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Structure and stability of rare-earth and transition-metal oxides

Luca Marsella and Vincenzo Fiorentini
SLACS, Sardinian LAboratory for Computational materials Science,
and Dipartimento di Fisica, Università di Cagliari, Cittadella Universitaria, I-09042 Monserrato (CA), Italy

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The structural parameters of rare-earth oxides lanthania (La_2O_3) and ytterbia (YbO), and of transition-metal oxides yttria (Y_2O_3) and lutetia (Lu_2O_3), candidate replacements of silica as gate insulators in nanometric Si electronics, are determined via *ab initio* calculations. The stability against formation of silica, silicides, and silicates for these oxides in contact with silicon is also investigated: we find stability against silica and silicide formation, but not against silicates.

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I. INTRODUCTION

In recent years, the performance needs of modern information technology have been forcing the size of Si-based ultra-large-scale-integrated (ULSI) devices into the domain of nanometric dimensions.[1,2] This implies the effective reduction of the physical thickness of insulating gate oxide layers in CMOS (complementary metal-oxide-semiconductor) devices. The natural oxide of Si technology, amorphous SiO_2, is now nearing its fundamental size limits, with physical thicknesses currently down to two unit cells. This leads to uncomfortably large (i.e., greater than 1 A/cm^2) leakage currents and increased failure probabilities.[1]

The main reason for the strong reduction of gate-oxide thickness in device downscaling is the need for increasing capacitances in the CMOS conducting channel. In a CMOS, the gate-oxide layer dominates the series capacitance of the channel. An increase in capacitance can thus be obtained reducing the dielectric thickness d/ε of the oxide layer, having physical thickness d and relative dielectric constant ε. Given its small dielectric constant, it is understandable that SiO_2 as a gate oxide has emerged as one of the downscaling bottlenecks. Clearly a replacement[1] will have to be found for silica as a gate insulator for Moore's law[3] on ULSI circuit component density—and hence circuit performance—to remain valid in the next decade.

One of the basic selection criteria for a gate oxide is its thermodynamical stability in contact with Si, barring the formation of undesired thin insulating layers (e.g., silica or silicates) at the Si-oxide interface, which would reduce the global capacitance of the CMOS conducting channel. Silicide formation during epitaxy of the chosen oxide on silicon is likewise undesirable as it will obviously alter the device properties.

In this paper, we focus our attention on a selection of transition and rare-earth metal oxides involving nominally trivalent metal cations: specifically, lanthania (La_2O_3), ytterbia (YbO), lutetia (Lu_2O_3), and yttria (Y_2O_3). We investigate via first-principles density-functional calculations their structure, energetics, electronic structure, and thermodynamic stability against silica, silicides, and selected silicates. We find all the investigated oxides to be stable against silica and silicides, not against silicates.

II. METHOD

Total-energy and force calculations are done within density-functional theory (DFT) using the VASP code[4] with the all-electron frozen-core projector-augmented-wave method,[5] using for O, Si, Lu, Yb (treated as divalent, see below), Y, and La respectively 5, 5, 6, 6, 7, and 8 projectors, with maximum angular momentum in the projector expansion of 3 for La and Y, and 2 for all other atoms. The use of an all-electron method is advisable in these compounds due to the relevance of d and f electrons in transition and rare-earth metals, and to the need to treat semicore states. The f shell is treated as frozen core in Lu and Yb (see also Sec. III A below). In the case of yttria and lanthania, both the local-density (LDA) and generalized-gradient (GGA) approximations to DFT have been used for comparison; only the GGA is used for ytterbium and lutetium oxides. As will be seen, GGA performs better in general.

To obtain accurate structures and formation enthalpies, we use a plane-wave cutoff of 360 eV (about 50% larger than the suggested maximum cutoff[4]). Monkhorst-Pack[6] grids are used for Brillouin zone integration, with the first-order Methfessel-Paxton[7] method for Fermi-surface smearing, where relevant. Mesh and smearing σ have been determined for each kind of material to obtain the desired accuracy: for metals we use the $8\times8\times8$ mesh and $\sigma=0.2$ eV, for silicides the $6\times6\times6$ mesh and $\sigma=0.05$ eV; for silicates and oxides, the $4\times4\times4$ and $\sigma=0.01$ eV. For hexagonal lattices, the mesh is centered at the Γ point to speed up convergence. The internal parameters of each structure have been optimized; the forces acting on the ions after optimization are below 10^{-4} eV/Å for oxides, 10^{-3} eV/Å for silicides and 0.01 eV/Å for the more complex silicates. These technical settings ensure a convergence of the computed total energies to around 1–10 meV.

