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Oxide interfaces for novel electronic applications

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Abstract

Oxide heterostructures have been shown to exhibit unusual physics and hold the promise of novel electronic applications. We present a set of criteria to select and design interfaces, particularly those that can sustain a high-density two-dimensional electron gas (2DEG). We describe how first-principles calculations can contribute to a qualitative and quantitative understanding, illustrated with the key issue of band alignment. Band offsets determine on which side of the interface the 2DEG will reside, as well as the degree of confinement. We use hybrid density functional calculations to determine the band alignments of a number of complex oxides, considering materials with different types of conduction-band character, polar or nonpolar character and band insulators as well as Mott insulators. We suggest promising materials combinations that could lead to a 2DEG with optimized properties, such as high 2DEG densities and high electron mobilities.

1. Introduction

The next generation of electronic devices faces the challenge of adequately containing and controlling extremely high charge densities within structures of nanometer dimensions. Silicon-based electronics has been extremely successful. Silicon metal–oxide–semiconductor field effect transistors (MOSFETs) are based on a two-dimensional electron gas (2DEG) that is formed at the interface between Si and a dielectric, and electrostatically controlled by a gate voltage. As devices are scaled to atomic dimensions the capacitance density and the switched

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current density must both increase [1]. Atomic-scale transistors must be thin and be able to control extremely high charge densities ($> 10^{13} \text{ cm}^{-2}$). Silicon devices typically have 2DEG densities around 10^{12} cm^{-2} . Nitride-based devices can sustain densities an order of magnitude higher. To go beyond that, novel materials that can support extremely high charge densities and high electric fields need to be explored.

Complex oxides have recently emerged as an attractive materials system to support these developments. The demonstration of a 2DEG at the $\text{SrTiO}_3/\text{LaAlO}_3$ (STO/LAO) interface [2–4] has triggered an avalanche of research. 2DEG densities up to $3 \times 10^{13} \text{ cm}^{-2}$ can be achieved in STO/LAO, but unprecedentedly high densities of $3 \times 10^{14} \text{ cm}^{-2}$ have since been demonstrated at $\text{STO}/\text{GdTiO}_3$ (STO/GTO) interfaces [5]. In addition, the interfaces have been reported to display unique behavior such as ferromagnetism [3] and superconductivity [6]. Metal–insulator (Mott) transitions that are inherent to some of the complex oxides could offer even greater prospects for enhanced functionality or novel device concepts [7, 8].

The materials and heterostructures that have been explored to date are clearly only a small subset of the vast number of materials combinations that could, in principle lead to interesting phenomena. Systematic experimental exploration of all of these combinations is clearly unfeasible—not least because high-quality growth techniques have proven essential to bring out the unique properties [5, 9]. Computations and simulations can greatly assist in the process of identifying suitable prospects: first and foremost, by building greater understanding of the phenomena, so that searches can be better informed and more focused—but also by screening and exploring a greater number of materials and junctions than is experimentally practical. Such a search should be guided by a set of criteria that the materials and their heterostructures should satisfy to develop a high-performance 2DEG-based device.

In this paper we propose a list of physical criteria that complex oxides and their interfaces should meet and explain how these requirements can be used in conjunction with electronic structure theory and device simulations to intelligently sort through candidate systems. We will illustrate the approach with select examples of cutting-edge first-principles calculations based on density functional theory (DFT). In particular, we present comprehensive data for band alignments across a range of oxides that are being considered as candidate materials. Since the band offsets at heterojunctions control confinement, accurate knowledge of these quantities is a prerequisite for device design.

The attention that has been focused on oxides and their interfaces is of course based on the tremendous progress that has been made in epitaxial growth [2, 10–12]. These achievements provide us with confidence that sensible proposals for new structures based on computational designs stand a good chance of being experimentally executable.

Section 2 discusses the fundamentals of formation of a 2DEG at an interface, particularly the case where electrons are provided by ‘polar-discontinuity doping’. In section 3 we present our list of criteria. Section 4 elaborates on band alignments, first explaining the first-principles methodology, then summarizing the results. Section 5 summarizes the paper and provides an outlook.

2. Formation of a two-dimensional electron gas and polar discontinuity doping

To realize a 2DEG, two ingredients are required: confinement and a source of electrons. Confinement is provided by forming a heterojunction: electrons are located in a semiconducting

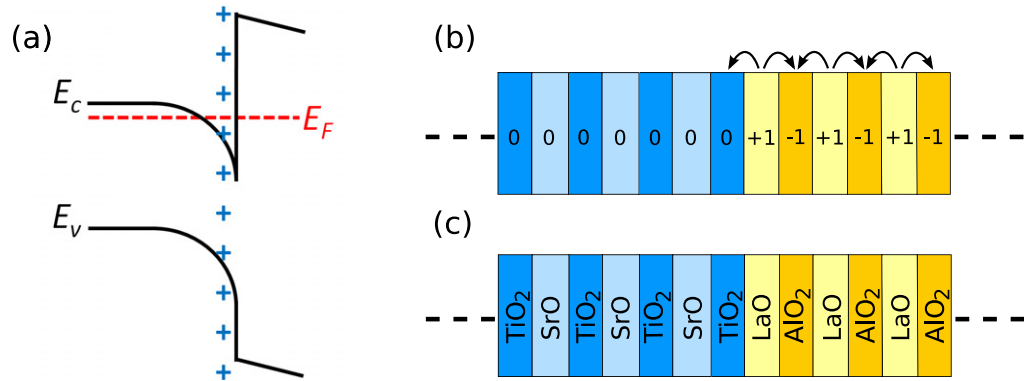


Figure 1. (a) Illustration of charge at a heterojunction resulting from an intrinsic interface layer of donors, providing a high density of carriers as well as electrostatically confining them to the interface. (b) Schematic representation showing an interface between a nonpolar and a polar material. Charges on layers are indicated, and arrows indicate electron transfer between layers in the polar material. At the interface, an excess $1/2$ electron is present. (c) Polar discontinuity at the STO/LAO interface.

