Research article

Ab initio calculation of band alignment of epitaxial La$_2$O$_3$ on Si(111) substrate

Alberto Debernardi

CNR-IMM, ss Agrate Brianza, via C. Olivetti 2, I-20864, Agrate Brianza, Italy, European Union

* **Correspondence:** Alberto.Debernardi@mdm.imm.cnr.it; Tel: +39-039-603-7804; Fax: +39-039-688-1175

Abstract: By means of plane wave pseudopotential method we have studied the electronic properties of the heterostructure formed by an high dielectric constant (κ) oxide, the hexagonal La$_2$O$_3$ epitaxially grown with (0001)-orientation on Si (111) substrate. We found that for La$_2$O$_3$ both the dielectric constant along the growth direction and the band gap are larger in the epitaxial film than in the bulk. By super-cell techniques we have computed the band alignment of the junction finding a valence band offset and a conduction band offset of $\sim$ 1.6 eV and $\sim$ 1.7 eV respectively. We demonstrate that the band alignment can be engineered by δ-doping the interface: our simulations show that, by doping the interface with S or Se monolayer, the valence (conduction) band offset increases (decreases) of about 0.5 eV without the formation of spurious electronic states in the semiconductor band-gap. The simulation of the critical thickness of pseudomorphic Lanthana film complete the work. Our results are relevant for the realization of a new generation of devices based on ultra-scaled complementary metal oxides semiconductors (CMOS) technology.

Keywords: High-κ Oxides; Lanthana; Band-engineering; ultra-scaled CMOS; *ab initio* simulation

1. Introduction

Moore's law, predicting the continue scaling down of microelectronic devices to smaller and smaller sizes, has encountered a serious limitation in the replacement of conventional silicon dioxide (SiO$_2$) that is used as gate insulator. In fact, when the oxide thickness is reduced to just few atomic layers, electrons can tunnel directly through the SiO$_2$ film, preventing the device to work. The ideal candidate to substitute SiO$_2$ would be an oxide with a high dielectric constant

(high-κ); the oxide must have a high-enough band-offset with the substrate to maintain a small electric current in the gate oxide (leakage). Further, the interface between the oxide and silicon must be free of any active defect causing electronic states in the semiconductor band-gap, which would degrade the electronic properties of the device. Among the possible candidates to substitute SiO_2 in advanced complementary metal-oxide-semiconductor (CMOS) devices, hexagonal La_2O_3 has recently attracted considerable interest for the high value of the dielectric constant of this phase (measurements gives $\kappa = 27\pm3$,[1, 2] in agreement with first principles value of $\kappa = 26$[1]) when compared to the experimental value of the dielectric constant of the cubic La_2O_3 (16$\pm$2)[1], or to the values of dielectric constant of different high-κ oxides, such as ZrO_2 ($\kappa \sim 20$)[3] or HfO_2 ($\kappa \sim 14$)[3]. Electronic and vibrational properties of hexagonal La_2O_3 can reliably be computed *ab initio*[1], predicting for the bulk dielectric constant an anisotropy that is less than 1%.[1] The results of Ref. [1] would make hexagonal La_2O_3 a promising material for the future generation of ultra-scaled CMOS devices, provided that the conduction band offset with the Si substrate would be large enough to produce a negligible leakage through the gate oxide.

The latter problem is one of the targets of the present article. By means of state-of-the-art density functional simulations we have computed the band offset of hexagonal La_2O_3 epitaxially grown on Si(111) substrate. At variance with the conventional (001) orientation,[4] the Si(111) oriented substrate has in-plane lattice parameter similar to the one of the hexagonal La_2O_3, allowing epitaxial growth and a defect free interface. In industrial processes employing Silicon as a substrate, the (001) orientation of the substrate is usually preferred with respect to the (111) orientation, because the latter forms an interface with SiO_2 that presents a density of defect which is about four time the density of defects formed at the SiO_2/Si(001) interface (see, e. g., Ref. [4]). As it will be shown in the present work, an oxide almost lattice matched with the Si(111) substrate can growth epitaxially without forming any active defect in the gap.

An accurate engineering of the junction between the Silicon substrate and the epitaxial high-κ oxide is required to minimize the interface trap density and the carrier scattering, and thus to obtain reliable, high performance devices. For this reason a considerable effort has been devoted to grow epitaxial, sharp, and well-ordered Silicon/high-κ oxides interfaces. In particular, thin crystal films of Praseodymia and of Ceria, two high-k oxides, has been grown epitaxially on Si substrate (111) oriented, by Cl passivation of the Si surface.[5, 6] The epitaxial growth of La_2O_3 film on Silicon substrates (111) oriented has been recently reported.[7, 8, 9] The experimental data regarding the crystal structure of La_2O_3 epitaxial layers are quite intriguing: for film thickness lower than 2 nm the cubic (bixbyite) phase is measured,[8, 9] while for larger oxide thickness the hexagonal phase, having $La_2O_3(0001) \parallel Si(111)$, is observed.[7, 9]

Our results predict that Lanthanum sesquioxide film can grow epitaxially up a to thickness of several decades of nanometers. We computed for the $La_2O_3(0001)/Si(111)$ junction a valence band offset of ~ 1.6 eV, and a conduction band offset of ~ 1.7 eV (remarkably higher than the minimum value of 1.0 eV required for the next generation CMOS transistors,[10] as devised in the international technology road-map for semiconductors[11]), suggesting the capability of hexagonal La_2O_3 to be used as gate oxide in future ultra scaled-devices. Further, we will show that it is possible to modify the band-offset of about 0.5 eV (i. e. $\sim 30\%$) without creating electronic states in the semiconductor band-gap by δ-doping the interface with S or Se monolayer.