III. RESULTS AND DISCUSSION

A. Structures

The nominal electronic ground states of the metals cations involved in the materials at issue are Y: [Kr] $4d^1\ 5s^2$; La [Xe] $5d^1\ 6s^2$; Yb [Xe] $4f^{14}\ 6s^2$; Lu [Xe] $4f^{14}\ 5d^1\ 6s^2$. They all behave as trivalent cations in the solid state, forming sesquioxides X_2O_3, except Yb. Ytterbium is a critical mixed-valence case, and forms both the monoxide YbO and

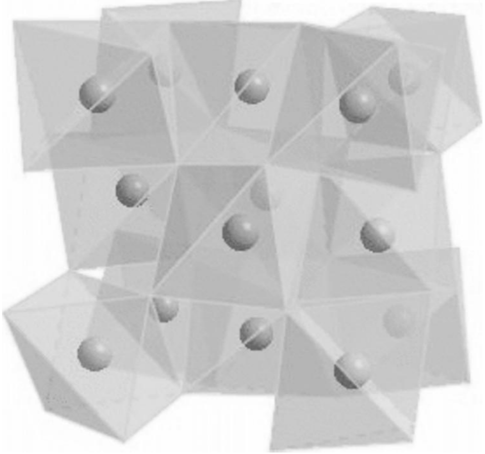

FIG. 1. Cubic cell of the bixbyite structure (from http://webelements.com).

the sesquioxide Yb_2O_3, behaving as divalent or trivalent cation, respectively. We did not attempt to treat the Yb *f* shell as partially occupied: correlation effects falling out of the applicability range of DFT are likely to play a major role there.[8] We therefore considered Yb as divalent, studying only the monoxide variant YbO, whereby the strictly divalent behavior of Yb has been confirmed in self-interaction-correction calculations.[8]

The bulk phases of the cations are metallic, and crystallize in the hexagonal close-packed structure, except ytterbium which is face-centered cubic.[9] The experimental structure of Y and Lu oxides is that of bixbyite, symmetry group T_h^7, which (in the present single-cation case) can be described as a body-centered lattice with a 40-atoms basis.[10] The primitive cell consists essentially of eight rotated defected-fluorite cells (see Fig. 1). La oxide is hexagonal, D_{3d}^3 group.[10] Ytterbium monoxide has the NaCl structure.[9] For the sesquioxides, we examine the competition of the hexagonal and cubic bixbyite structure, finding the correct energy ordering.

The stable structure for the studied silicides (XSi_2, with X the metal cation) has been found to be that of aluminum diboride.[10] For the silicates, we adopt the structure[11] of apatite $Ca_5(PO_4)_3O$, where in our case metal atoms replace Ca, and Si atoms replace P. Since this structure is quite large and complex (hexagonal lattice with a 42-atoms basis, space group C_{6h}^2), the calculations are performed only with yttrium and lanthanum as metal cations.

TABLE I. Lattice parameters for oxides. Yttria and lutetia are bixbyite, lanthania is hexagonal, YbO is NaCl. Experimental data are from Ref. 9 for YbO, and Ref. 10 for all others.

Oxide		a (Å)	$\frac{c}{a}$
Y_2O_3	LDA	10.515	1
	GGA	10.700	1
	exp	10.604	1
La_2O_3	LDA	3.865	1.553
	GGA	3.937	1.562
	exp	3.937	1.557
Lu_2O_3	GGA	10.355	1
	exp	10.391	1
YbO	GGA	4.743	1
	exp	4.870	1

TABLE II. Internal parameters for bixbyite Y_2O_3 and Lu_2O_3. Experimental data are from Ref. 10.