layer in which the energy of the conduction band (CB) is lower than in an adjacent barrier material. These electrons are confined to the vicinity of the interface in a (roughly) triangular potential well, which is formed by electrostatics (through application of a gate voltage) and/or because electrons are attracted to the interface by positive charges. As to the source of carriers: in a depletion-mode MOSFET, the carriers in the channel are provided by doping of the channel, while in the more common enhancement-mode MOSFET, they arise from electrostatic manipulation of the band structure: a positive gate voltage pulls the CB below the Fermi level, creating an inversion layer in the p-type substrate in which electrons from the n-type source can flow [13]. In high electron mobility transistors (HEMTs), the electrons are typically provided by modulation doping [13]. III-nitride based transistors offer higher confinement and 2DEG densities due to polarization fields intrinsic to the wurtzite structure of the nitride semiconductors. Modulation doping has recently been demonstrated for an oxide heterojunction between STO and $\text{SrTi}_{0.95}\text{Zr}_{0.05}\text{O}_3$ [14].

One could hypothesize a structure in which the source of electrons would be intrinsic to the heterojunction itself: i.e. an atomically thin layer of donors right at the interface between the two materials (see figure 1(a)). This would have the advantage of providing a very high density of electrons right where they are needed, and simultaneously confining them due to electrostatic attraction of the electrons to the positively charged donor centers. One might think that delta doping of semiconductors could achieve this goal; however, in practice delta doping is impossible to achieve with atomic precision, and any randomness in the doping profile will cause a high degree of scattering and lower the mobility.

It turns out to be possible, however, to create such a layer of delta doping intrinsically at the interface between two materials. As a generic example, consider two materials, one polar and the other nonpolar. Assume these materials have a cubic crystal structure, with lattice parameters that are close enough that a properly bonded interface can be formed. Looking along the (001) direction, we can picture the nonpolar material as consisting of atomic layers that are all charge neutral (i.e. the electronic charge in each layer exactly equals the ionic charge). The polar material, on the other hand, consists of layers that are charged; in the example of figure 1(b),

charges of +1 and -1 per unit cell are assumed. The presence of such charges arises, of course, from an imbalance in the electronic and ionic charges, and arises in any material that has at least partially ionic character. Many ionic crystals exhibit such polar behavior, although regular semiconductors such as GaAs can also be considered in this fashion [15]. The local charges arise from the fact that electrons in one layer are transferred to adjacent layers: if a layer ends up with a net positive charge of +1, it is because $1/2$ electron has been transferred to the layer to its left, and $1/2$ electron to the layer to its right, leaving those layers with a net negative charge.

The bulk of the material remains, overall, charge neutral. But an interesting phenomenon occurs if an interface is formed between a polar and a nonpolar material (figure 1(b)): the layer in the polar material adjacent to the nonpolar material donates $1/2$ electron to the right, i.e. to a ‘bulk-like’ layer in the polar material. It is also trying to donate $1/2$ electron to the layer to its left—but that layer belongs to a nonpolar material and does not need that electron to satisfy its bonding. This electron is therefore in principle available as a free electron, and the atomic layer on the polar side of the interface effectively acts as a layer of donors with a density of $1/2$ of the areal density of atoms at the interface. In most materials, this is on the order of a few times 10^{14} cm^{-2} ; i.e. a huge density compared to what is typically achieved in 2DEGs at conventional interfaces. We will refer to this situation as ‘polar discontinuity doping’ of interfaces.

In case all of this sounds far-fetched: a concrete example was discussed in the context of conventional semiconductors such as Ge and GaAs as early as 1978, by Harrison *et al* [16]. Unfortunately, an implementation with such semiconductors has not proved feasible, mainly because the interfaces have a tendency for intermixing and/or the surfaces of semiconductors tend to be heavily reconstructed, rendering it difficult to obtain the abrupt interfaces required for self-doping. We note that the nitride interfaces, such as the AlGaIn/GaN interfaces employed in HEMTs, do not exhibit polar-discontinuity doping. The nitrides, because of their wurtzite structure, exhibit *polarization discontinuities*, which enhance the density and confinement of the 2DEG—but (contrary to some early reports) the electrons in this 2DEG still need to be externally supplied, either by extrinsic doping or from surface states.

Interestingly, perovskite oxides do seem to enable the formation of the abrupt polar/nonpolar interfaces required for self-doping; indeed the by now famous STO/LAO interface falls into this category, as illustrated in figure 1(c). Our recent work, based on a combination of first-principles calculations and macroscopic Schrödinger-Poisson simulations, demonstrated that the electrons in the 2DEG are truly intrinsic to the STO/LAO interface and generated by the polar discontinuity [17]. This work also demonstrated that the electrons in the STO CB are delocalized over several atomic layers—in contrast to models where electrons are purported to reside in ‘ Ti^{3+} ’ states on the STO side. Such a localization of electrons would be inconsistent with the high mobilities that have been observed.

3. Criteria

In this section we describe a set of key parameters and criteria that determine the formation of a 2DEG at a given interface, or influence the 2DEG characteristics. These include the structural quality, the polar/nonpolar discontinuity at the interface, the electronic structure of the individual materials, band alignments and parameters that affect the mobility of the electrons in the 2DEG.

3.1. Structural quality

3.1.1. Lattice parameters. The lattice parameters of the materials to be joined at an interface should be close enough to allow for strong epitaxial bonding without formation of misfit dislocations. Perfect matching is not required; in fact, a slight lattice mismatch can be advantageously used to induce pseudomorphic strain that can be used in band-structure engineering, as discussed in section 3.5.1 below. Strain has also been found to be a useful parameter to affect other properties such as ferroelectricity, as has been established both experimentally [18] and computationally [19].

