

# Pt-incorporated anatase TiO<sub>2</sub>(001) surface for solar cell applications: First-principles density functional theory calculations

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First-principles density functional theory calculations were carried out to determine the low energy geometries of anatase TiO<sub>2</sub>(001) with Pt implants in the sublayers as substitutional and interstitial impurities as well as on the surface in the form of adsorbates. We investigated the effect of such a systematic Pt incorporation in the electronic structure of this surface for isolated and interacting impurities with an emphasis on the reduction in the band gap to visible region. Comprehensive calculations, for 1 × 1 surface, showed that Pt ions at interstitial cavities result in local segregation, forming metallic wires inside, while substitution for bulk Ti and adsorption drives four strongly dispersed impurity states from valence bands up in the gap with a narrowing of ~1.5 eV. Hence, such a contiguous Pt incorporation drives anatase into infrared regime. Pt substitution for the surface Ti, on the other hand, metallizes the surface. Systematic trends for 2 × 2 surface revealed that Pt can be encapsulated inside to form stable structures as a result of strong Pt-O interactions as well as the adsorptional and substitutional cases. Dilute impurities considered for 2 × 2 surface models exhibit flatlike defect states driven from the valence bands narrowing the energy gap suitable to obtain visible-light responsive titania.

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## I. INTRODUCTION

The wide-gap semiconductor titania (TiO<sub>2</sub>) has raised great interest primarily because of its catalytically active surfaces, long-standing stability, nontoxicity, and availability of single-crystal samples.<sup>1-3</sup> The most common phases of titania are known to be anatase, rutile, and brookite, among which anatase phase proves to be the most promising for photoelectrochemistry,<sup>4</sup> visible-light photocatalysis,<sup>5-7</sup> rocking-chair lithium batteries,<sup>8</sup> and optoelectronics.<sup>9</sup>

Hengerer *et al.*<sup>10</sup> studied the stability of anatase TiO<sub>2</sub>(101) and (001) facets, and found that it is possible to obtain clean and structurally perfect anatase surfaces. Single crystals of anatase TiO<sub>2</sub> exhibit stronger photocatalytic activity than rutile phase titania.<sup>11,12</sup> The natural crystallographic (001) surface of anatase is most often considered for catalytic applications among its various facets.<sup>13</sup>

Titania is active under UV irradiation while it is almost inert to solar spectrum by absorbing only 2%-3% of the sun light. Hence, narrowing the band gap to visible range is particularly important for practical photocatalysis. Such applications utilize excess electrons incorporated by various impurities. Resultant defect states fall in the band gap of TiO<sub>2</sub> sensitizing it for visible-light induced catalytic purposes. Usual way of defect formation is achieved by oxygen vacancy which reduces the oxide. However, merely the vacancy driven defect states are not enough for high level of activity.

Many attempts have been made to functionalize the titania surfaces for solar cell applications by impurities in the form of ion doping or dye sensitization.<sup>7,14-18</sup> Moreover, by acting as charge trap sites, such impurities are proposed to help in retarding the fast charge-hole recombination rates, which inherently exist in most of the semiconductors as TiO<sub>2</sub>.

Doping TiO<sub>2</sub> with metallic as well as nonmetallic elements has been extensively studied for powdered photocatalysts. Anatase phase of TiO<sub>2</sub> doped with N, S, C, and B has been reported to exhibit relatively high level of visible activity.<sup>18-23</sup> Supportingly, Wang *et al.*,<sup>17</sup> in their theoretical study, showed that N doping narrows the band gap of TiO<sub>2</sub> by bringing impurity states in the vicinity of valence-band maximum (VBM). Such an enhancement can also be obtained by transition-metal ion doping which reduces the gap allowing visible-light absorption by providing intraband states near the conduction-band or valence-band edges.<sup>14,24,25</sup> Yet, it depends on the role of dopants as recombination centers or as charge traps. For instance, Co<sup>3+</sup> and Al<sup>3+</sup> impurities serve as electron-hole recombination sites, significantly decreasing the photoreactivity. Pt ion doping has been successfully shown to enhance visible activity functioning as charge generation centers which produce free and trapped charges.<sup>7,14</sup>

Metal ion doping in the form of Ti substitution has been proposed also for titania based dye-sensitized solar cells (DSSC) which gain visible-light activation through dye molecule surfactants. In this manner, DSSC photovoltaic efficiencies have been found to be remarkably better for doped TiO<sub>2</sub> by preventing injected dye electron recombination between the electrolyte and the substrate.<sup>15</sup> On the other hand, Pt incorporation is not merely limited to powdered photocatalytic systems. Recently, Kitano *et al.*<sup>16</sup> successfully developed visible-light responsive Pt-loaded TiO<sub>2</sub> thin-film photocatalysts which achieve separate H<sub>2</sub> and O<sub>2</sub> evolution from water without requiring dye sensitization.

Encapsulation of Pt in titania due to the strong metal support interaction (SMSI) under reducing-gas atmosphere has been reported by Pesty *et al.*<sup>26</sup> Later, Zhang *et al.*<sup>27</sup> showed that neutral Pt atoms can thermally diffuse into TiO<sub>2</sub> lattice

under oxidizing atmosphere. They also argue that these diffused Pt atoms can substitute for  $\text{Ti}^{4+}$  when oxidized to  $\text{Pt}^{2+}$  or else they form interstitial impurities as well.

In this paper, we have investigated the effect of Pt incorporation in both the lattice and the electronic structure of stoichiometric anatase  $\text{TiO}_2(001)$  in the form of strongly interacting and noninteracting impurities on and in the surface. The aim is to shift the activity to visible region for solar cell operation. This is done so by band gap narrowing which is useful for photovoltaic devices. We have considered Pt as adsorbates on the surface, and as substitutional and interstitial impurities in the subsurface layers encapsulated by the slab.

## II. METHOD

We performed total-energy and electronic-structure calculations using the Vienna *Ab Initio* Simulation Package (VASP) implementation<sup>28</sup> of the gradient-corrected [Perdew-Burke-Ernzerhof (PBE)] (Ref. 29) density functional theory (DFT). The electron-ion interaction has been described by the projector augmented waves (PAW) method<sup>30,31</sup> using plane-wave basis sets.

The naturally occurring rutile and anatase polymorphs of titania are basically formed as a result of different modifications of the same  $\text{TiO}_6$  unit. This building block is arranged as a distorted octahedron with a Ti cation at the center and six oxygen at the vertices. The stacking pattern of these octahedra results in simple tetragonal (st) conventional unit cells for both of rutile and anatase polymorphs. However, in the case of anatase, the primitive unit cell is a body-centered tetragonal (bct) Bravais lattice. Since the conventional cell for anatase contains two bct units, the calculations assuming an st unit cell might cause misleading deductions such as the energy-band-gap type. We considered bulk properties of anatase phase of  $\text{TiO}_2$  as the starting point, both for building up the surface slab models and for obtaining the bulk-projected electronic structures. In this manner, we calculated, for example, the bulk lattice parameters to be  $a=3.801$  Å,  $c=9.468$  Å, and  $u=0.2095$  with a  $D_{4h}^{19}(I4_1/amd)$  space-group symmetry using bct unit cell. These results agree well with the corresponding experimental values<sup>32</sup> which were reported as  $a=3.785$  Å,  $c=9.514$  Å, and  $u=0.208$ . Besides, our PAW-GGA calculations for these structural properties are consistent with the other available theoretical results<sup>33–36</sup> and exhibit a better agreement with the experimental findings.

For the stoichiometric anatase  $\text{TiO}_2(001)$  surface, we considered an oxygen terminated supercell model involving six  $\text{TiO}_2$  layers with a vacuum region of  $\sim 13$  Å. These zigzag-like  $\text{TiO}_2$  layers consist of three atomic layers in which bridging oxygen atoms are out of the level Ti plane. Each of the oxygen at the back surface of such a bulk termination needs  $1/3$  electrons to be saturated. This cannot be accomplished by hydrogenation with integral charge. Indeed, it leads hydrogen driven surface states to appear just above the VBM as a consequence of the excess charge induced by this hydrogenation. Therefore, instead of saturating the back surface we chose a virtually symmetrical slab model which produces the same electronic properties coming from the top

and the bottom (001) surfaces. We call it as virtually symmetrical because it lacks perfect mirror symmetry along the axis perpendicular to the surfaces. In this sense it is not a trivial surface to model. On the other hand, our choice bears no mistakes since we use plane-wave basis sets with periodic boundary conditions.

In order to elucidate the role of Pt incorporation on the electronic behavior of anatase  $\text{TiO}_2(001)$  surface, we considered strongly interacting and isolated impurities on and inside the corresponding supercells. Pt adsorption on  $(1 \times 1)$  surface, for instance, corresponds to 1 monolayer (ML) coverage so that the shortest Pt-Pt distance is attained. When one considers Pt with  $(2 \times 2)$  construction, namely, 0.25 ML, Pt-Pt distance becomes 7.53 Å on the surface which leads to almost isolated impurities.

Because of the symmetrical nature of the slab model, supercell thickness becomes important particularly when Pt penetration depth increases. Implanted Pt atoms from the top and back surfaces should not interact inside the slab. In addition, the central part of the model slab must possess bulk-like properties. In this manner, even though none of the atoms were fixed to the bulk positions in the geometry optimizations, the atoms at the central part retained their original bulk positions for shallow enough Pt penetration. Moreover, the number of layers have been chosen so that increasing the slab height by one more layer did not alter the calculated results significantly. However, our tests showed that six  $\text{TiO}_2$  layers are not enough for Pt impurities placed deeper than 3.4 Å from the surface oxygen which corresponds to the second  $\text{TiO}_2$  sublayer. Therefore, we have used eight  $\text{TiO}_2$  layer thick slab model for such Pt impurities inside the slab.

Our convergence tests showed that the electronic wave functions can be expanded into plane waves up to an energy cutoff value of 400 eV and that the surface Brillouin-zone integrations can be carried out with a  $k$ -point sampling of  $(8 \times 8 \times 1)$  and  $(4 \times 4 \times 1)$  Monkhorst-Pack meshes<sup>37</sup> for  $(1 \times 1)$  and  $(2 \times 2)$  surface unit cells, respectively. In both cases, these choices gave a total-energy convergence up to a tolerance value smaller than 0.1 meV. All geometry optimization calculations were carried out using conjugate-gradient algorithm based on the reduction in the Hellman-Feynman forces on each constituent atom to less than 10 meV/Å.

