Abstract

To further miniaturize microelectronic devices, the semiconductor industry is replacing the conventional SiO$_2$ dielectrics and the poly-Si gate with high dielectric constant oxides (such as HfO$_2$) and metals with appropriate effective work functions (EWF). But the thermal instability of EWFs and the difficulty to control EWFs to desirable values are currently postponing widespread application of metal electrodes. In this proposal, we attempt to understand the possible mechanisms for the EWF instability and assess the feasibility of various approaches to tune EWFs (e.g., modulating metal compositions, controlling interfacial structures) using density functional theory (DFT) calculations combined with statistical thermodynamics.
1. Introduction

In the last four decades, the silicon-based microelectronics industry has successfully produced faster, denser and cheaper integrated circuits by continuously scaling the dimension of the metal-oxide-semiconductor (MOS) field effect transistors. The conventional MOS stack is composed of poly-Si, SiO$_2$ and Si [cf. Fig. 1 (a)]. During the device miniaturization process, the thickness of SiO$_2$ layer has been progressively reduced to maintain its capacitance. It has been noticed since the late 1990s that simply scaling the transistors to meet Moore's Law [1] would face its biggest challenge because the SiO$_2$ layer is getting too thin, thereby introducing a significant leakage current in the insulating layer and deleteriously affecting circuit reliability and performance [2, 3]. In the meantime, the poly-Si electrode is becoming another roadblock because of its high resistivity and depletion problem. Thus, the transition from SiO$_2$ and poly-Si to a high dielectric constant dielectric (or “high k”) and a metal electrode (see Fig. 1) is an attractive pathway to drive the progression of Moore's Law. Such a replacement will allow for thicker physical dielectric layers while still providing the necessary capacitance [4, 5]. Some electronic products based on these new classes of transistors (using HfO$_2$ as oxide and metal as electrode) are already in production since 2007. [6]

However, the gate electrode choice problem is very complicated and has not been fully resolved. A critical property that guides the choice of the metal electrode is its effective work function (EWF) when in contact with the dielectric. EWF is defined as the energy offset between the metal Fermi level ($E_F$) and the oxide vacuum level ($E_{vac}$) (cf. Fig. 2). As schematically shown in Fig. 2, EWF is determined by

![Fig. 1: The MOS gate architectures. (a) Classic technology based on poly-silicon-silica contacts. (b) Emerging devices based on metal-high dielectric constant oxide contacts.](image)

![Fig. 2: Schematic draw of the band alignment of metal-oxide. $E_{vac,m}$ and $E_F$ are the vacuum level and Fermi level of the metal. $E_{vac,o}$, CBM, VBM and $E_F$ are the vacuum level, conduction band minimum, valence band maximum and band gap of the oxide, respectively. $D_{int, net}$ is the interface dipole moment.](image)
the vacuum work function (WF) of the metal itself and the dipole moment \( D_{\text{inet}} \) due to the charge transfer occurring at the metal-oxide interface. The relationship between the three could be described by \( EWF = WF + 4\pi D_{\text{inet}}/A \), where \( A \) is the interface area. The specific values that EWFs should have to be useful in p-type and n-type transistors are 4 eV and 5.1 eV, respectively, such that \( E_F \) is aligned with the conduction band and valence band edges of the silicon substrate. In the past, such a “tunability” has been achieved by p-doping or n-doping the poly-Si electrode. Migration to a metal electrode that can display the right EWFs thus requires a control over the vacuum work function (e.g., through the electrode composition variation) as well as the interface dipole moment (e.g., through the metal-oxide interface structure modulation). [9, 10]

In the last several years, extensive studies have been performed on different kinds of conductive materials to get the ideal EWFs, including pure metals, bi-metal alloys, metal nitrides, conducting metal oxides and metal silicides. But after post-gate annealing (~1000 °C), the EWFs of most studied electrode materials shift towards the midgap of the silicon substrate (~ 4.6 eV). [11, 12, 13] For example, the EWFs of Pt on top of HfO\(_2\) decreased from 4.9 eV to 4.6 eV after high temperature annealing. [11] On the other hand, 700 °C annealing increased the EWF of TaTi on top of SiO\(_2\) from 4 eV to 4.3 eV. These phenomena have been presumed to be a consequence of the interface dipole moment change in the presence of interfacial O defects, but there is no direct evidence. In this sense, a better understanding of the EWF shift upon annealing is essential for widespread application of metal gate electrodes.