3.1.2. Point defects. Point defects, in particular oxygen vacancies, have often been invoked as sources of electrons in the STO/LAO 2DEG [20–24]. Our first-principles calculations indicate that both in STO and LAO oxygen vacancies have relatively high formation energies [25, 26]. However, this is an issue that would need to be evaluated in new materials being considered for heterostructures, and the methodology for addressing point defects is well established [27, 28].

3.1.3. Intermixing. Cation intermixing has been shown to occur for STO/LAO interfaces [29, 30], and recent experiments also indicate a strong effect of cation (non)stoichiometry on the 2DEG density [31]; such intermixing or (non)stoichiometry will interfere with the ability to obtain the full density 2DEG. Based on DFT calculations (in the generalized gradient approximation) Qiao *et al* [30] reported that intermixed interfaces are thermodynamically more stable than abrupt interface. This is a common feature at semiconductor interfaces; it does not mean that abrupt interfaces cannot be obtained using suitable growth techniques. Recent abrupt STO/GTO interfaces grown with molecular beam epitaxy without evidence of intermixing have been reported [5, 32].

3.2. Avoiding the ‘polar catastrophe’

The interface between STO and LAO has often been described in terms of a ‘polar catastrophe’ [29]. This stems from regarding the system purely in terms of the ionic charges. In the description outlined in section 2, no divergence of the potential occurs if the electrons that are generated by the polar discontinuity are kept (in CB states) locally at the interface. A divergence in potential only occurs if a net charge is present at the interface—which would be a consequence of electrons leaking away.

Electrons will leak away if the system is such that those electrons can be transferred to unoccupied states at lower energy. When a thin layer of LAO is grown on STO, the LAO surface (which is usually AlO_2 -terminated, as in figure 2(a)) exhibits partially occupied surface states in the lower part of the band gap, i.e. well below the energy of the electrons in the CB of STO. Electrons therefore prefer to occupy those states; the transfer of electrons from the interface to the surface sets up an electric field across the LAO layer, as shown in figure 2(b). This leads to a potential that increases toward the surface in the LAO layer, up to the point where the partially occupied surface states cross the Fermi level. The fraction of electrons that are transferred depends on the energetic position of the surface states and the thickness of the LAO layer. Below a critical layer thickness, *all* of the electrons are transferred to the surface, consistent with experimental observations [33]. Only for large enough thickness is the potential buildup sufficient to bring the surface states above the Fermi level. This situation has often been

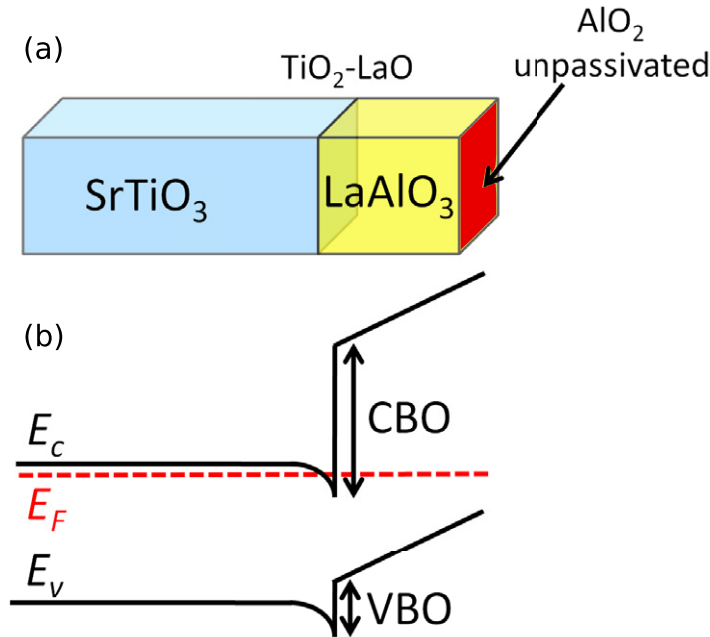


Figure 2. (a) Schematic representation of a structure with a thin LAO layer on top of STO. (b) Corresponding band diagram. The LAO surface serves as a sink of electrons when unpassivated, reducing the 2DEG density.

described as charge transfer *from* the LAO surface *to* the interface [34, 35], i.e. as if the surface acts as a source of electrons. However, as should be evident from section 2, the electrons actually originate at the interface.

We elaborated on this model in [17]. It also explains why the observed 2DEG density at STO/LAO interfaces is one order below the expected value of 1/2 electron per unit cell [20, 23, 33, 36]. For the present purposes, the question is: how can the loss of electrons from the interface be avoided? The key, clearly, is to avoid the presence of unoccupied states that drain away electrons from the interface. This can be addressed in two ways.

3.2.1. Surfaces. If the overlayer (the layer with the larger band gap) is terminated at a surface, unoccupied surface states in the band gap should be avoided. First-principles calculations can assess surface reconstructions and the associated electronic structure. Such calculations have been performed for many semiconducting systems (see, e.g. in nitrides [37]), but for oxides very few studies have been performed to date. This will be a very fertile and necessary area of investigations.

It should clarify, for instance, why heterostructures with a GTO, rather than an LAO overlayer, exhibit a 2DEG with a density of $3 \times 10^{14} \text{ cm}^{-2}$ [5]. Clearly, the GTO surface behaves differently from the LAO surface, and first-principles calculations can address this difference. The calculations can also address how modifications of the surface could prevent surface states from serving as a sink of electrons [17].

3.2.2. Interfaces. In [17] we demonstrated that STO/LAO/STO double heterostructures, with mirror-symmetric $\text{TiO}_2\text{-LaO}$ interfaces, lead to a 2DEG density corresponding to 1/2 electron

per unit cell at each interface. One can explain this based on the symmetry of the structure, which forces the electrostatic potential to be essentially flat across the LAO layer (as opposed to exhibiting a slope); Gauss' law then tells us that the net charge density at each interface (integrated over the width of the 2DEG) has to be zero, i.e. no electrons leak away from the interface. An alternative viewpoint is that the interface that terminates the LAO layer does not contain any unoccupied states that can act as a sink for electrons.