## III. RESULTS AND DISCUSSION

Anatase phase of bulk titania is found to have an indirect gap of 2.08 eV with the valence-band top being at about two-thirds of the way along  $\bar{\Gamma}X$ . Direct gap is slightly larger, 2.12 eV. The calculated gap values are underestimated as expected due to inherent shortcomings associated with the local-density approximation (LDA) while the experimental gap is 3.20 eV.<sup>38,39</sup> A more recent work reports this value to be 3.5 eV.<sup>40</sup> The calculational underestimation can be overcome by incorporating self-energy corrections going beyond the ground-state DFT. Indeed, Thulin and Guerra<sup>33</sup> reported a quasiparticle corrected gap of 3.79 eV which is overestimated and closer to the result 3.68 eV obtained by Calatayud *et al.*<sup>34</sup> using nonlocal B3LYP functional. A comparison of

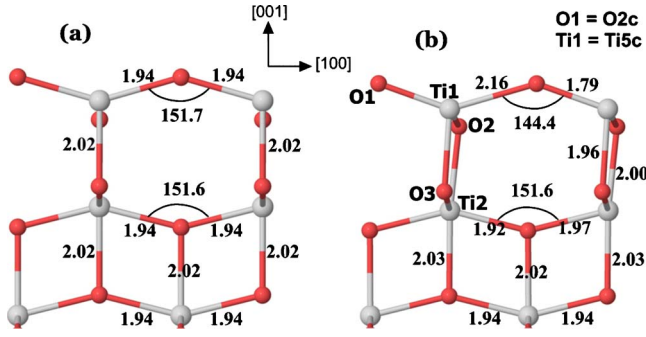


FIG. 1. (Color online) Atomic arrangements of the anatase TiO<sub>2</sub>(001)-2×2 structure. Side views of the (a) ideal and (b) relaxed surface unit cells, only up to eight atomic layers, are shown here. Ti and O atoms are denoted by light gray and red (dark) balls, respectively. All bond lengths are given in angstroms and all angles are presented in degrees.

our bulk band structure (not shown) with the ones reported in these references revealed a perfect match except the gap width, hence, indicating a scissors type rigid shift of the whole conduction band. Therefore, despite the underestimated gap, the band structures presented in this work can be considered within this context.

The (001) plane of anatase polymorph is known to be catalytically important as it constitutes commercial catalysts.<sup>41,42</sup> Yet, a theoretical investigation on the electronic structure of this surface is still needed. Therefore, we first consider the oxygen terminated (001) clean surface. The (1×1) unit cell forms in the shape of a square with a side of 3.765 Å over this plane [see the top view in Fig. 3(a)]. In fact, the (2×2) periodicity has also similar formation [see the top view in Fig. 5(a)]. Because of the bulk termination, the surface layer is composed of fivefold coordinated Ti and twofold coordinated O atoms which are denoted as Ti 5c and O 2c in Fig. 1, respectively. Bridging O 2c atoms make two equidistant bonds with Ti 5c's along [100] possessing a mirror plane symmetry on the ideal surface [Fig. 1(a)]. The outward position of O 2c forms a Ti 5c-O 2c-Ti 5c angle of 151.7°. In the ideal geometry, equatorial bond lengths are 1.94 Å while the axial bonds measure 2.02 Å. This conspicuously symmetrical structure gets distorted upon relaxation in consistency with the previous theoretical studies.<sup>43,44</sup> The Ti 5c-O 2c bond lengths become significantly inequivalent being 2.16 and 1.79 Å mainly because of the relatively larger displacement of surface oxygen along [100] compared to the Ti1 and Ti2. Moreover, Ti 5c-O 2c-Ti 5c angle reduces to 144.4° since O 2c's move outward the surface plane while the relaxation of Ti 5c's in the reverse direction is substantially larger than the other atoms near the surface. This relaxation pattern applies to both of the surface unit cells as all calculated values related to the atomic rearrangements presented in Table I for (1×1) surface are consistent with those of (2×2). Also, in agreement with the results of previous theoretical studies,<sup>43,44</sup> our geometry optimizations gave negligibly small displacements along [010]. Lazzeri *et al.*,<sup>43</sup> additionally, reported that the planar O2-Ti1-O3-Ti2 ring becomes slightly skewed making a dihedral angle of 6.0° with the (100) plane. However, as can readily be seen in

TABLE I. Geometric structure of anatase TiO<sub>2</sub>(001) surface. Atomic labels refer to Fig. 1. Calculated values for atomic displacements with respect to ideal bulk positions are given in Å.

Surface	Label	[100]	[010]	[001]
1×1	O1 (O 2c)	0.194	-0.011	0.034
	O2	0.223	-0.010	-0.038
	O3	-0.117	-0.011	-0.031
	Ti1 (Ti 5c)	0.003	-0.009	-0.091
	Ti2	0.011	-0.011	-0.011
	2×2	O1 (O 2c)	0.195	-0.011
2×2	O2	0.224	-0.010	-0.037
	O3	-0.117	-0.011	-0.030
	Ti1 (Ti 5c)	0.004	-0.010	-0.088
	Ti2	0.015	-0.013	-0.012

Fig. 1(b), our calculations suggest that the Ti1-O3 bond shortens to 1.96 Å and makes an angle of 2.46° with (100) plane whereas O2-Ti2 bond has a skew angle of 6.0° and a length of 2.00 Å. This can be attributed to the high reactivity of the surface with an indication that not only O 2c but also threefold coordinated O2 and O3 give contribution to the surface electronic properties.

An ideal-like structure in which atomic relaxations are only observed in the direction perpendicular to the surface is found to be energetically higher by 0.09 and 0.37 eV per unit cell for (1×1) and (2×2), respectively. The existence of this symmetry preserving structure was also reported by Calatayud and Minot<sup>44</sup> for (1×1) as well as for larger unit cells. Minimum energy structure cannot be reached unless the optimization is started from a slightly distorted ideal geometry. Relatively small atomic displacements as presented in Table I lead to weak energy differences between the minimum-energy structure and the ideal geometry. Therefore, these weak energy differences can be seen as an indication of high thermodynamic stability for anatase (001). Indeed we calculated the surface energies in both of the (1×1) and (2×2) cases to be 0.92 and 0.94 J/m<sup>2</sup> for relaxed and unrelaxed surfaces, respectively. The surface energy is defined as

$$E_{\text{surf}} = \frac{1}{2A} (E_{\text{TiO}_2} - nE_{\text{TiO}_2}^{\text{bulk}}),$$

where  $E_{\text{TiO}_2}$  is the total energy of the slab and  $nE_{\text{TiO}_2}^{\text{bulk}}$  refers to the energy of the bulk supercell containing an equal number of TiO<sub>2</sub> units as the slab.  $A$  corresponds to the exposed unit-cell area while the factor of 1/2 appears because the slab is symmetrical having two faces. Our calculated values are in good agreement with the GGA-PBE results ( $E_{\text{surf}}^{\text{rel}}=0.98$  and  $E_{\text{surf}}^{\text{unrel}}=1.12$  J/m<sup>2</sup>) of Lazzeri *et al.*<sup>43</sup> and, with the GGA-PW91 results ( $E_{\text{surf}}^{\text{rel}}=0.89$  and  $E_{\text{surf}}^{\text{unrel}}=1.04$  J/m<sup>2</sup>) of Calatayud and Minot,<sup>44</sup> LDA results are reported to give systematically larger surface energies.<sup>43,45,46</sup> The lack of accurate experimental measurements to compare with prevents us to discuss which exchange-correlation scheme does more reliably describe the surface properties.

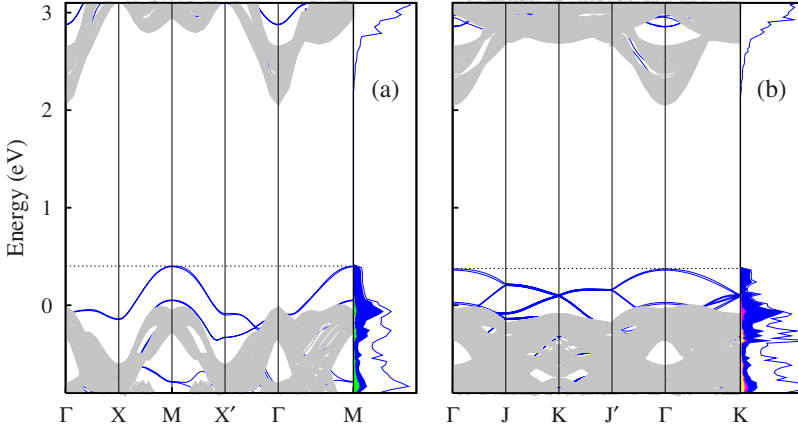


FIG. 2. (Color online) Energy bands for the clean anatase  $\text{TiO}_2(001)$  for (a)  $1 \times 1$  and (b)  $2 \times 2$  surfaces. Some of the important LDOS contributions to TDOS are shown. Projection of bulk continuum is also depicted as shaded areas.

The major surface bands derived from the valence bands are spilled out into the energy-band gap. Figure 2 shows the energy bands for the clean surface of anatase  $\text{TiO}_2(001)$ , having  $(1 \times 1)$  and  $(2 \times 2)$  periodicities, and the bulk band continuum (shaded regions) projected on the corresponding surface Brillouin zones, respectively. Fermi level is at 0.40 eV relative to the valence-band top and the surface states are filled causing the gap to narrow down to 1.68 eV (from the bulk gap value of 2.08 eV). These results for  $(1 \times 1)$  surface are in consistency with those of  $(2 \times 2)$  as presented in Fig. 2(b) and in Table II. The gap is indirect with surface state having a maximum at  $M$  point for  $(1 \times 1)$  while it is direct with the corresponding maximum at  $\Gamma$  for  $(2 \times 2)$  due to the surface Brillouin-zone folding. Conduction band makes a minimum at  $\Gamma$  in both cases and is bulklike with all the surface solutions being resonance states within the bulk band region except for the pocket states. The right-most panel shows the total density of states (TDOS) and important local contributions [local density of states (LDOS)] to it. The sur-

face states in the gap derived mainly from the twofold coordinated surface oxygen ( $\text{O } 2c$ ) are seen to have the form of a jump discontinuity at  $E_F$ , typical of two-dimensional van Hove singularity in the DOS due to the critical point at  $M$  (or  $K$ ). The contribution of  $\text{O}2$  to the LDOS, being comparably much less than that of  $\text{O } 2c$ , comes from the lower part of the surface states closer to the valence-band top. The DOS from  $\text{O}3$  (and similarly from  $\text{Ti } 5c$ ) extends to the valence bulk continuum affecting the surface states even less than  $\text{O}2$  does. Evidently, the DOS analysis at the upper region of the valence bands indicates that the energy levels of  $\text{O } 2c$  lying higher than those of fully coordinated oxygen must show higher reactivity.