More recently, implanting dopants at the metal-oxide interface has shown some promising trends. [14, 15] Rather than shifting away from desired values as reported for pure metal-oxide stacks, EWFs in doped stacks could shift towards the ideal values of 4 eV or 5.1 eV upon annealing. For example, incorporating Al at TiSiN-HfSiO\(_x\) interface increased the EWF from ~ 4.8 eV to ~ 5 eV after 1000 °C annealing. On the other hand, a La doped TiN-HfO\(_2\) interface eventually displayed an EWF of 4.1 eV. [16] However, only few dopants have been studied and the physical mechanism responsible for these specific shifts of EWF values is not clearly understood or well explored.
2. Proposed Research Plan

2.1 Research Objectives

In this proposal, we plan to address the issues discussed above and assess the feasibility of various approaches to tune EWFs (e.g., modulating metal compositions, controlling interfacial structures) using density functional theory (DFT) calculations combined with statistical thermodynamics. The knowledge obtained here may guide the optimization of the current metal/high-k/Si transistors and in the design of the next generation of transistors (e.g., those involving high mobility semiconductors such as Ge and GaAs).

The primary objectives of this proposal are three-fold, and include (1) understanding factors that control the vacuum work function of metals, (2) determining stable metal-oxide interface structures, and (3) controlling the interface dipole (and consequently the EWF). Each of these three objectives is described briefly below.

1) Vacuum work function of metals: This part of the study will involve the investigation of the surface stabilities and work functions of Pt, TiC<sub>x</sub>N<sub>1-x</sub> and TaC<sub>x</sub>N<sub>1-x</sub>. The impact of bulk composition, surface orientation and surface chemistry on vacuum work function values will be identified. Knowledge about the relative surface stability obtained in this part will provide guidance for our subsequent interfacial work.

2) Equilibrium interface structure: Considering the strong correlation between the interface structure and the EWF, this part aims at creating interface phase diagrams for metal-oxide heterostructures (e.g., Pt-HfO<sub>2</sub>, TiC<sub>x</sub>N<sub>1-x</sub>-HfO<sub>2</sub>) as a function of temperature (T) and O<sub>2</sub> pressure (P<sub>O<sub>2</sub></sub>). These phase diagrams will identify the interfacial oxygen content at a given (T, P<sub>O<sub>2</sub></sub>) condition and enable an atomic-scale understanding of the phase transformations at the metal-oxide interfaces during the annealing process.

3) EWF in M-HfO<sub>2</sub>, M-DL-HfO<sub>2</sub> and M-MNL-HfO<sub>2</sub>: Next, we plan to control the dipole moment at M-HfO<sub>2</sub> interfaces (M stands for metal, such as Pt and TiC<sub>x</sub>N<sub>1-x</sub>) by changing the interfacial O concentration, introducing interfacial dopants and inserting a molecular nanolayer, as schematically illustrated in Fig. 3 (a), (b) and (c), respectively.