In STO/LAO, growing such symmetric interfaces has proven very difficult [38]. Once again, STO/GTO has proven to be different, with superlattices containing a number of periods having been demonstrated [5]. One reason is that symmetric interfaces are inherent in the STO/GTO system, due to the TiO_2 layer that is common to both the STO and GTO structure, i.e. there is only one type of interface possible, containing an $\text{SrO}/\text{TiO}_2/\text{GdO}$ sequence of layers. In contrast, STO/LAO exhibits two types of interfaces, namely SrO/AlO_2 and TiO_2/LaO , and it is apparently not possible to control the growth process to force symmetric interfaces.

3.3. Electronic structure

3.3.1. Density of states. Achieving a high electron density in the 2DEG obviously depends on the density of states (DOS) of the CB. Oxides with CBs comprised of transition-metal d states (as is the case in STO) will tend to provide high DOS, since d bands tend to have relatively low dispersion. Low dispersion also implies large effective mass, which could limit mobility. Fortunately, these issues can be decoupled, as discussed in section 3.5.1 below. In oxides with CBs arising from sp bonding, the DOS should be carefully evaluated. Accurate first-principles calculations provide reliable band structures, which in turn directly determine DOS. For modeling purposes, effective masses can also be extracted from the calculations [39]. We note that parabolic band models are often inadequate.

3.3.2. Wavefunction spread and dielectric constant. Tight confinement of the electrons in the 2DEG is beneficial since it avoids capacitance degradation. The characteristic length for the wave-function spread decreases with increasing effective mass. Just like for the DOS, a high effective mass in the direction perpendicular to the interface is thus beneficial.

The dielectric constant is also a key parameter in confinement: the higher the dielectric constant, the less tightly the electrons are confined to the interface. An interesting complication arises due to the fact that dielectric constants can depend on the strength of the electric field [40]. The tight confinement of electrons means that the confining potential well is narrow, corresponding to large electric fields, which in turn will affect the confinement of the 2DEG near the interface. The confinement problem therefore needs to be solved self-consistently. For STO, the dielectric constant is known to decrease with applied field [41].

3.3.3. Breakdown strength. To render the 2DEG useful for device applications, being able to modulate these high electron densities is essential. This requires a high breakdown strength, which is the product of dielectric constant and breakdown field [42]. Breakdown field tends to scale as the square of the band gap. Conventional semiconductors such as Si and GaAs exhibit breakdown fields on the order of 0.1 MV cm^{-1} , while the value for GaN ($E_g = 3.5 \text{ eV}$) is around 3 MV cm^{-1} . The perovskite oxides discussed here have band gaps comparable to that of GaN, so we expect a similarly high breakdown field. Since the dielectric constants of complex oxides are larger than those of conventional semiconductors, the breakdown strengths will be superior.

3.3.4. Metal/insulator transitions. Some of the complex oxides in which the CB is comprised of d states behave as Mott insulators, i.e. an occupied d band is split into an occupied lower Hubbard band (valence band (VB)) and an unoccupied upper Hubbard band (CB). Changing the occupation of these d states can trigger a metal–insulator transition [44], which has been proposed as the basis for a novel ‘charge-gain’ transistor structure [7]. The physics of these Mott insulators is an active area of research, and first-principles calculations can contribute to both qualitative and quantitative understanding, as will be demonstrated below.

3.3.5. Alloying. Forming alloys increases the flexibility in device design and band-structure engineering, as was already demonstrated with the example of modulation doping at STO/SrTi_{0.95}Zr_{0.05}O₃ interfaces [14]. To first order, the electronic properties of alloys can be obtained by linear interpolation between the end compounds but nonlinearities (such as band-gap bowing) can often be significant, and can be obtained from first-principles calculations [43].

3.4. Band alignments

In our discussion of the STO/LAO interface in section 2 and figure 2, we showed a band alignment in which the CB minimum (CBM) in STO lies well below the CBM in LAO. Given the large difference in band gaps between STO (3.2 eV) [45] and LAO (5.6 eV) [46], and considering that the VB offset is expected to be small (because the VB states are mainly derived from 2p states of oxygen, which is the common anion [47]), this seems like a reasonable assumption. However, for many other materials combinations this alignment is not *a priori* known. The alignment is a key parameter for heterojunction design, both qualitatively (since it determines which material the electrons will reside in) and quantitatively (since the CB offset needs to be sufficiently large to ensure adequate confinement).

While the alignment can be determined experimentally, very few results have been reported for oxide interfaces to date. First-principles calculations are a powerful tool for determining such alignments, as has been demonstrated in the many calculations reported for semiconductors [48–50]. Because of the importance of this topic, and to serve as an illustration of the power of the first-principles approach, we devote a separate section of this paper to the band alignment problem (see section 4).

3.5. Mobility

For electronic devices, the mobility of electrons in the 2DEG needs to be high. This is actually a major problem for many oxides: low-temperature mobility is high (32 000 cm² V^{−1} s^{−1} in STO at 1.8 K [51]) but decreases to low values at room-temperature (10 cm² V^{−1} s^{−1} in STO at 300 K [52]). While cooling to cryogenic temperatures may be acceptable in some applications, widespread adoption will clearly depend on the ability to achieve higher room-temperature mobilities. Two main factors enter: carrier effective masses and scattering.

3.5.1. Effective mass. To achieve high mobility, the effective mass of carriers should be small. At first sight this seems incompatible with the requirement for a high DOSs, but as pointed out in [53], clever band-structure engineering can circumvent the issue. Effective masses may exhibit an anisotropy, either intrinsic due to the symmetry of the material, or induced by strain. The orientation of the heterostructure should then be chosen such that light electron masses

occur in the in-plane direction (particularly, the transport direction), while the out-of-plane direction should exhibit heavy electron masses, which lead to large densities of states.