We have also calculated the  $(1 \times 1)$  and  $(2 \times 2)$  clean surface band structures for the ideal-like geometries in which  $\text{Ti } 5c$ - $\text{O } 2c$  bond symmetry is preserved. In this case, the surface states move upward in the gap region reducing the energy-band gap by 0.29 eV. Moreover,  $\text{O } 2c$  driven states elevate from the bulk valence band up into the gap increas-

TABLE II. Calculated values of some key parameters for Pt- $\text{TiO}_2(001)$  anatase system: work function, Fermi energy relative to bulk valence top, and change in energy-band gap, as well as Pt-depth relative to surface oxygen, Pt-O distance, and Pt-Ti distance for each model. Labeling of models follow from Figs. 3 and 5, for  $(1 \times 1)$  and  $(2 \times 2)$  surfaces, respectively.

Surface	Model	$W$ (eV)	$E_F$ (eV)	$\Delta E_g$ (eV)	$h_{\text{Pt}}$ (Å)	$d_{\text{Pt-O}}$ (Å)	$d_{\text{Pt-Ti}}$ (Å)
$1 \times 1$	Clean	6.88	0.40	0.00			
	(s1)	5.83	1.51		-0.46	1.94(O 2c),1.96(O2),2.18(O3)	
	(s2)	5.36	1.85	-1.45	-3.04	1.95(O3,O4),2.02(O2,O5)	
	(a)	4.16	1.84	-1.53	0.76	1.97(O1)	2.55(Ti1)
	(b)	5.21	1.95	-1.55	0.54	1.96(O1)	2.61(Ti1), 2.71(Ti1)
$2 \times 2$	Clean	6.77	0.38	0.00			
	(s1)	6.13	1.12	-1.13	-0.68	1.92(O 2c), 2.10(O 2c), 1.99(O3)	
	(s2)	6.25	0.88	-0.50	-3.04	1.99 (O3,O4), 2.02 (O2,O5)	
	(a)	5.86	0.96	-0.58	1.24	1.90(O1)	2.36(Ti1)
	(b)	5.61	1.41	-1.03	0.24	1.95(O1),2.07(O3)	2.30(Ti1),2.78(Ti1)
	(c)	5.64	1.80	-1.42	0.02	1.99(O1)	2.80(Ti1)
	(d)	5.71	1.51	-1.13	-2.91	1.97(O3),2.06(O3)	2.72(Ti1),2.63(Ti2),2.86(Ti2)
	(e)	5.69	1.49	-1.11	-3.59	2.01(O4)	2.71(Ti2),2.77(Ti2),2.91(Ti3)
(f)	5.62	1.56	-1.18	-5.29	2.01(O5)	2.88(Ti2),2.75(Ti3)	

ing the number of available surface states. These elevations are not always rigid. For instance, the highest lying surface state exhibits some differences between the ideal-like and the minimum-energy configurations. At  $\Gamma$  point, this surface state coincides with the valence-band top in the lowest energy structure as shown in Fig. 2(a), whereas it lies 0.29 eV above the valence band in the case of the ideal-like configuration, attesting a prominent change in the character of this state. Therefore, these differences altogether suggest that the relaxations of atoms near the surface, noticeably, influence the surface electronic band structure, in contrary to what was asserted by a previous theoretical work.<sup>45</sup>

In practice, titania surface is covered with less than a monolayer or even dilute metal adatom concentration in catalysis applications. Hence, we systematically studied Pt implantation in anatase TiO<sub>2</sub>(001) with  $(1 \times 1)$  and extensionally with  $(2 \times 2)$  periodicities starting from the surface layer up to seven atomic sublayers corresponding to a depth of  $\sim 5.1$  Å. First, for Pt doped TiO<sub>2</sub> surfaces, we substitute Pt atoms for the fivefold Ti atoms (Ti1), closest to the surface layer, and in place of the bulk Ti atom (Ti2) at the second TiO<sub>2</sub> layer. We refer to these substitutional cases as (s1) and (s2), respectively. Second, we considered Pt atoms positioned at interstitial sites in oxygen atomic layers where Pt is strongly coordinated with the nearest-neighbor oxygen. The trend from strongly interacting Pt impurities at 1 ML to isolated ones at 0.25 ML coverages is expected to help predict the more dilute experimental situations.

### A. Contiguous impurities

Pt-implanted TiO<sub>2</sub>(001)- $1 \times 1$  system has been considered with all possible adsorptional, substitutional, and interstitial configurations starting from above the surface to inside the slab. Pt impurities in and on the  $(1 \times 1)$  surface are separated from each other by 3.76 Å. Although this is much larger than the Pt dimer length, it still maintains a distance close enough for a strong interaction. Pt is found to be stable at two adsorption cases which are presented in Fig. 3. In the first case, Pt adsorbate binds to both Ti 5c and O 2c at bridge position forming a Ti 5c-Pt-O 2c angle of 51°. Pt-Ti 5c bond length is 2.55 Å which is significantly close to Pt dimer length while Pt-O 2c distance is 1.97 Å. Structural properties of Pt for all the cases studied in this work such as Pt-O and Pt-Ti bond lengths as well as the Pt penetration depths are presented in Table II. The twofold binding of Pt to Ti 5c and O 2c compensates their undercoordination by charge transfer. Hence, the system undergoes a relaxation in favor of reducing the difference between the two inequivalent bond lengths (Ti 5c-O 2c) on the surface layer. [See Fig. 3(a.)] Similarly, both of the Ti1-O3 and Ti2-O2 bonds get equal in length to a value of 2.01 Å making a dihedral angle, with the (100) plane, of 5.9° and of 4.6°, respectively. Ti 5c-O 2c-Ti 5c angle, on the other hand, increases slightly to 146.1° due mainly to the downward relaxation of O 2c relative to its nearest-neighbor Ti 5c atoms. In fact, the surface does not show a significant reconstruction upon Pt adsorption, for this case, and is characterized dominantly by the relaxation of surface oxygen.

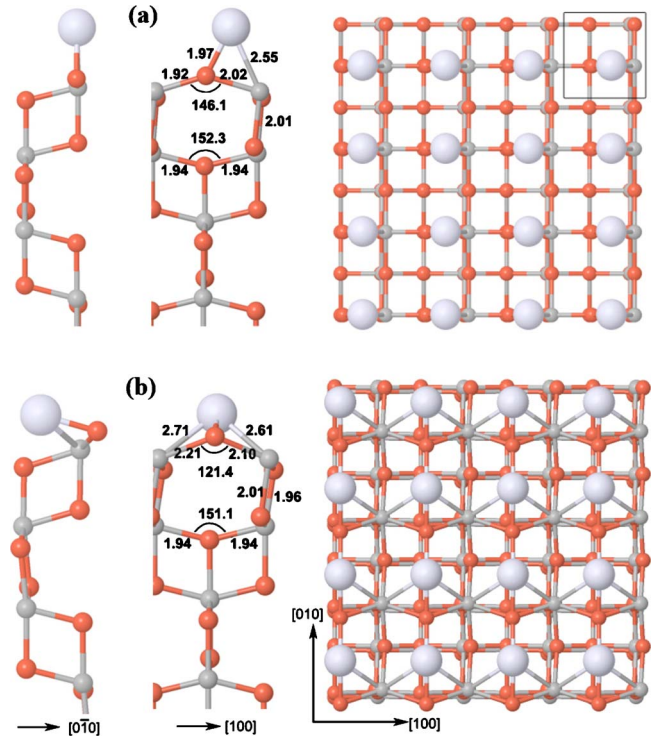


FIG. 3. (Color online) Pt on anatase TiO<sub>2</sub>(001)- $1 \times 1$  surface. Front, side, and top views for the two adsorption cases: (a) on the bridging oxygen bond and (b) off the bridging oxygen bond. The surface unit cell is indicated in (a) right.

In the second case as shown in [Fig. 3(b)] Pt is fourfold coordinated with the surface atoms. It makes two equidistant bonds with O 2c's along [010] being 1.96 Å in length while Pt-Ti bonds are 2.71 and 2.61 Å. This small difference in bond lengths stems from the stronger coordination of Pt with neighboring O 2c's. This strong interaction forms O-Pt-O lines along [010] as shown in the top view of Fig. 3(b). In this geometry, Pt is 0.22 Å closer to the surface relative to the previous case. Ti 5c-O 2c bonds are slightly inequivalent being 2.21 and 2.10 Å similar to the case of the clean surface. Nevertheless, Ti 5c-O 2c-Ti 5c angle gets subtly reduced to 121.4° prevalingly as a result of the elevation of O 2c in a strong coordination with the Pt adsorbate. The structure in case (b) is energetically 0.47 eV more favorable than that of case (a) because of the increased coordination of Pt with the surface atoms. Pt binding energy (BE) is calculated to be 2.70 and 2.93 eV/atom for the cases (a) and (b), respectively.

When Pt is substituted for Ti 5c, which is referred as s1, Pt-O3 and Ti2-O2 axial bond lengths increase substantially to 2.18 and 2.09 Å, respectively. Besides, Pt-O 2c equatorial bonds become almost equal being 1.95 and 1.93 Å with Pt-O 2c-Pt angle which reads 152.5°. In this structure, Pt-O3-Ti2-O2 side ring as a whole is skewed making a 5.2° dihedral angle with (100) plane. Pt is perfectly aligned with nearest-neighbor oxygen in the same lanes over the surface along [100] and [001] directions while being at the different atomic layers.