Firstly, combining the phase stabilities and the EWF values for M-HfO<sub>2</sub> interfaces with various interfacial O concentrations, we will attempt to understand the possible mechanisms for the EWF shift upon annealing (e.g., the O point defect). Next, we will investigate the impact of a doping layer (DL) on the stability of the interface and the values of EWFs. The doped stack is represented by M-DL-HfO<sub>2</sub> and the dopants will be
simulated in the form of a monolayer of oxides, i.e., La$_2$O$_3$, Al$_2$O$_3$, at the interface. Critical factors such as the dopant valence, electronegativity and thermal stability on the EWF shift (increase or decrease) will be analyzed. An effort will also be made to understand the usefulness and impact of stable molecular nanolayers (MNLs) at the metal-oxide interface to control the EWF. The MNLs composed of short organic chains (-CH$_2$-) and terminated by different species (e.g., S, Si, Hf, etc.) would be considered, because such a MNL has been reported to be stable between Cu and SiO$_2$ and able to enhance the interface toughness. [18] Although MNLs have not been applied before to tune EWFs, they have been successfully used to vary the vacuum work function of various metals. [19, 20] For example, a thin layer of methyl viologen on (111) Au surface reduced the WF from 5.1 eV to 3.3 eV. [19] Using MNLs at the metal-oxide interface may enable us to tune the interface dipole moment easily through changing the length and termination of MNLs, to prohibit the reaction between the electrode and dielectric layers, and hence postpone the degradation of transistors.

2.2 Methods

All the proposed work will be performed using DFT [21] combined with statistical thermodynamics. DFT is the replacement of the intractable many-electron, many-nuclei Schrödinger equation by a set of one-electron Kohn-Sham equations which are more practical to solve using modern computers. Recently, DFT calculations have become increasingly popular because they currently offer the best tradeoff between accuracy and computational efficiency with the capability of treating systems as large as ~1000 atoms. The accuracy of DFT calculations is described in Fig. 4, which plots the DFT results versus the corresponding experimental values. As we can see, the geometry, work function, schottky barrier height, conduction band offset and valence band offset
determined from DFT calculations are in good agreement with the experimental values.

In this project, all DFT calculations are performed using the VASP code [23]. A typical calculation of Pt-HfO₂ interface consisting of 120 atoms takes approximately 500 hours (21 days) on a single AMD 2.6 GHz processor. In order to finish these simulations in a tractable amount of time, calculations are performed in the Linux parallel computing environments located at IMS, the Connecticut Institute of Supercomputing and Visualization (CISV) within the UConn School of Engineering and the National Science Foundation (NSF) Teragrid.

![Fig. 4: The comparison between DFT and experimental results. (a) Lattice constant or bond length. (b) Other properties [e.g., schottky barrier height (SBH), conduction band offset (CBO), valence band offset (VBO) and work function (WF)]. [22]](image)

3. Completed Work

3.1 Work function of Pt, TiCₓN₁₋ₓ and TaCₓN₁₋ₓ [24, 25]

As one of the components of the EWF, controlling the vacuum work function is a promising way to achieve the ideal EWFs. Based on the work completed so far, we have demonstrated the ability to modulate the vacuum work function of metals, e.g. through control of compositions and/or surface chemistry.

The normally observed surface orientations for Pt, TiCₓN₁₋ₓ and TaCₓN₁₋ₓ, which are (001), (110) and (111), have been considered here. Table I lists all the possible stacking sequence for each metal along each of these three directions. We note that for Pt all planes are equivalent, but for a binary or ternary alloy, depending on the bulk
composition and orientation, the stacking sequence of planes and the composition within the planes can vary. The calculated work functions of all possible surface terminations are collected in Fig. 5, in which the circled data corresponds to the most stable surface termination of each metal or metal alloy determined using a detailed thermodynamic analysis [24, 25]. Several interesting observations can be made. (1) Our determination for the stable (111) Pt surface of 5.8 eV is in excellent agreement with the experimental value of 5.8 ~ 5.9 eV [21]. (2) The stable surfaces for TiC$_{x}$N$_{1-x}$ and TaC$_{x}$N$_{1-x}$ are mainly (001) type with surface composition depending on the bulk composition [cf. Fig. 5 (b) and (c)]. The work functions for these stable surfaces increase monotonically with the carbon ratio (x) in the solid solution. For example, from pure transition metal nitride to pure transition metal carbide, vacuum work function increases by ~ 1.4 eV for TiC$_{x}$N$_{1-x}$ and by ~ 0.6 eV for TaC$_{x}$N$_{1-x}$. (3) For each alloy composition, the work function depends significantly on the surface orientation and termination, varying as much as 2.5-4.4 eV for TiC$_{x}$N$_{1-x}$ (2.1-3.3 eV for TaC$_{x}$N$_{1-x}$).

