



# SrTiO<sub>3</sub> (001) surface and strained thin films: Atomic simulations using a tight-binding variable-charge model

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## ARTICLE INFO

### Article history:

Received 12 December 2012

Accepted 22 May 2013

Available online 30 May 2013

### Keywords:

Strontium titanate

Surface energy

Surface relaxation

Strained thin films

Variable-charge model

Density functional calculations

## ABSTRACT

The tight-binding variable-charge model SMTB-Q was used to study the properties of the (001) surfaces and ultra-thin films of the SrTiO<sub>3</sub> perovskite. First, the bulk properties of SrTiO<sub>3</sub> were successfully reproduced from a set of parameters independently determined for bulk SrO and TiO<sub>2</sub>. The formation energies, atomic relaxations and charge transfer for SrO- and TiO<sub>2</sub>-terminated SrTiO<sub>3</sub> (001) surfaces were then derived from 0 to 1200 K. The TiO<sub>2</sub>-terminated surface is more stable than the SrO-terminated surface by about 0.15 j m<sup>-2</sup> under 500 K. This difference decreases by a factor 3 at higher temperature. At 0 K, the surface energies ( $E_{\text{TiO}_2} = 1.10 \text{ j m}^{-2}$  and  $E_{\text{SrO}} = 1.20 \text{ j m}^{-2}$ ) are in accordance with the mean value yielded by ab initio calculations. A strong Sr displacement towards the SrO-terminated surface (0.33 Å) was observed in agreement with both experimental data and DFT calculations. In contrast, the other atomic relaxations included the Ti displacement towards the TiO<sub>2</sub>-terminated surface (0.13 Å), are in good agreement with ab initio results but strongly differ from experimental data ( $\approx 0.00 \text{ Å}$ ). The displacements of surface oxygen planes being small, one observes a splitting of the SrO and TiO<sub>2</sub> surface planes by 0.30 and 0.13 Å respectively. Moreover, the distance between the Sr and Ti planes is reduced by 19%. The charge transfers at the TiO<sub>2</sub>-terminated surface are comparable to those at the pure TiO<sub>2</sub> surfaces ( $-0.18$  and  $+0.14$ , for titanium and oxygen atoms respectively) leading to the increase of the Ti-O bond covalency near the surface. At the SrO-terminated surface, we found negligible charge transfers as at the pure SrO(100) surface. Moreover, we studied the effect of a 1.66% compressive strain (corresponding to the STO/Si(001) lattice mismatch) on the relaxation of thin films from 2 to 40 nm at 273 K. The atomic surface relaxations are not significantly modified apart from the Sr-Ti (resp. Ti-Sr) distances which relaxed by 25%. The ratio between out-of-plane and in-plane lattice parameters is in good agreement with the elasticity theory for a thickness up to 5 nm. Beyond 20 nm thick the film is almost fully relaxed.

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## 1. Introduction

The SrTiO<sub>3</sub> (STO) surfaces, like TiO<sub>2</sub> surfaces, constitute a model system in the surface science of metal oxides [1] and a very important system for technological applications. Thin STO films play a major role in electronic devices and related applications due to their desirable properties, such as high dielectric constant and chemical stability; consequently when deposited on silicon they are frequently used as the substrate material for high Tc superconducting films [2,3]. Therefore, many experimental and theoretical studies have been focused on STO surfaces. Particularly, the structure of the STO(001) surface, which can terminate in either SrO or TiO<sub>2</sub> planes, has been investigated by means of low energy electron diffraction (LEED) [4], medium-energy ion scattering (MRIS) [5] and surface X-ray diffraction [6,7]. Concurrently, theoretical studies have been performed, from first-principles with different methods and Hamiltonians: density functional theory (DFT) with the local density approximation (LDA) [8–10], the generalized gradient approximation

(GGA) [11], hybrid DFT [12], full-potential linear muffin-tin orbital method (FP-LMTO) [13] and from empirical shell-model [14,15]. Here, the STO(001) surface structure was studied by means of a recent variable-charge model, the so-called SMTB-Q model (Second-Moment Tight-Binding QEq) [16,17], based on a quantum description of oxides proposed by Goniakowski and Noguera [18,19]. The equilibrium charges are determined by a self consistent charge equilibration following the QEq approach [20]. The QEq formalism allows charges to vary in response to changes in the local environment of ions, which is a real progress compared with the fixed-charge shell-model. Note that it is the first time, to our knowledge that variable-charge simulations are performed for such complex oxide. Moreover, in the SMTB-Q model, the ionic-covalent metal-oxygen bond is described by means of the tight-binding formalism which takes into account the electronic structure of the oxide, in contrast to other variable-charge models [21–24]. In this approach, the covalent energy is a function of the ionic charges, which results in a great stability of the model with respect to charge transfers. This is particularly crucial when the crystal is submitted to strain or to the lack of periodicity in one direction by the presence of a surface. The parameters of the model are determined independently

