Vacuum 150 (2018) 29–34

Contents lists available at ScienceDirect

Vacuum

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

Stability and band offsets of nonpolar $(11\bar{2}0)$ ZnO on (001) $LaAlO_3$

Jianli Wang [a, b, *], Xinfeng Chen [a], Shuyin Wu [a], Dongmei Bai [c, **], Gang Tang [a], Junting Zhang [a], Catherine Stampfl [b, ***]

[a] School of Physical Science and Technology, China University of Mining and Technology, Xuzhou, 221116, China
[b] School of Physics, The University of Sydney, Sydney, New South Wales, 2006, Australia
[c] School of Mathematics, China University of Mining and Technology, Xuzhou, 221116, China

ARTICLE INFO

Article history:
Received 1 October 2017
Received in revised form
31 December 2017
Accepted 2 January 2018
Available online 5 January 2018

Keywords:
ZnO
$LaAlO_3$
Surface grand potential
Band offsets

ABSTRACT

Wurtzite-perovskite heterostructures consisting of a wide bandgap semiconductor and a high dielectric constant oxide afford the possibility of novel optoelectronic applications. In the present paper, the structural and electronic properties of nonpolar ZnO $(11\bar{2}0)$ on $LaAlO_3$ (001) substrates are studied by first-principles calculations. We study the initial adsorption of Zn and oxygen atoms on stoichiometric $LaAlO_3$ (001) surfaces, and find that Zn atoms are more strongly bound to the substrate than oxygen atoms. The surface phase diagrams indicate that Zn atoms may substitute La or Al atoms at the non-stoichiometric $LaAlO_3$ (001) surface. The atomic charges, electronic density of states, and band alignment are systematically analyzed for the optimized ZnO/LaO heterojunction. The band gap is found to be nonzero, and the conduction band offset and the valence band offset are 0.36 eV and 2.61 eV, respectively.

1. Introduction

Zinc oxide (ZnO) is a promising semiconductor material particularly for potential optoelectronic applications due to its wide direct band gap in the near ultraviolet region, and with a high exciton binding energy at room temperature [1]. ZnO-based metal-insulator-semiconductor field-effect transistors (MISFETs) with high quality gate dielectrics, are devices with high potential in very large scale integrated circuits [2] and logic circuits [3]. The continued miniaturization of highly integrated MISFETs stimulates great interest in developing high-quality heterojunctions between ZnO semiconductors and high dielectric constant gate dielectric materials. The perovskite, lanthanum aluminate ($LaAlO_3$ or LAO), has a dielectric constant of 25.1 [4] and a large bandgap of 5.7 eV [5], which makes it a promising candidate for future gate dielectric applications of ZnO-based MISFETs. It would therefore be desirable to integrate the ZnO semiconductor onto a single crystal LAO film. As wurtzite ZnO has no inversion symmetry, the alternate stacking of zinc ion (Zn^{2+}) layers with oxygen ion (O^{2-}) layers causes an electrostatic field along the common growth *c*-direction, which limits its applications for optoelectronic devices. Thus, nonpolar a-plane ZnO $(11\bar{2}0)$ is of interest to avoid undesirable internal electrostatic fields.

The deposition of a-plane ZnO epitaxial films has been reported on LAO (001) single crystal substrates [6–8]. The in-plane orientation relationships of a-plane ZnO domains with LAO are $[0001]_{ZnO}//[110]_{LAO}$ and $[1\bar{1}00]_{ZnO}//[1\bar{1}0]_{LAO}$ [7]. The hetero-interface itself becomes the device by further miniaturization in semiconductor device technology. A sharp ZnO/LAO hetero-interface is required to realize ZnO-based MISFETs structures, which dictate many of the characteristics of optoelectronic devices. To the best of our knowledge, there have been no theoretical studies of the atomic and electronic properties of ZnO/LAO interfaces to date. A promising candidate material should also exhibit a band offset of over 1 eV [9]. In this work we carry out first-principles investigations of the stability and band offsets of a-plane ZnO/LAO heterostructures, which is different to a superlattice structure and involves the vacuum [10–12]. The adsorption of ZnO $(11\bar{2}0)$ on LAO (001) is investigated to firstly find out the preferable geometry of ZnO/LAO heterostructures. We calculate the electronic density of states, Bader charge analysis, and the band alignment to gain a deeper understanding

