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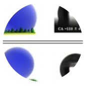

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First-principle study of ferroelectricity in $PbTiO_3/SrTiO_3$ superlattices

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Abstract

We performed the first-principles calculation to investigate the electronic structure and polarization behaviors in $PbTiO_3/SrTiO_3$ (PST) superlattices. The DOS (density of state) profiles show that there are strong hybridizations of atom Ti–O and Pb–O which play very important roles on ferroelectricity of the $PbTiO_3/SrTiO_3$ superlattices. Comparing to the corresponding paraelectric phase, we find the electrons of the PT ($PbTiO_3$) layers occupy lower energy states and electrons of the ST ($SrTiO_3$) layer occupy higher energy states. It is shown that the polarizations of the superlattices decrease with proportion of $SrTiO_3$ increasing. The constant polarization of local layer indicates that PST superlattices with small modulation lengthen can be approximately considered as a single ferroelectric material. Furthermore, according to electrostatic model, we find that directions of internal electric fields in PT and ST layers are opposite. In PST superlattices, internal electric field in PT layer leads to the loss of polarization of this layer, but the polarization of ST layer is induced by internal electric field of this layer. Compared to the value of the polarization in bulk $PbTiO_3$, polarization of PST is smaller.

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Keywords: Electronic distribution; Polarization behavior; Electric field; Electrostatic model

1. Introduction

Ferroelectric superlattices have attracted great attention because they provide new opportunities for ferroelectric device application. The properties of ferroelectric superlattices differ dramatically from their bulk materials, such as the polarization, dielectric constant and tunability etc. In recent years, various ferroelectric superlattices, such as $BaTiO_3/SrTiO_3$ [1–7], $PbTiO_3/PbZrO_3$ [8,9], $PbTiO_3/BaTiO_3$ [10], $PbZrO_3/BaZrO_3$ [11,12] and $PbTiO_3/SrTiO_3$ [13,14] have been prepared and studied. Furthermore, the three-component $(SrTiO_3)/(BaTiO_3)/(CaTiO_3)$ [15,16] superlattices have also been studied experimentally and theoretically.

$PbTiO_3$ is a very excellent ferroelectric material with large polarization and good piezoelectric properties. Many ferroelectric films and superlattices based on Lead titanate materials have been actively investigated for applications in transducers, infrared detectors, ferroelectric memories, etc., [17,18]. Thin films and the superlattices of $PbTiO_3$ with other perovskite compounds exhibit an enhancement in various interesting properties and are, thus, feasible to be used in some device designs. A $Pb(Zr,Ti)O_3/SrTiO_3$ multilayer with layer thicknesses in the 46–140 Å range was found to exhibit giant dielectric response over a broad temperature range [13]. It is well known there is improvement of ferroelectric properties and dielectric properties of $BaTiO_3/SrTiO_3$ superlattices corresponding to bulk

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$BaTiO_3$ due to effect of the misfit strains, which have been confirmed by the experimental and theoretical results [1,19]. $PbTiO_3/SrTiO_3$ superlattices have been fabricated by a sol–gel method and chemical vapor deposition method [13,14].

In this paper, we investigate the electronic structure and polarization behavior of $PbTiO_3/SrTiO_3$ superlattices grown on the $SrTiO_3$ substrate by using the first-principles calculation. DOS (density of state) profiles of PT and ST layer in 1×1 PST consisting of one PT layer and one ST layer show that there is strong hybridization of atoms Ti–O and Pb–O. Because of effect of misfit strain and internal electric field, electrons of ferroelectric PT layer and ST layer move towards the lower energy area and higher energy area, respectively. We also analyze polarization behaviors of four 5-periodicity superlattices. Our results show that polarization of PST is smaller than that of bulk $PbTiO_3$, and polarizations decrease with the proportion of $SrTiO_3$ of PST increasing. The similar results have also been obtained by the electrostatic models. We also reveal that the local polarization of each layer is almost constant through PST, and there are internal electric fields in each layer which induce polarization of ST layer and reduce polarization of PT layer.

2. Method

Based on the first-principles calculation, we study the electric density of state and polarization behaviors of PST ferroelectric superlattices. First-principle density-functional calculations were performed within local-density approximation (LDA) as implemented in the PWSCF package. The exchange-correlation energy was evaluated using Ceperley–Alder form with Perdew–Zunger parameterization [20–24]. We used Vanderbilt ultrasoft pseudopotentials [25] for all ions, treating the 5d, 6s, and 6p electrons of Pb, the 3s, 3p, 3d, and 4s electrons of Ti, the 4s, 4p, 5s electrons of Sr and the 2s and 2p electrons of O in the valence. The inclusion of the semi-core electrons in the valence states is necessary for an accurate description of these oxides. A kinetic energy cut-off of 30 Ry was used and the augmentation charges were expanded up to 270 Ry. Integrals over the Brillouin zone was performed using Monkhorst–Pack scheme where the k-point mesh used is $6 \times 6 \times 3$. The spontaneous polarizations were calculated by the berry-phase method developed by King-Smith and Vanderblit [26–30].

