



Ultra-thin oxide films for band engineering: design principles and numerical experiments[☆]

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ABSTRACT

The alignment of band energies between conductive oxides and semiconductors is crucial for the further development of oxide contacting layers in electronic devices. The growth of ultra thin films on the surface of an oxide material can be used to introduce a dipole moment at that surface due to charge differences. The dipole, in turn, alters the electrostatic potential – and hence the band energies – in the substrate oxide. We demonstrate the fundamental limits for the application of thin-films in this context, applying analytical and numerical simulations, that bridge continuum and atomistic. The simulations highlight the different parameters that can affect the band energy shifting potential of a given thin-film layer, taking the examples of MgO and SnO₂. In particular we assess the effect of formal charge, layer orientation, layer thickness and surface coverage, with respect to their effect on the electrostatic potential. The results establish some design principles, important for further development and application of thin-films for band energy engineering in transparent conductive oxide materials.

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1. Introduction

Traditional design of transparent conducting oxides (TCOs) for technological application has concentrated on engineering the optical absorption and the electronic conductivity, through doping and defect chemistry [1–5]. Increasingly it is becoming important to optimise different parameters in order to realise the potential of TCOs in new technological applications. In the context of thin-film photovoltaics the interface between TCOs and semiconductors is of great importance. For optimal device performance and lifetimes it is necessary to form a stable interface between the TCO and the semiconductor, it is also necessary to have an appropriate alignment of the electronic energy levels across the interface.

The alignment of the electronic energy levels is the so called band alignment and is analogous to the Schottky barrier formed at metal–semiconductor interfaces [6,7] in traditional semiconductor devices. The Schottky barrier contributes to the contact resistance (depending on doping levels) according to the thermionic model [8]:

$$R_c = \frac{k}{qA^*T} \exp\left(\frac{q\phi_b}{kT}\right) \quad (1)$$

Here ϕ_b is the Schottky barrier, or band offset in the case of semiconductor–semiconductor interfaces. Usually, the smallest possible band

offset is desirable for optimal device performance. Recently a lot of effort has been focused on establishing universal alignments of band energies in important semiconducting materials [4,9–15]. Developing a database of universally aligned energies allows for the prediction of appropriate material combinations for minimal band offsets. In some cases it may be impossible to realise such a combination of band energies for a given semiconductor. It is desirable, therefore, to be able to manipulate the band energies of either the semiconductor, the contact, or both in order to reduce the offset.

Surface dipoles in materials are well known to result in shifting the electrostatic potential, and hence workfunctions, of metals and semiconductors. Indeed, the effect of halide atoms adsorbed onto a metal surface on the metal workfunction was reported in the 1920s by Ives, Langmuir and Becke [16–18] and on Si and Ge semiconductor workfunctions more than 40 years ago [19]. More recently self-assembled monolayers have been used to tune energy levels for organic photovoltaic and organic light emitting diode (OLED) devices [20–22]. The effect of LiF buffer layers in OLED devices has recently been attributed to its dipole forming effects [23]. Modern synthetic techniques, for example molecular beam epitaxy and atomic layer deposition, make the realisation of atomically thin surface layers of one material on another possible. Therefore it is reasonable to envisage the possibility of the growth of an ultra-thin layer of one oxide on the surface of another, resulting in a surface dipole, shifting the band energies in the substrate oxide.

Using Tasker notation [24], oxide surfaces can be split into three categories. Type I: individual layers are charge neutral, no net dipole [e.g. MgO(001)]; type II: individual layers are charged, but groups of layers are charge neutral and non-polar [e.g. Al₂O₃(0001); TiO₂(110)]; type III: groups of layers have a net dipole [MgO(111); SrTiO₃(100)].

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Type III surfaces are unstable with respect to chemical or surface reconstructions. In this contribution we consider only thin film growth on type I surfaces. We use these models to establish a number of general design principles, which can be applied to achieve band engineering through surface layer modification. We consider first a simple analytical electrostatic model of a single dipole on the surface of a material, demonstrating the effects of dipole charge and orientation. To bridge between continuum and atomistic theories, we apply an electrostatic simulation of a model consisting of polarisable point charges in a rocksalt structure (MgO) with Parry summation [25] to consider a case closer to the realistic systems. The general principles outlined in this work can be used to inform the selection of potential candidate thin-film layers for band engineering purposes and will serve as a screening for candidate materials combinations for further high level quantum mechanics simulations and experimental synthesis.

2. Models

2.1. Analytical

The ionization potential (IP) is defined as the energy required to remove an electron from the highest energy state in the lattice to the vacuum level. The contributions to the IP can be partitioned, similarly to the workfunction in the work of Bardeen [26], into the binding energy of the electron in the lattice and the energy required to pass through the electrostatic double-layer at the surface. We approximate the electrostatic potential due to the surface layer as resulting from the dipole caused by the ionic charge separation in the oxide capping material. The underlying oxide has a zero net dipole moment in the bulk, due to alternating dipole layers cancelling one another, with only the surface layer potentially contributing to the dipole. Commonly the surface layer can reconstruct to cancel out the dipole [27,28], however polar surfaces are well documented, for example the (0001) surface of wurtzite structured ZnO [29].