* Corresponding author. School of Physical Science and Technology, China University of Mining and Technology, Xuzhou, 221116, China.
** Corresponding author.
*** Corresponding author.
E-mail addresses: jlwang@cumt.edu.cn (J. Wang), dmbai@cumt.edu.cn (D. Bai), catherine.stampfl@sydney.edu.au (C. Stampfl).

https://doi.org/10.1016/j.vacuum.2018.01.002
0042-207X/

of the electronic properties of nonpolar ZnO/LAO heterostructures.

2. Methodology

The density functional theory (DFT) calculations are performed using the plane-wave projector augmented-wave (PAW) method [13] with a plane-wave energy cutoff of 600 eV, as implemented in the VASP code [14]. The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) [15] scheme is employed in the structural optimization. A more accurate Heyd-Scuseria-Ernzerhof (HSE) hybrid functional [16] with a fraction of Fock exchange of 0.4 [17,18] and a range separation parameter of 0.2 $Å^{-1}$ is applied to obtain an accurate band structure. In HSE hybrid functionals, a part of the nonlocal Hartree–Fock (HF) type exchange is admixed with a semilocal XC functional giving the following expression [16]:

$$E_{XC}^{HSE} = \alpha E_X^{HF,SR}(\mu) + (1-\alpha)E_X^{PBE,SR}(\mu) + E_X^{PBE,LR}(\mu) + E_C^{PBE},$$

where α is the exchange mixing coefficient and μ is the screening parameter that controls the decomposition of the Coulomb kernel into short-range (SR) and long-range (LR) exchange contributions. We use GGA-PBE for the structural optimization and accurate HSE hybrid functional for the electronic band structure calculation due to the significant computationally demanding nature of the latter approach, which has been successfully used in previous studies [17,19–21]. The atomic positions are optimized until the maximum force on each atom is smaller than 0.02 eV/Å. The criterion to stop the relaxation of the electronic degrees of freedom is set by both the total energy and the band structure energy differences between two consecutive steps to be less than 10^{-4} eV. The Brillouin-zone integrations are carried out using a Gaussian smearing [22] of sigma = 0.05 eV, and we employ a Monkhorst-Pack [23] sampling scheme with k-point grids of $20 \times 20 \times 20$ for bulk LAO and $10 \times 10 \times 8$ for bulk ZnO. The LAO lattice constant of the optimized cubic perovskite structure is $a_{LAO} = 3.812$ Å [24] (using the GGA). The calculated indirect band gap of LAO is 5.73 eV (using the HSE) and is in agreement with the previous theoretical value of 5.677 eV [25] and the experimental value of 5.7 eV [5]. The ZnO lattice constants of the optimized wurtzite structure are $a_{ZnO} = 3.278$ Å and $c_{ZnO} = 5.330$ Å (using the GGA) and are in good agreement with the previous theoretical values ($a_{ZnO} = 3.292$ Å, $c_{ZnO} = 5.306$ Å [26]) and the experimental values ($a_{ZnO} = 3.2498$ Å, $c_{ZnO} = 5.2066$ Å [27]). The DFT calculation (using the HSE) predicts an energy gap of 3.47 eV for bulk ZnO, which is consistent with the previous theoretical value of 3.40 eV [17] and the experimental band gap of 3.44 eV [1]. The theoretical lattice mismatches between ZnO $(11\bar{2}0)$ and LAO (001) are 1.13% and 5.32% for $\langle 110\rangle_{LAO}$ (45° rotation angle of $\langle 100\rangle_{LAO}$) along the directions of ZnO [0001] and $[10\bar{1}0]$, respectively.

