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# Schottky barrier height at metal/ZnO interface: A first-principles study

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The Schottky barrier heights (SBHs) of various metals on ZnO are investigated by first-principles calculation. The SBHs decrease linearly with increasing metal work function, which follows the prediction of the metal-induced gap states (MIGS) model. The pinning factor  $S$  is calculated to be 0.56 which indicates moderate pinning effect. A closer look at the interfacial electronic structure shows the dominant rule of oxygen in forming the MIGS. To extend the concept of MIGS model to the band alignment between semiconductors, a calculation is performed on Si/ZnO interface. Si is found to have a type-II band alignment with ZnO, the conduction band offset (CBO) and valence band offset (VBO) are calculated to be 0.5 eV and 2.5 eV respectively. The results agree with the experimental values and the predicted values based on the charge neutrality level (CNL) method.

Keywords: Schottky barrier heights; metal/ZnO interface; Si/ZnO interface; band alignment; first-principles calculation

## 1. Introduction

ZnO is a wide band gap, n-type semiconductor [1-3]. The Schottky barrier contact of ZnO with metal and the Schottky barrier height (SBH) are of great importance for numerous electronic applications such as field-effect transistors, UV emitters and photovoltaic devices [4-6]. Within the Schottky-Mott rule, the SBH is proportional to the energy difference between metal work function and semiconductor electron affinity. So by varying the work function of the contact metal, the SBH can be controlled. However, the SBH values obtained from experiment results do not match the predicted ones in most cases. This is due to the Fermi level pinning effect caused by the localized surface states, including the semiconductor intrinsic surface state known as the metal-induced gap states (MIGS) and extrinsic states like defects, grain boundaries and impurities [7-9]. However, the influence of these factors on the SBH remains unclear because of the complex underlying theory. The effect of gap states on the SBH can be defined by Equation (1) [10,11]:

$$\phi_n = S(\phi_M - \phi_S) + (\phi_S - \chi_S) \quad (1)$$

where  $\phi_n$  is SBH,  $S$  is the pinning factor which varies between 0 (for a strongly pinned interface, i.e., Bardeen limit) and 1 (for no pinning interface, i.e., Schottky limit),  $\phi_M$  is the metal work function,  $\chi_S$  is the electron affinity of the semiconductor, and  $\phi_S$  is the reference pinning energy of the semiconductor. In the intrinsic case, the reference pinning energy is known as the charge neutrality level (CNL) of the semiconductor.

SBHs have been studied extensively at the metal/ZnO interface, while most of them focus on the ZnO wurtzite structure, both experimentally [4,12-14] and theoretically [15-17]. For the theoretically ones, most of them suffer from the unreasonable band gap value of ZnO, a limited range of metals tested, and a resulting rather disordered range of SBH values [15,16]. In this work, we focus on the zinc blende ZnO and consider a much wider range of metals. Besides, we also calculated the interface band alignment between ZnO and semiconductor to extend the application of MIGS model to interface between semiconductors to predict the band alignment [10,11]. Si as the most common semiconductor is chosen here as a typical example. Also, as one of the most famous structures for

solar cell applications, the interface band alignment between ZnO/Si is of great significance. Despite some experimental reports [18-20], little theoretical work has been done on the interfacial bonding and band line-up for ZnO/Si.

## 2. Calculation Method

This work was conducted with the CASTEP code [21]. We used the Perdew-Burke-Ernzerhof version of the generalized gradient approximation (GGA-PBE) exchange-correlation functional and norm-conserving pseudopotentials with a plane-wave cutoff energy of 680 eV. Pseudopotentials for oxygen were generated by the OPIUM method. For such density functional theory (DFT) calculations, GGA substantially underestimates the band gap values, especially for ZnO, whose calculated band gap is 0.88-0.98 eV but the experimental value is 3.40 eV [22]. Hybrid functionals can be used to correct the underestimation, but it is more time-consuming and is more difficult to converge for metallic systems. An alternative way is to include the Hubbard-type U interactions in LDA or GGA functionals. The GGA+U approach corrects the delocalization of electrons in Zn-3d states to help opening the band gap. Some previous studies on ZnO with the GGA+U method used an unphysically large U for Zn-d [16], which is not realistic. Instead, here we include a U term on Zn-3d (6 eV) and also on the O-2p states (8 eV) [23]. With this more reasonable combination of U values, the band gap can be adjusted to 2.60 eV and the optimized zincblende cell has lattice parameter of 4.73 Å. Although the calculated band gap is still smaller than the experimental data, the focus of this work is on the change in SBH with work function, which is not affected by the absolute band gap.