During relaxation, Atomic coordinates within supercells were relaxed along [001] within space group $P4mm$ until the Hellmann–Feynman forces are less than 5.0×10^{-4} Ry/bohr. The in-plane lattice constant (a) was fixed as the calculated lattice constant of $SrTiO_3$, while the out-of-plane lattice constant (c) was allowed to vary. In the berry-phase calculation, twelve k-points/string along [001] was used in the irreducible wedge to gain well-converged results.

3. Results

3.1. Structure characteristics

In our calculations, the initial structure of every PST superlattice is considered as a stack of cubic perovskite structure $PbTiO_3$ and $SrTiO_3$. In Table 1, $PbTiO_3$ and $SrTiO_3$ cubic lattice parameters have been obtained: $a_{PT} = 7.338$ bohr and $a_{ST} = 7.285$ bohr, which are in agreement with previous results [28,29,31]. In comparison with the experimental lattice parameters, there is a typical underestimate of LDA. According to formula: $\eta = \frac{a_{PT} - a_{ST}}{a_{ST}}$, the small misfit strain 0.75% of PST can be obtained. Thus the effect of strain on polarization of PST superlattices is very limited. After 1×1 PST superlattice has been optimized, the tetragonality c/a of PST is found to be 1.015. And tetragon $PbTiO_3$ in our calculation has shown tetragonality 1.035. It is very strange that tetragonality of $PbTiO_3$ is much larger than that of $PbTiO_3$ layer with small compressive strain in PST. Furthermore, the polarization of 1×1PST and $PbTiO_3$ are 32.18 and 74.67 $\mu C/cm^2$ by the berry-phase calculation, respectively. Compared to the value of the polarization in bulk $PbTiO_3$, we find that the polarization in PST is reduced sharply. The reason of this phenomenon including effects of internal electric fields and the misfit strains will be discussed in following sections.

3.2. Electronic structure

Electronic DOS profiles of paraelectric $SrTiO_3$ and ferroelectric ST layer in PST are shown in Fig. 1. These valence bands consisting of 2p electrons of O atom, 5s electrons of Sr atom and 3d electrons of Ti will be considered. The conduct bands are composed of 3d bands of Ti, 5s bands of Sr and 2p bands of O atom. The 2p electrons of O atom and 3d electrons of Ti atom mainly range from 5 eV to 10 eV in valence bands, showing the strong hybridization between Ti and O. However, only small part of 5s electrons of Sr atom in this area confirms the weak interaction between Sr and O atom. The highest occupied energy and the lowest unoccupied energy of electrons in ST layer of PST are 10.45 and 12.76 eV, respectively. And the corresponding energies are 10.13 and 12.36 eV in paraelectric $SrTiO_3$. When $SrTiO_3$ transits from paraelectric phase to ferroelectric phase, electronic distribution moves toward higher energy area because of paraelectric character of $SrTiO_3$ being in ground state. Energy of ferroelectric ST layer in PST should be higher than that of paraelectric $SrTiO_3$, due to the effect of the polarization in PT layer

Table 1
Lattice parameters (in bohr) and Born effective charge in cubic perovskite $ATiO_3$ (A refers to ion Pb and Sr)

Compound	a_0	$Z^*(A)$	$Z^*(Ti)$	$Z^*(O_1)$	$Z^*(O_2)$
$PbTiO_3$	7.338	3.93	7.01	−5.8	−2.58
$SrTiO_3$	7.285	2.55	7.08	−5.62	−2.02