In our models we consider the effect of capping a non-polar surface of rutile structured SnO₂. In the case of the non-polar surface the entire dipole electrostatic field will be due to the capping layer. Effects of carrier induced band bending or space-charge formation are not considered.

The separations of the poles in the dipole correspond to the interatomic bonding distances of the constituent ions in the bulk lattice of the capping layer. Having established these criteria we now estimate how the presence of a range of capping materials can bend the electronic bands in SnO₂.

The dipole moment of the surface is

$$\vec{p} = q\vec{d} \quad (2)$$

Where \vec{d} is the ionic separation and q is the absolute value of the charges on the ions. As stated earlier we assume the dipoles to be normal to the surface, therefore the separation only has a z component.

The magnitude of the band bending effect of the dipole is dependent on the dielectric screening of the lattice. For the single dipole scenario, we are interested in the dipole field in a region similar in magnitude to the charge separation which gives rise to the dipole. In this instance the electrostatic potential of the dipole, in the z dimension is

$$V_{Dip}(z) = \frac{1}{4\pi\epsilon^o} \frac{\vec{p}}{z^2} \quad (3)$$

where ϵ^o is the static dielectric screening of the lattice and \vec{z} is the distance from the centre of the dipole. The total electrostatic potential of the lattice at a point z is given by

$$V(z) = V_{Lat}(z) + V_{Dip}(z), \quad (4)$$

where $V_{Lat}(z)$ is the bulk macroscopic electrostatic potential of the lattice.

The dielectric screening tensor of SnO₂ is anisotropic, therefore different values of ϵ^o must be used depending on the surface orientation. For the (001) surface, we use $\epsilon_{33}^o = 9.86$ [30].

2.2. Numerical

For consideration of a more realistic arrangement of charges corresponding to a metal halide monolayer on a substrate oxide, we use pairwise interatomic potentials following the Born model as implemented in the General Utility Lattice Program [31] code. We model LiF on the non-polar MgO (001) surface. LiF is commonly employed as an electron blocking layer at both high and low workfunction electrodes [32–35] due to the dramatic improvement of device performance. The point charge models are constructed based on the MgO lattice, which has a cubic structure (space group Fm $\bar{3}$ m) with a lattice constant of 4.212 Å. The MgO region is constructed with charges of $+/- 2e$ at alternating lattice sites. The LiF layer is represented with charges of $+/- 1e$ at alternating lattice sites. The MgO crystal is terminated with the non-polar (001) surface and the LiF layer is placed 3 Å above the surface. We simulate the system as a 2D surface and calculate the electrostatic potential using a corrected Parry summation method [25]. In order to account for the charge screening effects of polarisation we represent the O and F ions using a core-shell model [36]. The interactions between the ions are then a combination of short-range Buckingham potentials from the parameter set of Binks [37] and long-range Coulomb interactions. The model reproduces the experimental static and high-frequency dielectric constants of MgO to reasonable accuracy.

3. Results

3.1. Analytical

In the analytical model we first consider a one-dimensional system, with a *single* dipole at one terminal, which could be thought of as an isolated molecule. The electric field of a dipolar molecule is presented in Fig. 1(a). Note that at either side of the dipole centre the electrostatic field decays to a common level; the vacuum level. Also note that immediately to the left of the negative charge the electrostatic potential is increased, whilst to the right of the positive charge the electrostatic field is decreased.

Using the textbook analytical model described we calculate the effect of placing a single dipole on the (001) surface of SnO₂. The material is represented by the zz component of the dielectric tensor. The results for the effect of the magnitude of the polar charges are presented in Fig. 1(b), where we set a distance between the dipolar molecule and the SnO₂ surface (\vec{z} in Eq. (3)) to 3 Å. With the negative pole of the dipole directed towards the surface, we can obtain a maximum band bending of between -0.4 and -2.1 eV at the surface, depending on the formal charges of the poles, from $q = 1$ to $q = 6$. In this model, the band bending decays with $1/r^2$ and the length of decay is inversely proportional to the dielectric constant of the material.

In addition to considering the effects of charge and separation of the dipole, we now also consider how the orientation of the dipolar species at the surface affects the band bending. Fig. 2 presents the effect of orientation, in this case the formal charges of the dipole poles are $q = \pm 2$ and the separation of the poles is 3 Å. The centre of the dipole remains 3 Å from the centre MgO region, with the poles rotated about the fixed centre, so that the dipole vector forms an angle (γ) with a vector parallel to the surface of the MgO, as illustrated in Fig. 2. For a single dipole on the material surface, the maximum effect is not when the dipole is perpendicular to the surface, but rather occurs at about 45°. These models represent some fundamental limits when considering the effect of single dipolar molecule on a material surface and demonstrate how the arrangement and charge of the dipole layer can affect the band

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