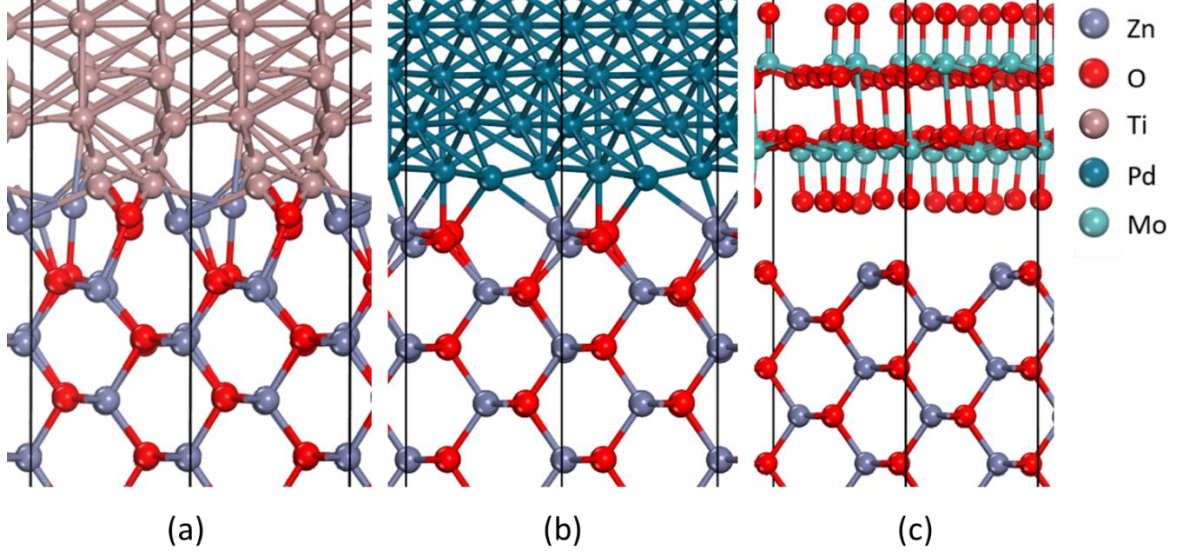
The calculations are carried out on the zincblende phase of ZnO, so as to use the higher symmetry and non-polar (110) face. For metal/ZnO interface, we focus on the (110) face which has no dangling bonds thus the effect by the intrinsic surface states can be ignored. The lattice mismatch between metals and ZnO are listed in Table 1. Four bilayers of metals and five bilayers of ZnO were used. Since the metal work function is not so sensitive to the lattice constant, metal was strained to match the ZnO surface slab. The interface was built using the interface supercell slab with a 15 Å vacuum slab. For the Si/ZnO interface, ZnO (111) was chosen because it is more energetically favorable and the negligible lattice mismatch (< 1%) guarantees a smaller model size.

**Table 1:** Lattice matching of metal and ZnO (110) face. Take Ti as an example,  $2 \times 2 = \sqrt{3} \times \sqrt{3}$  means that  $2 \times 2$  sized supercell of Ti (110) surface is fitted with  $\sqrt{3} \times \sqrt{3}$  sized supercell of ZnO (110) face.

Metal	ZnO	Lattice Mismatch (%)
Hf	$1 \times 1 = 1 \times 1$	2.05
Zr	$1 \times 1 = 1 \times 1$	0.82
Ag	$2 \times 2 = \sqrt{3} \times \sqrt{3}$	4.79
Ti	$2 \times 2 = \sqrt{3} \times \sqrt{3}$	9.10
Ru	$\sqrt{3} \times \sqrt{3} = \sqrt{2} \times \sqrt{2}$	2.35
Os	$\sqrt{3} \times \sqrt{3} = \sqrt{2} \times \sqrt{2}$	3.31
Re	$\sqrt{3} \times \sqrt{3} = \sqrt{2} \times \sqrt{2}$	4.84
Rh	$\sqrt{3} \times \sqrt{3} = \sqrt{2} \times \sqrt{2}$	2.83
Au	$2 \times 2 = \sqrt{3} \times \sqrt{3}$	5.03
Pd	$\sqrt{3} \times \sqrt{3} = \sqrt{2} \times \sqrt{2}$	5.61
Ni	$\sqrt{2} \times \sqrt{2} = 1 \times 1$	7.74
Pt	$2 \times 2 = \sqrt{3} \times \sqrt{3}$	0.39
MoO <sub>3</sub>	$2 \times 3 = \sqrt{6} \times \sqrt{6}$	0.53 in a, 1.02 in b
Si	$\sqrt{3} \times \sqrt{3} = 2 \times 2$	0.01