2. Method and computational technicalities

Our simulations are obtained, within the density functional theory, by plane-wave pseudopotential techniques, with generalized gradient approximation of Perdew, Burke and Ernzerhof[12] as implemented in the PWSCF package (Plane-Wave Self-Consistent Field).[13] We use state of the art ultra-soft [14, 15] pseudopotential in the separable form introduced by Kleinmann and Bylander[16]; O, S, and Se pseudopotentials have 6 valence electrons, while Si and La pseudopotentials have 4 and 11 valence electrons, respectively. Integration of electronic states is performed by means of special point techniques, by using a (12,12,1) Monkhorst-Pack grid [17] for the super-cell describing the interface. The valence electronic density was expanded on a plane-wave basis set with a kinetic energy cutoff of 50 Ry, while for the augmentation density of ultra-soft pseudopotentials a cutoff of 400 Ry was used.

At variance with estimations obtained with the so-called metal-induced gap states model[18, 19] based on the complex bulk band structures, we calculate the band offset by simulating a Si/La_2O_3 junction by the super-cell techniques. For a given stacking sequence of atomic planes at the interface, this method accounts the atomic relaxation and the structural relaxation of epitaxial layers along the growth direction. Further, it provides reliable predictions of electronic properties of the heterostructure (see e.g. Ref. [20, 21] and references therein).

We consider epitaxial La_2O_3 (0001)-oriented on Si(111) substrate. In fact, with this orientation the (111) plane of silicon (diamond structure) has a triangular surface lattice having the same symmetry of the La_2O_3 (0001) plane; further the resulting in-plane (i.e. parallel to the surface) lattice parameter of La_2O_3, a_{hex}, presents a small lattice mismatch (about $\sim 2\%$ according to the experimental values reported below) with the lattice parameter of the Si substrate, suggesting the possibility of epitaxial grown with this orientation.[22] The dielectric constants are calculated with the same method and technicalities used in Ref. [1], the interested reader can refer to this work an to the references therein for further computational details.

3. Results and Discussion

Lanthanum sesquioxide, La_2O_3, is and hexagonal crystal (space group $C\bar{3}m$) with lattice parameters $a_{hex} = 3.933$ Å [1] and $c_{hex} = 6.147$ Å[1]. Lanthanum atoms are in the (2d) position $\pm(1/2\,2/3\,u)$ (as usual, atomic positions are expressed in crystal units) with $u \equiv u_{La} = 0.245$;[23] one oxygen is placed in the (1a) position 000, while the other two oxygens are in the (2d) position with $u \equiv u_O = 0.645$.[23]
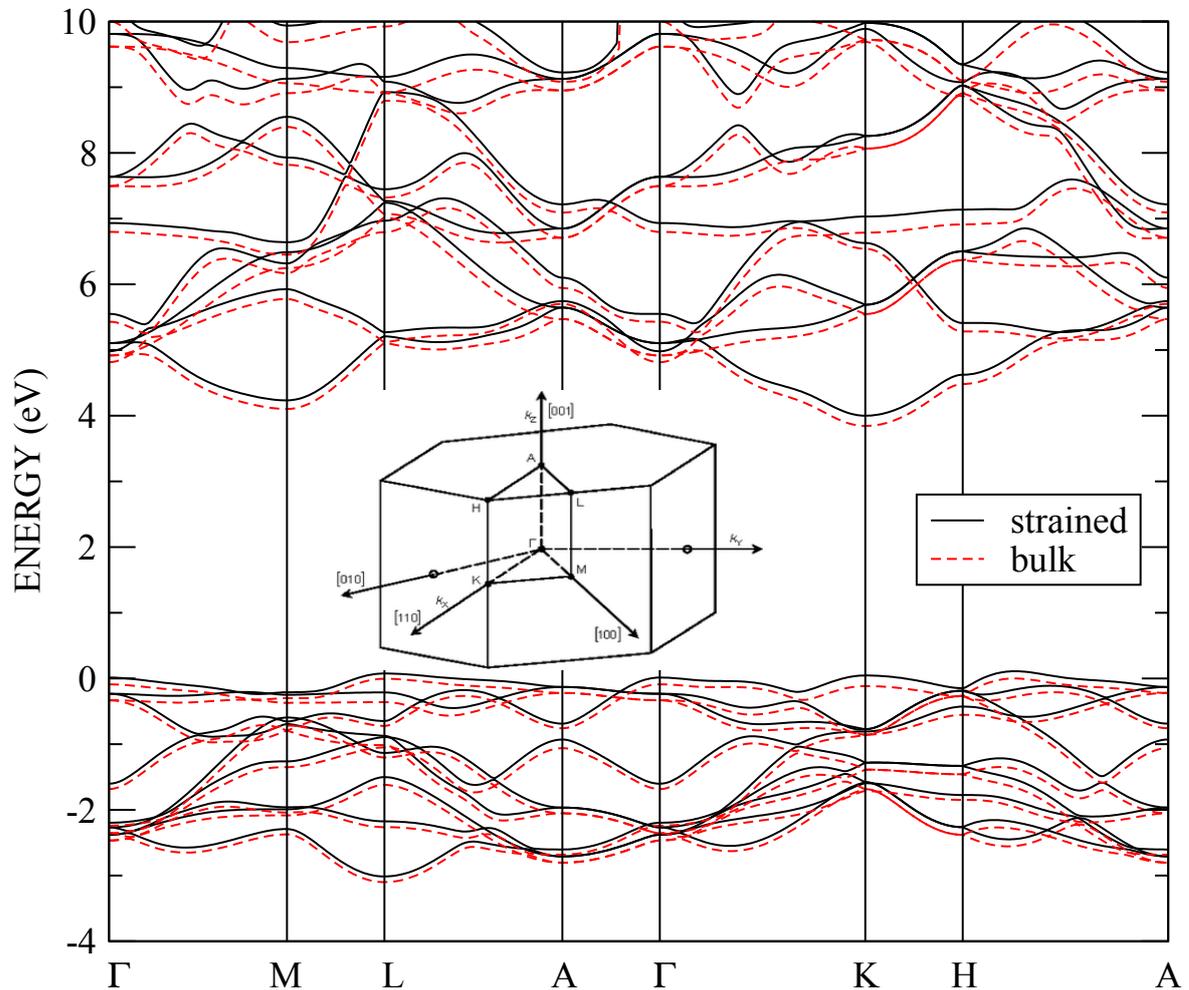
Figure 1. Electronic band-structure of bulk (red dashed line) and epitaxial (black solid line) hexagonal La$_2$O$_3$, along some high symmetry directions. The zero of the energy corresponds to the top of valence band of bulk crystal. The corresponding Brillouin zone is displayed as an insert.

