Modeling the structure of the TiO$_2$(rutile)/SrTiO$_3$ heterointerface

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**Abstract.** The structure of the TiO$_2$(rutile)/SrTiO$_3$ interface is modeled using the density functional theory method. Based on calculations, the most stable structure of the heterointerface is determined, for which there are noticeable differences in the structure of the bordering TiO$_2$ and SrTiO$_3$ layers. This determines mainly the ionic nature of interfacial bonding and the metallic nature of the interface, which can contribute to an increase in the number of charge carriers and the formation of a 2D electron gas. In addition, oxygen vacancies and under-coordinated O and Ti atoms are observed on the bordering TiO$_2$ layer, indicating excess energy of the heterointerface. The results obtained serve as a basis for using theoretical methods to evaluate the effect of dopants on the thermoelectric properties of TiO$_2$−SrTiO$_3$ biphasic ceramics.

**1. Introduction**

Currently, most of the energy is produced by heat engines, which leads to a low efficiency of electricity generation due to the dissipation of most of the heat. Therefore, secondary exhaust heat processing is highly promising for energy efficiency improvement. This gives rise to interest in high-temperature thermoelectric materials.

Earlier [1], the authors of this study presented the concept of creating a new thermoelectric material based on a two-phase ceramic TiO$_2$−SrTiO$_3$ system. Its peculiarity is that a 2D electron gas does not occur as usual in a specially formed thin layer of some substance, but spontaneously on the TiO$_2$/SrTiO$_3$ heterointerface (modulation doping).

In [2–4], the conditions for the formation of a 2D electron gas at the interface between thin TiO$_2$(anatase) and SrTiO$_3$ films were studied in detail, but the formation of biphasic high-density TiO$_2$−SrTiO$_3$ ceramics requires sintering temperatures above 1 000 °C. Under these conditions, a phase transition of titanium dioxide (anatase→rutile) is possible. It is known [1] that the lower boundary of the rutile conduction band is lower than that of strontium titanate. This implies that the formation of the TiO$_2$ rutile phase does not significantly affect the thermoelectric properties of the TiO$_2$−SrTiO$_3$ biphasic ceramics, in which a connected network of 2D electron gas must be formed at
2. Simulation Details

Calculations of energy and electronic structure were performed in the framework of DFT using the Quantum-ESPRESSO package [7]. The PAW approach [8] and the exchange-correlation functional of GGA were used for modeling, Perdew et al. [9] (PW91). DFT/PAW method combines simplicity of first-principles pseudopotential and accuracy of linearized augmented planewave method. PAW is an all-electron technique, which enables one to determine potential using all-electron density. That is why PAW proved to be as one of the most robust approximations for electronic structure modelling of crystals. DFT/PAW using the GGA PW91 functional allows to obtain reliable data on the structure and properties of TiO$_2$/SrTiO$_3$ interface [4].

The single-particle Kohn-Sham wave function was expanded using plane waves with a cutoff energy of 450 eV. When calculating the interface structure, a 10 Å vacuum region was embedded in supercells along the normal to the boundary, which eliminated undesirable interactions between the plate and its periodic images. The total energy was reduced to an accuracy of 2 meV per atom using the above parameters. When optimizing the structure of individual plates and the heterointerface, the convergence criterion was 0.05 eV/Å.

3. Results and discussion

The accuracy of the chosen method was evaluated by performing a series of calculations of the SrTiO$_3$ and TiO$_2$ bulk energies and electronic structures. The following optimal SrTiO$_3$ and TiO$_2$ bulk lattice constants were obtained: $a = 3.983$ Å, $b = 4.660$ Å and $c = 3.003$ Å. The calculated lattice constants are 102% of the experimental value for SrTiO$_3$ [10] and 101.5% for TiO$_2$ [11]. The band gap of bulk SrTiO$_3$ is calculated to be 1.69 eV, which is close to the theoretical values of 1.78 eV according to Zhang et al. [12] and 1.84 eV according to Fabricius et al. [13], but significantly less than the experimental value of 3.25 eV [14]. The estimated band gap of the rutile form of titanium oxide is 1.72 eV, which is also less than the experimental value of 3.00 eV [15]. Such differences between the experimental and calculated energies can be attributed to the well-known disadvantage of the DFT method, which consists in underestimating the band gap of semiconductors.