Y_2O_3		u	x	y	z
	LDA	−0.0326	0.3907	0.1514	0.3797
	GGA	−0.0327	0.3908	0.1516	0.3799
	exp	−0.0314	0.389	0.150	0.377
Lu_2O_3					
	GGA	−0.0330	0.3912	0.1521	0.3800

B. Lattice and internal parameters

The lattice parameters have been calculated using the Murnaghan equation of state, appropriate for crystals at moderate compressions,[12] with an accuracy of 0.001 Å. Table I lists the calculated lattice parameters for oxides in comparison with experimental values, where available. The LDA and GGA perform as expected (−1 and +1%, respectively) for yttria, whereas LDA gives a rather contracted lattice for the other oxides. Overall the agreement between GGA and experiment is within 1% or better.

In Table II we list the internal parameters of bixbyite-structure yttria and lutetia and in Table III those of hexagonal lanthania, as defined in Ref. 10. In the bixbyite structure, all oxygens are fourfold coordinated with four different distances from the cations (2.19, 2.22, 2.24, and 2.29 Å in lutetia, and 2.25, 2.28, 2.30, and 2.36 Å in yttria). The cations are all six-fold coordinated; one cation out of four in the primitive cell has six neighboring oxygens at the same distance (2.24 Å in lutetia, 2.30 Å in yttria), the others have three pairs of neighboring oxygens at three distinct distances (2.19, 2.22, and 2.29 Å in lutetia, 2.25, 2.28, and 2.36 Å in yttria); cation second neighbors are other cations at 3.46 Å. An X-ray absorption fine-structure (XAFS) experiment should therefore detect, in the radial pair distribution function, four quasi-nearest-neighbor peaks centered within approximately 0.1–0.2 Å of each other, all at the same intensity, for both oxygen and the cation x-ray edges (for the cation this is due to 1/4 of them having 6 neighbors and 3/4 just two neighbors).

C. Relative stability: bixbyite vs hexagonal

The relative stability of the cubic bixbyite structure against the hexagonal lanthanum-oxide structure is investi-

TABLE III. Internal parameters for hexagonal La_2O_3. Experimental data are from Ref. 10.

La_2O_3		u	v
	LDA	0.2446	0.6453
	GGA	0.2471	0.6452
	exp	0.245	0.645

gated for yttria and lanthania. Calculations are performed in the LDA, at the nominal[4] cutoff of 250 eV for both oxides. The result is that bixbyite Y_2O_3 is more stable by 0.14 eV per formula unit over the hexagonal phase; conversely, hexagonal La_2O_3 is more stable than bixbyite by 0.20 eV per formula unit. In both cases the volume per formula unit in the bixbyite structure is about 11–12% larger than in the hexagonal phase. These results agree with the experimental findings and confirm the ability of this kind of calculations to predict structural preferences even for complex structures (see Note added in proof).

D. Thermodynamical stability in contact with Si

To predict the thermodynamical stability of the oxides in contact with Si, their formation enthalpies are calculated from the computed energies per formula unit (the formation enthalpy is the energy difference between a compound and the parent bulk phases of the constituents, a negative value indicating stability of the compound), and compared to those of competing compounds involving silicon. For amorphous silica, we take the experimental[13] value $\Delta H_{SiO_2} = -8.2$ eV.

The weighting factors for the various enthalpies are stoichiometric coefficients arising from chemical equilibrium conditions. For example, the reaction involving yttrium oxide and silica is

$$2\,Y_2\,O_3 + 3\,Si \leftrightarrow 4\,Y + 3\,SiO_2\,.$$

Indicating with E the total energies of the various bulk phases involved, the reaction is balanced if

$$\begin{aligned} 4\,E_Y + 3\,E_{O_2} + 3\,E_{Si} + 2\,\Delta H_{Y_2O_3} \\ = 4\,E_Y + 3\,E_{Si} + 3\,E_{O_2} + 3\,\Delta H_{SiO_2}, \end{aligned} \tag{1}$$

or

$$\Delta H_{Y_2O_3} = \tfrac{3}{2}\,\Delta H_{SiO_2}. \tag{2}$$

That is, yttria is stable against decomposition into silica and metallic yttrium if $\Delta H_{Y_2O_3} < \tfrac{3}{2}\Delta H_{SiO_2}$. Similar relations between enthalpies are determined by the equilibrium of reactions having yttrium silicides and silicates as final products:

$$\Delta H_{Y_2O_3} = 2\Delta H_{YSi_2}, \tag{3a}$$

$$\Delta H_{Y_2O_3} = \tfrac{2}{5}\Delta H_{Y_5(SiO_4)_3O}\,. \tag{3b}$$

Analogous relations with the same coefficients hold for lanthanum and lutetium oxides. In the case of ytterbium oxide, instead, the equilibrium conditions are simpler:

$$\Delta H_{YbO} = \frac{1}{2}\Delta H_{SiO_2} \tag{4a}$$

$$\Delta H_{YbO} = \Delta H_{YbSi_2} \tag{4b}$$

TABLE IV. Formation enthalpies (eV per formula unit) of oxides vs silicides and silicates, multiplied by the weighting factors given in Eqs. (2) to (4). The experimental formation enthalpy of silica is −8 eV.