In our simulation the bulk lattice parameters are computed by imposing the vanishing of the stress in the bulk unit cell. We obtain for the hexagonal La$_2$O$_3$ the following lattice parameters: a_{hex} = 3.895 Å, c_{hex} = 6.157 Å, u_{La} = 0.2502, and u_O = 0.6438, that well reproduce the experimental data. The computed lattice parameter of Si is (the experimental data taken from literature are reported in parenthesis): a_{fcc} = 5.468 (5.431)[23] Å; the latter value corresponds to a lattice parameter of the Si(111) surface a_{hex} = 3.867 (3.840)[23] Å, giving a theoretical

lattice mismatch of less than $\sim 1\%$, that satisfactory reproduces the experimental fact that -with the considered orientation - substrate and oxide have similar in-plane lattice parameters. The mismatch produces a small strain of the epitaxial oxide, with a computed in-plane stress of ~ 16 Kbar; along the growth direction the lattice parameter of the epitaxial oxide is free to relax, and the calculated lattice constant, $c_{hex}^{epi} = 6.194$ Å, is only a fraction of percent larger than the bulk theoretical value reported above. As can be noticed from Fig. 1, the strain due to epitaxial growth of La_2O_3 does not substantially affects the band structure of hexagonal La_2O_3 and the computed band-gap slightly increases from the bulk value of 3.84 eV to 3.89 eV of the strained structure.
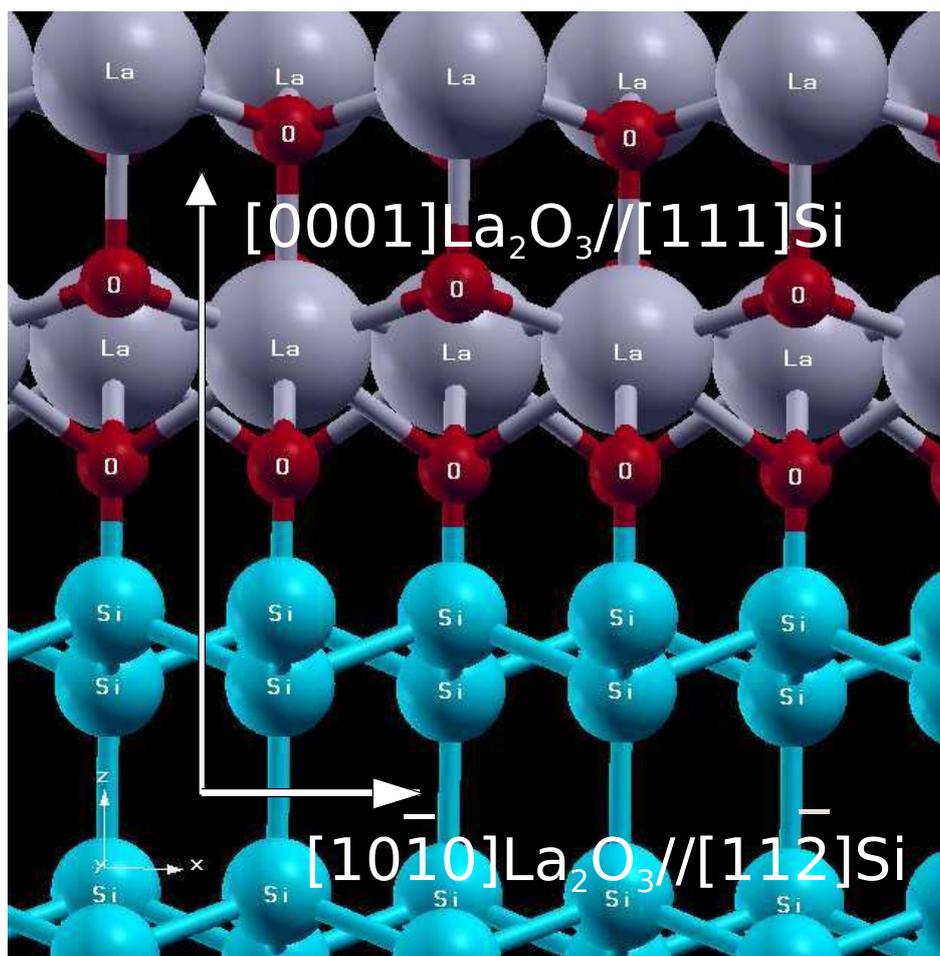
Figure 2. Interface used in the calculation of the $La_2O_3(0001)/Si(111)$ heterostructure.

The experimental band-gap of bulk hexagonal La_2O_3 is 5.5 eV,[24] while the experimental band-gap of bulk Silicon is 1.11 eV [25]. Our computed Silicon band-gap is 0.614 eV, in agreement with the results present in literature which are obtained by the same (or by a similar) technique. It is well known that, within the density functional theory, the computed band-gaps are usually underestimated with respect to the experimental values (for further discussion and references see e.g. Ref.[26]).

The dielectric constants are also modified in the strained structure. By taking, as usual, the z-axis along the growth direction we obtain for the dielectric constants of hexagonal epitaxial La_2O_3 (in parenthesis the corresponding bulk values): $\kappa_{xx} = \kappa_{yy} = 24.5$ (26.2), and $\kappa_{zz} = 28.0$ (26.0). According to our results, in the epitaxial oxide the dielectric constant along the growth direction (that in a CMOS transistor is the component of the dielectric tensor having technological interest) increases by $\sim 8\%$ with respect to the bulk value, producing an improvement in the dielectric properties of La_2O_3 film.