One way to avoid the problem of electrons occupying the Ti 3d-derived bands would be to replace STO with a material that instead contains 4d or 5d-derived bands (as in SrZrO₃ or SrHfO₃), or s or p-derived bands (as in BaSnO₃). The less localized nature of these states will result in smaller electron effective masses, potentially leading to higher mobilities.

Strain can be used to engineer the ordering of CB valleys as well as effective masses. Strain can be induced through pseudomorphic growth, in which a material is grown epitaxially on a substrate with a different lattice constant. This leads to tensile or compressive strain as the in-plane lattice constant is expanded or contracted to match that of the substrate, and the out-of-plane lattice constant adjusts according to the elastic properties of the layer. This approach is widely used in silicon technology, particularly in SiGe heterostructures; in addition, other methods of process-induced strain have been developed in silicon technology [54].

Understanding the effects of strain on the band structure is thus of great importance, and first-principles calculations can yield detailed and comprehensive information. For STO, we reported strain-induced changes of the energetic ordering and effective mass of CB states results based on hybrid functional calculations (a methodology discussed in more detail in section 4.2) [39].

3.5.2. Scattering. Ionized impurity scattering can lead to strong decreases in mobility; this is an important reason why modulation doping (in which carriers are located in a different spatial region from the ionized donors) is widely applied in HEMTs. One might think that the high density of effective donor centers at the polar/nonpolar interface (figure 1(a)) would lead to unacceptably high scattering rates. This does not happen, however, because these charged centers are arranged in a perfectly periodic array, which does not lead to scattering—the analogy being the charged atomic cores that constitute the periodic lattice in which valence electrons move in a crystal. However, any deviation from periodicity (e.g. due to interfacial roughness) will lead to reductions in mobility.

In addition to impurity scattering, scattering from optical phonons leads to a strong reduction of mobility at finite temperatures, responsible for the large difference in mobility at low and room temperatures.

4. Band alignments

Band alignments of complex oxides can be obtained by a variety of experimental methods; to date, mainly x-ray photoelectron spectroscopy (PES) has been employed, but the focus has been almost exclusively on STO/LAO. First-principles theory is a powerful tool for obtaining these offsets, but the calculated values for VB offsets that have been reported to date differ significantly in both magnitude and sign. The sign determines whether the VB maximum (VBM) is higher in STO or in LAO; we adopt the convention that at an A/B interface the VB offset is positive if the VBM in B is higher in energy than in A. DFT calculations, using either the local density approximation (LDA) or the generalized gradient approximation (GGA) approximation, for superlattices with symmetric TiO₂–LaO terminations resulted in VB offsets of -0.15 eV (GGA) [55], 0.51 eV (LDA) [56] and 0.9 eV (GGA) [57]. Qiao *et al* (GGA) [30] also reported a VB offset of 0.7 eV for a perfect interface, and 0.2 eV for an interface that included cation intermixing.

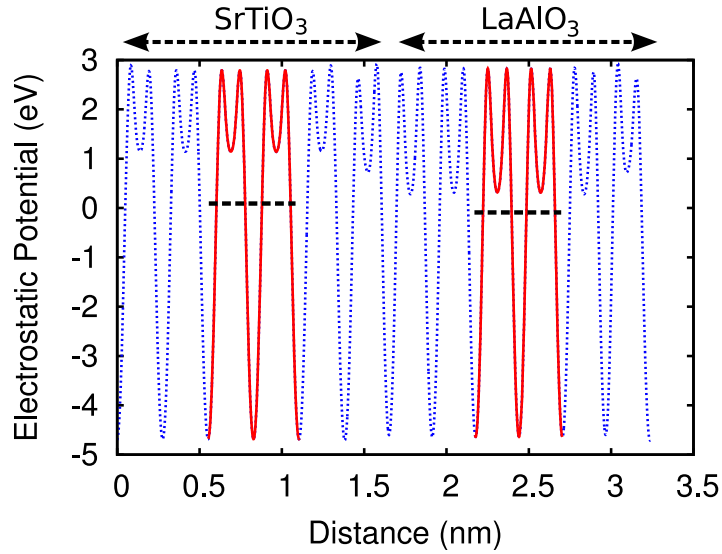


Figure 3. Planar-averaged electrostatic potential plotted along the [110] direction for the STO/LAO heterostructure (blue dotted line). Bulk-like regions in the center of each layer are highlighted (red solid lines), and the average potentials determined for these regions are shown as dashed black lines.

In the following section we will outline the methodology followed in our own calculations. We note that band-alignment results are relevant not only for the case of polar-discontinuity-doped (polar/nonpolar) heterostructures but also for interfaces between nonpolar materials, such as STO/SrZrO₃ [58]. As noted in section 2, modulation doping at STO/SrTi_{0.95}Zr_{0.05}O₃ interfaces was recently reported [14].

4.1. Methodology

Band alignments are in principle properties of a specific interface; i.e. a new calculation should be performed for every pair of materials. In practice however, it turns out that band offsets for lattice-matched nonpolar interfaces exhibit transitivity [48, 50, 59] i.e. if the offsets A/B and B/C are known, the offset A/C can be derived. This implies that the offsets can be obtained based on the alignment of the band structure of each material on an absolute energy scale (e.g. with respect to the vacuum level).

Surface calculations can in principle be used to obtain this alignment [43, 60]. In the present work we obtain the band alignments from explicit interface calculations [49]. First, separate calculations for each bulk material are performed in which the VBM and CBM are determined with respect to the average electrostatic potential in the respective material. Then, the average electrostatic potentials in the two materials are aligned by performing a calculation for a superlattice and determining the difference in the average electrostatic potential in the bulk regions of the heterostructure, i.e. far enough from the interface (see figure 3). Therefore, the thickness of each material in the superlattice has to be large enough to contain a bulk-like region.