On the other hand, Pt substitution for bulk Ti (Ti2), namely, s2, results in a structure which reflects similar topo-

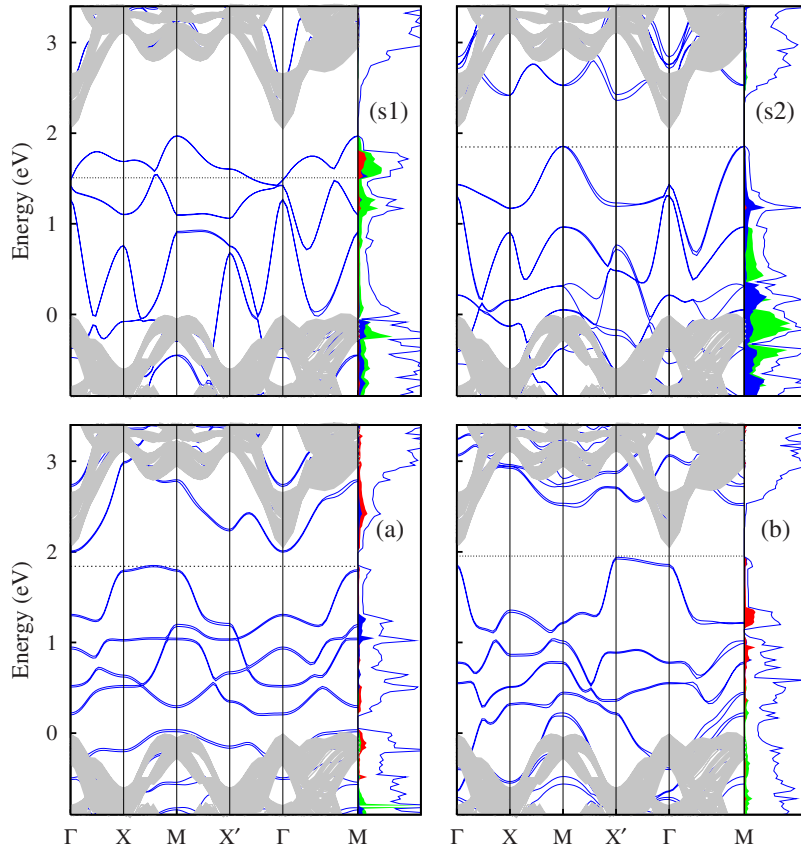


FIG. 4. (Color online) In the upper row: (s1) energy bands for Pt impurity atom substituted for surface-Ti ion in the anatase  $\text{TiO}_2(001)-1 \times 1$  surface and (s2) those for Pt impurity atom substituted for the second-layer Ti ion. Some of the important LDOS contributions to TDOS are shown. Projection of bulk continuum is also depicted as shaded areas. In the lower row: (a) energy bands due to interstitial Pt on anatase  $\text{TiO}_2(001)-1 \times 1$  surface as in Fig. 3(a) and (b) that as in Fig. 3(b).

logical characteristics with the ideal clean slab [shown in Fig. 1(a)]. Pt-Ti2 replacement at  $1 \times 1$  unit cell drives the structure from the relaxed to an ideal-like geometry. Even though Pt replaces Ti2, the axial bond lengths extend slightly to 2.02 Å. Similarly, the difference in bond distances of Pt with the neighboring fully coordinated oxygen become negligibly small being 1.95 Å. The only substantial displacement with respect to the relaxed structure is obtained for O 2c which moves up a little bit so that Ti 5c-O 2c bond lengths become symmetrized with a value of 1.96 Å forming an isosceles Ti 5c-O 2c-Ti 5c triangle having an obtuse angle of 146.9°.

Pt can also be considered at the interstitial sites in between the fully coordinated level oxygen. Starting from such a configuration, the surface expansively reconstructs with a local segregation as a result not only of the SMSI but also of the stress induced by the web of closely spaced Pt impurities inside the slab. For instance, when we place Pt in between two O2 atoms (referring to Fig. 1), it pushes the first  $\text{TiO}_2$  layer (O1-Ti1-O2 group) upward breaking Ti1-O3 and Ti2-O2 bonds. Meanwhile, Pt moves in between O1 and O3 forming new equidistant axial bonds (1.98 Å) on a straight line which makes an angle of 26.6° with the (100) plane. Since O1 and O2 coordination numbers interchange, O2 is further elevated up forming zigzag Ti 5c-O 2c pattern, this time along [010] direction with bond lengths of 1.85 and 2.08 Å. In summary, Pt interstitial at O2 level for  $(1 \times 1)$  surface segregates the first and the second  $\text{TiO}_2$  layers by 2.0 Å relative to the separation of those in the clean surface.

The coordination of Pt with nearest-neighbor oxygen in these model cases signifies the strength of Pt-O electrostatic

interaction so that Pt is very dominant in disturbing the surface atomic arrangements. These impurity driven rearrangements modify the electronic band structure to a significant extent by bringing new defect states as well as perturbing the already existing surface states that originate from the distorted lattice bondings.

The electronic structure for the geometries in Figs. 3(a) and 3(b) with Pt ions as surface impurities are presented in Figs. 4(a) and 4(b), respectively. Moreover, in Fig. 4(s1) and 4(s2), those for the substitutional impurity at the surface (replacing Ti1) and that in the bulk (replacing Ti2 in the subsurface layer) are shown, respectively.

For the first case of adsorbates shown in Fig. 4(a), the energy gap is full of six defect states, five of which are occupied and one that is close to the conduction band is empty. Fermi level is at 1.84 eV. The system has a narrow gap of only 0.15 eV. The gap is indirect and the highest occupied defect state makes a maximum at midway, otherwise almost flatband, along  $\bar{X}M$ . The lowest unoccupied band is also a defect state making a minimum at  $\Gamma$  and having the shape of the lowest conduction band along most directions except around  $X'$ . Its LDOS has a two-dimensional character as expected, and is a result of antibonding interactions between electrons from Pt and O1 ions. The lower group of four bands all have Pt contributions with three upper bands having contributions from O1. Especially, the flatband at 1.0 eV causing a peak in the LDOS and the peak above that are mainly due to O1 ion, whereas the lowest of the four has contributions mainly from O2 ion. This band and the one below, separated by a pseudogap, which is barely above the valence-band top, are of the same character, namely, of Pt and O2.

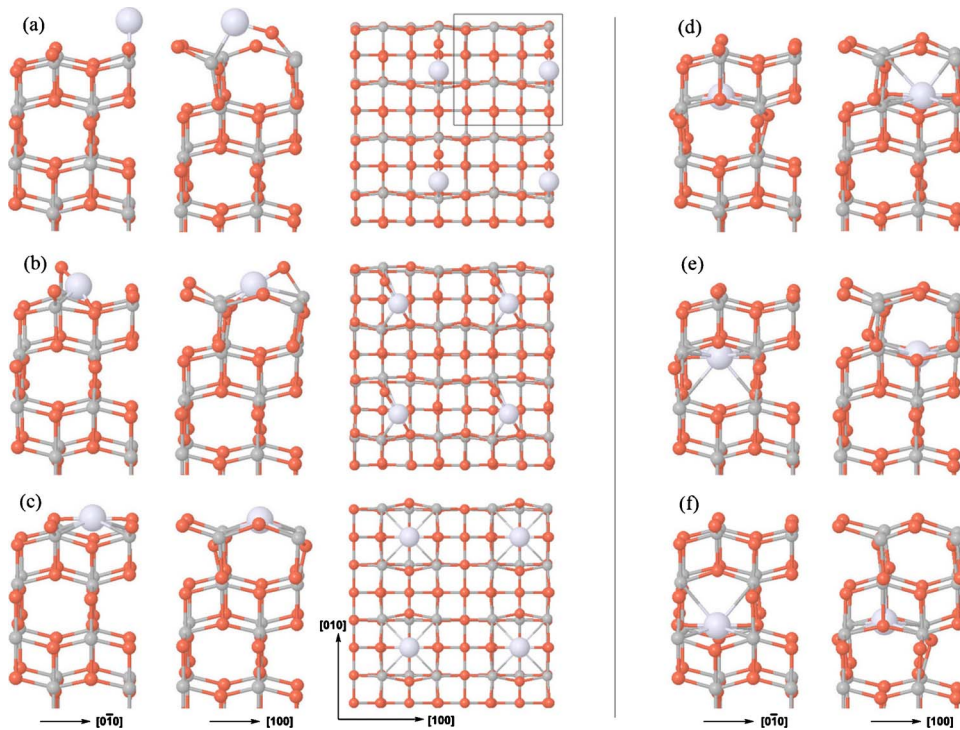


FIG. 5. (Color online) Interactions of single Pt atom with anatase TiO<sub>2</sub>(001) surface (in order of penetration depth of the Pt atom): (a) Pt adsorbed on the surface, (b) surface oxygen supported by Pt with SMSI, and [(c)–(f)] stable structures of Pt in the surface. Pt atom is shown in white and denoted by the biggest sphere while Ti is in gray and O is represented as small red (dark) balls.

The second adsorbate case described in Fig. 3(b) is energetically more preferable than the first one as they both contain equal number of atomic species. In this case [see Fig. 4(b)] the same five defect states fill the bulk band gap as in the previous case. All of them lie below the Fermi level which is at 1.95 eV relative to valence-band top and the gap is 0.13 eV, again small. The lowest unoccupied state being bulklike this time is the conduction-band minimum at  $\Gamma$ . The empty defect state is higher in energy. The highest occupied defect state has a maximum at  $X'$ ; however the band is almost flat along  $\overline{X'\Gamma}$  making the gap nearly a direct one. The band is also flat in some part of the way along  $\overline{\Gamma M}$ , both causing higher densities in the LDOS picture. The contribution by the O1 ion is mainly in the upper defect bands in the energy range between  $E_F$  and about 0.2 eV below that along with Pt ion while that by O2 is mainly in the lower defect states starting from the highest peak at about 0.6 eV down into the valence bands.

In the case of surface substitutional, the bulk energy gap is full of four defect states as seen in Fig. 4(s1), lower two of which are fully occupied and the upper two are almost half filled each. Therefore the system shows metallic behavior. Fermi level is at 1.51 eV relative to the valence-band top. These two upper bands cross each other along high-symmetry directions of the surface Brillouin zone at three places, namely, very close to the  $\Gamma$  point along  $\overline{X'\Gamma}$ , and passed midway along the  $\overline{\Gamma M}$  and  $\overline{XM}$  directions. The LDOS due to Pt ion as well as some due to neighboring two oxygen ions O1 and O2 are coming from these bands dispersed around the Fermi level. The two lower bands are surface states due to oxygen ions O1 and O2.

Figure 4(s2) shows the band structure for the subsurface substitutional where the energy gap is full of four defect states that are all occupied. Fermi level is at 1.85 eV relative to the valence-band top giving rise to an indirect energy gap

of 0.23 eV. The LDOS of the highest occupied defect band having a sharp peak due to the almost flat part along  $\overline{X'\Gamma}$  is contributed by Pt ion and its neighboring oxygen ions. This band is pretty similar in shape to the half-filled one in (s1) case that makes a maximum at  $M$ . Next piece of LDOS between 0.3 and 0.9 eV is due to the surface oxygen O1. This band was observed to be similar to the clean surface band due to O1 in Fig. 2(a), especially around  $M$  point along all three directions. The band that is hardly visible above the valence-band top at  $M$  point is also similar to the second band of clean surface at the same region. Since the Pt ion is deeper than skin of the surface region in this case the surface is healed and the surface states are back. The van Hove singularity at about 0.9 eV, where this band ends at the right-most  $M$  point in Fig. 4(b), is also evident just like the one at  $E_F=0.40$  eV in Fig. 2(a).