3.1. Band alignment

We simulate the $La_2O_3(0001)/Si(111)$ interface by a hexagonal periodically repeated super-cell containing 55 atoms (24 Si, 12 La, and 19 O) with the basis vectors, a, oriented along the primitive lattice vector of Si(111) plan. The length of the basis $a = \frac{a_{Si}}{\sqrt{2}}$, where $a_{Si} = 3.866$Å, is kept fixed to the theoretical lattice parameter of bulk-Si. The height $c = 75.88$ Å of the super-cell was obtained relaxing the structure along the growth direction to have a negligible stress along this direction (< 4 Kbar after the relaxation procedure).

We consider an oxygen terminated interface, i.e. along the growth direction the atomic-plane sequence is: ...Si, O, La, O, O, La, ..., as displayed in Fig. 2, with the O at the interface corresponding to the $(1a)$ position of La_2O_3 to ensure the stoichiometry of the interface; according to recipe proposed in Ref. [27] this type of termination produces an interface free of defects in the gap, as can be noticed by looking to the top panel of Fig. 3 where we display the total density of states (TDOS) of the super-cell structure in an energy range corresponding to the Si band-gap (the zero of the energy corresponds to the top of the valence band of Si). In the top panel of Fig. 3 we also display the projected density of states (PDOS) on the atomic orbitals of the O atom at the interface; in the energy range considered, only energy levels corresponding to p-atomic orbitals have non-vanishing density of states (DOS); in the panel, the p-states PDOS is displayed as a red dashed line, with double peaks structures in the PDOS at energy $4 \div 5$ eV lower that the top of the valence band.

The band alignment is obtained by computing the average of the electron density of the heterostructure $La_2O_3(0001)/Si(111)$, according to the procedure exposed in Ref. [28]. The resulting electrostatic potential is displayed in Fig. 4 as a (blue) dashed line, giving the potential lineup of the two materials. The band structure of the bulk semiconductor and of the strained (bulk) oxides are then added to this averaged potential to obtain the band-offset of the junction. The scheme of the band alignment is displayed in Fig. 5. The computed band-offset between the semiconductor and the oxide are $\Delta E_{vbo} = 1.58$ eV for the valence band-offset, and $\Delta E_{cbo} = 1.68$ eV for the conduction band-offset. The former (latter) result estimates the potential barrier that an hole (electron) in the Si valence (conduction) band maximum (minima) has to overcome to be injected into the gate oxide, thus producing a leakage current.

As mentioned at the end of Section 3 the band-gaps of bulk compounds evaluated by density functional theory are usually underestimated with respect to the corresponding experimental values. However, since in the present case this fact is expected to produce an underestimation of the computed conduction band offset, it does not affect (but it rather enforces) one of the main result of the present work, namely that, according to our calculations, the conduction band offset is large enough to prevent leakage current.
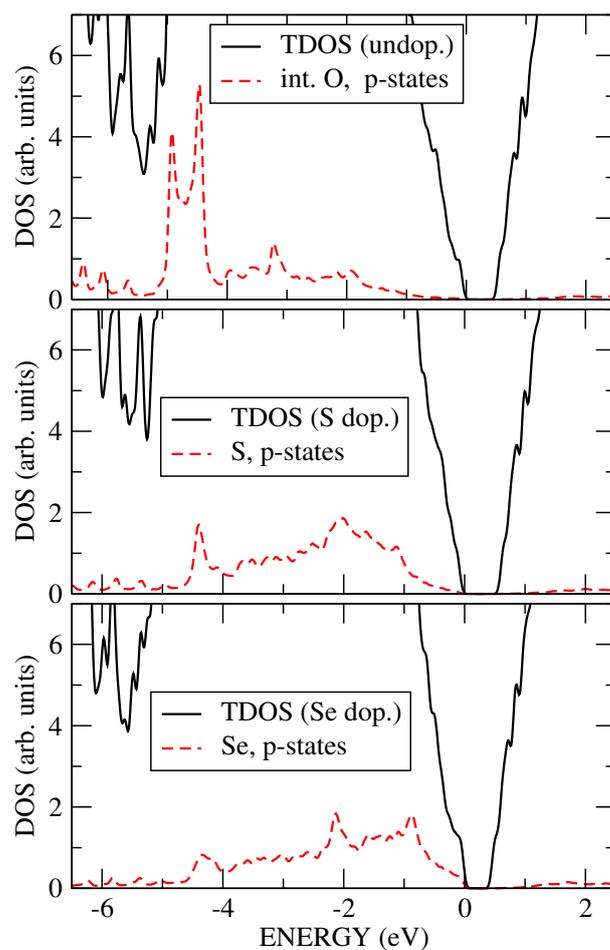
Figure 3. Total density of state (black solid line) and projected density of states on p-orbitals of interfacial atoms (red dashed line) for the three super-cells considered in the article. The zero of the horizontal axis corresponds to the top of the valence band. The top panel corresponds to the $La_2O_3(0001)/Si(111)$ interface, while the middle and bottom panels correspond to δ-doped interfaces with S or Se atoms respectively.

According to this results, hexagonal La_2O_3 presents a band offset with Si suitable for the use as gate oxide in the next generation CMOS devices.

To provide further evidence of the latter assertion, we consider two recipes to improve the estimation of band-offset by taking into account the experimental values of band-gaps of the bulk materials constituting the junction. In the first recipe, we correct ΔE_{cbo} by taking the value of valence band-offset form our *ab initio* simulation and then, instead of using the theoretical band-gaps as usually done in the standard *fully ab initio* method described above, we use the experimental values of bulk Silicon (1.11 eV) and of Lanthanum sesquioxide band-gaps. In the following estimation we use a La_2O_3 band-gap equal to 5.57 eV, to take into account the small increase ($\sim$ 1.3%) of the band-gap, with respect to bulk free-standing value, predicted by our simulation for epitaxial La_2O_3 (however, the corresponding values of ΔE_{cbo} by taking the bulk experimental value of 5.5 eV, can be straightforward computed). We obtain for the conduction band-offset $\Delta E_{cbo} = 2.89$ eV.