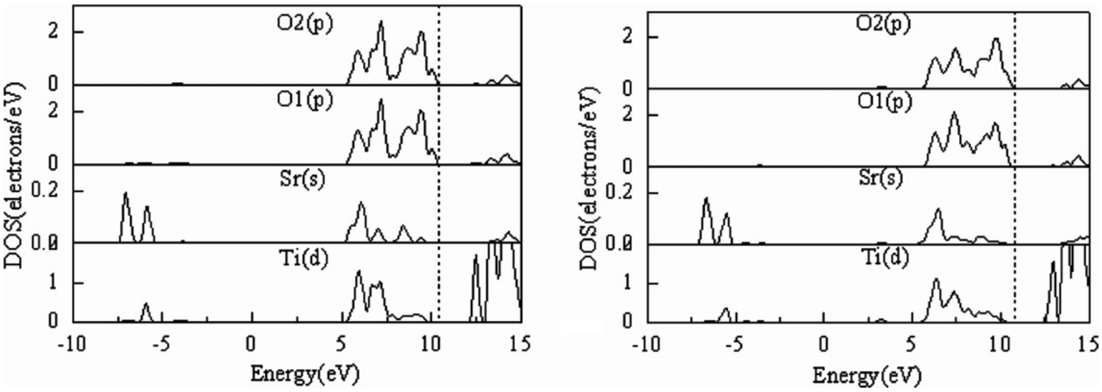

Fig. 1. DOS profile of paraelectric $SrTiO_3$ (left) and ferroelectric $SrTiO_3$ (right) layer in PST.

and the misfit strain between ST and PT layers. It is found that the DOS peak of ST layer become smoother than that of its paraelectric state, which indicates that redistribution of electrons inducing the ferroelectricity of ST layer.

Fig. 2 describes the electronic DOS profiles of paraelectric $PbTiO_3$ and ferroelectric PT layer in PST. It is shown in Fig. 2 that valence bands contain 2p electrons of O atoms, 6s and 6p electrons of Pb atom and 3d electrons of Ti atom. There are mainly 3d bands of Ti atom, 2p bands of O atoms and 6p bands of Pb in conduct bands. Comparing DOS of paraelectric $PbTiO_3$ with that of PT layer in PST, we found that there is similar distribution of 2p electrons of O atoms and 3d electrons of Ti atom in area between 5 eV and 10 eV, which implies strong hybridization between Ti and O atoms. The distribution of 6s and 6p electrons of Pb atom is similar with that of 2p electrons of O atoms, so the interaction between Pb and O atoms is very strong. The previous work [28] has shown the strong interaction between Pb and O atom is a critical reason why bulk $PbTiO_3$ has excellent ferroelectric properties. So strong interaction of Pb–O has important effect on the ferroelectric properties of PT layer in PST. In paraelectric $PbTiO_3$, the highest occupied energy and the lowest unoccupied energy of electrons are 11.06 eV and 13.21 eV, respectively. And the corresponding values become 10.54 eV and 12.76 eV in PT layer of PST, respectively. Contrary to ST layer of PST, electronic distribution of PT layer move toward low energy area. $PbTiO_3$ in ground state is ferroelectric phase, so ferroelectric phase have lower energy than paraelectric phase. Electrons of ferroelectric PT layer in PST should distribute at lower energy area in comparison with that of paraelectric $PbTiO_3$. The DOS profile of PT layer in PST becomes smoother than that of paraelectric $PbTiO_3$ due to electronic redistribution. It represents the stronger interaction of Pb–O and Ti–O which is origin of ferroelectricity of PT layer of PST.

3.3. Polarization behavior

In Table 2, it is shown that the tetragonality c/a and polarization of various period-5 superlattices of PST. The polarization of PST is smaller than that of bulk $PbTiO_3$. With the proportion of $SrTiO_3$ increasing, the polarization of PST superlattices declines continuously. Because of small misfit strain between PT and ST layers, the polarization 80.81 $\mu C/cm^2$ of 5/0 PST is slightly larger than that of bulk $PbTiO_3$, Where 5/0 PST means that there are five PT layers and no ST layer in period-5 superlattices of PST. When a PT layer is replaced with ST layer, the polarization is reduced nearly by 30%. The 3/2 and 2/3 PST superlattices are detected to be 50% and 30% of polarization of bulk strained $PbTiO_3$. When there is only one PT layer in 5-periodicity PST superlattices, the polarization becomes small value 8.89 $\mu C/cm^2$. The polarization behaviors of