## B. Dilute impurities

TiO<sub>2</sub>(001)-(2×2) unit cell prevents charge transfers between the impurity sites by providing a 7.53 Å Pt-Pt separation together with local screening effects through the slab. Therefore, both the geometric and the electronic structures show significant differences from the (1×1) counterparts. For instance, Pt interstitials can be stable inside (2×2) slab without segregation effects as opposed to the case with (1×1) surface. For the incorporation of Pt ion as an adsorbate or as an interstitial, we examined a total of six cases that are shown in Figs. 5(a)–5(f), in the first three of which the Pt is situated on/in the surface and in the last three the Pt ion is below the surface layer.

In the first case, [Fig. 5(a)], Pt adsorbate is twofold coordinated with nearest-neighbor Ti 5c and O 2c along the O1-Ti1 row. Pt raises the O 2c upward by 0.92 Å and pushes it in [100] direction by 0.83 Å from its relaxed lattice position.

As a result of the SMSI, bond distances from Ti 5c to Pt, Pt to O 2c, and O 2c to the next Ti 5c, which are connected successively through line segments in a row, become 2.36, 1.90, and 180 Å, respectively. The other O1-Ti1 row remains to be less effected by the presence of Pt adsorbate with Ti 5c-O 2c bonds, 2.11 and 1.81 Å in length, making a Ti 5c-O 2c-Ti 5c angle of 144.4° as in the case of relaxed clean surface. Among the side bonds, other than the skewing toward  $[\bar{1}00]$ , merely the Ti1-O3 one, which connects to the promoted O 2c, is elongated by 0.04 Å with a dihedral angle of 7.23° bearing a subtle difference from the values calculated for the (2×2) clean surface. Moreover, the distances and angles are not distorted considerably in the second TiO<sub>2</sub> layer near the surface.

The structure shown in Fig. 5(b), being the lowest energy configuration among adsorptional and interstitial cases, undergoes a more complex atomic rearrangement upon Pt adsorption. The adsorbate migrates to a bridge position in between Ti1 and O2 with bond lengths of 2.78 and 2.07 Å for Pt-Ti1 and Pt-O2, respectively. As a consequence of the SMSI, the nearest-neighbor O 2c is pushed from its lattice site upward above the midpoint between Ti1 and Pt forming a triangle. It is aligned perpendicular to the surface, with O 2c-Ti1 and O 2c-Pt sides of 1.81 and 1.95 Å, respectively. In this geometry O 2c elevation above the Pt adsorbate is calculated to be 0.83 Å. Another triangle forms between the consecutive Ti1 on the Ti1-O1 row, neighboring O2 and Pt which lies at the vertex connecting the two triangular atomic arrangements in a fourfold coordination with these surface atoms. In this second triangle Pt-Ti1 bond distance becomes 2.30 Å. Furthermore, the two Ti 5c-O 2c bonds become slightly distorted, 1.81 and 2.17 Å in length, with Ti 5c-O 2c-Ti 5c angle of 143.9° on the second Ti1-O1 row. The only noticeable difference occurs in the Ti1-O3 bond which extends to 2.16 Å. All other side bonds preserve the skewing similar to the (2×2) clean surface results.

The third adsorptional model adopts a more neatly symmetrical structure among Pt/TiO<sub>2</sub>(001)-(2×2) cases as shown in Fig. 5(c). Pt resides at the midpoint between two undercoordinated surface oxygen with a bond length of 1.99 Å. Meanwhile, Pt also makes equidistant bonds with four Ti 5c's, each of which 2.8 Å in length. This extended bond distance (see Table II) entails a rather weak Pt-Ti 5c interaction on the surface. As a result of this isotropic fourfold coordination with surface Ti's, the axial Ti1-O3 bonds become aligned parallel to [001] direction. On the other hand, the two Ti2-O2 bonds, being coplanar with the Pt, are the only slanted ones which make two dihedral congruent angles of 12.3° with the (100) and  $(\bar{1}00)$  planes.

When Pt is substituted for one of the surface-Ti ion (Ti1), the Pt-O3 bond, although unaltered in length, noticeably differs from Ti-O3 bonds by skewing more from 2.21° to 18.21°. Due to the excess charge incorporated by the substitutional impurity, the Pt-O2-Ti1 row exhibits slight distortions in bonds and angles. Resultant two Pt-O 2c-Ti 5c angles become 141.8°/153.5° with Pt-O 2c and Ti 5c-O 2c bond distances of 1.92/2.10 and 2.01/1.82 Å, respectively. On the other hand, the Ti1-O2-Ti1 row retains the values as those of the clean surface.

As in the case of (1×1), Pt substitution for Ti2 results in the reduction in the skewness in the axial bonds as they align parallel to [001] direction. While the axial bond lengths assume an ideal-like value of 2.02 Å, the nearest-neighbor equatorial Pt-O distances become 1.99 Å which describes a slightly extended value over the Ti-O equatorial bond length of 1.94 Å. Therefore, the only substantial displacement is obtained for the atoms at the surface TiO<sub>2</sub> layer along  $[\bar{1}00]$ . This rearrangement reduces the skewness but preserves the nonsymmetric nature of Ti 5c-O 2c bonds which read 2.14 and 1.81 Å with a Ti 5c-O 2c-Ti 5c angle of 144.8°. In other words, as the number of Pt substitutions for four possible Ti2 ions increases, the structure adopts an ideal-like geometry which gains a plane mirror symmetry as in the case of s2-1×1.

For anatase TiO<sub>2</sub>(001)-(2×2) surface, being contrary to the (1×1) cases, Pt is found to be stable once it penetrates into the interstitial cavities, starting from the O3 level, as shown in Figs. 5(d)–5(f). Pt ions are encapsulated by the slab in an octahedral position at the midpoint between the two level oxygen in interaction with the six nearest-neighbor Ti's. The location of the encapsulated Pt is determined dominantly by the strong Pt-O interaction, as being at the same depth with and in the middle of, the fully coordinated two level oxygen. This leads to two structural ramifications as fingerprints. First, two oxygen atoms whose interconnecting line is perpendicular to O-Pt-O bonding, in the closest (preceding or succeeding) oxygen atomic layer, are slightly repelled out from their lattice positions as a result of the induced stress due to the excess charge brought by the impurity. This is not solely specific to interstitial cases. We obtained the very similar result for the adsorptional model in Fig. 5(c). Second, Pt ion, making equidistant equatorial bonds with, maintains four Ti's at the corners of a square shape which can be seen through [001] direction. This is due mainly to Pt impurity rather than the TiO<sub>2</sub> lattice itself since the third adsorptional case [see top view of Fig. 5(c)] adopts surface Ti's in the same geometry. This is so that Ti1-O3 axial bonds are aligned parallel to [001] as opposed to their slanted posture in the clean surface. Evidently, similar arguments apply for the first two interstitial cases [Figs. 5(d) and 5(e)], as well. This time Pt holds Ti2's in a squarely manner causing Ti2-O2 bonds to align vertically with respect to the surface plane. When Pt penetrates deeper than the second TiO<sub>2</sub> layer into the cavities, the symmetry breaking over the Ti 5c-O 2c bonds and the skewness of Ti1-O3-Ti2-O2 ring, similar to the clean surface can finally be reproduced. This corresponds to the last interstitial model as shown in Fig. 5(f). Therefore, Pt implants induce a local stress causing nearby atoms to slightly rearrange from their lattice positions in the TiO<sub>2</sub>(001)-(2×2) surface as a result of the strong Pt-O interaction.

The electronic structure for the geometries in Fig. 5(a)–5(f) with the interstitial impurity are presented in Fig. 6(a)–6(f), respectively, and moreover in Figs. 6(s1) and 6(s2), those for the substitutional impurity at the surface (replacing Ti1) and that in the bulk (replacing Ti2 in the subsurface layer) are shown, respectively.

For the first adsorbate case described in Fig. 5(a), the impurity bands due to the interaction between Pt and the



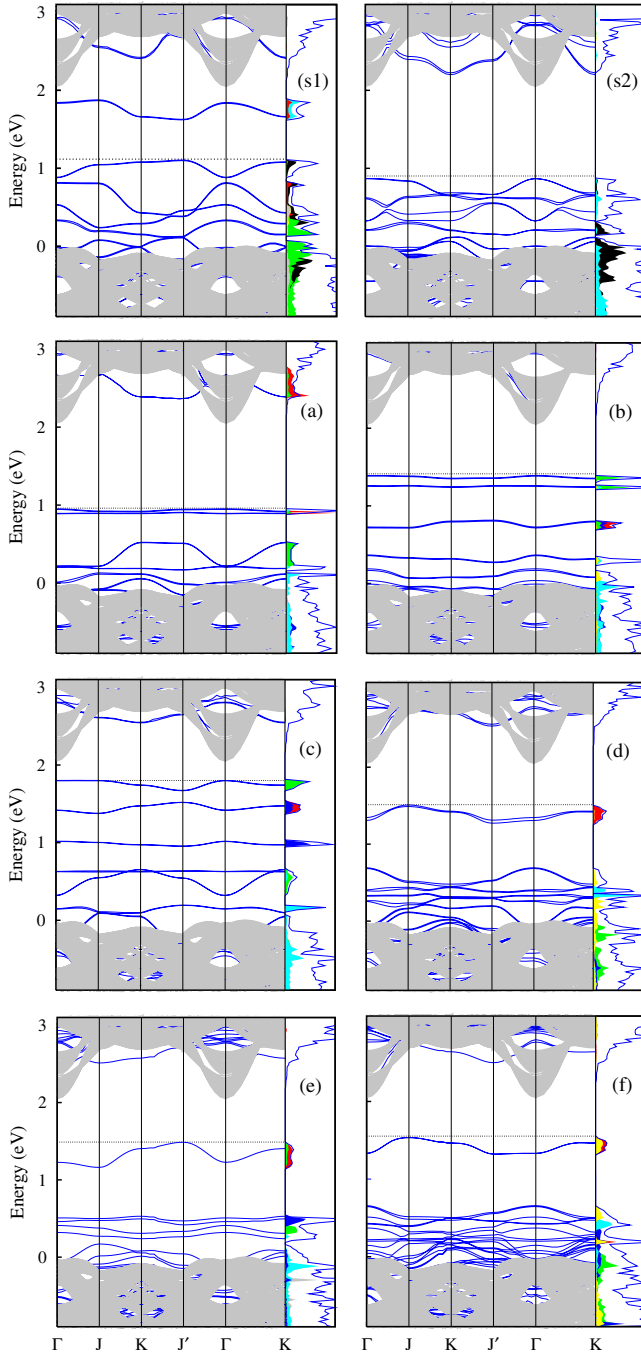


FIG. 6. (Color online) (s1) Energy bands for the anatase TiO<sub>2</sub>(001)-2×2 surface with Pt adsorbed as a substitutional impurity at a surface-Ti site, (s2) at a subsurface-Ti site, and [(a)–(f)] for the interstitial impurity cases in Figs. 5(a)–5(f).