If we compare these results for ΔE_{cbo} with the experimental value of $\Delta E_{cbo} = 2.3$ eV reported in Ref. [24], we can notice that the *fully ab initio* value of $\Delta E_{cbo} = 1.68$ eV underestimates the experimental data of about 27%, as expected according to the above discussion, while the ΔE_{cbo} *corrected with experimental bulk band-gaps* over-estimates the experimental value of about the same amount (26%). We remark that in the latter recipe only ΔE_{cbo} is corrected on the basis of experimental data, while the valence band-offset remain unchanged.

A better estimation of the band alignment can be obtained with the following recipe, that we propose in the present paper, to correct symmetrically both valence and conduction band off-set by taking into account the experimental values of bulk band-gaps of the two materials composing the junction. In this second recipe, that we call the *ab initio Fermi energy line-up*, we consider, as reference the theoretical line-up of the Fermi energies of the two compounds, Si and La_2O_3, forming the junction. The Fermi energy is usually defined at absolute zero, and at this temperature it is equal to the electron chemical potential. The Fermi energy of undoped semiconductors or insulators at T=0 K is exactly at the middle of the band-gap.[29]

We take our theoretical value of valence band offset and add to it 1/2 of the *theoretical* values of bulk band-gaps of the two materials (Silicon and bulk strained hexagonal Lanthanum), to obtain the *ab initio* line-up of the two Fermi energies; from this reference value, the valence and conduction band-offset are computed by using the experimental values of bulk band-gaps.

With this procedure, that we call *ab initio Fermi energy line-up* plus *experimental bulk band-gaps,* we obtain $\Delta E_{vbo} = 2.17$ eV and $\Delta E_{cbo} = 2.29$ eV; the latter result is in perfect agreement with the reported experimental value.

3.2. Critical thickness

For completeness, we have estimated the critical thickness, t_c, that an epitaxial La_2O_3 film can reach on Si(111). We have calculated t_c *ab initio*, in a similar way as exposed in the work of Fiorentini and Gulleri [30]. In the following we give a brief account of the method we used.

An epitaxial layer of thickness t is energetically favored with respect to the fully relaxed layer when the following inequality is fulfilled:

$$E_{surf}^{Si} + E_{surf}^{La_2O_3} \geq E_{form} + \Delta E_{epi} * t/t_s. \tag{1}$$

The equal sign holds if $t = t_c$. The left hand side of Eq. 1 represents the cost in energy to form two non-interacting surfaces and it is given by the sum of the surface energy of Si(111),

E_{surf}^{Si}, plus the surface energy of La$_2$O$_3$(111), $E_{surf}^{La_2O_3}$. The right hand side of Eq. 1 represents the sum of the formation energy[31] of the interface, E_{form}, plus the energy of the epitaxial layer of thickness t, where ΔE_{epi} is defined as the difference between the bulk energy of the unit cell of the oxide calculated in the same strain structure of the super-lattice minus the energy of the free-standing structure, and t_s is the value of the lattice parameter of the strained oxide along the growth direction (z-axis); in the present case we have $t_s = c_{hex}^{epi}$. We remand the interested reader to Refs. [30, 31] for further computational details.

The formation energy depends on the growth condition: O-rich favoring oxygen excess, while O-poor favoring oxygen deficit. From a theoretical point of view, this corresponds to fix the chemical potential of the constituents. In our case the chemical potential of Lanthanum, μ_{La}, and of Oxygen, μ_O, are not independent: O-rich (O-poor) condition means La-poor (La-rich) condition. O-rich (i.e. La-poor) condition corresponds to chose μ_O equal to the value of the molecular oxygen, $\mu_O = \mu_{O_2}$, while La-rich (i.e. O-poor) condition corresponds to chose μ_{La} equal to the value of the La element, computed in the hexagonal structure.

Our results are obtained by taking (hereafter the values of the surface energy are referred to the (1x1) unit cell) the Si surface energy equal to 1.179 eV, value computed by K. D. Brommer et al [32] for the Si (111) surface with 7x7 reconstruction and a La$_2$O$_3$ surface energy equal to 0.559 eV that we estimated for the La$_2$O$_3$(0001) surface by relaxing a slab (with the same cut-off used in the super-cell calculation of the junction) composed of five La$_2$O$_3$ unit layers separated by $\sim$ 4.8 nm of vacuum.

We obtain a critical thickness ranging from $t_c = 43$ nm (La-rich condition) to $t_c = 172$ nm (O-rich condition), according to the arbitrary in the choice of the chemical potential. This means that the oxide layer can grow up to a thickness of decades of nanometers, conserving its epitaxial structure (and, at least in principle, a defect-free interface); a results that can be expected from the fact that the oxide and the substrate have similar lattice parameter. Incidentally, we notice that the film thickness of 6 nm[9] and 20 nm,[7] reported so far in literature for epitaxial La$_2$O$_3$ on Si(111) are compatible with our predictions.

