Strain induced ferroelectricity in the SrZrO₃/SrTiO₃ superlattice: First principles study

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Abstract

The lattice distortion strain induced ferroelectricity in SrZrO₃/SrTiO₃ superlattice is studied using first principles density functional theory. Within the tetragonal symmetry $P4mm$, the lattice distortion from the lattice mismatch in the superlattice structure is determined through energy minimization. This kind of lattice distortion leads to the formation of spontaneous polarization in the superlattice, although neither SrZrO₃ nor SrTiO₃ is ferroelectric. From analysis of the relative displacements of the cations and anions, we have found that the SrZrO₃ cell may make a greater contribution to the polarization in the SrZrO₃/SrTiO₃ superlattice than the SrTiO₃ cell. An extremely large polarization of 42.7 μC/cm² has been predicted.

Perovskite oxides with the chemical formula ABO₃ have attracted great interest due to their ferroelectric, piezoelectric, ferromagnetic and superconductive properties. These properties make them a very important class of materials for many applications, such as nonvolatile memory, optical waveguides, laser frequency modulations, piezoelectric transducers, etc. [1–3]. One generic representative of perovskite oxides is strontium titanate SrTiO₃ (STO), which is called an incipient ferroelectric (or quantum paraelectric) oxide because its ferroelectric phase transition is assumed to be suppressed by quantum fluctuations [4]. STO has cubic perovskite structure at room temperature and experiences a cubic–tetragonal phase transition at 105 K. Since it has a high dielectric constant and is a candidate for replacing SiO₂ as a gate oxide in metal oxide semiconductor devices, STO has been extensively studied both experimentally and theoretically. Strontium zirconate SrZrO₃ (SZO) is another perovskite which undergoes relatively complex phase transitions. With increasing temperature, its structure phase changes from orthorhombic ($Pnma$) to orthorhombic ($Cmcm$) at 970 K, then to tetragonal ($I4/mcm$) at 1020 K, and finally to cubic ($Pm3m$) at 1360 K [5]. SZO is of interest due to its promising use in high voltage and high reliability capacitor applications. Recently it has been investigated as a possible material for high k gate dielectrics [6].

Neither STO nor SZO is ferroelectric. However, ferroelectricity has been observed recently in artificial (SZO)$_m$/(STO)$_m$ superlattices fabricated by molecular beam epitaxy (MBE) [7]. It has been surmised that the reason for the ferroelectric properties is mainly due to the lattice distortion introduced by the lattice mismatch between SZO and STO. To see how this kind of lattice mismatch affects the ferroelectric properties, we perform first principles calculations on an ultrashort (SZO)$_1$/(STO)$_1$ superlattice to obtain its geometrical structure, polarization behavior, as well as its electronic structure.

The unit structure of the (SZO)$_1$/(STO)$_1$ superlattice used for calculation is schematically shown in Fig. 1. It is a ten-atom supercell with one SZO and one STO along the z-direction sharing the same in-plane lattice constant a. The calculations are carried out using the density functional theory (DFT) plane-wave pseudopotential method implemented in the PWscf code [8]. The exchange–correlation potential is treated with the local density approximation (LDA) [9]. Vanderbilt ultrasoft

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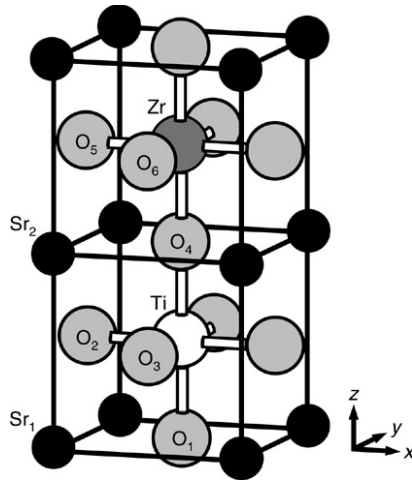*E-mail address:* yangk@mail.sdu.edu.cn (K. Yang).

Fig. 1. Unit structure of the $(SZO)_1/(STO)_1$ superlattice used in the calculations. The solid, light gray, dark gray and open circles represent the Sr, O, Zr and Ti atoms, respectively.

pseudopotentials [10] are employed. A plane-wave energy cut-off of 30 Ry has been adopted. A $(6 \times 6 \times 3)$ Monkhorst–Pack grid [11] is used for the Brillouin zone integration with Zr (4s, 4p, 4d, 5s), Ti (3s, 3p, 3d, 4s), Sr (4s, 4p, 5s), and O (2s, 2p) treated as valence. During the relaxation, both the in-plane lattice constant a and the out-of-plane lattice constant c, as well as the atomic positions, are allowed to relax within the tetragonal symmetry of space group $P4mm$.

