Structural distortion and charge redistribution in $SrTiO_3$ (111) polar surfaces

Yan Yin [a], Jianli Wang [b, **], Huiping Zhu [a], Kai Lv [a], X.S. Wu [a, *]

[a] Laboratory of Solid State Microstructures and School of Physics, Nanjing University, Nanjing 210093, China
[b] Department of Physics, China University of Mining and Technology, Xuzhou 221116, China

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ABSTRACT

The structural and electronic properties of the $SrTiO_3$ (111) polar surfaces are studied using first-principles calculations. The structural distortions for Ti termination are larger than that for SrO_3 termination. A negative charge density of $-0.55e$ is concentrated at the surface of Ti termination, which may explain the recent finding of two-dimensional electron gas exits at the $SrTiO_3$ (111) surface. A positive charge density of $0.64e$ is accumulated at the surface of SrO_3 termination. The nonstoichiometric TiO and SrO_2 terminations are also considered. Oxygen octahedrons tilt to the opposite direction in the adjacent cells along the stacking direction. TiO and SrO_2 terminated slabs are both insulating with surface charge modified relatively small. The surface energies for all the $SrTiO_3$ (001), (011) and (111) surfaces are calculated to compare the surface stability.

1. Introduction

$SrTiO_3$ (STO) is a typical transition metal oxide and is widely used as a substrate for the creation of high-T_c superconductors [1], large negative magnetoresistance [2] or other functional materials [3,4]. The discovery of a high-mobility electron gas at the $LaAlO_3$/$SrTiO_3$ heterointerface [5] has attracted much attention, and gives rise to the development of oxide electronic devices [6,7]. Recently, two-dimensional electron gas (2DEG) has also been observed at the surfaces of (001) [8,9], (110) [10] and (111) [11] oriented STO. The findings have sparked a new research of metallic oxide surfaces to improve this material's technological importance. But the origin of the 2DEG remains elusive. Therefore, a microscopic understanding of the electronic based on oxide material's surface is imperative.

The STO (001) nonpolar surfaces and (011) polar surfaces have been well studied experimentally [12–14] and theoretically [15–18], while STO (111) polar surfaces are relatively less studied. The STO (111) surface exhibits a stable (1 × 1) structure in experiment [19]. Two terminated surfaces, SrO_{3-x} and Ti terminations,

have been observed by scanning tunneling microscopy combined with reflection high-energy electron diffraction under specific preparation conditions [20]. Recently, an atomically flat single-terminated surface has been successfully obtained on the (111)-oriented STO [21]. In theory, the semi-empirical Hartree-Fock calculations discussed polarity effects at the (111) surfaces, and argued that the compensation for the polar orientations is achieved through anomalous filling of surface states [22]. A quantum espresso simulation (QE) investigated the surface electronic structure and thermodynamic stability of the STO (111) slabs, finding that Ti terminated (111) surface should be experimentally realizable, and the Ti-terminated slab is possible to create 2DEG [23]. We have extended this existing work by (i) studying the distortions of oxygen octahedron and by (ii) performing a deeper analysis of the anomalous filling of surface states in the STO (111) polar surfaces.

In the present, we focus on different STO (111) surfaces: the two stoichiometric Ti and SrO_3 faces, and two nonstoichiometric TiO and SrO_2 terminations. In the following, after a brief description of the computational details, we calculate the surface energies for all the STO (001), (011) and (111) surfaces to compare the surface stability, and then we analyze the surface relaxations, structural distortions and electronic properties for the STO (111) stoichiometric and nonstoichiometric terminations.

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* Corresponding author.
** Corresponding author.
E-mail addresses: jlwang@cumt.edu.cn (J. Wang), xswu@nju.edu.cn (X.S. Wu).

2. Computational method

The calculations are performed using density-functional theory (DFT) [24] within the Perdew−Burke−Ernzerhof − generalized gradient approximations exchange-correlation functional [25] as implemented in the VASP code [26] and projector augmented wave pseudopotentials [27]. The energy cutoff for the plane-wave basis set is 500 eV. A $12 \times 12 \times 12$ (bulk) and a $6 \times 6 \times 1$ (slab) Monkhorst-Pack k-point mesh are used for the Brillouin zone integration. Increasing the mesh to $8 \times 8 \times 1$ for slabs calculations, the computed total energies decrease by less than 20 meV. The structural relaxation is permitted until the force acting on each atom is less than 0.02 eV/Å.

The lattice constant of bulk STO is calculated to be 3.945 Å [18], which is in good agreement with the experiment value (only a 1% deviation) of 3.905 Å [28] as well as other theoretical results [29,30]. The computed band gap of bulk STO (1.77 eV) is consistent with Ref. [31], and it is smaller than the experiment value (3.2 eV) [32], which is a common case for the DFT. The (111)-oriented STO slabs are composed of alternately stacked charged planes, Ti^{4+} and SrO_3^{4-}, giving rise to a divergent electrostatic potential. In order to avoid the dipole−dipole interactions between periodic slabs [33], twenty-five-layer symmetric slabs are adopted, which are terminated by the same crystalline planes, with 10 Å vacuum widths on each side (see Fig. 1). According to classical electrostatics, ideal polar surfaces are unstable [34], and a polar surface can be stabilized by modify either the charges or the stoichiometry in the surface layer [35]. Thus two nonstoichiometric TiO and SrO_2 terminations are also discussed in this work.