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for the two binary oxides SrO and TiO<sub>2</sub> and then are used to derive bulk and surface properties of STO after a small correction, taking advantage of the transferability of the SMTB-Q model. Moreover, the effect of strain on thin films from 2 to 40 nm-thick was studied at 273 K. More precisely we applied a 1.66% compressive strain parallel to the (001) surface which corresponds to the lattice mismatch between STO and Si(001) in assuming that the silicon substrate imposes a clamping effect to the STO film deposited on it.

The paper is organized as follows. In Section 2, the SMTB-Q model is shortly described (Section 2.1) and the parameters of the model are determined for bulk SrO and TiO<sub>2</sub> (Section 2.2). In Section 2.3, the transferability of the model is discussed and the bulk properties of STO were derived. In Section 3, surface properties of SrO, TiO<sub>2</sub> and STO (energetic, atomic relaxations and charge transfer) are studied and the results are compared with ab initio calculations performed with the CRYSTAL06 code [25], and with experimental data when available. In Section 4, the effect of a strain on the relaxations of thin films is investigated. Section 5 contains our conclusions.

## 2. Bulk SrO, TiO<sub>2</sub> and SrTiO<sub>3</sub>

### 2.1. The SMTB-Q model

In this model, the cohesive energy,  $E_{\text{coh}}$ , of a simple binary oxide  $M_nO_m$  is the sum of four terms:

$$E_{\text{coh}} = E_{\text{ion}} + E_{\text{coul}} + E_{\text{cov}} + E_{\text{rep}}, \quad (1)$$

with:

$$E_{\text{ion}} = \sum_A (E_A^0 + \chi_A^0 Q_A + \frac{1}{2} J_{AA}^0 Q_A^2) \quad (2)$$

$$E_{\text{coul}} = \sum_A \sum_{B < A} Q_A Q_B J_{AB} \quad (3)$$

$$E_{\text{cov}} = - \sum_{i(i=M,O)} \left\{ \sum_{\substack{j(j=O,M) \\ r_{ij} \leq r_c}} \xi_M^2 \exp \left[ -2q_M \left( \frac{r_{ij}}{r_{OM}^0} - 1 \right) \right] \Delta Q_M \right\}^{1/2} \quad (4)$$

$$E_{\text{rep}} = \sum_{i(i=M,O)} \sum_{\substack{j(j=O,M) \\ r_{OM} \leq r_c}} A_M \exp \left[ -p_M \left( \frac{r_{ij}}{r_{OM}^0} - 1 \right) \right] \quad (\text{metal-oxygen pairs}) \\ + \frac{1}{2} \sum_{O, r_{OO} \leq r_c} B \exp \left( \frac{r_{OO}}{\rho} \right) \quad (\text{oxygen-oxygen pairs}). \quad (5)$$

$E_{\text{ion}}$  (Eq. (2)) is the ionization energy developed up to the second order with respect to the charges  $Q_A$  on atom  $A$ ,  $E_A^0$  is the energy of the neutral atom and  $\chi_A^0$  and  $J_{AA}^0$  are the electronegativity and the hardness of the atom  $A$  respectively.  $E_{\text{coul}}$  (Eq. (3)) is the electrostatic energy.  $J_{AB}$  is the Coulomb interaction between the unit charges on centers  $A$  and  $B$ . Following Rappé and Goddard [20],  $J_{AB}$  are Coulomb integrals between two single s-type Slater orbitals  $\rho_A(r) = N_n r^{n-1} e^{-(2n+1)/4R_A}$ , where  $N_n$  is the normalization constant,  $n$  is the quantum number of the outer valence orbital and  $R_A$  is the covalent radius of atom  $A$  in the original QEq formulation [20]. In fact, the real significance of  $R_A$  is a little more complex in a solid, because it must depend both on the coordination number of the atom and on the interatomic distance and is then considered as an adjustable parameter. At short distance, the Coulomb interaction is shielded, leading to a decrease of the absolute value of the electrostatic energy compared with the one obtained with point-charge models. The expression of the covalent energy,  $E_{\text{cov}}$  (Eq. (4)), is derived from the quantum model developed by Noguera and Goniakowski [18,19], recalled in the Appendix A. This expression is obtained from Eq. (A5) by extending the covalent interaction over all neighbors of every atom

