Effect of oxygen in the effective work function of Pt/HfO$_2$.

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I. Introduction

Metal-oxide interfaces are important for many applications such as catalysis, oxidation resistant metals, vacuum seals, thermal barrier coatings, and recently in microelectronics [1]. The continued scaling of the traditional metal oxide semiconductors (CMOS) has required thinner gate oxides, in particular the thinning of the SiO$_2$ layers resulted in a the leakage of current in the dielectric [2]. The solution proposed to this problem was the replacement of SiO$_2$ for a high dielectric constant (k) material such as HfO$_2$. A similar scaling problem was imminent for poly-Si gate technology, and added to this there was observed the incompatibility of this material with the high-k dielectric. The option for these problems was the adoption of a high-k gate dielectric to replace SiO$_2$ and suitable metal gates to replace poly-Si.

Different materials have been consider as option for the replacement of SiO$_2$ in the traditional transistor, for instance, ZrO$_2$, HfO$_2$, La$_2$O$_3$, etc. In the other hand, different metal elements and compounds have been studied for the substitution of poly-Si.

Between different materials, Pt and HfO$_2$ represent a good option for the replacement of poly-Si and SiO$_2$ respectively. Pt is a late metal transition, has high work function and high chemical stability while HfO$_2$ is stable and hard metal oxide and has a high dielectric constant.

After the implementation of the new material, different issues arise to be addressed to further improve, between these; it was observed that the flat band voltage ($V_{fb}$) shifts after post-deposition annealing. This condition is presented with most effect in metal gates with high work functions used in p-type MOSFET [3].

The $V_{fb}$ shift can be interpreted as the change in the work function of metal gates interfaced with high-k materials. Between the causes of the $V_{fb}$ shift, the presence of oxygen vacancies is considered one of the principal factors.

Although the defect formation energies of the oxygen vacancies in HfO$_2$ is relatively high, they can be easily generated in actual devices by with the help of the oxidation of underlying silicon.

The control of the changes in the work function could be one option to control the flat band voltage ($V_{fb}$) shifts in the new transistor.

This term paper is divided in fifth sections; the first shows the introduction in semiconductor devices, the second the procedure for the calculation of the work function and effective work
function. The third section shows the effect of the oxygen vacancy in the effective work function and its relation with the charge transfer, the fourth section present some relations between the oxygen content and the effective work function and the fifth section the conclusions.

1. Concept in Semiconductor Devices

To understand better the concepts developed in this document, I will include a brief explanation of some basic definitions.

In semiconductors physics, the filled energy band is called the valence and, it is after all occupied by the valence electrons, the empty band immediately above is called the conduction band. The zero energy is usually taken at the top of the valence band. The energy gap separating the two bands is the band gap. For a metal the Fermi energy lies at the boundary between filled and empty state.

In Figure 1 a metal oxide interface is observed with its respective energy levels.

![Energy band for a metal oxide interface.](image)

Figure 1. a) Energy band for a metal oxide interface.

The properties of a perfect crystal of a pure element or perfectly stoichiometric compound are called intrinsic properties, whereas the influence of added impurities or defects give rise to extrinsic properties [11].
2. Work Function

The work function is defined as the minimum energy required to extract one electron to an infinite distance from the surface.

In a metal the work function is the energy difference between the Fermi energy and the vacuum energy.

2.1 Calculation of the Work Function

The metal work function ($\Phi_m$) can be calculated using DFT in two steps.

The first step includes the calculation of the bulk material which will provide the information of the Fermi energy ($E_F$).

After the bulk calculation, a slab calculation is carried out to obtain the information of the vacuum level (energy).

The electronic potential of both calculations has to be correlated to apply the definition:

$$\Phi_m = V(\infty) - E_F$$

Where $\Phi_m$ is the metal work function, $V(\infty)$ is the electrostatic potential in the vacuum and $E_F$ is the Fermi energy on the bulk metal.

2.2 Calculation of the effective work function

When the metal is in contact with the oxide, the effective work function ($\Phi_{\text{eff}}$), a measure of the alignment between the band edges of the Si substrate and the metal Fermi level, need a different approximation compared to the defined for the calculation of the metal work function.

The metal work function in an oxide can differ significantly from its vacuum work function due to the formation of interfaces dipoles, which are usually attributed to the presence of interface states in the band gap of the oxide.

Different models have been proposed to explain the origin of these states, some of the leading models describe them as surface state [6], metal induced band gap states (MIGS) [7] or disorder induced band gap states (DIGS) [8].