### 3. Results

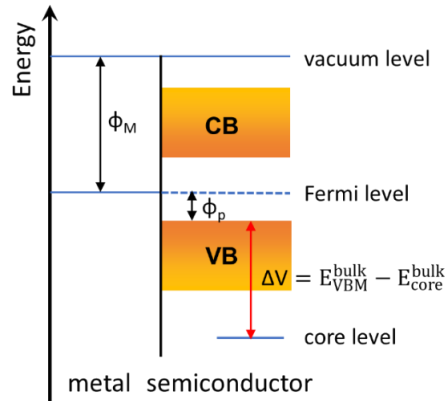
After the relaxation of metal/ZnO contact, interfacial atomic rearrangement occurs. Several relaxed interface structures are demonstrated in Fig. 1. It is seen that the surface roughness induced at the Pd/ZnO is negligible, indicating the formation of weak interfacial bonding without disturbing the bulk ZnO structure, while significant interfacial deformation is observed for Ti/ZnO case due to the high activity of Ti. Here we also include the metal oxide MoO<sub>3</sub> (Fig. 1(c)), taking advantage of its high work function [24]. The layer distance between MoO<sub>3</sub> and ZnO after geometry relaxation is about 2.70 Å, indicating the weak van der Waals interlayer bonding owing to the layered structure characteristics of MoO<sub>3</sub>.



**Fig. 1.** Relaxed atomic structure of (a) Ti/ZnO (b) Pd/ZnO (c) MoO<sub>3</sub>/ZnO interfaces, with atom species labelled.

The p-type Schottky barrier height is the difference between the valence band maximum (VBM) and metal Fermi level  $E_F$ . However, the localized states formed due to contact of metal and ZnO make it difficult to extract the SBH value directly from interfacial band plot. Therefore, we used Kraut's core-level method [25-27] to increase the precision in determining the VBM, which follows the assumption that the energy difference between VBM and core level states stays the same despite the environment condition. SBH can be derived from Equation (2), where  $E_{core}^{int}$  is the core level state in interfacial model:

$$\phi_p = E_{core}^{int} + \Delta V - E_F \quad (2)$$

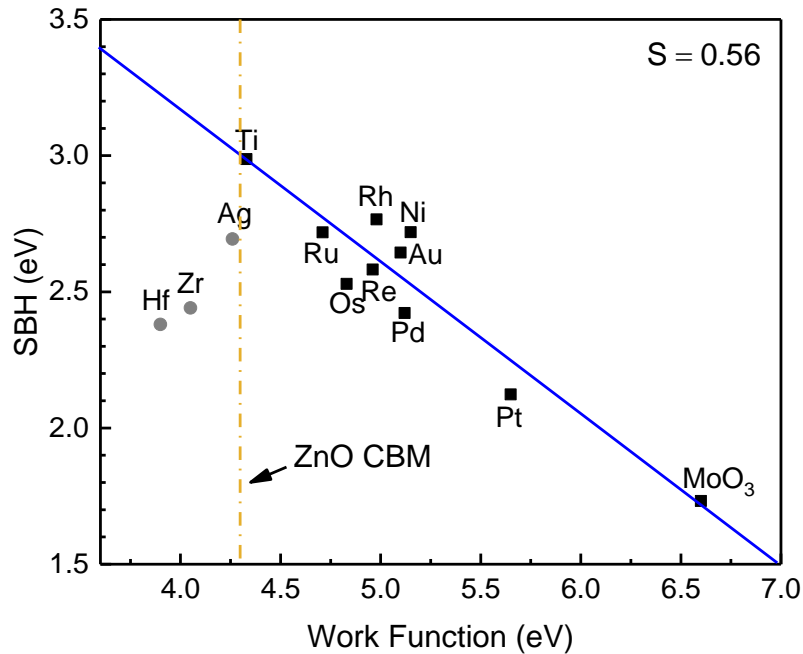


**Fig. 2.** Schematic diagram of core level alignment scheme. The energy difference between core level state and valence band maximum of the bulk crystalline ZnO ( $\Delta V$ ) is labelled.

