. 6. Band gap of the surface structures as a function of the Pd coverage.

about 1.5 eV after the Pd row has been formed or if the surface cations of Sn²⁺ or Pd⁺ types are present at surface. Clearly, this can alter surface conductivity, reactivity and optical parameters. For instance, supposing a thin film (thickness 20 nm) with each adsorbate (0.35 ML coverage) causing a donation of one conduction electron, the conductivity of the film can be doubled [57]. The enhancement of reactivity is attributed to decrease of global chemical hardness, which is approximately half of the gap [58,60]. Roughly, Sn and Pd sites may behave almost similarly, since electrostatic potentials (with respect to positive charge) around these atoms are similar and much lower than around oxygen sites [38,47]. Towards dissociation of oxygen, the Sn²⁺ ion of reduced surface has been predicted to be more reactive than the corresponding Pd⁺ ion [59]. This is in agreement with the smallest gap of the reduced surface.

In Fig. 7 the band structure of the reduced surface with substitution of in-plane oxygen by Pd (Fig. 2a) is shown with the corresponding projected bulk band structure of SnO₂ crystal. The alignment of the projected bulk band structure relative to the surface slab band structure is fixed to match the valence band minima at the Γ point [12]. The band structure illustrated is roughly similar with the other surfaces in which Pd⁰ type of atoms are presented (Figs. 2a,c and 3a). In these cases the uppermost disperse and delocalized

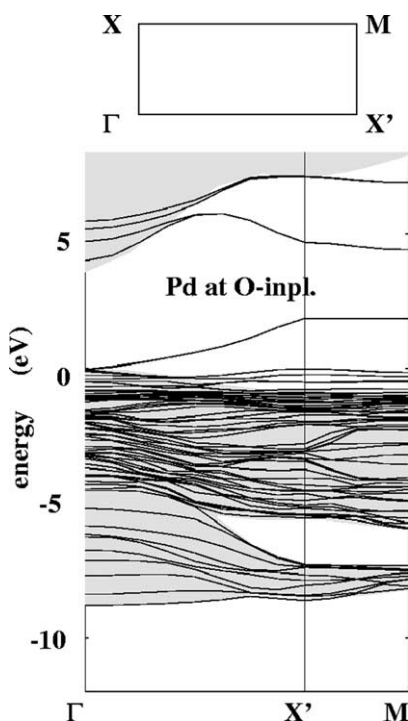


Fig. 7. Surface bands of the Pd/SnO₂(1 1 0) surface slab model corresponding to geometry shown in Fig. 2c. The shaded region is the projected bulk band structure. Part of the first Brillouin zone with high symmetry points, where valence band maxima and conduction band minima are found.

valence band are associated with modest contribution of palladium s and p types in addition to dominating Pd-d type contribution. Particularly, in the case of the geometry of Fig. 2c, also other surface atoms contribute including p-states of bridging oxygens and in-plane oxygen. Occupied Pd type of states, entirely of d-type, are found near the top of the valence band (above -4 eV in the scale of Fig. 7). In the case of the surface with Pd⁺ type of ion (Fig. 5a), the Pd contribution instead extends throughout the valence band and is also found at energies of deep lying O-2s type of levels (below -17 eV from the top of the valence band). The latter contribution is almost vanished in the case of the Pd⁰ atoms. The above results are in qualitative agreement with photoelectron spectroscopy of Pd doped SnO₂ systems [61] and Pd on other metal oxide supports [32], which do not distinguish different types of palladium adatoms.

The large dispersion of the highest occupied levels can result from sdp-hybridizations [32,51,62] and by overlap between e_g type of states (z^2 orbital) of Pd adatoms [36]. The high curvature at the top of the valence band implies that holes can have large mobility along [0 0 1] direction at the surface, once the palladium rows are formed. This can, in principle, influence to the surface conductivity especially when bands at surface are bent upwards [29]. On the other hand, at lower Pd coverage, the uppermost states have much less dispersion, and more generally, electrons are majority charge carriers of SnO₂ due to its donor impurities. The conduction band minimum is found at the Γ point, except for the case where Pd adatoms are on reduced surface with every second Pd absent from the continuous Pd row. In this case the dispersion of conduction band has a large anisotropy. Excluding this surface model, effective masses of electrons range between 0.5 and $1.5 m_e$ depending on direction, being heavier than in SnO₂ crystal. The evaluated effective masses of SnO₂ crystal were between 0.29 and $0.53 m_e$, to compare with the experimental values between 0.2 and $0.3 m_e$ [63]. Smallest effective masses were evaluated for the stoichiometric surface along [0 0 1] direction ($0.5 m_e$), for surface model of Fig. 4 and in the case of Pd adatoms on reduced surface if every second Pd is absent from the continuous Pd row ($0.3 m_e$). Thus, at low coverages, Pd adsorption can enhance conductivity by electrons of stoichiometric thin film due to increase of charge carrier concentration rather than influencing on the effective masses.

Evaluated charge differences, with respect to free palladium atom, indicate significant excess electron charge distributions between Pd⁰ and the nearest Sn atoms, in addition to the positions of Pd⁰ atoms. Thus, there is a covalent Pd–Sn bonding, which is supported also by a positive bond populations of the corresponding Pd–Sn bonds. These charge distributions obviously are a reason for large (negative) Mulliken charges of Pd⁰ atoms, which are almost equal to those of oxygen ions. However, this may be artefact related to Mulliken population analysis, which is known to be sensitive to the choice of atomic orbitals. Some covalent bonding is observed also between

palladium and bridging oxygen in the geometries of Fig. 3.

5. Conclusions

The Pd/SnO₂(110) adsorbate/substrate system has been studied in the case of low Pd coverage. Calculations show that Pd can adsorb to various anionic and cationic sites depending on surface reduction and external conditions. At anionic sites Pd–Sn bond lengths significantly exceed Sn–O lengths in bulk and surface. It can be predicted that on perfect stoichiometric (110) support, clustering of Pd results, while on reduced surfaces, the palladium–metal oxide interaction may also cause deformations of the supporting surface layer by Pd substitution of surface layer atoms. Strong binding of Pd with surface tin atoms can enhance release of oxygen from stoichiometric surface, which makes tin sites on surface more reactive. Reduced surface containing Sn²⁺ type of ions has smaller band gap that is slightly below the gap of the Pd/SnO₂ surfaces considered.

Surface in-plane oxygen vacancies are found to be preferred adsorption sites (E_{ads} above 4 eV), some of which are expected to be or become available in the case of oxygen deficient surfaces. Fourfold and fivefold coordinated surface tin atoms provide adsorption sites also. Binding is weaker at the stoichiometric (110), (100) and (101) surfaces than at the reduced (110) surfaces. In these cases, Pd is bound with bridging oxygen and/or surface tin atoms. The weak attraction between palladium adatoms can enhance the alignment and nucleation of Pd adatoms along [001] surface direction, especially in the case of stoichiometric (110) surface. Least coordinated (3 or 4) surface tin atoms of the reduced SnO₂(110) surfaces are predicted to be preferred substitution sites of Pd among tin atoms. The observed substitution reactions may be connected with the experimentally observed formation of tin alloy on Pd/SnO_{2-x} surface.

Once the continuous Pd rows has been formed, or the surface cations of Sn²⁺ or Pd⁺ types are present at the surface with large density, the thin film conductivity can be increased due to the de-

crease of the band gap and de-localization of conduction band states. This may be associated with increased reactivity, over the stoichiometric surface and over the case in which some in-plane oxygen sites are occupied by Pd.

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