3.3. δ-doped interfaces

Several compounds have the hexagonal structure of Lanthanum sesquioxide, in particular, two of them, an oxysulfide, La$_2$O$_2$S, and an oxyselenide, La$_2$O$_2$Se, have also a chemical composition similar to La$_2$O$_3$, since O, S and Se are in the same column of the periodic table of elements. In the two former compounds, the S or Se atom replaces the O atom in the $(1a)$ position[23] in the unit cell of La$_2$O$_3$. La$_2$O$_2$S according to first principles calculations [33] is predicted to have an high-κ. Our simulation, gives for La$_2$O$_2$S (the *ab initio* results computed by Vali[33] are reported in parenthesis): $\kappa_{xx} = \kappa_{yy} = 18.1$ (15.85), $\kappa_{xx} = \kappa_{yy} = 18.1$ (15.85), and $\kappa_{zz} = 15.8$ (15.15). Our computed lattice parameters $a_{hex} = 4.03$ Å(3.9905), $c_{hex} = 6.93$ Å(6.8391), $u_{La} = 0.2825$ (0.28), $u_O = 0.6266$ (0.63), are in good agreement with experimental data [23]: $a = 4.0509$ Å, $c = 6.943$ Å, $u_{La} = 0.29$, $u_O = 0.64$.
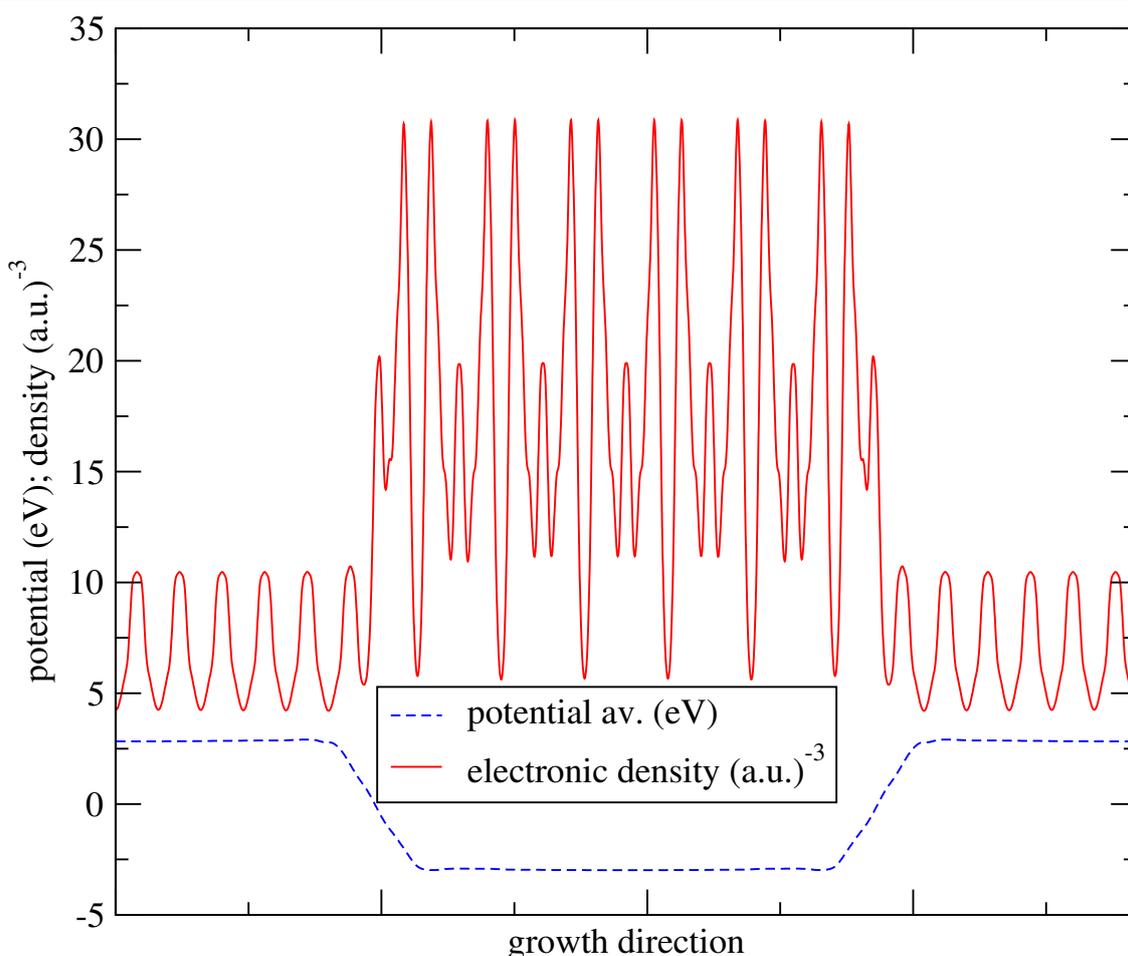
Figure 4. (Red) solid line: profiles along the growth direction of electronic density (the average is made on planes parallel to the interface). (Blue) dashed line: the electrostatic lineup potential. The structure at the center of the figure corresponds to the La$_2$O$_3$ slab, the structure close to the borders corresponds to the Si slab.

For La$_2$O$_2$Se we computed $\kappa_{xx} = \kappa_{yy} = 15.1$ and $\kappa_{zz} = 12.6$, while for the lattice parameters we obtained $a_{hex} = 4.071$ Å, $c_{hex} = 7.158$ Å, $u_{La} = 0.2910$, $u_O = 0.6222$, that well reproduce the experimental data:[23] $a_{hex} = 4.070$ Å, $c_{hex} = 7.124$ Å.

We re-call that in the stoichiometric interface considered in the present work the O atom placed at the interface corresponds to the $(1a)$ position[23] of the unit cell of hexagonal structure of La$_2$O$_3$, that in La$_2$O$_2$S (La$_2$O$_2$Se) that is occupied by the S (Se) atom. It this therefore quite natural, in order to modify the band-offset of the junction by changing the chemical composition of the interface, to consider a δ-doped interface with with S (Se) substituting the interfacial $(1a)$ O atom, since the $(1a)$ atomic position corresponds to the position already occupied by S (Se) atoms in Lanthanum-oxysulfide (oxyselenide). After atomic relaxation, we have computed the electronic states and the band alignment of S and Se δ-doped interfaces in a similar way as the un-doped one. We display only the results obtained by the standard *fully ab initio* method. The