In Fig. 3, the p-type SBHs are plotted with different metal work functions [28]. We set the borderline between high work function metals and low work function metals as the conduction band minimum (CBM) of ZnO. The electron affinity (i.e., the energy difference between the vacuum level and CBM) is calculated to be 4.31 eV by GGA+U in our work, slightly smaller than the 4.6 eV given previously by sX functional in Ref. [10,11]. For those high work function metals, a strong linear relationship can be observed between SBH and work function, therefore the MIGS model is proved to be suitable for ZnO [10,11]. The high work function MoO<sub>3</sub> helps to get a more reliable fitting line [24,26]. A best fit line is plotted on Fig 3 and the absolute value of slope is the Fermi-level pinning factor  $S$ , which is 0.56 in this case. According to the empirical formula of Mönch [29]:

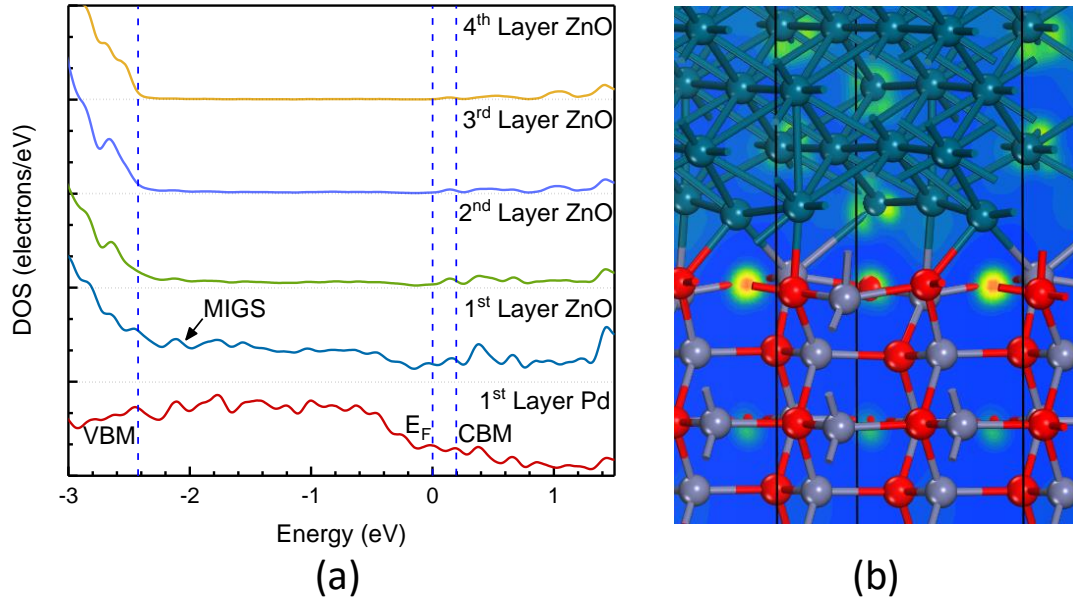
$$S = \frac{1}{1+0.1(\varepsilon_{\infty}-1)^2} \quad (3)$$

where  $\varepsilon_{\infty}$  is the dielectric constant. In the case of ZnO,  $\varepsilon_{\infty}=4.0$ , so the empirical value of  $S$  should equal to 0.53, which is close to our calculated value ( $S=0.56$ ) and further proves that MIGS model holds for ZnO. Low work function metals are also included in Fig. 3. However, these lie below the best fit line. The deviation from the fit line is because the metal work functions enter the conduction band of ZnO, where the density of metal-induced states is negligible compared to the high density of conduction band states. The pinning by MIGS is no longer the dominant factor thus the MIGS model is not applicable.