Cation	oxide	silicide	silicate
Y	−19.41	−2.96	−29.41
La	−18.84	−3.87	−29.74
Lu	−20.18	−2.30	
Yb	−7.15	−1.07	

Calculated enthalpies are converged to better than 10 meV in all cases, occasionally better than 1 meV. In general, formation enthalpies calculated within GGA-DFT are in reasonable agreement with experiment, so the present results should be quantitatively reliable (thermodynamic tables[13] give $\Delta H_{Y_2O_3} = -19.7$ eV/formula unit and $\Delta H_{La_2O_3} = -23$ eV/formula unit, which compare favorably to fairly with our values of −19.4 and 18.4 eV, respectively).

For as regards stability, the results summarized in Table IV indicate that all oxides are far more stable than silica, and that their decomposition into silica and metal is not energetically favorable. Furthermore, all oxides are stable against silicide formation, as the formation enthalpies of silicides are minor in all cases on the scale set by the oxides. However, yttria and lanthania are not stable against the formation of silicates. While we did not study directly Lu and Yb silicates, from the data available it seems quite reasonable to extend this conclusion to those cations as well.

Our predictions are for zero temperature, but we do not expect entropic effects at finite temperature to change any of our conclusions. While this is obvious for the formation enthalpies of the various compounds (silicides, silicates, etc.), which differ by several electron-volt, it is also highly probable for the energy order of the bixbyite and hex phases, which would require unlikely large entropy differences (~10 k_B at room temperature) to be reversed.

E. Electronic structure

Here we present the orbital- and site-projected density of states (DOS) of yttrium and lanthanum oxides to give a feeling for the nature of the electronic states in these systems. The typical DOS projected on oxygen atoms in both Y_2O_3 and La_2O_3 has the expected dominant p character in the upper valence band (not shown). As to the cations, the orbital-projected DOS at a La atom in (1/3,2/3,u) in Wyckoff

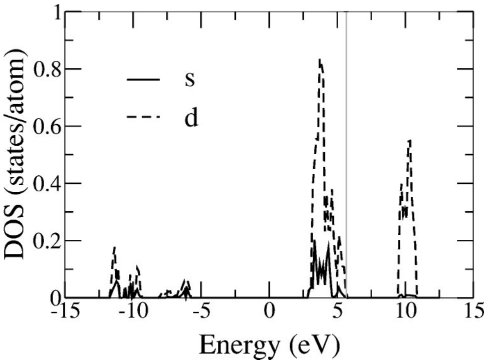

FIG. 2. s and d orbital-projected DOS at La $(\frac{1}{3},\frac{2}{3},u)$ in La_2O_3.

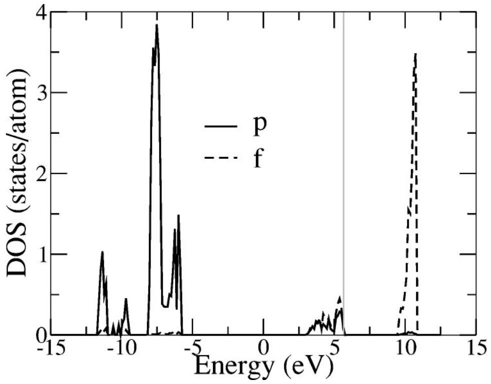

FIG. 3. *p* and *f* orbital-projected DOS at La $(\frac{1}{3},\frac{2}{3},u)$ in La_2O_3.

coordinates[10] in La_2O_3 is displayed in Fig. 2 for *s* and *d* orbitals, and in Fig. 3 for *p* and *f* orbitals (the projected DOS for the other independent La atom is quite analogous). The thin gray line indicates the valence-band top. The band gap is in both cases around 4 eV. Experimental values (carrying considerable uncertainties so far) are[2] 5.7 eV for La_2O_3 and 6.2 eV for Y_2O_3. This underestimate is due to the well-known DFT error in predicting fundamental energy gaps.[14] The most sizable character in the upper valence band is *d* like, with some lesser, but comparable, admixture of *s* and *f* states (the latter are unbound in the atom); the conduction band, while containing some *d* admixture, is prevailingly *f* like.

