Computational Materials Science 156 (2019) 286–291

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Letter

From $LaAlO_3/SrTiO_3$ to $LaAlO_3/KNbO_3$: Improving the transport properties of two-dimensional electronic gas in created $+1/+1$ interfaces

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ARTICLE INFO

Keywords:
Two-dimensional electron gas
First-principles
$KNbO_3$
Heterostructure
Ferroelectric polarization

ABSTRACT

The discovery of two-dimensional electron gases at $LaAlO_3/SrTiO_3$ heterointerface makes it a promising candidate for new generation of nano-devices. Further enhance of interfacial transport properties is the main challenge. To increase the limit of interfacial carrier densities of two-dimensional electron gas (2DEG) of well-studied $LaAlO_3/SrTiO_3$ heterostructure from 0.5 to 1 e^- per unit cell, we replaced substrate $SrTiO_3$ by $KNbO_3$ to acquire the $+1/+1$ interface with one extra electron donor and less localized valence electrons. First-principles calculations are used to study $(LaBO_3)_m/(KNbO_3)_{6.5}$ (B = Al, Ga; m = 2–8) heterostructures. The studied heterostructures all show n-type metallic state without critical thickness, and the distribution of charge densities of different monolayers can be modulated by the polarization effect of $KNbO_3$. The interfacial carrier density of studied heterostructures perform one order of magnitude larger than $LaAlO_3/SrTiO_3$ because of the increased intrinsic carrier limit. With the increase of $LaBO_3$ (B = Al, Ga) layer thickness, the interfacial carrier density rises up to $1.26 \times 10^{14}\,cm^{-2}$, and the electron effective masses decrease monotonically, resulting in higher carrier mobility and around 6 times larger electrical conductivity. This work proved an effective approach for tuned interfacial 2DEG and future device engineering.

1. Introduction

Since Ohtomo and Hwang [1] reported the conducting heterointerface of an ultrathin $LaAlO_3$ (LAO) film deposited on a $SrTiO_3$ (STO) substrate, much effort has been devoted to explore the novel properties of two dimensional electron gas (2DEG) between two insulator perovskites, including superconducting [2], magnetism [3,4], electronic phase separation [5] and photocatalysis [6]. In particular, the 2DEG located in $LaTiO_3/SrTiO_3$ (LAO/STO) interface has high interfacial carrier density and mobility [7], which makes it promising for high-mobility all-oxide electronic devices.

Generally, first principle calculations are based on LAO/STO heterostructure, in which the STO substrate can be seen regarded as stacks of neutral $(SrO)^0$ and $(TiO_2)^0$, while LAO film can be seen as alternating positively charged $(LaO)^+$ and negatively charged $(AlO_2)^-$ monolayer, moreover, LAO is epitaxial grown on STO substrate [1]. There will be potential divergence in LAO film, with increase of LAO unit cell thickness [8], causing polar catastrophe [9]. In this scenario, when the thickness of LAO unit cell reaches to critical value, half an electron is transferred from electron donor $(LaO)^+$ monolayer to electron donor $(TiO_2)^0$ monolayer, resulting in conducting state of interface [9]. For above atmosphere, the theoretical calculated charge carrier density is predicted to be $3.3 \times 10^{14}\,cm^{-2}$, while several experiments on oxygen annealed and under high oxygen grown samples have turned down the carrier density to be about $1–2 \times 10^{13}\,cm^{-2}$ [3,7,10–12], which are underestimated about one order of magnitude.

To acquire high interfacial charge carrier density and mobility, many theoretical considerations and experimental studies have been carried out. The carrier density can be controlled by varying the sample fabrication process or by electrostatic gating [13], for instance, varying the thickness of LAO unit cell [14] or controlling oxygen growth pressure can modulate the interfacial carrier density and mobility [11,15,16]. What's more, the carrier density can also be induced by electrostatic gating of the conducting interface separated from ferroelectric materials [17,18] and be reversibly tuned by inducing mechanical strain [19–21].