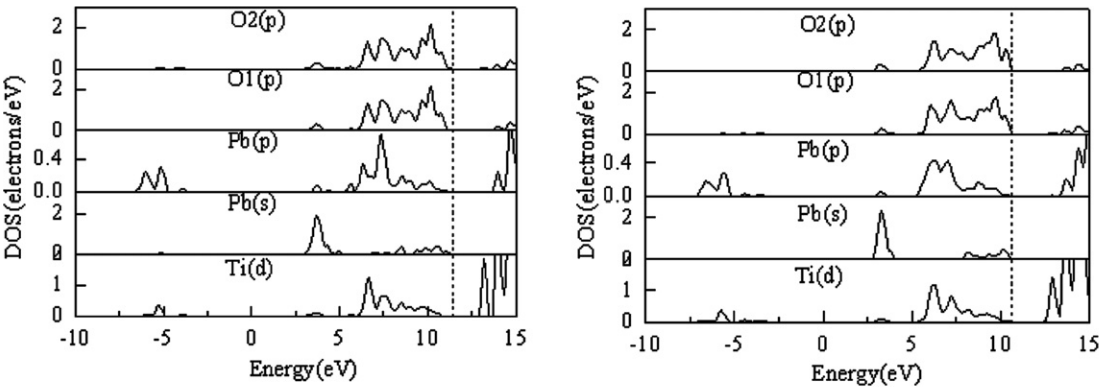

Fig. 2. DOS profile of paraelectric $PbTiO_3$ (left) and ferroelectric $PbTiO_3$ (right) layer in PST.

Table 2
Structural parameters computes computed for superlattices with in-plane lattice constant $a = 7.285$ bohr, and with m layers $PbTiO_3$ and n layers of $SrTiO_3$

m/n	c/a	P ($\mu C/cm^2$)
5/0	5.24	80.81
4/1	5.14	57.75
3/2	5.09	40.28
2/3	5.05	24.75
1/4	5.015	8.9
0/5	5	0

superlattices are insufficiently interpreted only from the results of first-principle calculation.

$$P_l = \frac{1}{V_l} \sum_{i} Z^*_{li} \Delta u_{li} \tag{1}$$

Here $\Delta u_{li} = u_{li} - u^0_{li}$.

Since the intricate relation between eptiaxial strain and chemical composition of layers plays an important role to determining the polarization behaviors of superlattices, polarization of local layer is calculated using Eq. (1). In Eq. (1), V_l is the volume of local layer l, and Δu_{li} and Z^*_{li} are the displacement and the effective charge of ion i in cell l, respectively. u_{li} and u^0_{li} represents the coordinate of atom i along [001] in cell l of ferroelectric and paraelectric PST, respectively. In each case, we average out contributions of oxygens in the planes bounding elementary cell, and cations at the corners set the volume of the cell. The dynamic effective charges of atoms have been calculated by finite difference method, as listed in Table 1. The results are in agreement with previous results [28,29,31]. The polarization of local layers in PST superlattices is shown in Fig. 3. The polarization of local polarization is almost constant through each superlattice. The polarization of PT layer in PST is smaller than that of bulk $PbTiO_3$ and the ST layer is polarized from paraelectric phase.

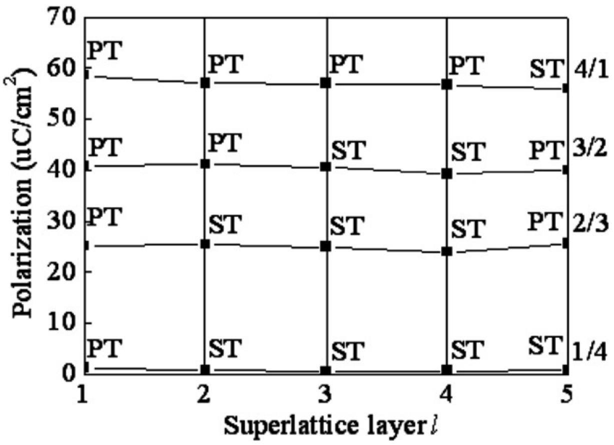

Fig. 3. Polarization of local layer of PST superlattices.

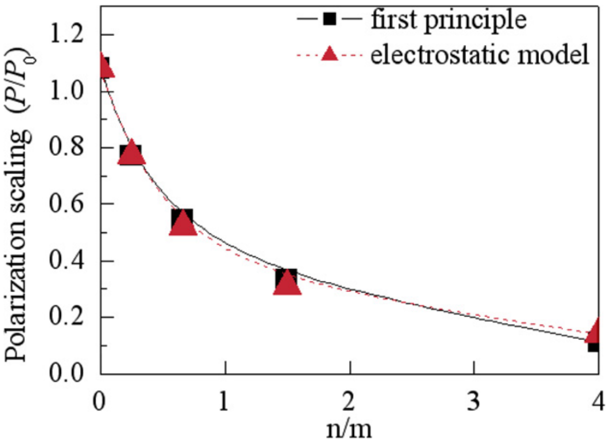

Fig. 4. Polarization in PST superlattices from first-principle and electrostatic model.

