Energy band alignment at interfaces of semiconducting oxides: A review of experimental determination using photoelectron spectroscopy and comparison with theoretical predictions by the electron affinity rule, charge neutrality levels, and the common anion rule

Andreas Klein *

Technische Universität Darmstadt, Department of Materials and Earth Sciences, Petersenstrasse 32, D-64287 Darmstadt, Germany

ABSTRACT

The energy band alignment at interfaces of semiconducting oxides is of direct relevance for the electrical function of electronic devices made with such materials. The most important quantities of the interface determined by band alignment are the barrier heights for charge transport given by the Fermi level position at the interface and the band discontinuities. Different models for predicting energy band alignment are available in literature. These include the vacuum level alignment (electron affinity rule), branch point or charge neutrality level alignment governed by induced gap states, and an alignment based on the orbital contributions to the density of states (common anion rule). The energy band alignment at interfaces of conducting oxides, which have been experimentally determined using photoelectron spectroscopy with *in situ* sample preparation, are presented. The materials considered include transparent conducting oxides like In_2O_3, SnO_2, ZnO, and Cu_2O, dielectric and ferroelectric perovskites like $(Ba,Sr)TiO_3$ and $Pb(Zr,Ti)O_3$, and insulators like Al_2O_3. Interface formation with different contact partners including metals, conducting and insulating oxides are addressed. The discussion focuses on the energy band alignment between different oxides. A good estimate of the band alignment is derived by considering the density of states of the materials involved.

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1. Introduction

Interfaces of semiconducting oxides, which are the subject of this contribution, are relevant e.g. for numerous electronic devices like thin film solar cells [1,2], (organic) light emitting diodes [3], thin film transistors [4], and information technology [5]. The energy band alignment at semiconductor interfaces, determined by the Schottky barrier heights at semiconductor/metal interfaces and by the valence and conduction band discontinuities at semiconductor heterointerfaces, largely determines the functionality of devices [6]. Large barriers prevent charge transport across the interface and are required, e.g., for electrodes of capacitors and for gate dielectrics of field effect transistors. Small barriers enable charge transport across an interface, a prerequisite for ohmic contacts.

Furthermore, the doping limits of semiconductors, i.e. the maximum achievable electron and hole concentrations, are discussed in terms of a *pinning level*, which is at a similar level when the valence and conduction bands of different materials are aligned on a common energy scale [7,8]. Materials with a deep lying valence band maximum are difficult to dope p-type, while n-type doping becomes

difficult for a high conduction band minimum energy. The band alignment, which is typically a unique quantity for a given material combination, is therefore not only of practical importance, but also related to fundamental properties of the materials.

Intensive research has been performed in the last 25 years of the 20th century to understand the physical mechanisms underlying the energy band alignment of inorganic semiconductors [9–13]. Induced gap states have been identified as the origin of the Fermi level pinning at interfaces of covalently bonded semiconductors including the elemental and the III–V semiconductor compounds. Semiconductors with more ionic bonding like the II–VI chalcogenides and oxides, are known to exhibit less strong Fermi level pinning [14]. While considerable theoretical and experimental data on band alignment of chalcogenides are available (see compilation in [13]), no systematic data on interfaces of oxide materials have been published so far. Theoretically derived energy band alignments of a number of oxides were published by Robertson and coworkers [8,15,16]. These alignments are, however, not deduced from interface supercell calculations, which typically reveal accurate values for the offsets [12], but either from electron affinities, i.e. vacuum level alignment, or from charge neutrality level, or valence band maximum alignment, respectively. To which extent these band alignments are adequate can hardly be assessed without a comparison with experimental data.

* Tel.: +49 6151 166354; fax: +49 6151 166308.
  E-mail address: aklein@surface.tu-darmstadt.de.

Energy band alignments of various interfaces of semiconducting oxides are collected in this contribution. The energy bands are aligned on a common energy scale. The observed energy band alignment is discussed in terms of the different models. It is proposed that neither vacuum level nor charge neutrality level alignment, but rather the common anion rule provides the best estimate for band alignment at oxide heterointerfaces, as it does also for other II–VI semiconductors [17].

2. Experimental determination of band alignment by photoelectron spectroscopy

2.1. Experimental procedures

The procedure to determine energy band alignment using photoelectron spectroscopy (PES) has been outlined by Waldrop and coworkers [18]. It has been extensively used to study semiconductor interface formation [9–11]. Binding energies in PES are measured with respect to the Fermi energy of the spectrometer system and can be easily calibrated by measuring the Fermi edge emission of a metallic sample. For semiconductor samples, the onset of emission at low binding energy corresponds to the valence band maximum at a binding energy of $E_F - E_{VB}$. The core levels of the semiconductor should exhibit a binding energy with respect to the valence band maximum $E_{CL}^{VB} = E_B(CL) - E_{VB}$, which is characteristic for the given material and can be determined for the substrate and the contact material at the beginning and the end of an interface experiment, respectively. The interface experiments begins with the preparation of a substrate surface and continues by stepwise deposition of the contact material until the substrate emission lines are completely attenuated. Using Al Kα radiation as excitation for PES ($h\nu = 1486.6$ eV), this corresponds to a thickness of the contact material of ~10 nm. To follow the evolution of the chemical and electronic properties, the contact material has to be deposited in multiple steps, starting with films of sub-nanometer thickness.