( $M$  or  $O$ ) up to the second-moment cut-off radius  $r_c$  generally located between the 4th and 5th neighbors [27].  $r_{OM}^0$  is the equilibrium first neighbor  $OM$  distance,  $\xi_M$  and  $q_M$  are adjustable parameters. Eq. (5) represents the short-range pair repulsion between ions.  $A_M$ ,  $p_M$ ,  $B$  and  $\rho$  are adjustable parameters. Cation-cation short-range interactions are neglected because the  $M$  outer orbitals are empty in an insulator. Note that the extension of Eqs. (1)–(5) to ternary systems is straightforward, Eq. (A6) that must be used at the place of Eq. (A5).

According to the QEq scheme [20], the equilibrium ionic charges in the crystal are those which minimize  $E_{\text{coh}}$  (more exactly, the part of  $E_{\text{coh}}$  which depends on the charges), and we obtain (see Appendix B):

$$\left( \chi_O^0 - \chi_M^0 \right) + J^{\Sigma} Q = 2m\beta\sqrt{Z_O} \frac{(n_{\text{cov}} - 4 + 2Q)}{\sqrt{(2-Q)(n_{\text{cov}} - 2 + Q)}}, \quad (6)$$

where the expression (A4) for  $E_{\text{cov}}$  were used for sake of simplicity of the writing (the use of Eq. (4) is straightforward). In contrast, in previous variable-charge models [21–24], the covalent energy does not depend on the charges, and the equilibrium oxygen charge is simply given by:

$$Q = \frac{(\chi_M^0 - \chi_O^0)}{J^{\Sigma}}. \quad (7)$$

### 2.2. Parameters of the model for bulk SrO and TiO<sub>2</sub>

For a particular oxide, the parameters of the model are adjusted in order to reproduce the lattice parameters, the cohesive energy and the elastic properties. These parameters can be separated into two groups. The first group, the QEq parameters, includes the electronegativity  $\chi_A^0$ , the hardness  $J_{AA}^0$  (Eq. (2)) and the effective radius of the Slater orbitals,  $R_A$  of each species ( $A = M, O$ ).  $\chi_O^0$  and  $J_{OO}^0$  are adjusted to electron affinity of oxygen.  $\chi_M^0$  and  $J_{MM}^0$  are adjustable parameters and must be reasonably compatible with the ionization energies of  $M$ . The second group, the short-range (SR) parameters, includes  $\xi_M$ ,  $q_M$  (Eq. (4)),  $A_M$ ,  $p_M$ ,  $B$  and  $\rho$  (Eq. (5)). The values of the two sets of parameters for SrO and TiO<sub>2</sub> are reported in Table 1. Note that oxygen parameters are the same in the two cases, apart  $R_O$  which slightly depends on  $Z_O$  (6 in SrO, 3 in TiO<sub>2</sub>).

In Table 2, the calculated and experimental properties are compared. Lattice parameters, cohesive energies and bulk modulus are very well reproduced and the elastic constants fit satisfactorily, the maximum deviations being 36% for  $C_{12}$  of SrO and 22% for  $C_{33}$  of TiO<sub>2</sub>. It is necessary, here, to emphasize a point. To select a set of parameters to describe some properties of a compound is always a compromise. There are several satisfactory sets of parameters (which are not very different from each other) according to the accuracy wanted on any particular

**Table 1**

Parameters of the SMTB-Q model for SrO and TiO<sub>2</sub>. The second column of results is relative to this work and the third column to a previous work on TiO<sub>2</sub> [17].

	SrO	TiO <sub>2</sub>	TiO <sub>2</sub> [17]
$\chi_O^0$ (eV)	6.57	6.57	7.543
$J_{OO}^0$ (eV)	10.22	10.22	12.162
$\chi_M^0$ (eV)	4.9	0.0	0.0
$J_{MM}^0$ (eV)	3.56	10.572	10.572
$R_O$ (Å)	0.52	0.543	0.617
$R_M$ (Å)	0.767	0.734	0.6933
$\xi_M$ (eV)	1.423	1.087	1.12
$\beta$ (eV)	1.423	0.928	0.956
$q_M$	1.935	2.096	2.16
$A_M$ (eV)	0.342	0.134	0.1
$p_M$	6.274	12.61	15.48
$B$ (eV)	580.44	580.44	580.44
$\rho$	0.354	0.354	0.354
$r_{OM}^0, r_c$ (Å)	2.58, 8.0	1.95, 6.0	1.95, 6.0

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