The experimental lattice constant of cubic SZO at equilibrium is 4.154 Å [5], which is larger than the 3.905 Å of cubic STO [12], leading to a 6.4% lattice mismatch. Our calculated lattice constants of cubic SZO and STO are 4.096 Å and 3.850 Å, respectively, which are slightly smaller than their corresponding experimental values. This underestimation of the lattice constant is an artifact of the LDA method. However, it is very interesting to note that the calculated lattice mismatch is 6.390%, which is in good agreement with the experimental value. The SZO and STO cells in the superlattice will experience mutual strain from each other due to the lattice mismatch. The equilibrium in-plane lattice constant a of the $(SZO)_1/(STO)_1$ superlattice is determined to be 3.958 Å from the structural optimization. This indicates that in the superlattice, the SZO unit cell undergoes an in-plane compressive strain, whereas the interface constraint leads the STO cell to experience an in-plane tensile strain. The calculated local c/a parameter is 1.094 for the SZO cell, and 0.947 for the STO cell. In other words, the SZO cell is elongated along the z-direction, but the STO cell is shortened. The in-plane lattice constant a, 3.958 Å, is used in all the following calculations.

Due to the imposed symmetry, the displacement of each atom in the supercell of the $(SZO)_1/(STO)_1$ superlattice is along the z-direction. The fractional coordinates of the atoms in the relaxed structure are listed in Table 1, where O_2 and O_5 are symmetrically equivalent to O_3 and O_6, respectively. In the relaxed supercell, the origin is chosen such that the sum of the z-shifts is identically zero. The $(SZO)_1/(STO)_1$ superlattice can be regarded as consisting of four different metal–oxygen layers alternating along the z-direction, which

Table 1
Fractional coordinates of atoms in the $(SZO)_1/(STO)_1$ superlattice

Atom	Fractional coordinates		
	x	y	z
Sr_1	0.0	0.0	$0.00 - 0.0063$
O_1	0.5	0.5	$0.00 + 0.0154$
Ti	0.5	0.5	$0.25 - 0.0123$
O_2	0.0	0.5	$0.25 + 0.0038$
O_3	0.5	0.0	$0.25 + 0.0038$
Sr_2	0.0	0.0	$0.50 - 0.0422$
O_4	0.5	0.5	$0.50 - 0.0088$
Zr	0.5	0.5	$0.75 - 0.0103$
O_5	0.0	0.5	$0.75 + 0.0284$
O_6	0.5	0.0	$0.75 + 0.0284$

Table 2
Relative displacements of metal and O atoms along the z-direction in each layer of the $(SZO)_1/(STO)_1$ superlattice

Layer	Relative displacements	
	Fractional	Absolute (in Å)
Sr_1–O_1	0.0217	0.1753
Ti–$O_2(O_3)$	0.0161	0.1301
Sr_2–O_4	0.0334	0.2698
Zr–$O_5(O_6)$	0.0387	0.3126

Positive values denote that O atoms locate above the metal atoms.

are denoted as Sr_1–O_1, Ti–$O_2(O_3)$, Sr_2–O_4, and Zr–$O_5(O_6)$, respectively. It can be clearly seen from Table 1 that all atoms shift away from their ideal positions. The largest shift occurs on the Sr_2 atoms. All the metal atom move towards the negative z-direction. The shift direction of the O atoms is different for different O atoms. The bottom-face-center O_1 atom and the side-face-center O_2 and O_3 as well as O_5 and O_6 atoms shift toward the positive z-direction, which is the opposite direction from the metal atoms. But the O_4 atom at the middle-face-center shifts toward the negative z-direction, along the same direction as the metal atoms. The displacement of the O atoms in the SZO cell (i.e. O_5 and O_6) is in the same direction as that of the O atoms in the STO cell (i.e. O_2 and O_3), but with larger magnitude. Since the polarization comes from the relative displacement of the cations and anions, in Table 2 we list the relative displacements of metal atoms and O atoms along the z-direction in each layer. The positive (negative) values denote that O atoms locate above (below) the metal atoms. It can be seen from Table 2 that all four of these displacements are positive values, which means that the dipoles of all the layers are parallel, thus favoring the occurrence of ferroelectricity in the $(SZO)_1/(STO)_1$ superlattice. Also we can find from Table 2 that the largest relative displacement is between Zr and $O_5(O_6)$ in the SZO cell. This result implies that the SZO contributes more to the polarization of the superlattice than STO does.

The polarization for the $(SZO)_1/(STO)_1$ superlattice is obtained as 42.7 $\mu C/cm^2$ using the Berry phase method. This value is much larger than the calculated polarization of 15.4 $\mu C/cm^2$ [13] and 23.1 $\mu C/cm^2$ [14] for the $(BaTiO_3)_1/(SrTiO_3)_1$ [$(BTO)_1/(STO)_1$] superlattice. The lattice mismatch in the $(BTO)_1/(STO)_1$ superlattice is about 2.5%, which is much smaller than the 6.4% mismatch in the