The procedure of an interface experiment using PES is illustrated in Fig. 1. The valence band discontinuity is derived from the binding energy difference of substrate and film core levels ΔE_{CL}, which can be measured if the thickness of the deposited film is less than 3–5 times the inelastic mean free path of the photoelectrons. The latter is a function of the kinetic energy of the photoelectrons and varies in the range of 0.5–3 nm [19]. In the idealized case, ΔE_{CL} does not depend on the thickness of the deposited film. However, non-constant ΔE_{CL} may occur in the case of strong band bending or if the electronic structure of the deposited film is not yet fully developed, e.g. if the crystallographic structure of the film depends on film thickness [1,20,21]. For a reliable determination of band alignment a series of depositions with stepwise increasing film thickness is therefore recommended. If several core level lines are available, it is also important to check if the ΔE_{CL} of different substrate and film core levels reveal the same values. Valence band discontinuities can further be determined from photoelectron spectroscopy by valence band difference spectra [9,22], although this procedure is less reliable and less frequently applied.

2.2. Results

A number of band alignments at several oxide interfaces are summarized in Table 1. Only a few direct determinations of interfaces between different oxides are currently available. The difficulty in determining band alignment at oxide heterointerfaces directly comes from the common anion (O) in both materials, which prevents the use of this core level in the procedure for the determination of the band alignment. In order to increase the set of data to be discussed, which is important for the discussion of generalized rules for the estimation of energy band alignment, additional interfaces with common contact materials are included. The relative band edge energies
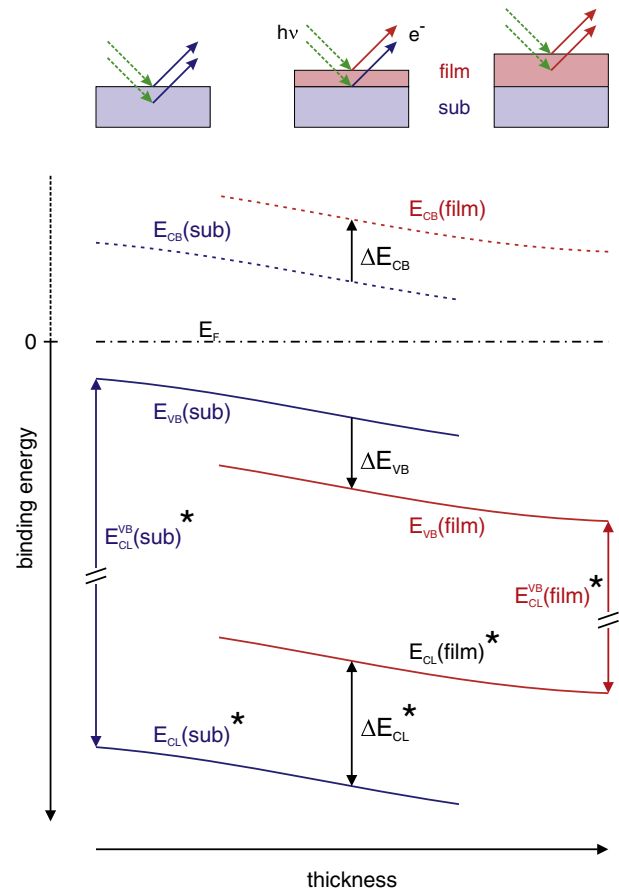

Fig. 1. Determination of energy band alignment between two semiconductors by photoelectron spectroscopy. Experimentally determined quantities are indicated by asterisks.

of two oxides AO_x and BO_y can then be derived using transitivity according to $\Delta E_{VB}(AO_x/BO_y) = \Delta E_{VB}(AO_x/C) + \Delta E_{VB}(C/BO_y)$. A number of data are available for interfaces of oxides with the II–VI semiconductor CdS, which is due to the fact that CdS is a common contact material to oxides in CdTe and Cu(In,Ga)Se$_2$ thin film solar cells [23].

Not all band alignments of the interfaces listed in Table 1 show transitivity. This is particularly the case for the interfaces of different transparent conductors with CdS. The origin of the deviation from transitivity lies in the restricted variation of the Fermi level in the two materials [47]. Assuming transitivity of the band offsets at the SnO_2/CdS and the SnO_2/In_2O_3 interface, the valence band offset at the In_2O_3/CdS interface is predicted as $\Delta E_{VB} = -1.5$ eV, while a direct determination reveals an offset of only $\Delta E_{VB} = -0.8$ eV. In the direct experiment, a larger valence band offset does not occur as it would require either a Fermi level position in In_2O_3 ~1.0 eV above the conduction band minimum. Such high doping levels are not possible in In_2O_3 [8,48,49]. On the other hand, a larger valence band offset would be possible if the Fermi level in CdS is near midgap (~1.2 eV above the valence band maximum). Such Fermi level positions were, however, never observed in our evaporated CdS films, which is most likely related to the defects in the material. Similar effects, which can lead to a significant dependence of the band alignment on interface preparation, have also been observed at the interfaces between CdS and ZnO [1], In_2S_3 and ZnO [50], and Cu_2O and Sn-doped In_2O_3 (ITO) [25]. The band alignment can therefore strongly be affected by the accessible range of Fermi level in the respective materials.

In order to develop rules for the prediction of energy band alignment, it is important to identify an intrinsic band alignment, which