data corresponding to the *correction recipes* to adjust the *ab initio* data with experimental bulk band-gaps (see Section 3.1), can be straightforwardly computed by the interested reader.
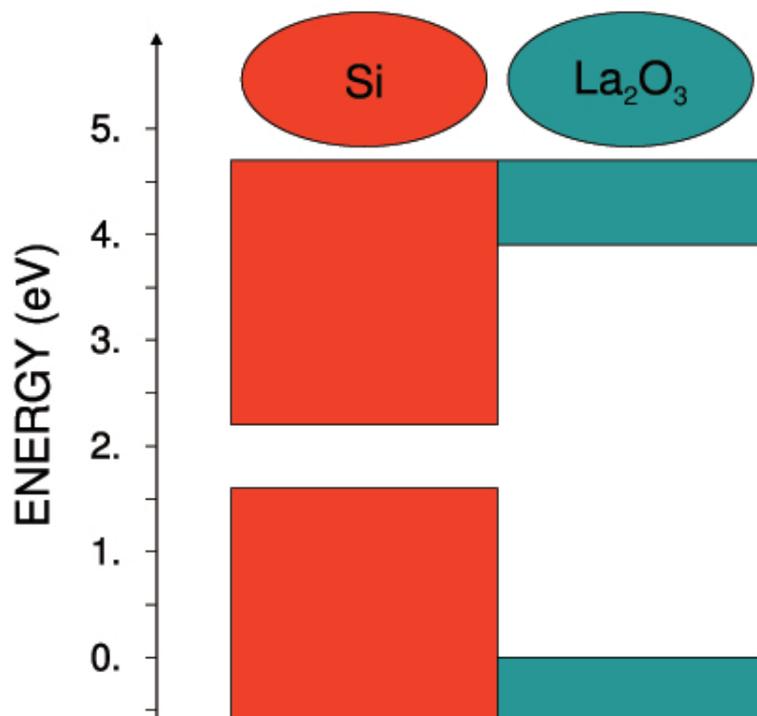
Figure 5. Scheme of the band alignments at the La$_2$O$_3$(0001)/Si(111) junction (fully *ab initio* data).

We found that for the S-doped interface $\Delta E_{vbo} = 2.08$ eV, and $\Delta E_{cbo} = 1.18$ eV; while for the Se-doped interface $\Delta E_{vbo} = 2.04$ eV and $\Delta E_{cbo} = 1.24$ eV; this means that the valence (conduction) band-offset can be significantly increased (decreased) of about 0.5 eV (i.e. about 30%) by δ-doping the interface with a monolayer of S or of Se.

Remarkably, no impurity states are induced in the gap by δ-doping, as can be noticed by looking to the middle and to the bottom panel of Fig. 3, where the TDOS (of the whole super-cell) and the PDOS (of interfacial atoms) are reported for the S and Se δ-doped interface respectively. We take the energy of valence band maximum as the zero of the energy scale. By comparing the PDOS of interfacial S or Se atoms with the PDOS of O atom at the interface of the un-doped structure (top panel of Fig. 3), we can notice that, by effect of δ-doping, in the range of energies from -3 eV up to about -1 eV, the PDOS of S and of Se are larger than the corresponding PDOS

of interfacial O of un-doped structure; while the double peak structure, present in the PDOS of the un-doped structure at $\sim$ -4.5 eV, almost disappears in S and in Se PDOS.

In the introduction, we mentioned the use of passivating agents (such as Cl or H) on Si(111) surface to promote epitaxial growth of high-κ oxides; the employment of this technique to growth Si(111)/high-κ oxide interfaces, calls for a brief discussion about the possibility to exploit the use of passivating molecules in future experiments to obtain a shift in the band-alignment similar to the one predicted by our simulations for δ-doped heterostructures. For this reason, we briefly summarize the general criteria that have inspired our choice of doping elements.

To prevent leakage in the ultra-scaled devices, the production of interfaces free of spurious electronic states in the band-gap, acting as electrical traps, is a must. To fulfill this demand the doping elements, that we used in the present work to engineer the band offset, were chosen according to the following requirements: i) the dopants should produce in the oxide substitutional defects, and they should have the same oxidation states (they are isovalent) of the element they substitute, to avoid the formation of dangling bonds that can produce electronic levels in the band-gap. ii) the epitaxial layer of the doped oxide should share the crystallographic structure with Lanthanum sesquioxide, where the dopants (S,Se) are placed in a well defined crystallographic position (1a). For perfect interfaces, this reduces, at least in principles, the possibility of chemical disorder, produced by the dopants that randomly occupy substitutional sites of the crystal structure. Instead, as in the case of Lanthanum oxysulfide and Lanthanum oxyselenide, the dopant are energetically favored to place in a pre-determined stacking order, producing a δ-doped interface. This property also discourages the formation of amorphous oxide layer. In fact, the amorphization of epitaxial layer can be expected when one introduce doping elements having coordination number different to the one of O [(1a) Wyckoff position] in La_2O_3 sesquioxide. S and Se fulfill both requirements and, according to the above results, they produce defect-free interfaces.

In light of recent experimental results reporting that the termination of substrate dangling bonds by Cl strongly favors abrupt Lanthana-Silicon interfaces,[8] and on the basis of our theoretical results, a possible suggestion is to passivate the Silicon (111) surface with molecules like S-Cl$_2$, Se-Cl$_2$ (or S-H$_2$, Se-H$_2$), thus forming Si-S-Cl, Si-Se-Cl (or Si-S-H, Si-Se-H) surface bonds. Presumably, this passivation can provide an element like S (or Se) that can be incorporated in the first layer of Lanthanum sesquioxide, producing Lanthanum oxysulfide (oxyselenide) and an enhancement of valence band offset that can further improve the suppression of leakage currents through gate oxide in ultra-scaled p-channel CMOS devices.

4. Conclusion

On summary, by means of plane-wave pseudopotential techniques we predicted that high-κ Lanthanum sesquioxide films (0001)-oriented can growth epitaxially on the almost lattice-matched Si(111) substrate up to a critical thickness of decades on nanometers maintaining a defect free interface. We have computed the valence and conduction band offset of La_2O_3(0001)/Si(111) heterostructure. In particular, the conduction band offset of the fully *ab initio* calculation is found to be $\sim$ 1.7 eV. This offset makes this oxide completely suitable to prevent leakage in the forthcoming generation of ultra-scaled CMOS structures. Further, we

have shown that it is possible to modify the band-offset of about 30% by δ-doping the interface with S or Se atoms without creating interfacial electronic states in the gap, thus providing a suitable mechanism for the band-offset engineering of the junction. These results make the high-κ Lanthanum sesquioxide an extremely promising candidate as gate oxide in the next-future CMOS nano devices.