<table>
<thead>
<tr>
<th>Bulk composition</th>
<th>Pt</th>
<th>TiC$<em>{x}$N$</em>{1-x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Direction</td>
<td>x = 0</td>
<td>x = 0.25</td>
</tr>
<tr>
<td>(001) Pt</td>
<td>TiN</td>
<td>TiCo$<em>{0.5}$N$</em>{0.5}$</td>
</tr>
<tr>
<td>and</td>
<td>TiN</td>
<td>TiCo$<em>{0.5}$N$</em>{0.5}$</td>
</tr>
<tr>
<td>(110) Pt</td>
<td>TiN</td>
<td>TiCo$<em>{0.5}$N$</em>{0.5}$</td>
</tr>
<tr>
<td></td>
<td>TiN</td>
<td>TiCo$<em>{0.5}$N$</em>{0.5}$</td>
</tr>
<tr>
<td>(111) Pt</td>
<td>TiN</td>
<td>T</td>
</tr>
<tr>
<td>Pt N CN$_3$ CN</td>
<td>CN</td>
<td>C$_3$N</td>
</tr>
<tr>
<td>Pt Ti Ti Ti Ti Ti Ti</td>
<td>Ti</td>
<td>Ti</td>
</tr>
<tr>
<td>Pt N CN$_3$ CN</td>
<td>CN</td>
<td>C$_3$N</td>
</tr>
</tbody>
</table>

Table I: The stacking sequences of Pt and TiC$_{x}$N$_{1-x}$ along the <001>, <110> and <111> directions. TaC$_{x}$N$_{1-x}$ has similar stacking sequences as TiC$_{x}$N$_{1-x}$, which are not listed here.

Fig. 5: Work functions of all surface terminations considered: (a) Pt, (b) TiC$_{x}$N$_{1-x}$, and (c) TaC$_{x}$N$_{1-x}$. The circled data correspond to the work function of the most stable surface termination for each bulk composition which is determined based on a separate surface energy analysis.
Particularly noteworthy are the C₃N₁ₓₓ-terminated (111) surfaces which display the highest work function.

### 3.2 Interface phase diagrams for Pt-HfO₂ [26]

Compared to the bulk vacuum work function, the interface dipole is gaining a lot of research interest as a promising way to tune EWFs, because it could be controlled by the interface structure. As described in ref. [11-13], the O vacancy or interstitial density at the interface may change with the annealing condition and hence affect the dipole moment. However, such an interfacial structure change is difficult to identify experimentally. Here, combining DFT results and thermodynamics, we have identified stable Pt-HfO₂ interface structures as a function of temperature and O₂ pressure. The approach employed in this part could be also applied to other interface or surface systems.

Our interface model is created by placing (111) Pt on top of (001) monoclinic HfO₂ (m-HfO₂). The former is stretched to match the latter. The corresponding interface configuration is represented by Pt:Θ₀: HfO₂, where Θ₀ is the interfacial O coverage, ranging from 0 to 2 monolayers (ML). Three representative interface structures are shown in Fig. 6. When Θ₀ = 0, the Pt and HfO₂ parts are bonded through Pt and Hf atoms. When Θ₀ = 1, one half of the interfacial O atoms passivates the interfacial Hf atoms and the other half bonds to interfacial Pt atoms. When Θ₀ > 1, the extra O atoms sit between the two Pt layers next to the interface. As shown in Fig. 6, the local structure of Pt-O bonding at the Pt: 2: HfO₂ interface mimics a distorted platinum oxide.