neighboring promoted-oxygen O1' (prime for bonded neighbor) are grouped in three sets within the bulk band-gap region [see Fig. 6(a)]. Two of them being almost conjugate of each other are in the energy ranges of 2.3–2.6 and 0.15–0.5 eV, respectively, while the bands in the third group, being almost flat, producing a sharp peak in the LDOS picture, are located in between the other two groups at around 1 eV. This is the highest occupied set of states of mainly Pt-O1' character with some contributions from the O 2s. The Fermi level is at 0.96 eV, and since the lowest unoccupied band is the

bulk conduction band, having a minimum at  $\Gamma$  the energy gap is direct and 1.12 eV in width. The conjugate bands are dispersed along  $k_y$  but flat along  $\Gamma J$  and  $KJ'$ . The empty one is in resonance with the bulk bands around  $\Gamma J$  and localized in the gap otherwise. Due to this asymmetry in localization the LDOS is also not symmetric in shape. The filled one being in the gap has a symmetrical one-dimensional (1D) LDOS coming from Pt-O1' interaction, with a smaller mixture of Pt and larger mixture of O1', which is the other way around in the empty conjugate state. In addition to bonding to O1', Pt causes slight repositioning to other surface oxygen, as a result of which, a little contribution comes from O1 along the same line as Pt-O1' [see Fig. 4(a)] in the upper part of the delocalized 1D peak. The lower peak of the same LDOS is degenerate with a contribution due to a new flat-band of O2 character adjacent to the edge of the above band. The lower two bands are surfacelike and again of O2 characters.

The case shown in Fig. 5(b) is the most favorable one with the lowest total energy among all (except the substitutional cases since they belong to different stoichiometry which prevents a direct comparison of their total energies) and its electronic nature is again a semiconductor, like all the other dilute impurity cases. Comparing its energy bands [see Fig. 6(b)] with the case of Fig. 6(a), the empty impurity band (not shown) is now pushed up into the bulk continuum of the conduction band. The two flat peaks (Pt-O1'), split by 0.15 eV, are also raised in energy causing the Fermi level to be at 1.41 eV, and decreasing the (direct) energy gap to 0.67 eV. They have also contributions from O1 and O2'. The next lower band (due to Pt-O1'-Ti1-O2 chain) is now much less dispersed and it is separated from the impurity band below, being no longer degenerate at  $\Gamma$  as in case of Fig. 6(a). The fifth (shown) band is also due to Pt-O1' and Ti1-O1 interactions.

Figure 5(c) shows the last of the adsorbate cases where Pt is situated very symmetrically on the O1 layer. All four Ti1's are equivalent; two of the four O1's are bonded to the Pt interstitial, and two of the four O2's are displaced as seen in top view of Fig. 5(c). Consequently, there are eight bands fallen into the gap. The first one from the top, again empty, is within the conduction band, with localization around  $K$ , and conjugate to the sixth band. It is mainly of Pt character. The second band is the highest occupied O1'-related surface band which makes a maximum at  $\Gamma$  and flat along  $\Gamma J$ . The Fermi level is at 1.80 eV and the (direct) gap is 0.28 eV, the narrowest gap of all cases. The third band at about 1.5 eV is an impurity band due to Pt-O2' interaction of larger Pt mixing, whereas the fourth band, at about 1 eV, has a sharp peak of same character with larger O2' mixing. The fifth band is a perfect flat one due to displaced O 2s since Pt pushes O 2s off their lattice positions causing these stress-induced flat going states that reflect major oxygen character due to relatively weaker neighboring interactions. The sixth band is a rather dispersed two-dimensional surface band of O1', O2, and O1 characters, in decreasing order of contribution, which is almost the mirror image of the empty first band above. They are both very symmetric with respect to  $k_x$  and  $k_y$  as expected [see top view of Fig. 5(c)]. The last two, the seventh and eighth bands, are impurity bands of mainly O2',

O2, and slightly of O1' and Pt contributions.

Since the geometric structures, shown in Fig. 5(d)–5(f), of the Pt ions as bulk interstitials (subsurface and deeper) in their nearest-neighbor environment are equivalent, their electronic band structures are also very similar, especially for (d) and (f). It is expected that as the Pt ion is placed deeper into the bulk [see Fig. 6(d)–6(f)], the band structure will alternate as “(d) and (e).” The empty defect band lies partly in the gap. The second impurity band being filled is due to Pt-O1'(O2,O3',O4') interactions, and making a maximum at  $J$ ,  $J'$ , and  $J$  in cases (d), (e), and (f), respectively. Similarly, the Fermi level is situated at about 1.5 eV and the energy gap is about 0.5 eV (see Table II). The lower filled bands are the mixture of surface bands and less dispersed impurity bands due to Pt interstitials.

When the surface Ti is substituted by a Pt impurity on a  $2 \times 2$  reconstruction, the gap is filled by several impurity bands as seen in Fig. 6(s1). One of them is far above in the conduction-band region and partly fallen into the gap. The next lower one is an empty band making a minimum at  $J'$  point around  $\sim 1.6$  eV. The bandwidth is about 0.2 eV due to the interaction between the Pt substitutional impurity with its neighbors O3' and O1'. Below is the highest occupied band of surfacelike state dispersed by the interaction between surface Ti and O2'. This band makes a maximum,  $E_F = 1.12$  eV, at  $J'$  point as well, causing the 0.57 eV gap to be a direct one and narrowed as compared to the 1.70 eV gap for the clean surface. The band is nearly flat along  $\overline{JK}$  and  $\overline{KJ'}$  which results in a sharp peak in the LDOS at Fermi level. Having the upper empty band going almost flat along  $\overline{KJ'}$  as well, causing parallel bands in this direction, one may expect an enhancement in the optical transitions rate. The two bands further below are due to O3'-Pt-O1' and Ti-O2' bonding interactions, respectively. Moreover the bands below those look more like, roughly, the surface states of clean (001).

In the case of placing the substitutional Pt ion at the second layer, we have a bulklike impurity problem where the surface layer is chemically similar to the clean surface with four Ti ions exposed. This is also evident in the band structure shown in Fig. 6(s2). The empty states fallen from the conduction band into the forbidden gap but still above the conduction-band minimum are very symmetric with respect to  $k_x$  and  $k_y$  directions. And in the optical gap, most of the bands look surfacelike with impurity bands passing through them. The Fermi level is at 0.88 eV and the gap of 1.20 eV is again a direct one at  $\Gamma$  like in the clean surface case. The difference of 0.50 eV is partly (about 0.30 eV) due to the unreconstruction of the clean surface with the subsurface impurity substitution. The Pt based impurity state is almost flat at around 0.2 eV above the valence-band top.

The strong dispersion of defect bands seen in  $(1 \times 1)$  cases and the rather less dispersed nature of these bands in  $(2 \times 2)$  models originating from the Pt impurities signify the role of Pt-Pt interaction in relation to Pt concentration. Furthermore, the distinguishable flatness of the impurity bands shown in Figs. 6(a) and 6(b) arise from the minimal coordination of Pt adsorbate with the surface ions as a result of its spatial location, in addition to the diluteness of these impurities.

1 ML Pt substitution for undercoordination drives anatase into a metallic state. At the same coverage Pt adsorption and substitution for the second-layer Ti in this surface yields a low band-gap semiconducting system which would be active in the infrared region. On the other hand, anatase  $\text{TiO}_2(001)$  can be functionalized for visible activity by Pt impurities implanted with a  $(2 \times 2)$  periodicity for all models except the (c) case [see Fig. 5(c)] which corresponds to a band gap narrowing of 1.42 eV. For this impurity concentration, this represents the maximum value close to those of the 1 ML cases. LDOS analysis indicates that the number of defect states derived from the valence bands increase with the coordination of Pt with O1 and O2 ions which is also maximum due to its high-symmetry relaxed position. Therefore, even though platinized  $\text{TiO}_2$  is known to give visible-light activity,<sup>7</sup> our calculations show that band gap narrowing depends on the impurity concentration and the coordination number of Pt with the near surface oxygen.

### C. Analysis of the electronic density

The topological analysis of the charge density gives accurate information about the bonding characteristics for the neighboring atoms. Therefore, one needs a qualitative description of the interatomic charge distributions which can be computed by employing Bader analysis based on atom in molecule (AIM) theory. To do so, the real-space cell is partitioned into Bader volumes delimited by local zero-flux surfaces of the electron-density gradient vector field. Then, these volumes can be integrated around an atomic region to calculate the local charge depletion and accumulation. We obtained these atomic properties using the AIM formalism that is implemented with a recent grid-based algorithm.<sup>47</sup> The Bader charge results for Pt and surface region Ti and O atoms are presented in Table III in the cases of  $(1 \times 1)$  and  $(2 \times 2)$  unit cells. For  $(2 \times 2)$  surface, there are four possible Ti (or O) ions to choose from which are at the same atomic layer. We have preferred to provide the calculated values for the ones that are closer to the Pt impurity in order to make a better comparison with the  $(1 \times 1)$  counterparts.

In the case of clean surface, a deep lying Ti ion, which should reflect bulklike properties, transfers an amount of 0.443 electronic charges to each of the neighboring oxygen losing its last atomic shell. Hence, this fully coordinated Ti ion accumulates a Bader charge of +2.66e. A bulklike oxygen, on the other hand, gets a valence charge state of  $-1.33e$ . Calatayud *et al.*<sup>34</sup> computed these values for the bulk anatase  $\text{TiO}_2$  as  $Q_{\text{Ti}}=2.96e$  and  $Q_{\text{O}}=-1.48e$  using a different exchange-correlation scheme. The Bader charge accumulation around the ions is also sensitive to the determination of integration regions with boundaries delimited by zero gradient of the electronic density. Although we obtained slightly lower charge states for Ti an O ions resulting in a relatively less polarized bonding, in quite an agreement both results obey the same stoichiometry by correctly adding up to charge neutrality of  $\text{TiO}_2$  and are smaller than the nominal oxidation states obtained for a generic ionic oxide such as MgO. As a result, a polarized covalent bonding develops between charged Ti cations and O anions.

TABLE III. The valence charge accumulation based on Bader analysis for Pt-TiO<sub>2</sub>(001) anatase system. Atom labels follow Fig. 1. The charges for lattice atoms that are closest to Pt are presented in the case of (2×2) slab.