The MIGS model propose that $\Phi_{\text{eff}}$ depends on the metal work function $\Phi_m$, the charge neutrality level energy $\Phi_{\text{CNL}}$ and a Schottky pinning factor $S$ [4] as
\[ \Phi_{\text{eff}} = \Phi_{\text{CNL}} + S(\Phi_m - \Phi_{\text{CNL}}) \]

In the MIGs model, the S factor is expected to depend only on the oxide. It is taken to vary empirically with the electronic part of the oxide constant \( \varepsilon_{\infty} \) as:

\[ S = \frac{1}{1 + 0.1(\varepsilon_{\infty} - 1)^2} \]

The value of \( \varepsilon_{\infty} \) is 4.0 for HfO\(_2\) which gives a result for S of 0.52, however this value overestimates the intrinsic Fermi level pinning; the essential problem was not to distinguish between intrinsic and extrinsic pinning mechanisms. Schaffer et al. [9] then showed that the effective work function of Pt was very dependent on its oxygen content and its treatment in a forming gas or oxidizing anneals. These data clearly indicates that \( \Phi_{\text{eff}} \) shifts on p-type metals are an extrinsic effect.

Robertson et al. [4] using this information found that the value of S for HfO\(_2\) was related with the value of S for SiO\(_2\). Assuming a value of S = 1 for SiO\(_2\), they found that S~ 0.82 for HfO\(_2\).

The authors explained that the benefit of the MIGS model is that it does not require any atomic model of the metal-oxide interface; it only depends on bulk material properties. However, it does not show the dependence on interfacial chemistry or atomic correction which is an incorrect approximation.

Moreover, in this paper is reported the calculation of the slope of the valence band offset (VBO) of metals on HfO\(_2\) calculated with DFT and corrected with GW (explain below) Vs \( \Phi_m \) experimental which gives a value of S = 0.92. The difference between the graphical, the experimental and the empirical formula of S values (0.92, 0.8 and 0.5 respectively) is due to the wide gap system.

Another important observation is that there is an offset between the barriers for polar and non-polar interfaces of 0.8 eV. The charges in the insulator create image charges in the metal. For the non-polar case, the distribution looks like a bulk insulator. For the polar case, there is a net dipole layer created at the oxide–metal interface, and this adds an extra band offset. This implies that the MIGs model gave a reasonable prediction of the band offsets when the interfaces are non polar.
An additional method for the calculation of $\Phi_{\text{eff}}$ was proposed by Fonseca et al. [2], they considers some experimental values to determine the $\Phi_{\text{eff}}$. In this method $\Phi_{\text{eff}}$ is dependent of the band gap of the dielectric ($BG_d$), the electron affinity ($EA_d$) and the VBO as:

$$\Phi_{\text{eff}} = BG_d + EA_d - VBO$$

Where $BG_d$ is taken to be the experimental band gap of the dielectric, and $EA_d$ the experimental electron affinity, with values of 5.7 eV and 2.9 eV respectively.

The VBO value can be obtain from two methods. The first one is by the electronic potential and the second one by the projected density of states (PDOS).

Figure 2, shows a graph of PDOS as function of energy, where the parameters $E_F$, $E_V$ and $E_{VBO}$ are observed.

However, in this equation the determined VBO value is scaled by the experimental (5.7 eV) to calculated dielectric (3.9 eV) band gap ratio to obtained good results.

![Figure 2. Calculation of VBO using PDOS.](image)

### 2.3 GW correction in the band gap offset

Within DFT applied for infinite systems the main source of error in the evaluation of the electronic levels and the transition energies reside in the used of the Kohn Sham eigenvalues.

The GW approximation (GWA) to the manybody problem, as proposed by Hedin and Lundquist [10], offers this more accurate description of the band structure of materials, by treating
explicitly the energy differences associated with the addition or the removal of one electron to or from the system.

They corrected the Khon-Sham eigenvalues by using the equation

\[(T + V_{est} + V_{hartree})\psi_i^{qp}(r) + \int dr' \sum (r, r'; \epsilon_i^{qp}) \psi_i^{qp}(r') = \epsilon_i^{qp} \psi_i^{qp}(r)\]

where the eigenvalues \(\epsilon_i^{qp}\) are complex numbers, with their real parts equal to the energy of the pseudoparticles associated with the eigenfunctions \(\psi_i^{qp}\).

