11th International Conference
on Advanced Materials

Rio de Janeiro Brazil
September 20 - 25

ICAM2009

Density Functional Theory Study Electronic and Structural Properties of (001) Surface for $SrZrO_3/SrTiO_3/SrZrO_3$ and $SrTiO_3/SrZrO_3/SrTiO_3$ Interface Systems

A. F. Gouveia[(1)*] and J. R. Sambrano[(1)]

(1) Grupo de Modelagem e Simulação Molecular, DM, UNESP – Universidade Estadual Paulista, Bauru, SP, Brazil; e-mail: gouveia@fc.unesp.br

* Corresponding author.

Abstract – The structural and electronic properties of (001) surface for $SrZrO_3/SrTiO_3/SrZrO_3$ and $SrTiO_3/SrZrO_3/SrTiO_3$ selected surfaces were investigated by means of density functional theory applied to periodic calculations at B3PW level. The relaxation effects for two symmetric terminations are analyzed. The electronic and energy band properties and density of states are discussed. For the interfaces systems the fundamental energy gap is direct for $SrZrO_3/SrTiO_3/SrZrO_3$ and indirect for $SrTiO_3/SrZrO_3/SrTiO_3$.

The $SrZrO_3$ (SZ) and $SrTiO_3$ (ST) crystals have attracted considerable attention due to their ferroelectric and piezoelectric properties, yielding attractive models for experimental and theoretical academic research. Correlations between theoretical and experimental techniques can bring clarification about the structure of these materials. In this work we report periodic calculations based on DFT theory with the B3PW hybrid functional. The calculations were performed by using the CRYSTAL06 computer code. The atomic centers have been described by Hay-Wadt small core [3] for Sr atoms, ECP HAYWSC 311d31g [4] for Zr atoms, HAYWSC-411(311d)G [4] for Ti atoms and 6-31d1 [4] for O atoms.

The cubic phase of both perovskites has a space group symmetry *Pm3m* and lattice parameter ***a*** = 4.109 Å for SZ and ***a*** = 3.944 Å for ST. A optimization procedure of the lattice parameters has been performed, yielding ***a*** = 4.106 Å e ***a*** = 3.850 Å for SZ e ST, respectively. From this optimized parameters two surfaces structures (001) have been modeled for the SZ and ST, alternating between a plan containing atoms of Zr or Ti and O (MO_2-termination) and another plane containing atoms of Sr and O (SrO-termination).

The choice of the number of layers for the theoretical calculations was performed considering the cleavage energy (E_s^u) not optimized, $E_s^u = \frac{1}{4}[E_{SrO} + E_{MO_2} - nE_{bulk\ SZ\ or\ ST}]$. Thus, calculating the surface energies for the models, using the formula: $E_s(i) = E_s^u(i) + E_{rel}(i)$, where i denotes SrO, ZrO_2 or TiO_2 and E_{rel} is the relaxation energies, defined as: $E_{rel}(i) = ½\,[E_{slab}(i) - E_{slab}^u(i)]$, where $E_{slab}(i)$ is the slab energy after relaxation. The analysis yields convergence for 23 layers for each model. Consequently, 23 layers may be sufficient to describe the surface geometry for the properties analysis.From the model of 23 layers, a new surface structure have been modeled for interfaces $SrZrO_3/SrTiO_3/SrZrO_3$ (SZ/ST/SZ) and $SrTiO_3/SrZrO_3/SrTiO_3$ (ST/SZ/ST), where the terminations are the same of bare models. The cleavage energy for the interface models is redefined as: $E_s^u = \frac{1}{4}[E_{SrO} + E_{MO_2} - nE_{bulk\ SZ} - nE_{bulk\ ST}]$. Table 1 shows the band gap for all periodic models.

The results show that for the SZ the band gap is indirect for ZrO_2-termination and direct for SrO-termination. On the other hand, for the ST the band gap is indirect for both terminations. Whereas the deposition of films is carried out in form of layers on a substrate, we observed that the construction of the SZ/ST/SZ interface leads a decrease of the band gap for both terminations and the bad gap became direct for MO_2-termination. For the ST/SZ/ST interface there is an increase of the band gap, if we compare with the bare model.

Table 1: Calculated band gaps (eV) for bare and interfaces models

	SZ	ST	SZ/ST/SZ	ST/SZ/ST
MO_2 – termination	4,62*	2,36*	3,17**	2,79*
SrO – termination	4,46**	1,49*	1,44**	3,23*

M = Zr ou Ti, * indirect band gap between *M* and *Γ* and ** direct band gap at *Γ* point.

Acknowledgements: CNPq, Fapesp and UNESP

[1] Sambrano, J.R., *et al*; *J. Mol. Struct.*, **2007**, 813, 49.
[2] Piskunov, S., *et al*; *Surf. Sci.*, **2005**, 575, 75.
[3] Mike Towler Home Page: www.tcm.phy.cam.ac.uk/~mdt26/crystal.html
[4] Crystal Home Page: www.crystal.unito.it/