In the present work, the band alignments were determined by systematically using STO as one of the materials in the interface calculations. STO was chosen because it is widely used as

a substrate due to the availability of large single crystals with high crystalline quality. It also exhibits reasonably good lattice matching to the other materials considered here.

Usually the two materials have different equilibrium lattice parameters, posing an additional complication in the calculation of band alignments. In this case, we perform the interface calculation fixing the in-plane lattice parameters to those of the non-STO material, and allow the out-of-plane lattice parameter of STO and the atomic positions near the interface (cation layer of each material, and interface oxygen layer) to relax.

In general, the volume of the STO in the superlattice will end up at a value different from its equilibrium value due to the Poisson effect, i.e. a material that is compressed (stretched) in the plane tends to expand (contract) in the perpendicular direction according to the Poisson ratio. The superlattice calculations thus provide the alignment of the electrostatic potential between strained STO and another material in its equilibrium structure. Combined with bulk calculations for STO in the same strain state, this provides the band alignment between a complex oxide in equilibrium and a strained STO overlayer.

We are often interested, however, in the ‘natural’ band alignment between the materials at their equilibrium volume. To obtain this alignment, we have to account for the effect of the volume change in the STO. This is done by performing a similar calculation as for the band alignment at a heterojunction, but instead calculating the alignment of the electrostatic potential between strained and unstrained volumes of the same material [61], in a homojunction supercell with equilibrium in-plane lattice parameters.

Finally, we discuss the issue of the interface orientation. Many of the oxide interfaces grown to date have been grown along the [001] direction, where a polar discontinuity occurs at the interface. However, if we carry out the calculations for a superlattice including this polar discontinuity, we unavoidably introduce the ionic doping at the interface and the compensating 2DEG, and the presence of these charges and the resulting dipole could affect the calculated band alignment. For the record, we are of the opinion that these additional effects are not part of the true intrinsic band alignment, for reasons that have been discussed at length in previous publications [48, 59]. Indeed, in the absence of the polar-discontinuity-doping effects, we expect only small differences between band alignments for different orientations. We have tested this in the case of alignments between nonpolar materials, in which the 2DEG is absent in the [001] direction, and found that calculations for this direction (with up to eight layers of each material in the superlattice) produce results that are within 0.05 eV of those obtained for [110].

One could argue that the 2DEG-related effects may be present in experimental determinations of the offsets—however, that is an issue that depends on the details of how the experiments are carried out. In the calculations, if we did include these effects by using the [001] direction, we might also introduce additional uncertainties due to incomplete description of the 2DEG in our limited-width superlattices. Indeed, while the thickness of the layers in our superlattices is adequate to describe the rapid convergence of the electrostatic potential to its bulk value away from the interface, we do not claim to accurately describe the full spatial extent of a 2DEG.

We have avoided all these issues by performing our calculations for superlattices with an (110) interface orientation. No polar discontinuity exists in this orientation, since the planes parallel to the interface are composed of $(\text{SrTiO})^{4+}$ and $(\text{O}_2)^{4-}$ on the STO side and, for example, $(\text{LaAlO})^{4+}$ and $(\text{O}_2)^{4-}$ on the LAO side. For the cubic oxides we used superlattices containing six layers of each material in the [110] direction, with an in-plane area of $a \times \sqrt{2}a$, and for the distorted oxides we used a superlattice with five layers of each material with in-plane area

$2a \times \sqrt{2}a$ in order to accommodate the lattice distortions. Convergence tests as a function of layer thickness indicated that increasing the thickness of each material from six layers to eight layers for the cubic materials changed the potential alignment by less than 0.05 eV, and for the distorted materials increasing the layers from five to seven changed the potential alignment by less than 0.1 eV.

4.2. First-principles methods

Our calculations are based on DFT [62, 63] with the screened hybrid functional of Heyd, Scuseria and Ernzerhof (HSE) [64] as implemented in the VASP code [65, 66]. We use the default mixing parameter of 25% and range-separation parameter of $0.2 \text{ \AA}^{-1}$. This choice of parameters yields band gaps close to the experimental values, as discussed in section 4.3. The use of HSE is essential not only for describing band gaps, but also for the correct position of the VBM with respect to the vacuum level [67, 68]. HSE also gives an energy gap within the Ti 3d states for the Mott insulators GTO and YTiO₃ (YTO). We use projector augmented wave potentials [69] to describe the interaction between the valence electrons and the ionic cores, and a 500 eV energy cutoff for the plane-wave expansion. Spin-polarization effects were taken into account for Mott insulators, required to properly describe the electronic structure.

4.3. Results for bulk materials

We considered ABO₃ perovskite oxides, with A = Ca, Sr, Ba, La, K, Y and Gd, and B = Ti, Zr, Hf, Al, Ta and Sn, as listed in tables 1 and 2. The materials investigated can be divided into cubic band insulators, distorted band insulators and distorted Mott insulators. Our choice of materials covers B-site transition metals from the 3d, 4d and 5d rows (Ti, Zr, Hf and Ta). The valences include +1, +2, and +3 for the A site, and +3, +4 and +5 for the B site. Our list also allows for comparing materials with CBs derived from d states versus s states (as in the case of BaSnO₃, SrSnO₃ and CaSnO₃).

The band insulators can be divided in nonpolar and polar according to the charge of the alternating planes along the [001] direction: STO, BaTiO₃ (BTO), CaTiO₃ (CTO), SrZrO₃ (SZO), SrHfO₃ (SHO), BaSnO₃ (BSO), SrSnO₃ (SSO) and CaSnO₃ (CSO) are nonpolar since the alternating planes consisting of either AO or BO₂ are all charge neutral. LAO and KTaO₃ (KTO) are polar: LAO is composed of alternating planes of (LaO)⁺ and (AlO₂)[−] and KTO is composed of (KO)[−] and (TaO₂)⁺. The Mott insulators, YTO and GTO are also polar materials along the [001] direction, with alternating planes of (TiO₂)[−] (Ti assumes valence +3 in these Mott materials) and (YO)⁺ or (GdO)⁺. We remind the reader that our band-offset calculations are all carried out with an (110) interface orientation, which does not exhibit any polar discontinuity.