On the surfaces of SrTiO$_3$(111) and the rutile form of TiO$_2$(100), two types of endings were taken into account (figure 1). In total, 4 possible interfaces were built within the framework of the above-mentioned orientation relations. The $W_{ad}$ (Table 1) adhesion energy was estimated by analogy with [4,16] to predict an energetically stable interface. The unrelaxed $W_{ad}$ value is calculated by subtracting the energy of the boundary layers in the equilibrium state from the energy value of the unrelaxed isolated plates. Then, for each isolated plate and heterointerface, the structure was optimized, which allowed obtaining a relaxed $W_{ad}$ value.

| Structure | Unrelaxed | Relaxed |
|-----------|-----------|---------|
| $a$       | 0.29      | 0.33    |
| $b$       | 0.07      | 0.01    |
| $c$       | 0.09      | 0.15    |
| $d$       | 1.56      | 1.44    |
Figure 1. Unrelaxed structures of the heterointerfaces between the rutile form of TiO$_2$ and SrTiO$_3$.

The highest value of $W_{ad}$ is observed for structure $d$ (figures 1 and 2), which can be explained by differences in the structure of the bordering TiO$_2$ and SrTiO$_3$ layers. This determines the predominantly ionic (with a small amount of covalency) nature of interfacial bonding and the metallic nature of the TiO$_2$(rutile)/SrTiO$_3$ interface, which can contribute to the formation of a 2D electron gas on the heterointerface. However, confirmation of this conclusion requires additional experimental studies. In addition, the possibility of forming a 2D electron gas can be influenced by the introduction of various alloying additives in TiO$_2$ (rutile) or SrTiO$_3$.

Figure 2. The relaxed structure of the heterointerface (structure $d$) between the rutile form of TiO$_2$ and SrTiO$_3$. 
In the relaxed structure of the TiO$_2$(rutile)/SrTiO$_3$ heterointerface on the bordering TiO$_2$ layer, two under-coordinated titanium and oxygen atoms are present in each unit cell, and oxygen vacancies are also observed (figure 2). In addition, in the second TiO$_2$ layer, some of the Ti atoms are under-coordinated. Additional calculations are required to determine the effect of the number or type of broken bonds on the heterointerface on the $W_{ad}$ value, but it can be assumed that the presence of under-coordinated atoms indicates the excess energy of the heterointerface.

4. Conclusions
Based on DFT calculations, the epitaxial stability of the TiO$_2$(rutile)/SrTiO$_3$ heterogeneous boundary has been estimated. Modeling has shown the stability of the heterointerface structure, for which the greatest differences are observed in the structure of the bordering TiO$_2$ and SrTiO$_3$ layers, which determines mainly the ionic nature of interfacial bonding and the metallic nature of the TiO$_2$(rutile)/SrTiO$_3$ interface and can contribute to the formation of a 2D electron gas. However, confirmation of this effect requires a series of additional experimental measurements. In any case, it is possible to change the thermoelectric properties of biphasic ceramics TiO$_2$-SrTiO$_3$ by introducing modifying additives.

After optimizing the structure of the TiO$_2$(rutile)/SrTiO$_3$ heterointerface, the TiO$_2$ boundary layer contains under-coordinated Ti and O atoms, as well as oxygen vacancies. This can be attributed to the excess binding energy of the rutile TiO$_2$ (100) and SrTiO$_3$ (111) layers. The results obtained can be used to calculate the structure of the TiO$_2$/SrTiO$_3$ interface with various alloying additives in TiO$_2$ and/or SrTiO$_3$, which helps to predict the optimal amount of the additive and its elemental composition.

Acknowledgements
This work was supported by the Russian Foundation for Basic Research (Project No.18-29-11044).

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