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Interactions of charged domain walls and oxygen vacancies in $BaTiO_3$: a first-principles study

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ABSTRACT

Ferroelectric domain walls have been promised for some potential applications due to their unique properties. In particular, the electrical conductivity of charged domain walls (DWs) allows a new dimension to ferroelectric functionalities. In this work, we construct two representative types of charged DWs, i.e. head-to-head (HH) wall and tail-to-tail (TT) wall, and employ the first-principles method to study the electronic structure of these charged walls in $BaTiO_3$ and the interactions between them and oxygen vacancies. It is revealed that the HH walls show the *n*-type conductivity, but the TT walls show the *p*-type conductivity. While embedded oxygen vacancies attract the TT wall and repel the HH wall, the interaction between the walls and oxygen vacancies depends on the vacancy occupation. This interaction enhances the conductivity of HH walls and reduces the conductivity of TT walls, and in particular a TT wall in binding with oxygen vacancies will drive the transition of *p*-type wall conductivity into *n*-type wall conductivity. The interaction of these walls with oxygen vacancies is discussed using the electrostatic model. This work represents a comprehensive understanding of electrical transport of charged DWs in ferroelectrics and possible roadmaps for manipulation.

1. Introduction

Ferroic domain structure has been a long-standing topic because it contains a characteristic scale essential for ferroic properties [1,2]. An understanding of domain structure in ferroics becomes highly necessary [3–5]. Attention is being paid to domain wall (DW) itself where the electronic structure is different from bulk [6,7]. It is known that ferroelectrics exhibit complex domain structures because of relaxation of depolarization energy together with other ingredients of physics [8]. A few of emergent phenomena associated with ferroelectric DW have been observed [9–16]. One concerned effect is the unusual electrical transport inside a wall. The enhanced wall electrical conductivity (hereafter abbreviated as wall conductivity) [17–20] may find relevant potential applications in microelectronics [21] and energy-conversion devices [22,23]. In addition, a wall can be multiferroic [24], further stimulating interest in electronic property inside a wall.

Although wall conduction has been observed in numerous ferroelectrics such as $BiFeO_3$ and $PbTiO_3$ [15,17,25–30], no clear correlation between wall configuration and its conductivity is understood, noting that wall conductivity can be observed in both small band-gapped $YMnO_3$ (~1.55 eV) and large gapped $BaTiO_3$ (BTO) (3.2 eV) [31,32]. So far, most observations have been focused on charged wall across which the continuity of electric polarization is broken. The head-to-head (HH) wall and tail-to-tail (TT) wall are two simple cases and usually have better conductivity than others [17–19,27]. A schematic representation in Fig. 1(a) shows three domains separated by two walls. The electrons in the outer shell of cationic ion near a HH wall would have higher energy, likely to be excited into the conduction band. This is equivalent to the *n*-type carrier doping. For a TT wall, the situation is just opposite, equivalent to the *p*-type carrier doping.

The above discussion hints potentials to mediate the wall conductivity by electric polarization [11,16,18,20]. The charge

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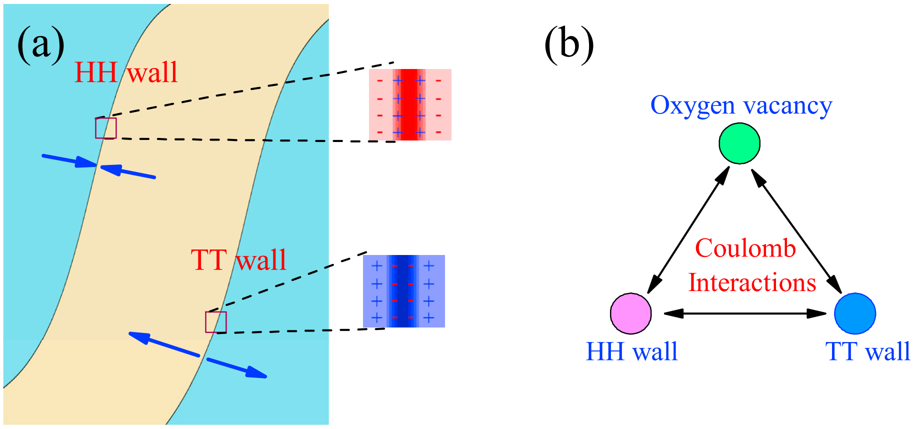

Fig. 1. (a) A schematic representation of HH wall and TT wall as neighbors. The blue arrows indicate the polarization, the symbol '+' and '−' denote the charges. (b) The interaction triangle between HH wall, TT wall, and oxygen vacancy. HH, head-to-head; TT, tail-to-tail.