For bulk calculations we considered both the five-atom simple cubic perovskite unit cells ($a \times a \times a$, where a is the lattice constant) and 20-atom distorted GdFeO₃ unit cells (roughly $\sqrt{2}a \times \sqrt{2}a \times 2a$). The latter allow for octahedral rotations and tilts that are characteristic of the room-temperature phase for a number of the complex oxides considered in the present work (see table 2). The calculations for the five-atom cubic unit cell were performed using a $6 \times 6 \times 6$ Γ -centered k-point mesh, and the calculations for the 20-atom cells were performed using a $4 \times 4 \times 2$ Monkhorst–Pack k-point mesh.

In the Mott insulators GTO and YTO, the VBM and CBM are derived from the Ti 3d states. Here the Ti atoms assume the +3 oxidation state, in contrast to the titanate band insulators

Table 1. Calculated and experimental lattice constants and band gaps of studied oxides in the simple cubic structure at room temperature. The simple cubic structure has an indirect ($R \rightarrow \Gamma$) band gap; the direct ($\Gamma \rightarrow \Gamma$) band gap is given in parentheses.

Material		Calculated			Experimental		
		a (Å)	E_g^{ind} (eV)	E_g^{dir} (eV)	a (Å)	E_g^{ind} (eV)	E_g^{dir} (eV)
SrTiO ₃	STO	3.903	3.27	3.63	3.905 [70]	3.20	3.75 [45]
BaTiO ₃	BTO	3.992	3.13	3.22	3.992 [71]		3.20 [72]
KTaO ₃	KTO	3.994	3.40	4.36	3.988 [73]	3.64	4.35 [74]
LaAlO ₃	LAO	3.787	4.88	5.04	3.791 [75]		5.6 [46]
BaSnO ₃	BSO	4.130	2.40	2.88	4.119 [76]		3.1 [76]

Table 2. Calculated and experimental lattice constants and band gaps of oxides stable in the GdFeO₃ distorted phase at room temperature. Note that GTO and YTO are Mott insulators, with band gaps still debated in the literature. The band gap is direct for the GdFeO₃ structure.

Material		Calculated				Experimental			
		a (Å)	b (Å)	c (Å)	E_g^{dir} (eV)	a (Å)	b (Å)	c (Å)	E_g^{dir} (eV)
CaTiO ₃	CTO	5.363	5.445	7.627	3.84	5.380	5.442	7.640 [77]	3.57 [78]
SrZrO ₃	SZO	5.786	5.833	8.198	5.36	5.791	5.811	8.196 [79]	5.6 [80]
SrHfO ₃	SHO	5.752	5.783	8.153	5.76	5.752	5.765	8.134 [81]	6.1 [80]
CaSnO ₃	CSO	5.511	5.675	7.892	4.31	5.532	5.681	7.906 [82]	4.4 [83]
SrSnO ₃	SSO	5.711	5.725	8.090	3.55	5.708	5.704	8.066 [84]	3.93 [85]
GdTiO ₃	GTO	5.350	5.726	7.624	2.05	5.393	5.691	7.664 [86]	–
YTiO ₃	YTO	5.324	5.697	7.611	2.11	5.316	5.679	7.611 [86]	–

discussed above in which the Ti atoms assume the +4 oxidation state. Starting from STO, replacing Sr by Y or Gd results in one extra electron per Ti that would occupy the CB. This extra electron causes the degenerate Ti 3d bands to split in an occupied lower Hubbard band, constituting the VB, and an empty upper Hubbard band, which constitutes the CB. This opening of a gap is accompanied by a structural distortion, with rotations and tilts of the TiO₆ octahedra; the size of the gap strongly depends on the lattice distortion.

The primitive cell of GTO and YTO contains 20 atoms, i.e. four formula units, as they both are stable in the GdFeO₃ distorted phase. Spin polarization is essential in the description of the ground state of GTO and YTO: the lower Hubbard band and the upper Hubbard band occur in the same spin-up channel, with a ferromagnetic ordering of the Ti moments.

4.4. Results for band alignments

The calculated band alignments are shown in figure 4 and listed in tables 3 and 4. In the band insulators the VB is composed mainly of O 2p states, with the VBM at the R point $\pi/(2a)(\pm 1, \pm 1, \pm 1)$ of the Brillouin zone of the cubic crystal structure. Because of the

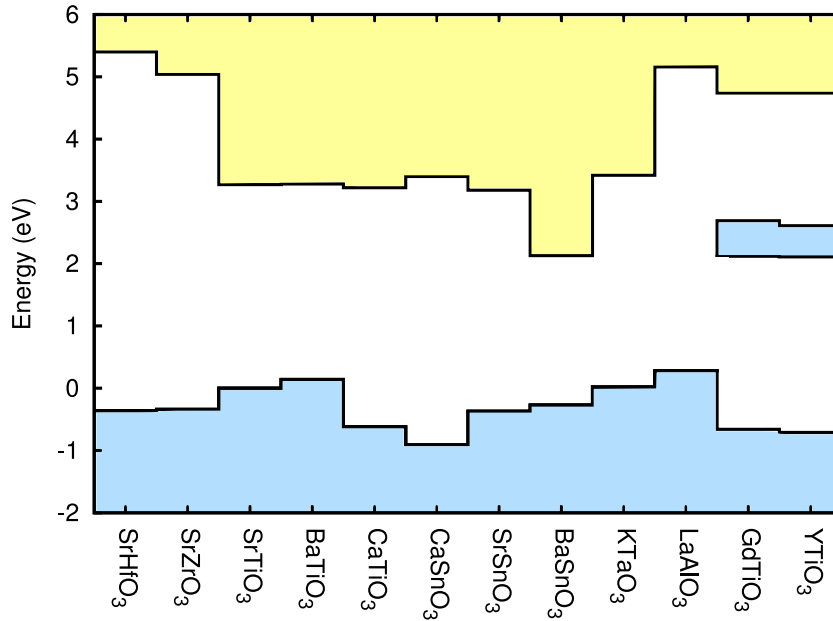


Figure 4. Natural band alignments for oxides considered in the present work. The VB maximum of STO was used as the zero of energy.

