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# The interface between a polar perovskite oxide and silicon from monoatomic lines

I. Devos\*

*Institut d'Electronique, de Microélectronique et de Nanotechnologie,  
Unité Mixte de Recherche CNRS 8520, Avenue Poincaré BP 69,  
F-59652 Villeneuve d'Ascq CEDEX FRANCE*

P. Boulenc

*ST Microelectronics, 850 rue Jean Monnet,  
F-38926 Crolles CEDEX FRANCE*

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## Abstract

We report a study on the interface of polar high- $\kappa$  materials with reconstructed Si(001)2x1 surface. LaAlO<sub>3</sub> is taken as a prototype material. The building of the interface is based on the prior growth of metal lines followed by oxidation. Electronic structure calculation of the interface within the DFT framework also helps to build it and understand bondings. Moreover, the conduction band offset is computed to be 1.89 eV, in agreement with electronic applications requirement. The results may provide a guidance for interface processing.

FIG. 1: Top(a) and side(b) view of the Al lines geometry. The atomic positions are those corresponding to the total energy minimum of our computations. The grey bars link Si dimers and the black bars link Al dimers forming the lines. Letters A to F refer to the in plane O atom position which are added to the lines.

The search for alternative dielectrics to silicon dioxide in MOS capacitors has recently focused on complex oxide materials with high dielectric constant (high- $\kappa$  materials). Many of them belong to the class of perovskites (cubic crystals with the chemical formula  $ABO_3$ ) which are thought to have a good ability to grow as crystalline films. The interface with Si is of crucial importance as it must avoid gap states and be structurally coherent with the film crystallographic structure.

Many works have been devoted to  $SrTiO_3$ , the prototype non-polar perovskite oxide. This oxide consists in an alternation of SrO and  $TiO_2$  layers along the (001) axis. As the oxidation states of Sr, Ti and O are respectively +II, +IV and -II, each plane is neutral and a SrO- $TiO_2$  bilayer is nonpolar. The interface  $rTiO_3/Si(001)$  has been greatly studied, both experimentally<sup>1</sup> and theoretically<sup>2,3,4</sup>.

In the search of the best candidate, the  $LaAlO_3$  crystal further raised out of the perovskite family. This was partly due to its better misfit to Si(001) surface (0.7 %). The conduction band offset is expected to be greater than 1 eV. A value has been computed<sup>5</sup> to be 1 eV within the "charge level model" which does not take the interface structure into account. Nevertheless, as the La, Al and O respective oxidation states are +III, +II and -II, the  $AlO_2$  and LaO layers are charged with -1 and +1 electrons and the crystal is polar. This polar aspect leads to more complex interface constructions than the previous  $SrTiO_3$  compound.

This letter focuses on the interface between a polar perovskite and Si(100)2X1, taking  $LaAlO_3$  as a prototype. The interface may begin with La or Al atoms deposition. For an interface starting with La, Ashman et al.<sup>6</sup> have shown that La atoms cover the Si surface by pairs. This scheme is coherent with the "electron counting model" where 2 La atoms provide 6 electrons to 6 Si dangling bonds, removing gap states and assuming a coverage  $\theta = 2/3$ . Klenov et al.<sup>7</sup> have grown a Si thin film on a  $LaAlO_3$  substrate and microscopy has shown that the interface is based on La pairs. This interface has been theoretically studied by Först et al.<sup>8</sup> to precise the Si network at the interface and the interface O contents which can not be resolved by the microscopy. The obtained Si network of the Si epitaxy is not

FIG. 2: Charge density map of the Al lines showing the high density areas along the Al-Si and Al-Al bonds (Si and Al atoms are respectively represented by grey and black balls). These area are evidenced by bold lines.

clearly coherent with the  $\text{LaAlO}_3$  epitaxy on the  $2\times 1$  reconstructed Si surface. In order to avoid dipole moment of the polar surface, Knizhnik et al.<sup>9</sup> have constructed theoretical interfaces by transfer of O from one boundary surface to the other in their  $\text{LaAlO}_3$  slab.

Our aim here is to construct an interface starting with Al atom deposition, compatible with the growth of  $\text{LaO-AlO}_2$  neutral bilayers, without midgap states.

We choose here to start the growth process by a well-known Al coverage of the Si surface based on monoatomic Al lines (built on Al pairs). Indeed, when one considers atoms whose preferred oxidation state is +III, the electron counting model leads to a coverage  $\theta = 1/3$  monolayer (ML). But it is not easy to find on the surface a position corresponding to a symmetry of order 3. Nevertheless it is well known for indium, Al and so on that the stable geometry (Fig.1) is realized at a coverage  $\theta = 1/2$  ML by pairs of adatoms which form monoatomic chains on the Si surface.<sup>10</sup> As coverage of Si by Al lines has been realized ten years ago, we take this surface as a starting point for the growth of  $\text{LaAlO}_3$ .

We have carried out electronic structure calculations of this template to get insight of the electron distribution and bonding at the surface. The ABINIT planewave code<sup>11</sup> is used with Hartwigsen Goedecker Hutter pseudopotentials.<sup>12</sup> The exchange correlation is given in the local density approximation (LDA). We consider a supercell consisting of a slab of 7 layers of Si atoms which bottom layer is fixed and saturated by hydrogen atoms, covered by the adatoms and a vacuum slab of 14 Å. Atomic positions are relaxed until forces reach 0.5 eV/Å. The charge density maps reported on Fig.2 clearly show high density regions between top Si atoms and Al atoms, representing the Si-Al bonding at the interface. One must also notice (Fig.2) the other high density region between pairs of Al atoms, corresponding to Al-Al bonding. Thus, one may understand that a pair of Al provides 4 electrons to 4 Si dangling bonds while the 2 Al share 2 electrons, leading to a coverage of  $\theta = 1/2\text{ML}$ . The electronic density of states (Fig.3 b) shows that the half filled state in the band gap of the  $\text{Si}(001)2\times 1$  (Fig.3 a) has really disappeared, in favor of the Si-Al bond creation [noticed as SiAl and SiAl\* on Fig.3 (b)]. Thus, electron counting model must be "extended" to take into account the bond pairing of adatoms.