This is equivalent to Khon-Sham equation if \(\sum (r, r'; \epsilon) = \delta(r - r')V_{xc}(r)\)

Making two assumptions

1) The difference between \(\sum = GW\) and \(V_{xc}\) is small.
2) The Khon-Sham wave function are close to the pseudoparticles wavefunctions

The Khon-Sham eigenvalues can be corrected

\[\epsilon_i^{qp} = \epsilon_i^{KS} + \langle \psi_i^{qp} | \sum (\epsilon_i^{qp}) - V_{xc} | \psi_i^{qp} \rangle\]

Because of the time consuming of this calculation, the authors applied GW to calculate the bulk electronic structure of the oxides alone thus correcting the DFT band edges shift obtained with GW.

Fonseca et al. calculated the band gap for m-HfO\(_2\) and also for c-HfO\(_2\), obtaining a value of 5.8 eV and 5.6 respectively, which shows that they obtained a good band gap in comparison with the experiments.

The authors used the band edge shifts obtained from GW calculations to correct DFT band offsets, which implies that the scaling of VBO theoretic and experimental is not necessary with this correction.

3. **Electronic structure of Pt/HfO\(_2\) interface with oxygen vacancy** [3].

Cho et al. [3] studied the electronic structure of Pt/HfO\(_2\) interface with oxygen vacancy. They suggest that the charge transfer between the oxygen vacancy and metal electrode can cause a large shift in the band offset.
3.1 Computational methods and model system

For the calculation for the effective work function of Pt the authors used VASP with a cutoff of 500 eV, k-point sample of 5 x 5 x 1, PAW pseudo-potentials and LDA exchange correlation. The vacuum used was 12 Å. As a model system they choose (1 x 1) unit cell of monoclinic HfO$_2$ (001) surface interface with (2 x $\sqrt{3}$) unit cell of Pt metal along (111) direction. To define the effect of the oxygen vacancy, they introduce vacancies in 8 different sites (Figure 3).

![Figure 3. Unit cell of the model structure. The oxygen vacancy positions are noted as 1-8.](image)

3.2 Results

Cho et al. [3] studied the effect of the oxygen vacancy in Pt/HfO$_2$ interface. They calculated the deformation energy of the surface at different positions of the oxygen vacancies, for two types of surfaces unrelaxed and relaxed (Figure 4). To do so, they used the following expression

$$\Delta \Omega = \Omega_l - \Omega_{l,bulk}$$

They found that for both type of calculations the total energies remain almost constant inside the slab but they drop sharply when the vacancy was right next to the metal layer. Moreover, they reported that when the atoms are allowed to relax, the binding energies increase by $\sim$2.0 eV due to the formation of additional Pt-Hf bonds at the interface regions. This strong binding of oxygen vacancy to the interface was attributed to the change in the transition level of the oxygen vacancy and formation of interfacial bonding.
The authors also reported the charge transfer per unit interface cell for vacancy positions 1 to 8 (Figure 5). They indicated that the charge transfer decreases monotonically as the oxygen vacancy moves away from the interface. When the vacancy is on 1 and 2 sites near the interface, the charge difference is about 0.1e but it decreases to 0.02e at the position 5.

Cho et al. [3] also calculated the band offset using PDOS in the clean interface and for the material with an oxygen vacancy in the fifth position (Figure 6), this calculation allow them to know the changes in the work function for these two cases.
Figure 6. The layer by layer position of the valence and conduction edges with respect to the metal Fermi level. Dashed lines represent the clean surface and the solid lines the result for the 5th vacancy of HfO$_2$.

The authors found that the oxygen vacancy localized in the fifth position decreases $\Phi_{eff}$ of Pt by approximately 0.6 eV. They conclude that due to the behavior of the VBO through the lattice, the shift in the $\Phi_{eff}$ is induced by the charge redistribution right at the interface, rather than throughout the HfO$_2$ slab, and that the VBO increase as vacancies segregated at the interface.

An important observation is that even though the charge transfer is small, the large lateral density results in a significant change in the band offset.

4. Pt/HfO$_2$ Interface Structures and Properties.

Fonseca et al.[2] studied the interface Pt/HfO$_2$ and determined the effective work function of this interface at different oxygen contents.

4.1 Computational details and interface model

For the calculation of the effective work function of Pt/HfO$_2$ the authors used VASP code with both LDA and GGA. Ultrasoft non local PPs were used for all the atomic species. K- space was done using a 5x5x1 k-point for the interface calculation based on the (1x1) m-HfO$_2$ unit cell.
vectors in the interface plane. The calculated oxygen adsorption energy on different sites of the Pt (111) surface used a model slab containing 9 Pt layers.