To estimate the electron distribution in the various surface configurations, we use here the Bader's topological charge analysis [36] to estimate the electron sharing between the O anions and the Sr and Ti cations, which corresponds to a partition of the total charge in atomic basins. The Bader charges of the bulk STO are +1.61 for Sr, +2.18 for Ti, and −1.26 for O, which are consistent with Ref. [15]. Charges are given in electron numbers. These numbers generally do not offer the exact valences, but the difference of them can be thought as the valence electrons change.

3. Results and discussion

3.1. Surface energies

To obtain the surface energy [17,37], we first calculate the cleavage energy (E_{cl}) which is needed to cleave the crystal into two unrelaxed complementary terminations. When the STO crystal is cleaved along the (111) surface, the complementary terminations are the Ti and SrO_3 faces, or TiO and SrO_2 terminations. We assume the cleavage energy distributes equally between the two complementary terminations. Therefore, the cleavage energies for Ti or SrO_3 terminations and TiO or SrO_2 terminations can be written as:

$$E_{cl}(Ti/SrO_3) = \frac{1}{4}\left[E_{slab}^{(unrel)}(Ti) + E_{slab}^{(unrel)}(SrO_3) - nE_{bulk}\right], \quad (1)$$

$$E_{cl}(TiO/SrO_2) = \frac{1}{4}\left[E_{slab}^{(unrel)}(TiO) + E_{slab}^{(unrel)}(SrO_2) - nE_{bulk}\right], \quad (2)$$

where $E_{slab}^{(unrel)}(A)$ is the total energy of unrelaxed symmetric slab with A termination, A = Ti, SrO_3, TiO, or SrO_2, E_{bulk} is the bulk energy per unit cell, n is the total number of bulk unit cells in the two complementary terminated slabs, and the factor of 1/4 corresponds to four surfaces created by crystal cleavage. Next, we compute the relaxation energy for A terminated slab,

$$E_{rel}(A) = \frac{1}{2}\left[E_{slab}(A) - E_{slab}^{(unrel)}(A)\right], \quad (3)$$

where $E_{slab}(A)$ is the total energy of A termination after relaxation. Then, we obtain the surface energy as the sum of the cleavage and relaxation energies,

$$E_s(A) = E_{cl}(A) + E_{rel}(A). \quad (4)$$

The fifteen-layer STO (001) terminated surfaces and nineteen-layer STO (011) terminated surfaces are also calculated for comparison following upper steps. For STO (001) surfaces, the complementary terminations are the TiO_2 and SrO terminations. For
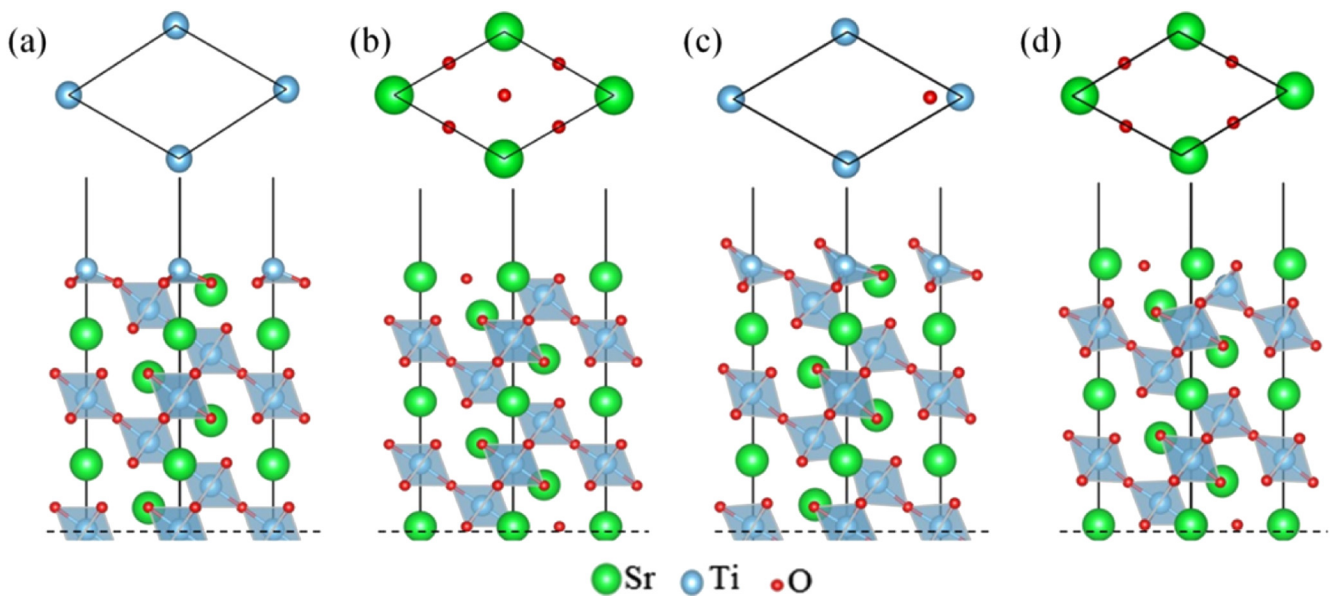
Fig. 1. The top and side view of the upper half slabs for the four STO (111) terminations: the stoichiometric (a) Ti and (b) SrO_3 terminations, the nonstoichiometric (c) TiO and (d) SrO_2 terminations. TiO and SrO_2 terminations may be obtained from stoichiometric surface by adsorption and desorption O atom. The modified surfaces in (c) and (d) are energy preferable, which are consistent with the previous study [23]. The dotted line indicates the central of the slab.