Surface	Model	O1	O2	O3	Ti1	Ti2	Pt
1×1	Clean	-1.26	-1.34	-1.33	+2.61	+2.64	
	(s1)	-0.79	-0.99	-1.15		+2.62	+1.63
	(s2)	-1.27	-1.20	-1.02	+2.57		+1.84
	(a)	-1.15	-1.34	-1.32	+2.52	+2.64	-0.03
	(b)	-1.17	-1.33	-1.31	+2.39	+2.64	+0.11
2×2	Clean	-1.26	-1.34	-1.33	+2.60	+2.64	
	(s1)	-1.07	-1.07	-1.33	+2.58	+2.63	+1.64
	(s2)	-1.26	-1.19	-1.18	+2.60	+2.64	+1.85
	(a)	-1.07	-1.35	-1.33	+2.49	+2.64	+0.02
	(b)	-1.08	-1.31	-1.33	+2.57	+2.65	+0.06
	(c)	-1.22	-1.32	-1.33	+2.54	+2.64	+0.07
	(d)	-1.26	-1.33	-1.23	+2.56	+2.56	+0.08
(e)	-1.23	-1.34	-1.27	+2.58	+2.55	+0.15	
	(f)	-1.26	-1.34	-1.31	+2.60	+2.59	+0.14

Naturally, the AIM charge values, presented in Table III, for (1×1) and (2×2) periodicities in the case of clean surface models exhibit a one-to-one correspondence as expected since the electronic properties (such as the band gap, work function, etc.) derived from their charge densities must represent the same surface. The oxidation states of surface layer ions affect the reactivity of single crystals of anatase (001). Hence, we computed the Bader charges for the undercoordinated ions as  $-1.26e$  for O1 and  $+2.61e$  for Ti1 being lower by  $\sim 5\%$  and  $\sim 1\%$  than that of the deep lying O and Ti, respectively. Moreover, bulklike charge states are adopted starting from O2 atomic layer which stays  $2.56 \text{ \AA}$  below the surface oxygen. Clearly, bulk termination bears slight differences in charge states of deep and surface ions, particularly in the case of surface oxygen, indicating a rather low reactivity of the clean (001) surface. This prediction is in good agreement with the experimental observations that clean surfaces of TiO<sub>2</sub> exhibit lower catalytic activity than stepped (101) and oxygen-defect (001) surfaces.<sup>12</sup>

Pt incorporation yields significant disturbance in the electronic density in the vicinity of the impurity site. Particularly, this effect is observed for the oxygen in the close proximity of Pt while the electron depletion from around the nearest-neighbor Ti ion remains minimal upon Pt deposition. From the data presented in Table III, the standard deviation in the Bader charges with respect to the reference clean surface values have been calculated to be 0.17, 0.14, and 0.12 for O1, O2, and O3 while the corresponding values are 0.09 and 0.04 for Ti1 and Ti2, respectively. Smaller deviations obtained for the deeper lying ions also imply a limited contribution of these atoms to the DOS and surface bands near the Fermi level. Therefore, for instance, we obtain the smallest band gap for the adsorptional case (c) among (2×2) structures although it has lower number of Pt-O interactions than interstitial configurations do.

When substituted for Ti ion either at the surface or in the slab, Pt cannot acquire the same oxidation state that Ti had.

This results in a relatively lower amount of charge accumulation around the neighboring oxygen resulting in a less polarized covalency between Pt and O. This is clear also, for instance, in the three-dimensional (3D) charge-density plot presented in Fig. 7, which belongs to the case (b) of Pt-TiO<sub>2</sub>(2×2) system. Ti's show lesser valence electronic density distributions around them, indicating strongly polarized covalent Ti-O bonding. The electron depletion from Pt to O1 is lower than that, for instance, from Ti2 to neighboring oxygen. Moreover, the charge density around O1 is noticeably smaller than that of O3 (and also of O2). In summary, Ti-O bond polarization, and therefore interaction, in TiO<sub>2</sub> lattice environment is stronger than that of Pt-O.

On the other hand, the strength of Pt-TiO<sub>2</sub> interaction can also be compared with respect to different model cases presented in Table III. Bader charges calculated for Pt ion suggest that it interacts with the lattice in the substitutional cases stronger than in the adsorptional and interstitial configurations.

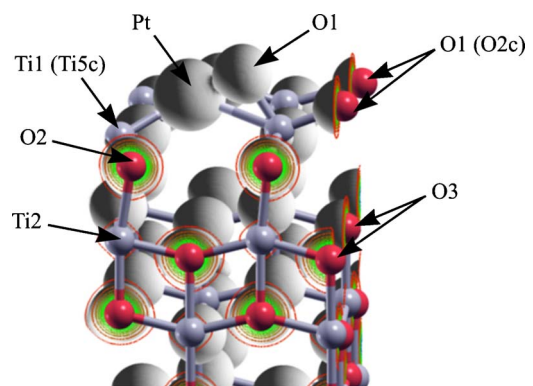


FIG. 7. (Color online) 3D charge-density plot for the “b-2×2” case of Pt on anatase TiO<sub>2</sub>(001) surface [Fig. 5(b)].

#### D. Thermodynamic stability of the phases

The  $(1 \times 1)$  and  $(2 \times 2)$  surface supercells comprise unequal amounts of atomic species. Moreover, adsorptional or interstitial cases, being stoichiometrically different from the substitutional ones, represent an addition of impurity instead of a Pt-Ti replacement. When the supercell total energies are considered, the lowest energy structures are  $b-1 \times 1$  [Fig. 3(b)] and  $b-2 \times 2$  [Fig. 5(b)] among the adsorptional/interstitial cases while they turn out to be  $s1-1 \times 1$  [Fig. 3(s1)] and  $s2-2 \times 2$  [Fig. 5(s2)] for the substitutional geometries at one and quarter ML concentrations, respectively. Therefore one cannot directly compare their stability by just looking at their supercell total energies.

We employed formalism of Qian *et al.*<sup>48</sup> and Northrup<sup>49</sup> to study the thermodynamic stability of the Pt-incorporated  $\text{TiO}_2(001)$  surfaces that have varying number of constituents at different concentrations. In this scheme, relative formation energy is defined as a function of the chemical potential of the excess atomic species as

$$E_{\text{form}} = E_{\text{Pt/TiO}_2} - E_{\text{TiO}_2} - \Delta n_{\text{Ti}} \mu_{\text{Ti}} - \Delta n_{\text{Pt}} \mu_{\text{Pt}},$$

where  $E_{\text{Pt/TiO}_2}$  and  $E_{\text{TiO}_2}$  are the total energies of the Pt-incorporated and bare  $\text{TiO}_2$  surfaces while  $\mu_{\text{Ti}}$  and  $\mu_{\text{Pt}}$  stands for the chemical potentials of Ti and Pt.  $\Delta n_{\text{Ti}}$  and  $\Delta n_{\text{Pt}}$  represent the differences in the number of atoms of each atomic species with respect to the reference clean surface. Formation energy in this form is a function of Ti and Pt chemical potentials. Equilibrium is reached when the chemical potential of a given species is equal in all the phases that are in contact with each other. Also, these phases must be in equilibrium with bulk anatase such that

$$\mu_{\text{Ti}} + 2\mu_{\text{O}} = \mu_{\text{TiO}_2}.$$

This relation interrelates chemical potential of Ti to O chemical potential that varies accordingly with the experimental conditions. The value of  $\mu_{\text{Ti}}$  must be smaller than that of the hcp Ti bulk solid phase which is an undesirable formation at the surface and is referred as the Ti-rich conditions. The other extreme is that when the surface oxygen are found in thermodynamic equilibrium with the molecular oxygen bath corresponding to O-rich conditions. Assuming it as an ideal gas, the intermolecular interactions can be neglected. Hence, the chemical potential of oxygen can be referenced to the value at the  $\text{O}_2$  molecule which is  $\mu_{\text{O}} = E_{\text{O}_2}/2$ . Therefore, Ti chemical potential relative to its bulk value  $\Delta\mu_{\text{Ti}} = \mu_{\text{Ti}} - \mu_{\text{Ti}}^{\text{bulk}}$  varies between  $\Delta\mu_{\text{Ti}} = 0$  (Ti-rich conditions) and  $\Delta\mu_{\text{Ti}} = -8.9$  eV (O-rich conditions), for  $\text{TiO}_2$ . Since the relative formation energy of phases is defined as a function of Ti and Pt chemical potentials, Pt is assumed to be in thermodynamic equilibrium with its fcc bulk solid phase that serves as a reservoir for Pt atoms. Hence,  $\mu_{\text{Pt}}$  is chosen to represent such an experimental condition. In fact, this corresponds to just another extreme for undesired Pt phases on the surface that can be avoided by  $\mu_{\text{Pt}} < \mu_{\text{Pt}}^{\text{bulk}}$ .

The formation energies are shown in Fig. 8(a) relative to that of the clean surface for 12 phases as a function of Ti chemical potential over the full range of its allowed values. They are normalized to a  $1 \times 1$  unit cell in order to compare

their thermodynamic stabilities. Pt adsorption at 1 ML coverage results in unstable surfaces with relative formation energies at 1.77 and 2.00 eV/ $1 \times 1$  for (b) and (a) adsorption modes, respectively. Substitutional cases at this concentration are the most unstable phases within the range of  $-8.56 < \Delta\mu_{\text{Ti}} < 0$  eV with increasing instability toward Ti-rich conditions while they become the most stable phases under O-rich conditions for  $-8.90 < \Delta\mu_{\text{Ti}} < -8.56$  eV in favor of substitution for Ti 5c ( $s1-1 \times 1$ ). For this latter experimental situation, in which the surface is in thermodynamic equilibrium with the molecular oxygen,  $s2-1 \times 1$  phase has a relatively higher formation energy by 0.10 eV/ $1 \times 1$  followed by  $s2-2 \times 2$  and  $s1-2 \times 2$  structures which are energetically less favorable by 0.26 and 0.33 eV/ $1 \times 1$ . Similarly, over the range  $-7.15 < \Delta\mu_{\text{Ti}} < 0$  eV, Pt substituted  $\text{TiO}_2(001)-(2 \times 2)$  surfaces are the most unstable structures among 0.25 ML phases whereas they turn out to be the most stable cases, in which the formation energy is slightly lower for  $s2-2 \times 2$  phase, over the range  $-8.56 < \Delta\mu_{\text{Ti}} < -7.15$  eV closer to O-rich conditions.