4.2 Results

Fonseca et al.[2] study Pt/m-HfO$_2$ at different oxygen content (0, 0.25, 0.5, 0.75 and 1 ML) at the interface. Figure 7. shows the structure for the first three content of oxygen. The oxygen free interface (0 ML) has only Pt-Hf bonds. Insertion of 1 oxygen per two Hf atoms (0.25 - ML) does not lead to the formation of Pt-O bonds, but reduces the number of Pt-Hf bonds. Pt-Hf bonds completely disappear at 0.75 ML-O at the interface, and the number of Pt-O bonds increases. Increasing the oxygen content to 1 ML-O results in significant roughening of the interface, which is caused by the repulsion between the oxygen ions at the interface. In this case the number of Pt-O bond increases to 6 with two oxygen atoms forming a single Pt-O bond.

Figure 7. Fully relaxed Pt/HfO$_2$ interface models containing different oxygen concentration (a) 0ML, (b) 0.25 ML and (c) 0.5 ML.
The authors calculated the valence band offset using PDOS analysis. They observed that the VBO drops sharply with the increase of oxygen concentration (Table 1)

Table 1. Calculated valence band offset and $\Phi_{\text{eff}}$ for Pt/m-HfO$_2$ interfaces with different O content.

<table>
<thead>
<tr>
<th></th>
<th>VBO (LDA) (eV)</th>
<th>VBO (GGA) (eV)</th>
<th>$\Phi_{\text{eff}}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0 ML</td>
<td>2.7</td>
<td>2.9</td>
<td>4.4</td>
</tr>
<tr>
<td>0.25 ML</td>
<td>2.2</td>
<td>2.0</td>
<td>5.7</td>
</tr>
<tr>
<td>0.5 ML</td>
<td>2.0</td>
<td>2.0</td>
<td>5.7</td>
</tr>
<tr>
<td>0.75 ML</td>
<td>1.3</td>
<td>1.3</td>
<td>6.7</td>
</tr>
<tr>
<td>1 ML</td>
<td>1.0</td>
<td>1.0</td>
<td>7.1</td>
</tr>
</tbody>
</table>

From the VBO the authors calculated the Pt $\Phi_{\text{eff}}$ on m-HfO$_2$ from the relation:

$$\Phi_{\text{eff}} = BG_d + EA_d - VBO$$

Where $BG_d$ and $EA_d$ are the dielectric band gap and electron affinity, respectively. To correlate the interface stoichiometry with the calculated VBO’s they used the experimental values for $BG_d$ and $EA_d$ (5.7 eV and 2.9 eV) and the VBO from Table 1 scaled by the experimental (5.7 eV) to calculated (3.9 eV) dielectric band gap ratio.

Fonseca et al. found that for stoichiometric interface conditions (0.5 ML-O) the Pt $\Phi_{\text{eff}}$ was 5.7 eV and for O-poor interface conditions (0 ML-O) the Pt $\Phi_{\text{eff}}$ was 4.4 eV. They found that this number were in good agreement with $\Phi_{\text{eff}}$ of Pt (111) for a clean surface and with the $\Phi_{\text{eff}}$ for Pt on m-HfO$_2$, respectively. The authors conclude that the good agreement between experimental and calculated $\Phi_{\text{eff}}$’s using the O-free interface is a strong indication that in fact, the HfO$_2$ interface is highly reduced and also that this results offer a clear explanation to the large difference measured for the Pt vacuum and effective work function.

5. Conclusions

The flat band voltage shift is one of the challenges for the new technology of transistor metal/HfO$_2$. 
The effective work function is interpreted as the change in the effective work function of metal gates interface with high k materials.

The calculation of the effective work function of Pt/HfO₂ has been studied by several authors using different techniques.

The calculation of the effective work function requires the consideration of the intrinsic and extrinsic states, as well as some corrections to obtain good agreement between the calculated and the experimental values.

The MIGS model gives a reasonable prediction of the band offset of non-polar interfaces.

GW correction gives a good band gap for m-HfO₂, which implies that now is possible the use of the BGₐ from DFT calculation, as well as, avoid the scaling of VBO.

The oxygen vacancy is strongly attracted to the interface and the charge transfer decreases as the vacancy moves away from the interface. Even though the charge transfer is small for oxygen vacancy inside the slab, the effective work function of Pt decreases as result of this charge transfer.

The good agreement between experimental and calculated $\Phi_{eff}$ using the O-free interface Pt/m-HfO₂ is a good indication that the HfO₂ is highly reduced and also that this results offer a clear explanation to the large difference measured for the Pt vacuum and effective work function.

The oxygen content and oxygen vacancies affect the $\Phi_{eff}$ of the Pt/m-HfO₂ interface. The control of $\Phi_{eff}$ is depending between other factors, of the oxygen content.

References