Figure 4 displays instead the orbital-projected DOS of one of the two independent Y cations in bixbyite-structure yttria (the other independent yttrium site is essentially equivalent). As typical of transition-metal oxides, the conduction band is mostly cation *d* like. The main qualitative difference thus stems, not unexpectedly, from the different contribution of *f* and *d* states in the La and Y compound. The *f* like conduction band appears to be narrower and flatter, thus presumably having a larger effective mass, which may be conducive to the use of La compounds as a gate oxide.

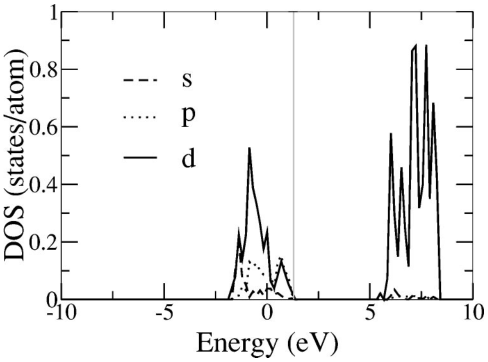

FIG. 4. Orbital-projected DOS at Y $(\frac{1}{4},\frac{1}{4},\frac{1}{4})$ in Y_2O_3.

IV. SUMMARY

We have reported calculations on the structure and energetics of a selection of rare-earth and transition-metal oxides. Detailed structural data were provided. The stability in contact with Si is evaluated: the oxides are stable against decomposition into silica and silicides, not against silicate formation, which is presumably to be expected during deposition of the oxide on Si.

Note added in proof. After submission we completed calculations for lutetia in the hex and bixbyite phases: as for yttria and unlike lanthania, in agreement with experiment we find bixbyite lowest in energy.

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[1] S. Thompson, P. Packan, and M. Bohr, Intel Technology J., 3rd quarter 1998 (http://www.intel.com/technology/itj/q31998/pdf/trans.pdf); D.A. Buchanan, IBM J. Res. Dev. **43**, 245 (1999); G.D. Wilk, R.M. Wallace, and J.M. Anthony, J. Appl. Phys. **89**, 5243 (2001).

[2] *Alternative Gate Dielectrics for Microelectronics*, edited by G. Wilk and R.M. Wallace, special issue of Materials Research Society Bulletin **27** (3) (2002).

[3] G.E. Moore, Electronics **83**, 114 (1965).

[4] G. Kresse and J. Furthmüller, Phys. Rev. B **54**, 11 169 (1996); http://cms.mpi.univie.ac.at/vasp/

[5] P.E. Blöchl, Phys. Rev. B **50**, 17 953 (1994); G. Kresse and D. Joubert, *ibid.*, **59**, 1758 (1999).

[6] H.J. Monkhorst and J.D. Pack, Phys. Rev. B **13**, 5188 (1976).

[7] M. Methfessel and A.T. Paxton, Phys. Rev. B **40**, 3616 (1989).

[8] A. Svane, W.M. Temmerman, Z. Szotek, L. Petit, P. Strange, and H. Winter, Phys. Rev. B **62**, 13 394 (2000).

[9] R. Wyckoff, *Crystal structures* (Wiley, New York, 1963), Vol. 1.

[10] R. Wyckoff, *Crystal structures* (Ref. 9), Vol. 2.

[11] R. Wyckoff, *Crystal structures* (Ref. 9), Vol. 4.

[12] F.D. Murnaghan, Proc. Natl. Acad. Sci. U.S.A. **30**, 244 (1944).

[13] E. Lax and C. Synowietz, *D'Ans-Lax Taschenbuch für Chemiker und Physiker* (Springer, Berlin, 1967).

[14] See, e.g., the review by W.G. Aulbur, L. Jönsson, and J.W. Wilkins, Solid State Phys. **54**, 1 (2000).