The surface models are simulated by a periodic supercell approach [28]. Surface calculations are performed using periodic $(\sqrt{2} \times \sqrt{2})$ R45° symmetric slab [24,29] models (where both surfaces have the same termination) with a fifteen LAO lattice constant (57.18 Å) wide vacuum region placed between the truncated LAO (001) surfaces (see Fig. 1), which ensures that the dipole moment between the periodic images in the *z*-direction (taken perpendicular to the surface) is sufficiently small [30]. We note that we used a small supercell, which does not necessarily correspond to a real superstructure due to computational limitations. Both LaO-termination and AlO_2-termination of the LAO (001) surface are taken into consideration because they can coexist in theory [24] and experiment [31,32]. The LAO slab contains 11 alternating

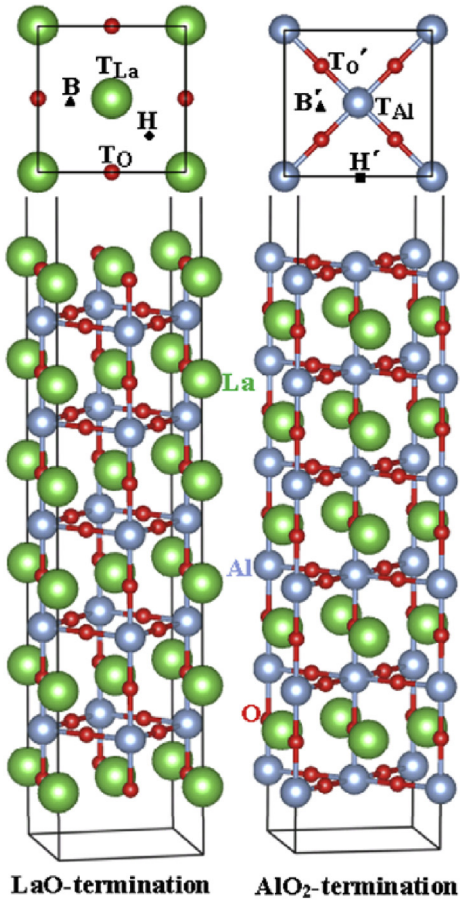

Fig. 1. Perspective view and top view of the LaO-termination and AlO_2-termination of the LAO $(\sqrt{2} \times \sqrt{2})$ R45° surface unit cell with the high symmetry adsorption sites indicated.

$(LaO)^+$ and $(AlO_2)^-$ atomic monolayers (MLs). The LaO-terminated slab contains six $(LaO)^+$ layers and five $(AlO_2)^-$ layers, and the AlO_2-terminated one contains six $(AlO_2)^-$ layers and five $(LaO)^+$ layers. The LaO-terminated surface consists of two La atoms (one La atom at the corner, the other La atom at the center of the unit cell) and two oxygen atoms (at the middle between the adjacent La atoms at the corner of the unit cell), while the AlO_2-terminated surface contains two Al atoms (one Al atom at the corner, the other Al atom at the center of the unit cell) and four oxygen atoms (at the middle between the Al atom at the corner and the Al atom at the center of the unit cell). Coordinates of all atoms are allowed to fully relax except for the three-central layer atoms of the LAO slab. For the LAO surface and interface calculations, we take different calculation parameters compared to those for the bulk calculations due to the high computational requirements. Specifically, the calculations are carried out with a $4 \times 4 \times 1$ Monkhorst–Pack **k**-point mesh. On increasing the mesh to $(6 \times 6 \times 1)$, the total energy difference is calculated to be less than 0.01%.

3. Results and discussion

We first focus on the initial adsorption of Zn and oxygen atoms on LAO (001). The electronic structure of isolated Zn or oxygen atoms is clearly chemically different to that of a ZnO crystal due to the different surrounding atomic environments. To determine the plausible adsorption geometry, we aimed to simulate the real experimental growth on the LAO substrate by considering where