In order to study the polarization behavior of PST superlattices accurately, the electrostatic model is proposed. Because the polarization of each layer through superlattice is constant, the electric displacement of PT layer is identical to that of ST layer. According to $D = \varepsilon_0 E + P$ [3,5,33–35]:

$$\varepsilon_1 E_1^{+} P_1 = \varepsilon_2 E_2 + P_2 \tag{2}$$

Here E_1 and E_2 correspond to electric field within PT layer and ST layer, and ε_1 and ε_2 are dielectric constant of $PbTiO_3$ and $SrTiO_3$, respectively. Short-circuit boundary demands the electric field must vanish within entire superlattice. The relation should be established as follows:

$$mE_1 = -nE_2 \tag{3}$$

In PT layer, the initial polarization $P_1 = P_{5/0}$, while the initial polarization $P_2 = 0$ for ST layer. So formula (2) becomes

$$P = \frac{P_{5/0}}{1 + \frac{n}{m}\left(\frac{\varepsilon_1}{\varepsilon_2}\right)} \tag{4}$$

From formula (4), polarizations P of PST can be obtained with chemical composition n/m. The ratio of polarization P/P_0 in PST from the first-principles calculation and electrostatic model with chemical composition n/m is shown in Fig. 4. From our results, we find that the polarization ratio P/P_0 is same by using two methods almost.

4. Discussion

By calculating electronic DOS profiles of PST, there is very strong interaction of Pb–O and Ti–O which is similar with previous results in single ferroelectric material. Compared with electrons of paraelectric $SrTiO_3$ and paraelectric $PbTiO_3$, electrons in ST and PT layer move toward higher energy area and low energy area, respectively. The two critical factors determining ferroelectric properties of superlattices are misfit strain and internal electric field. In PST, the energies of PT and ST layers suffering from the effect of misfit strain and internal electric field should be higher than those of $PbTiO_3$ and $SrTiO_3$ in ground state. Thus DOS of

ST layer move towards the high energy area. Energy of PT layer is higher than that of ferroelectric phase in ground state, but this energy still is lower than the energy of paraelectric $PbTiO_3$.

We will discuss the polarization behaviors of PST from two ways. First, the internal polarizing field is critical factor determining the properties of superlattices. There is the long-range interaction between ferroelectric layers through the intervening paraelectric layers in ferroelectric/paraelectric superlattices, which induced polarization of paraelectric layers [32,33]. In our study, the interaction between "upper–lower" two PT layers polarizes "middle" ST layers. The modulation lengths (total thickness of PST unit cell) of period-5 PST superlattices are very short. When the modulation wavelength is sufficiently short, this interaction leads the superlattices to behave as a single artificial ferroelectric material for $KTaO_3/KNbO_3$ superlattices. The constant polarization of local layers in PST indicates PST with short modulation lengthens can be regarded as a single artificial ferroelectric material, which is similar with $KTaO_3/KNbO_3$ superlattices. Second, according to electrostatic model, there is electric field in each local layer in PST because of the mismatch of polarization between $PbTiO_3$ and $SrTiO_3$ in ground state. If effect of misfit strain on polarization in PST is negligible, the polarization of each local layer mainly attributes to electric field in this layer. The electric fields in PT layer and ST layer have opposite signs. The electric field in PT layer suppresses its polarization, while the ST layer is polarized. The polarization of $BaTiO_3/SrTiO_3$ is improved with response to bulk $BaTiO_3$ [1], because polarization induced by the large misfit strain is larger than the declined polarization induced by internal electric field in BT layer, and both misfit strain and electric field polarize the ST layer. In PST, there is the enhanced polarization induced by small misfit strain which cannot compensate the reduced polarization by internal electric field in PT layer, and ST layer is polarized mainly by its internal electric field. Then the polarization of PT layer is consistent with that of ST layer. The polarization of PST is smaller than that of bulk $PbTiO_3$. Intrinsic relation between long-range interaction of PT layers and internal electric fields has not been revealed clearly.

5. Summary and conclusions

We utilized the first-principle calculation to investigate the electronic structure and polarization behavior of PST superlattices. The conclusions are summarized as follows:

(1) There is strong interaction between Pb and O atom and between Ti and O atoms in PST. Due to misfit strain and internal electric field, energy of ST layer is higher than that of paraelectric phase, while the energy of PT layer lies between energy of ferroelectric phase in ground state and energy of paraelectric phase.

(2) The polarization behaviors calculated by the first-principle agree well with results obtained by electrostatic model. With volume fraction of $SrTiO_3$ increasing, the polarizations of PST decrease continuously. The polarizations of PST are smaller than that of bulk $PbTiO_3$, because polarization induced by small misfit strains can not compensate the reduced polarization induced by internal electric field in PT layers.

(3) The PST superlattices behaviors as a single ferroelectric material due to small modulation lengthen, confirmed by the constant polarization of local layer calculated by first-principle method.

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