Apart from the modulation works mentioned above, the exploitation of other interfaces between ABO_3 perovskites (except $SrTiO_3$) is also proved to be effective for enhancing interfacial transport properties. LAO/STO heterostructure has an n-type $(LaO)^+/(TiO_2)^0$ interface with

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https://doi.org/10.1016/j.commatsci.2018.09.053
Received 8 August 2018; Received in revised form 24 September 2018; Accepted 25 September 2018

only one electron donor $(LaO)^+$ monolayer, while $(TiO_2)^0$ is neutral, which can be recorded as the +1/0 interface. Replacing the neutral layer with +1 layer (+1/0 interface to +1/+1 interface) can provide the system one more electron donor and increases the limit of interfacial carrier densities from 0.5 to 1 e^- per unit cell [22], which may be an operative way to change the electric structure of the system and obtain ultrahigh interfacial carrier density. It is proved that 2DEG can be created in $KNbO_3$: La superlattice's $(LaO)^+/(NbO_2)^+$ interface [23]. And our previous work $KNbO_3$: Y ultrathin film [22] also predicted an increased interfacial carrier density at the +1/+1 interface of $(LaO)^+/(NbO_2)^+$. Afterwards Wang et al. [24] predicted superior 2DEG in the polar/polar perovskite-oxide-based HS systems, and the spin-polarized 2DEG can be regulated via controlling the thicknesses of the $LaAlO_3$ and $BaTiO_3$ layers in $LaAlO_3/BaTiO_3$ superlattices [25]. Additionally, Cooper et al. [23] proved that the band effective mass of the oxide 2DEG is an intrinsic property of the bulk component material. Compared with $SrTiO_3$ as the substrate in LAO/KNO, $KNbO_3$ has less localized valence electrons [26], predicting possible higher carrier mobility.

In this work, based on the first principle, we studied $LaAlO_3/SrTiO_3$ heterostructure in which the heterostructure substrate ($SrTiO_3$) was replaced by $KNbO_3$ in aim at creating the +1/+1 interface with one extra electron donor and less localized valence electrons. Based on preview research of 2DEG in $LaGaO_3/SrTiO_3$ [27,28], we also explored $LaGaO_3$ as the film layer for its similar crystal structure with $LaAlO_3$ as well as smaller lattice mismatch with $KNbO_3$. We also discussed how interfacial electronic structure and transport properties going to change with adjusting LBO (B = Al, Ga) unit cell thickness. By studying the electronic structure, interfacial carrier density, electrons effective masses of $(LaBO_3)_m/(KNbO_3)_{6.5}$ (B = Al, Ga; m = 2–8) heterostructures, we analysed the carrier mobility and electrical conductivity, in order to provide an effective approach for tuned interfacial 2DEG and future device engineering.

2. Computational method

Our calculation is performed using density functional theory (DFT) operated within the Cambridge Sequential Total Energy Package (CASTEP) in Materials Studio (MS) [29]. The exchange-correlation effects are treated within the Wu-Cohen functional (WC) of the generalized gradient approximation (GGA) for geometry optimization [30]. After the systematic energy convergence test, the electron wave functions are expanded in a plane-wave basis set limited by a cut-off energy of 340 eV. The bulk and heterostructure interface calculations are performed using the 4 × 4 × 4 and 6 × 6 × 1 Monkhorst-Pack k-point mesh, respectively. For bulk electronic structure calculations, we use the screened exchange local density approximation (sx-LDA) [31] with 830 eV cutoff energy and 4 × 4 × 4 Monkhorst-Pack grid to obtain more accurate band structures. The self-consistent calculations are converged to 10^{-5} eV/atom and the structures are relaxed until the forces on the ions are less 0.03 eV/Å. A structure of $(LaBO_3)_m/(KNbO_3)_{6.5}$ (B = Al, Ga, m = 2–8) was built by stacking $(LaO)^+$-terminated $LaBO_3$ film on $(NbO_2)^+$-terminated $KNbO_3$ substrate along [0 0 1] direction, and m is the number of $LaBO_3$ unit cells. For convenient discussion, we won't clarify the number of $KNbO_3$ unit cells in following acritical, for all the calculated models of this paper containing 6.5 $KNbO_3$ unit cells. A 15 Å vacuum layer was added between the neighboring slabs with dipole correction to offset the in-built electric fields. The in-plane lattice constant was fixed to $KNbO_3$' experimental lattice constant 4.016 Å [32], with varying the out-of-plane lattice constant c and minimizing the total energy.