doping via various approaches could be a good scheme to improve the wall conductivity. On the other hand, the role of lattice defects in influencing transport properties has been well recognized, suggesting the defects-oriented strategy to improve wall conductivity. For instance, wall conductivity in $BiFeO_3$ thin films can be remarkably mediated by Fe^{4+} ions and Bi vacancies [9]. The interactions of walls with lattice defects may lead to DW variants in $PbTiO_3$ [10] and other systems [33–37]. Theoretical calculations [38] revealed that point defects may have lower formation energy inside walls as sinks on one hand and are pinned by immobile defects on the other hand [15]. For ferroelectric oxides, the role of oxygen vacancies (OVs) has been often discussed, including the accumulation and pinning in walls [39–41] as well as structural variations [30,32]. Here it is noted that an implanted OV is bivalent unless otherwise stated. Owing to the electrostatic interaction of an OV with its neighbors, the electronic structure and spatial configuration of a wall will be modulated. For a concrete case, attraction between OV and TT wall and repulsion between vacancy and HH wall are expected. Meanwhile, neighboring HH wall and TT wall also have electrostatic interaction. One can propose an interaction triangle connecting OV, HH wall, and TT wall, as shown in Fig. 1(b).

Nevertheless, such a triangle has not yet well understood [9,33,40]. First, the electronic structure and conductivity of a charged wall remain to be investigated in detail. Second, the correlation between wall conducting behaviors and charged defects deserves for attention. For simplifying consideration, one takes BTO as the object of present study. A charged wall can be generated by the super-bandgap illumination method at room temperature [13,42], and a metallic-like conduction with conductivity $\sigma \sim 10^9$ times larger than that inside domain is possible [16]. BTO is a ferroelectric in which the density of OVs can be mediated over many orders of magnitude, allowing the appearance of insulating, semiconducting, or metallic wall. Furthermore, earlier experiments [39,41] revealed that OVs can aggregate near some DWs, making their concentration much higher than other locations. This indicates the necessity for addressing the interactions between OVs and charged walls.

Owing to the complex interactions between charged wall and defects, a phenomenological study based on effective Hamiltonian is complex. The first-principles approach allows us to proceed from the specific atomic structure to study these complex interactions. In this work, we mainly address the electronic structure of HH wall and TT wall and their interaction with charged defects such as OVs.

2. Model and computational details

2.1. Structural model

We start from a simple model based on a tetragonal BTO lattice with fixed symmetry (P4mm) [43]. The optimized lattice constants after a full relaxation are $a = 3.9851$ Å, $c = 4.1773$ Å, in agreement with earlier results [44,45]. The lattice for the present calculation is a long strip supercell of $1 \times 1 \times L$ in dimension with electric polarization along the c-axis, as shown in Fig. 2a. The periodic boundary conditions are applied. In this case, the ground state must be a monodomain [15,46].

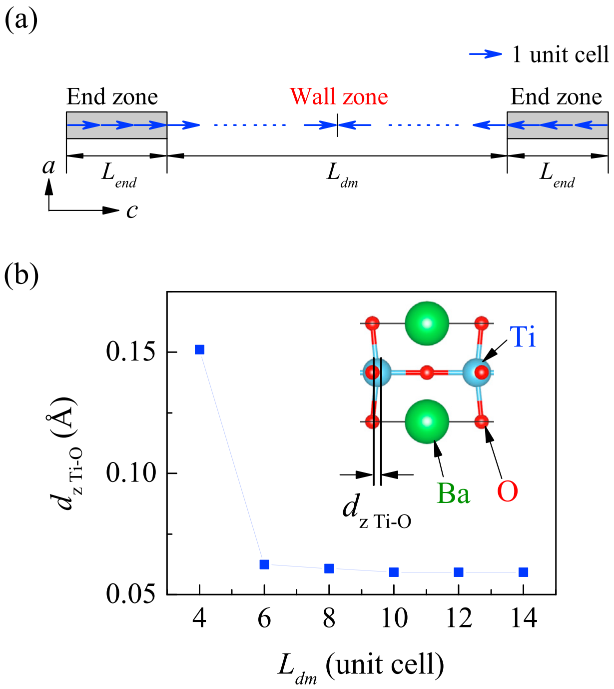

Fig. 2. (a) A schematic drawing of a wall zone. Each arrow indicates a BTO unit cell and also the polarization direction. The shaded areas at the two ends are the end zones of the lattice. (b) The distance of Ti atom and O atom near a domain wall along the c-axis, $d_{z\ Ti\text{-}O}$, as a function of L_{dm}. The inserted picture in (b) is an enlargement of the unit cell near the HH wall plane. BTO, $BaTiO_3$; HH, head-to-head.