Table 3. Natural band alignments between band insulators and STO. Valence- and CB offsets (VBO and CBO) are referenced to the STO band edges.

Material	VBO (eV)	CBO (eV)	Material	VBO (eV)	CBO (eV)
SrHfO ₃	−0.36	2.13	BaSnO ₃	−0.27	−1.14
SrZrO ₃	−0.34	1.74	SrSnO ₃	−0.37	−0.09
BaTiO ₃	0.14	−0.01	KTaO ₃	0.02	0.15
CaTiO ₃	−0.62	−0.05	LaAlO ₃	0.28	1.89
CaSnO ₃	−0.91	0.13			

Table 4. Natural band alignments between Mott insulators and STO. Offsets are given for the O 2p edge and the minimum and maximum of the lower Hubbard band (all referenced to the VBM of STO), and for the bottom edge of the upper Hubbard band (referenced to the CBM of STO).

	O 2p (eV)	LHB-bottom (eV)	LHB-top (eV)	UHB (eV)
GdTiO ₃	−0.66	2.12	2.69	1.47
YTiO ₃	−0.71	2.11	2.61	1.47

similarity of these VB states, one might expect them to be approximately aligned (an expectation that formed the basis for the common-anion rule for band offsets [47]). Figure 4 indeed shows that the variation of the VBM (and the O 2p edge for the Mott insulators) across the different materials is generally smaller than the variation of the CBM; still, the position of the VBM varies by as much as 1.2 eV, and thus a blanket application of the common-anion rule would lead to significant inaccuracies. The larger variation of the CBM reflects the variety in cations in these perovskites. For instance, in the case of STO the CBM is derived from the Ti 3d t_{2g}

states, while in SZO it is derived from Zr 4d t_{2g} states. Atomic Zr 4d states are higher in energy than Ti 3d states [15], placing the CBM in SZO at a higher energy than in STO. The CBM of SHO lies even higher. While insights like this are very useful to analyze and predict trends, quantitative results require full-fledged calculations.

For STO/LAO interfaces, a number of experimental results have appeared in the literature, all obtained with PES: Chambers *et al* [87] reported a VB offset for STO/LAO of $+0.24 \pm 0.20$ eV; Qiao *et al* [88]: 0.16 ± 0.10 eV; Segal *et al* [89]: 0.35 ± 0.18 eV and Berner *et al* [90]: 0.35 ± 0.10 . All of these values are in reasonable agreement with our calculated VBO of 0.28 eV. PES measurements of the STO/SZO band alignment produced a VBO of -0.5 eV [58], again close to our calculated value of -0.34 eV. For the Mott insulator GTO, our calculated offset between the VBM of STO and the top of the LHB is 2.69 eV, in good agreement with the measured value of 2.94 eV [91], lending further support to our approach.

4.5. Discussion

As described in section 2, a 2DEG can spontaneously form at a polar/nonpolar heterostructure. For the materials discussed in this paper, this includes a combination of any of the nonpolar band insulators with the polar LAO or KTO, or with the Mott insulators GTO or YTO. The band alignments reported in the previous section then determine on which side of the interface the 2DEG will reside—and whether the magnitude of the offset is sufficient to provide adequate confinement. For instance, the 0.17 eV offset between STO and KTO may only be marginal. This offset results in the interface electrons being confined to the STO. By combining KTO with, for example, SZO as a barrier, the electrons will be confined within KTO. This would both minimize the lattice mismatch compared to the STO/KTO case, and result in a 2DEG residing in higher-mobility KTO Ta 5d states.

Other potentially interesting combinations involve the stannates. BSO has already been flagged as a promising transparent conducting oxide material because of its high conductivity [92], with a CBM consisting of Sn s states. According to our band alignments, a heterojunction with KTO or LAO would create a 2DEG situated on the BSO side. Another way of increasing electron mobility would be to have the 2DEG reside in a material with CBs derived from 4d or 5d such as SZO or SHO, since such d states are less localized (and hence more dispersive) than the 3d states of STO. But due to the high-lying CB energies of these two materials, this might be difficult to achieve in practice.

The STO/GTO interface was the first interface to exhibit a full 2DEG density (1/2 electron per unit cell area) as expected from the polar discontinuity [5]. In accord with the band alignment shown in figure 4, the 2DEG resides on the STO side of the interface, and the Mott insulator GTO serves as a potential barrier. We expect this to hold in the case of STO/YTO as well, due to the similar band gap and band alignments. To achieve a ‘charge-gain’ transistor structure [7] in which the electron density in GTO or YTO can be modulated would require a band insulator with a CBM significantly higher than in STO; possibly SHO. Alternatively, Mott insulators with lower d-state energies could be explored.

5. Summary and outlook

The design of novel complex-oxide heterostructures can greatly benefit from first-principles calculations. We reported hybrid density functional calculations for band alignments, which

are useful for assessing and analyzing all types of heterostructures, including those in which a 2DEG would be formed by extrinsic doping as well as those exhibiting a polar discontinuity that leads to spontaneous formation of a 2DEG. We also proposed a list of criteria to screen useful heterostructures, highlighting in which areas first-principles calculations can contribute. The examples that were discussed illustrate that the first-principles computational approach can fruitfully contribute to the design of novel heterostructures.

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