FIG. 3: Electronic density of states around the forbidden band gap  $E_g$  of the Si (a) for the free surface where the arrow pins the half filled dangling bond (b) for the Al lines deposited at the Si surface(c) for the oxidized lines showing that the Si band gap is recover. Black and grey surfaces correspond to occupied and unoccupied states.

site	$\Delta E$ (eV)	$\Delta z$ (Å)	SM
A	0.00	1.49	4
B	1.02	0.84	2
C	0.10	2.04	1
D	1.01	2.68	1
E	2.90	0.95	1
F	7.22	0.92	1

TABLE I: O adatom on the Al line. Calculated energy variation ( $\Delta E$ ) between the respective relaxed positions ( $\Delta z$ ) and the multiplicity of the corresponding site (SM)

This Si covered by a half layer of Al is then oxidized by two approaches: i) considering electron counting arguments to obtain a neutral interface ii) computing with ab initio method the energy of the system with one O atom, for various O positions (A-F on Fig.1), in order to define the most stable ones. Let us first count the electrons. To construct a neutral interface, one considers that  $N$  O atoms need  $2N$  electrons. As the surface provides 2.5 electrons (1 electron from the dangling bonds and 1.5 electrons from the  $Al_{0.5}$ ), the interface is neutral with 1.25 O atoms. The interface stoichiometry is thus  $Al_{0.5}O_{1.25}$ . Now considering ab initio computations, each of the A-F site height positions is relaxed. The total energy values are reported in Tab.I. The A and C sites correspond to similar energies, and they are more stable than the others by more that 1 eV. This may be easily understood if one considers the trend of O atoms to go where a high electron density stands (on the Si-Al and Al-Al bond). These stable sites are fully filled and lead to the addition of 1.25 O monolayer, in agreement with a neutral surface.

The resulting  $Al_{0.5}O_{1.25}$  surface has been fully relaxed and its electronic structure has been studied. The Si-O bonding distance is similar as those in  $SiO_2$ . The Al-O distances (from 1.76 to 1.85 Å) are compatible with those in an  $AlO_2$  plane of  $LaAlO_3$ . Atoms in the

FIG. 4: Geometry of the relaxed supercell. O and Al atoms are represented respectively by white and black balls. Tiny and wide grey balls correspond to Si and La atoms.

$\text{Al}_{0.5}\text{O}_{1.25}$  layer are nearly in the same plane. Concerning the electronic density of states (Fig.3 c), the oxidation does not add states in the gap of the Al covered surface, and the Si gap is recovered.

In order to define the further growth over the  $\text{Al}_{0.5}\text{O}_{1.25}$  layer, the interface has also been capped by a neutral  $\text{LaAlO}_3$  bilayer. As a bilayer, both  $\text{LaO-AlO}_2$  and  $\text{AlO}_2\text{-LaO}$  sequences with various in plane positions have been constructed and relaxed. Their total energies are similar showing that the further growth on the interface will be similar whatever its structure would be. Furthermore, the perovskite structure of the relaxed bilayer is maintained, demonstrating the possibility of growing  $\text{LaAlO}_3$  over this interface.

Concerning applications, a key point is the conduction band offset which is wished to be greater than 1 eV to avoid tunnelling through the oxide barrier. As the interface between oxide and Si greatly influence the offset value, it is important to evaluate this offset for each interface. We have computed it for the  $\text{Al}_{0.5}\text{O}_{1.25}$  interface followed by the previous sequences. The computation are realized on supercells built on H - Si slice (13 Å) -  $\text{LaAlO}_3$  (19 Å) - Si slice (13 Å) - H containing a mirror plane in order to avoid the infinite adding of the interface electronic dipole. As the corresponding supercell contains a too large amount of atoms (230) to be reasonably relaxed by means of the ABINIT code, we make use of the SIESTA code<sup>13</sup> which mainly differs from the previous one by the use of local atomic orbitals. We make use of the same pseudopotentials and basis set as Knizhnik et al.<sup>9</sup>. The atomic basis for La, Al and O atoms is polarized simple zeta, it is polarized double zeta for Si atoms. The supercell has been fully relaxed in the Harris functional framework (until a maximum force tolerance of 0.1 eV/Å is reached). This relaxation leads to the same interface structure as those obtained for the bilayer computed with ABINIT (Fig.4). Then the electronic structure of the relaxed supercell is calculated in the Self Consistent Field framework, using a 2X2X1 k point grid. The average potential method is used to evaluate the band offsets.<sup>14</sup> The computed conduction band offsets is computed to be 1.89 eV which is greatly sufficient for applications in microelectronics.

In conclusion, we have derived an interface between a polar high- $\kappa$  perovskite and Si. The interface corresponds to the prior growth of metal lines followed by oxidation. It has

been shown that the  $\text{Al}_{0.5}\text{O}_{1.25}$  interface leads to consider that  $\text{LaAlO}_3$  is likely to replace  $\text{SiO}_2$  with a conduction band offset around 1.89 eV. More generally, this result is in favor of interfaces based on the B metal atoms in case of growth of the polar  $\text{ABO}_3$  perovskite on the  $\text{Si}(001)2\times 1$  surface.

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\* Electronic address: Isabelle.Devos@isen.fr

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