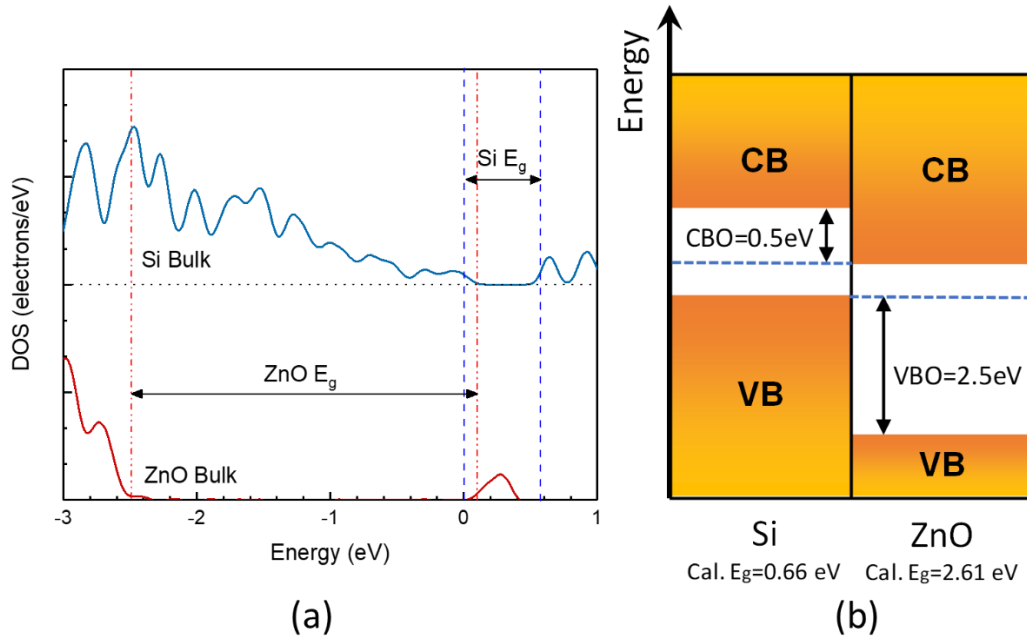
**Fig. 3.** p-type SBH values of metal/ZnO contacts, with best fit line plotted for high work function metals. Pinning factor  $S$  is derived to be 0.56. The borderline for high and low work function is determined by the calculated CBM of ZnO (4.31 eV). Low work function metals are also plotted on the graph with the grey round symbol for reference.

To further understand the influence of MIGS, the local density of states (DOS) of metal and individual ZnO layers in the interface model is shown in Fig. 4 (a). It is obvious that gap states emerge in the band gap of ZnO and decay away from the surface. MIGS almost disappear since the third layer of ZnO. Further analysis on the orbital filling condition near the interface indicates that orbital of O at the contact dominantly contributes to the MIGS formation as shown in Fig. 4(b).



**Fig. 4.** (a) Partial DOS of Pd and ZnO individual layers from the Pd/ZnO interface model, with VBM, CBM and Fermi level labelled. The blue, green, purple and yellow lines indicate the 1<sup>st</sup>, 2<sup>nd</sup>, 3<sup>rd</sup> and 4<sup>th</sup> layer (count from the interface) of ZnO, respectively. The red line indicates the 1<sup>st</sup> layer of Pd. The decay of MIGS can be observed through the layers. (b) Filling condition of orbitals with metal Fermi energy. The density of electrons is highest for O at the interface and decays as we go deeper into the bulk ZnO.

We also investigated the interface of Si/ZnO to extend the concept of SBH, i.e. the band offset between metal and semiconductor, to the band offset between two semiconductors. The density of states and band alignment of the interface are shown in Fig. 5. (a) and (b), respectively. Staggered gap (Type II) is observed with a calculated conduction band offset (CBO) equals 0.5 eV and valence band offset (VBO) equals 2.5 eV.



**Fig. 5.** (a) Partial DOS of Si bulk and ZnO bulk with VBM and CBM labelled. (b) Schematic band alignment diagram of Si/ZnO interface. The calculated band gap for Si bulk and ZnO bulk is shown.

Compare to the experimental band offsets values listed in Table 2, the VBOs show a large energy variation ranging from 2.55 eV to 3.15 eV. The VBO obtained in this work well agree with those

reported by Ref.[19,20] According to the theory proposed in Ref. [11], the band alignment can be predicted by matching the alignment of charge neutrality levels (CNL) of two semiconductors modified by the S factor, and the theoretical value of CBO and VBO turns out to be 0.9 eV and 3.2 eV with Type II band alignment [11]. The difference between our calculation and theoretical value may arise due to the formation of dipole at interface and the underestimated band gap.

**Table 2:** Band alignment comparison between our calculation, theoretical value and the experimental data.

$E_g$ of ZnO (eV)	$E_g$ of Si (eV)	VBO (eV)	CBO (eV)	Method	Data
2.61	0.66	2.50	0.50	DFT model	This work
3.40	1.12	3.20	0.90	CNL model	[11]
3.37	1.12	3.15	0.90	XPS	[18]
3.37	1.12	2.55	0.40	XPS	[19]
3.32	1.12	2.76	0.66	C-V	[20]

## 4. Conclusions

In conclusion, SBHs at metal/ZnO (110) interface are systematically studied. It is found that for metals with work functions higher than the ZnO CBM energy, SBHs are mainly influenced by MIGS. The pinning factor S for ZnO is calculated to be 0.56, which agrees with the value derived from the empirical formula. Further explanation of the pinning effect is supported by giving an insight into the local DOS and orbital filling condition of ZnO individual layers. Additionally, calculation of Si/ZnO interface shows a type-II band alignment, which agrees well with the experimental reports.

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