3. Results and discussion

3.1. Bulk perovskites

Firstly, we studied the material characters of the parent bulk perovskites $KNbO_3$, $LaGaO_3$, $LaAlO_3$ (KNO, LGO, LAO), as listed out in Table 1, which include the experimental and calculated lattice constants (a), lattice mismatch (f, respected to KNO). The lattice mismatch $f = (a_f - a_s)/a_s$, where a_f and a_s are the lattice constants of the film (LGO and LAO) and the substrate (KNO), respectively. The largest lattice mismatch for the studied heterostructures is 4.36% for LAO/KNO, which ensures all studied heterostructures can be successfully prepared by experiments [33]. Fig. 1 shows the band edge positions of the parent bulks, where the conduction band minimum (CBM) of electrons donor LGO and LAO is higher than the CBM of the electrons acceptor KNO, to guarantee that electrons can transfer from donor to acceptor for n-type metallic state.

Table 1
The material characters of the parent bulk perovskites $KNbO_3$, $LaGaO_3$, $LaAlO_3$.

	Experimental		Theoretical	
Compound	a (Å)	f (%)	a (Å)	f (%)
KNO	4.016[32]	0	3.988	0
LGO	3.875[34]	−3.51	3.905	−2.08
LAO	3.789[35]	−5.65	3.814	−4.36

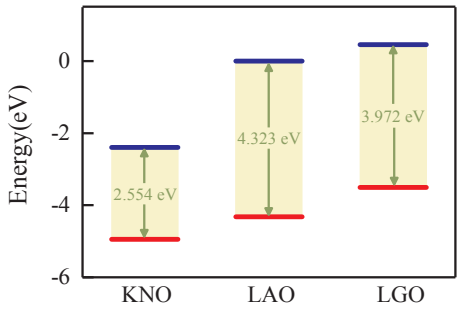

Fig. 1. The band edge positions of the parent bulks $KNbO_3$, $LaAlO_3$ and $LaGaO_3$.

Fig. 2 shows the calculated relaxed-lattice structures for LBO/KNO heterostructure. The effect of the relaxation is to polarize the cation and the anion planes near the interface which is similar to the relaxation for the well-studied $LaTiO_3/SrTiO_3$ interface [1,22,36]. Compared to the unrelaxed bond length 1.994 Å, the cation-anion bond length near the interface on LAO side shrank while it extended on the KNO side in LAO/KNO heterostructure, which grows on both side of LGO/KNO. Generally, the lattice distortion near the interface of LGO/KNO is smaller

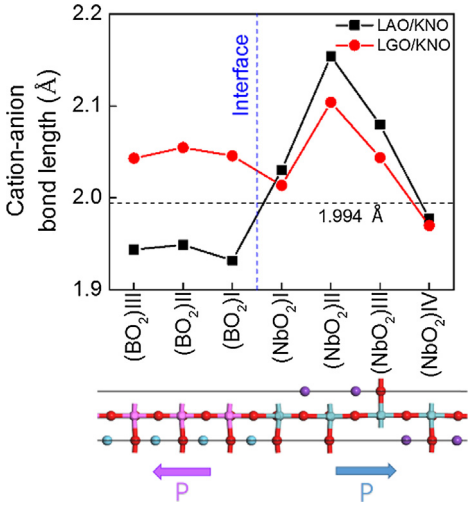

Fig. 2. The cation-anion bond lengths along z direction for LAO/KNO heterostructure.