Acknowledgments

Conflict of Interest

The author declares no conflicts of interest in this paper.

References

1. Scarel G, Debernardi A, Tsoutsou D, et al. (2007) Vibrational and electrical properties of hexagonal La_2O_3 films *Appl. Phys. Lett.* 91, 102901. *ibid.* (2007) 91, 189901(E).

2. Tsoutsou D, Scarel G, Debernardi A, et al. (2008) Infrared spectroscopy and X-ray diffraction studies on the crystallographic evolution of La_2O_3 films upon annealing. *Microelectron Eng* 85: 2411-2413.

3. See e.g.: Fanciulli M, Scarel G, editors Rare Earth Oxide Thin Films: Growth, Characterization, and Applications, *Topics in Applied Physics* 106, Berlin: Springer; 2007.

4. Stesmans A (2002) Influence of interface relaxation on passivation kinetics in H_2 of coordination P_b defects at the (111) Si / SiO_2 interface revealed by electron spin resonance. *J Appl Phys* 92: 1317

5. Gevers S, Flege JI, Kaemena B, et al. (2010) Improved epitaxy of ultrathin praseodymia films on chlorine passivated Si(111) reducing silicate interface formation. *Appl Phys Lett* 97: 242901.

6. Flege JI, Kaemena B, Höcker J, et al. (2014) Ultrathin, epitaxial cerium dioxide on silicon. *Appl Phys Lett* 104: 131604.

7. Edge LF, Tian W, Vaithyanathan V, et al. Stemmer S, Wang JG, and Kim MJ (2008) Growth and Characterization of Alternative Gate Dielectrics by Molecular-Beam Epitaxy. *ECS Transactions* 16: 213-227.

8. Flege JI, Kaemena B, Schmidt T, et al. (2014) Epitaxial, well-ordered ceria/lanthana high-κ gate dielectrics on silicon. *J Vac Sci Technol B* 32: 03D124.

9. Proessdorf A, Niehle M, Hanke M, et al. (2014) Epitaxial polymorphism of La2O3 on Si(111) studied by in situ x-ray diffraction. *Appl Phys Lett* 105: 021601.

10. See e.g. Houssa M, Pantisano L, Ragnarsson LA, et al. (2006) Electrical properties of high-κ gate dielectrics: Challenges, current issues, and possible solutions. *Materials Science and Engineering R* 51: 37-85.

11. ITRS Reports and Ordering Information. Available from: http://www.itrs.net

12. Perdew JP, Burke K, and Ernzerhof M (1996) Generalized Gradient Approximation Made Simple. *Phys Rev Lett* 77: 3865-3868; *ibid.* (1997) 78, 1396(E).

13. Giannozzi P, Baroni S, Bonini N, et al. (2009) QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *J Phys Condens Matter* 21: 395502.

14. Rappe AM, Rabe KM, Kaxiras E, et al.(1990) Optimized pseudopotentials. *Phys Rev B* 41: 1227-1230.

15. Vanderbilt D (1985) Optimally smooth norm-conserving pseudopotentials. *Phys Rev B* 32: 8412-8415.

16. Kleinman L, and Bylander DM (1982) Efficacious form for model pseudopotentials. *Phys Rev Lett* 48: 1425-i1428.

17. Monkhorst HK, Pack JD (1976) Special points for Brillouin-zone integrations. *Phys Rev B* 13: 5188-i5192.

18. Demkov AA,Fonseca LRC, Verret E et al. (2005) Complex band structure and the band alignment problem at the Sihigh-κ dielectric interface. *Phys Rev B* 71: 195306.

19. Peacock PW, Robertson J (2002) Band offsets and Schottky barrier heights of high dielectric constant oxide. *J Appl Phys* 92: 4712-4721.

20. Debernardi A, Peressi M, Baldereschi A (2005) Spin polarization and band alignments at NiMnSb/GaAs interface. *Comput Mater Sci* 33: 263-268.

21. Debernardi A, Peressi M, Baldereschi A (2003) Structural and Electronic properties of NiMnSb Heusler compound and its interface with GaAs. *Mat Sci Eng C* 23: 743-746.

22. Epitaxial grown of hexagonal $La_2O_3(0001)$ on Si (111) substrate has been reported by L. F. Edge, oral presentation, EMRS meeting 2006.

23. Wyckoff RWG (1963) *Crystal structures* Vol.1, New York: John Wiley & Sons.

24. Engströn O, Raeissi B, Hall S, et al. (2007) Navigation aids in the search for future high-κ dielectrics: Physical and electrical trends. *Solid-State Electron* 51: 622-626.

25. Yu PY, Cardona M (2010) *Fundamentals of Semiconductors* Heidelberg: Springer

26. Engel E, Dreizler RM (2011) newblock *Density Functional Theory* Heidelberg: Springer

27. Peacock PW, Robertson J (2004) Bonding, Energies, and Band Offsets of $SiZrO_2$ and HfO_2 Gate Oxide Interfaces. *Phys Rev Lett* 92: 057601.

28. Peressi M, Binggeli N, and Baldereschi A, (1998) Band engineering at interfaces: theory and numerical experiments. *J Phys D: Appl Phys* 31: 1273-1299.

29. Balkanski M, Wallis RF (2000) *Semiconductor Physics and Applications* New York: Oxford University Press Inc.

30. Fiorentini V, Gulleri G (2002) Theoretical Evaluation of Zirconia and Hafnia as Gate Oxides for Si Microelectronics. *Phys Rev Lett* 89: 266101.

31. Debernardi A, Wiemer C, and Fanciulli M (2007) Epitaxial phase of hafnium dioxide for ultra-scaled electronics. *Phys Rev B* 76: 155405

32. Brommer KD, Needels M, Larson BE, and Joannopoulos JD (1992) Ab initio theory of the Si(111)-(77) surface reconstruction: A challenge for massively parallel computation. *Phys Rev Lett* 68: 1355-1358.

33. R. Vali (2006) Electronic, dynamical, and dielectric properties of lanthanum oxysulfide. *Comp Mat Sci* 37: 300-305.