On the other hand, Pt interstitials are unstable relative to the formation energy of the clean surface by 0.18 eV/ $1 \times 1$  for (d), and by 0.11 eV/ $1 \times 1$  for (e) and (f) at  $(2 \times 2)$  reconstruction implying increased stability with increasing Pt penetration depth. These results suggest that practical interstitial applications might require thermal treatment. Therefore, our calculations for the stabilities of substitutional cases under O-rich conditions and of Pt interstitial phases are in good agreement with the experimental results of Zhang *et al.*<sup>27</sup> who suggested that neutral Pt atoms can thermally diffuse into  $\text{TiO}_2$  lattice under oxidizing atmosphere. They also argue that these diffused Pt atoms can either substitute for the  $\text{Ti}^{4+}$  sites when oxidized to  $\text{Pt}^{2+}$  (for which our calculations show a charge state of  $+1.85e$ ) or they occupy interstitial sites.

In contrary to those of the 1 ML phases, Pt adsorbates at 0.25 ML happens to be energetically more stable relative to bare surface by 0.17, 0.23, and 0.37 eV/ $1 \times 1$  for the (a), (c), and (b) adsorption phases, respectively, for the whole range of allowed Ti chemical potential. Besides,  $b-(2 \times 2)$  structure is also the most stable phase within  $-7.15 < \Delta\mu_{\text{Ti}} < 0$  eV which spans 80.3% of the whole range from Ti-low to Ti-rich conditions.

The phase diagram shown in Fig. 8(b) has been derived from the results obtained for the energetically more stable phases, presented in Fig. 8(a), for varying Ti and Pt chemical-potential values. Hence, high formation energy surfaces have not been considered due to their instability. Under Pt-rich conditions, which refer to the formation energies presented in Fig. 8(a), three most stable phases exist for varying chemical potential of Ti. Under Pt-rich and O-rich conditions the most stable phase is  $s1-1 \times 1$  in which all of the surface-Ti ions substituted with Pt. A small deviation from these conditions by slightly increasing the Ti chemical potential switches the phase to 0.25 ML concentration surface of  $s2-1 \times 1$ . For lower O concentrations  $b-2 \times 2$  surface is more stable and dominant over the range of allowed Ti chemical potential. Under Pt-poor conditions the phase diagram reproduces the clean  $\text{TiO}_2(001)$  surface with no impurities.

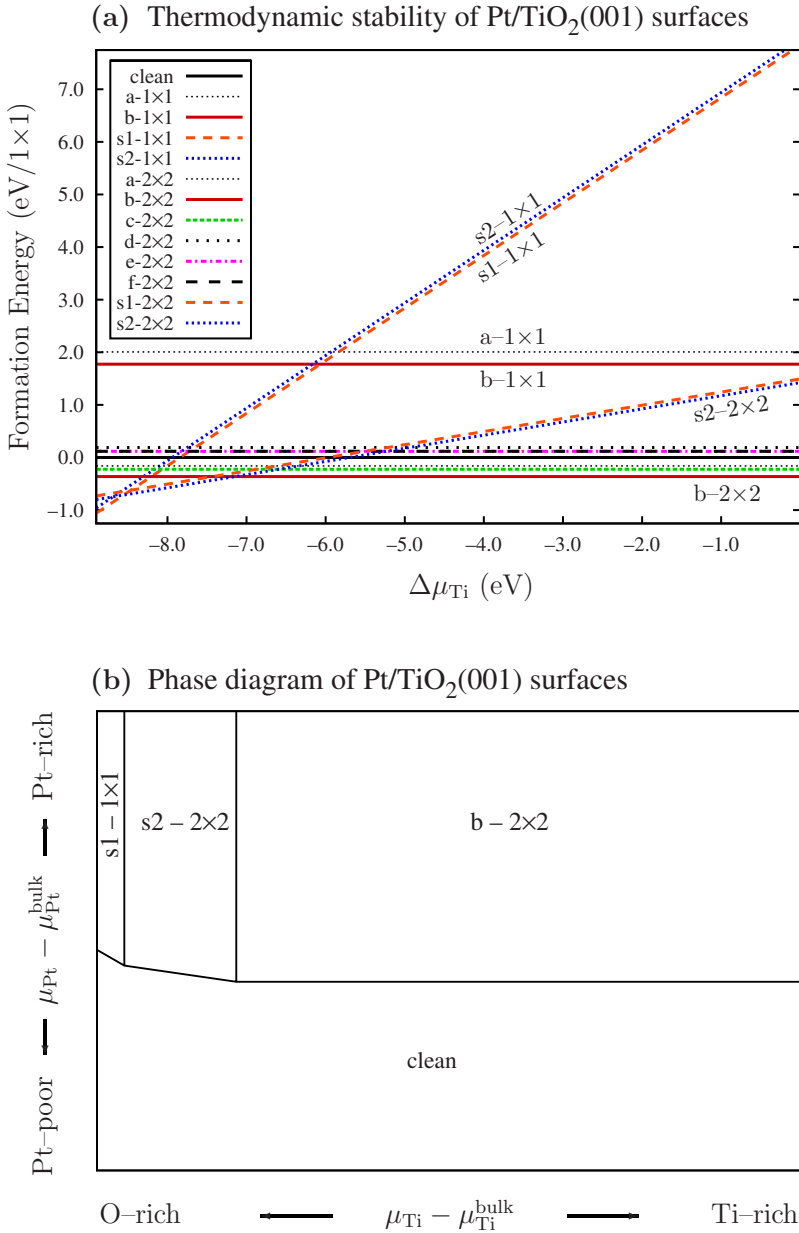


FIG. 8. (Color online) (a) Normalized formation energies of Pt-incorporated TiO<sub>2</sub>(001) structures relative to that of clean surface as a function of the Ti chemical potential. (For numerical figures, see Table IV.) Pt impurities are chosen to be in thermodynamic equilibrium with fcc Pt bulk phase. (b) Phase diagram of Pt/TiO<sub>2</sub>(001) surface as a function of Pt and Ti chemical potentials.

#### IV. CONCLUSIONS

We systematically studied the structural and electronic properties of Pt impurities in the form of adsorptional, interstitial, and substitutional cases for anatase TiO<sub>2</sub>(001) with (1×1) and (2×2) surface periodicities. The former represents full coverage while the latter corresponds to isolated impurities. Depending on the Pt concentration per unit-cell area, impurity-impurity electron coupling strength mediates the mode of atomic rearrangements as they are clearly different for (1×1) and (2×2) models. For instance, Pt adsorption at the bridge site obtained for 1 ML coverage in Fig. 3(a) is corresponded by the pattern shown in Fig. 5(a) at 0.25 ML coverage, in which surface oxygen is promoted by the adsorbate as a result of the SMSI. This difference is even more pronounced for interstitial cases. When implanted inside the slab for full coverage, Pt atoms form parallel metallic wires inside TiO<sub>2</sub> where interlayer distances slightly in-

crease due to local segregation while Pt impurities can be encapsulated by the (2×2) lattice at interstitial cavities to form structures without undergoing a major reconstruction.

In addition, another dominant factor in the formation of low energy Pt/TiO<sub>2</sub> structures is the nearest-neighbor Pt-O coordination which derives from the impurity-lattice oxygen charge transfer. Relative stabilities of these structures can be addressed to local disturbance on the potential-energy surface induced by the excess electrons brought by the impurities that consequently account for the enhancement of the electron trapping efficiencies.

Clean TiO<sub>2</sub>(001) possesses surface states derived from the valence bands in the energy-band gap near the VBM originating from the undercoordinated surface oxygen. The nature of these bands is sensitive to the minimum-energy rearrangement of the surface ions. Although this accounts for the observable responsiveness of TiO<sub>2</sub>(001), electronic charge-

TABLE IV. Numerical values for the formation energy of Pt/TiO<sub>2</sub> surfaces for adsorptional and interstitial phases (all in eV/1 × 1) referring to the constant valued functions depicted in Fig. 8. Relative formation energies are given with respect to that of the bare surface. Those of the substitutional phases not provided since they vary with varying Ti chemical potential due to different surface stoichiometry.

Phase	$E_{\text{form}}$ (Absolute)	$E_{\text{form}}$ (Relative)
Clean	0.76	0.00
a-1 × 1	2.76	2.00
b-1 × 1	2.53	1.77
a-2 × 2	0.59	-0.17
b-2 × 2	0.39	-0.37
c-2 × 2	0.53	-0.23
d-2 × 2	0.94	0.18
e-2 × 2	0.87	0.11
f-2 × 2	0.87	0.11

density analysis indicates a relatively lower reactivity with respect to defect surfaces.

In interaction with nearest-neighbor oxygen, Pt derives *s-p* hybrid impurity states from the valence bands, which lie above the VBM close to the Fermi level, as well as the ones from the conduction bands. The character of these defect states controls the narrowing of the energy-band gap. In addition to the Pt-O interaction, impurity-impurity coupling, depending on the Pt concentration, influences the position and the dispersion of defect states. Therefore, 1 ML cases exhibit strongly dispersed bands in the gap with a narrowing that refers to infrared activity and ultimately to metallization for Pt-Ti1 substitution and for interstitial Pt implantation. Having the highest symmetry adsorption mode, Pt at the midpoint between two O *2c*'s at 0.25 ML also exhibits a

band gap narrowing of 1.42 eV corresponding to infrared region similar to low band-gap Pt/TiO<sub>2</sub>(001)-(1 × 1) cases. Pt concentration, therefore, is not the only factor that controls the band gap narrowing. Our calculations show that the number of impurity driven states that fall into the gap is proportional to the coordination of Pt with O1 and O2. This explains the occurrence of 1.42 eV gap narrowing for 0.25 ML Pt concentration while all the remaining cases for (2 × 2) represent visible activity. Moreover, excess nonbonding charge due to the interaction of Pt with only one O1 in the adsorptional models in Figs. 5(a) and 5(b) brings rather flat going bands.

At 1 ML concentration under oxygen rich conditions Pt substituted TiO<sub>2</sub> tends to be more stable. As O chemical potential gets slightly lower, the phase adopts a (2 × 2) surface periodicity. Further decreasing  $\mu_{\text{O}}$  toward Ti-rich conditions, the most stable phase, dominant over the allowed range of experimental conditions, happens to be adsorption on the surface for 0.25 ML coverage (b-2 × 2), which is semiconducting in the visible region with a band gap narrowing of 1.03 eV. Consequently, anatase TiO<sub>2</sub>(001) can be functionalized for visible activity by Pt incorporation. We have shown how it relates to impurity concentration, to coordination number of Pt with the near surface oxygen, and to thermodynamic conditions which determine the chemical potential of constituent species, for useful applications.

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