The stable interfaces are those with minimum interface free energy (Y₀), which can be defined as:

\[ Y₀ = \left( G_{\text{Pt:Θ₀:HfO₂}} - n_{\text{Hf}}\mu_{\text{Hf}} - n_{\text{O}}\mu_{\text{O}} - n_{\text{Pt}}\mu_{\text{Pt}} \right)/A - \sigma_{\text{HfO₂}} - \sigma_{\text{Pt}} \tag{3} \]

where \( G_{\text{Pt:Θ₀:HfO₂}} \) is the Gibbs free energy for the heterostructure and \( A \) is the interface area.
area. \( n_{\text{Hf}} \), \( n_{\text{O}} \) and \( n_{\text{Pt}} \) are the number of Hf, O and Pt in the heterostructure. \( \mu_{\text{Hf}} \) and \( \mu_{\text{O}} \) are the chemical potentials of Hf and O in bulk \( m-\text{HfO}_2 \) and \( \mu_{\text{Pt}} \) is the chemical potential of fcc-Pt. \( \sigma_{\text{HfO}_2} \) and \( \sigma_{\text{Pt}} \) stand for the energies of the two free surfaces in the interface model and are treated as a constant because it is insensitive to the interface structure change. Moreover, \( \mu_{\text{Hf}}, \mu_{\text{O}} \) and \( \mu_{\text{Pt}} \) in Eq. (3) satisfy the following relationship.

\[
\mu_{\text{Hf}} + 2\mu_{\text{O}} = G_{\text{HfO}_2}
\]

\[
\mu_{\text{Pt}} = G_{\text{Pt}}
\]

where \( G_{\text{HfO}_2} \) and \( G_{\text{Pt}} \) are the Gibbs free energies for bulk \( m-\text{HfO}_2 \) and bulk Pt, respectively. Substituting Eq. (4) into Eq. (3) results in

\[
\gamma_{\theta_0} = \left[ G_{\text{Pt}:\theta_0:\text{HfO}_2} - n_{\text{Hf}} G_{\text{HfO}_2} - n_{\text{Pt}} G_{\text{Pt}} \right] / A - \sigma_{\text{HfO}_2} - \sigma_{\text{Pt}}
\]  

(5)

When \( \theta_0 = 0.5 \), the whole system is stoichiometric (\( n_{\text{Hf}}: n_{\text{O}} = 1:2 \)) and the interface energy is

\[
\gamma_{0.5} = \left( G_{\text{Pt}:0.5:\text{HfO}_2} - n_{\text{Hf}} G_{\text{HfO}_2} - n_{\text{Pt}} G_{\text{Pt}} \right) / A - \sigma_{\text{HfO}_2} - \sigma_{\text{Pt}}
\]  

(6)

Using \( \gamma_{0.5} \) as a reference, we can further define the relative interface energy as

\[
\gamma'_{\theta_0} = \gamma_{\theta_0} - \gamma_{0.5}
\]

\[
= \left[ G_{\text{Pt}:\theta_0:\text{HfO}_2} - G_{X:0.5:\text{HfO}_2} - (n_{\text{O}}-2n_{\text{Hf}})\mu_{\text{O}} \right] / A
\]  

(7)

This relative interface energy determines the stability of various interface structures and in turn the interface phase diagram. The Gibbs free energy terms can be written as a function of enthalpy and entropy.

\[
G = E + \Delta H(T, P) - T \times (S_{\text{vib}} + S_{\text{con}})
\]  

(8)

\( E \) is the enthalpy at 0 K, which can be obtained from DFT calculations, \( \Delta H(T, P) \) is the enthalpy deviation from \( E \) at temperature \( T \) and pressure \( P \), and \( S_{\text{vib}} \) and \( S_{\text{con}} \) are the vibration and configuration entropy, respectively. Substituting Eq. (8) into Eq. (7) and assuming that Pt: \( \theta_0 \): HfO\(_2\) and Pt: 0.5: HfO\(_2\) have similar \( \Delta H(T, P) \) and \( S_{\text{vib}} \), we can rewrite Eq. (7) as below

\[
\gamma'_{\theta_0} = \left[ E_{\text{Pt}:\theta_0:\text{HfO}_2} - E_{X:0.5:\text{HfO}_2} - kT \ln \Omega_{\theta_0} - (n_{\text{O}}-2n_{\text{Hf}})\mu_{\text{O}} \right] / A
\]  

(9)

where \( \Omega \) is the number of equivalent arrangements of \( \theta_0 \) O atoms at the interface. Considering the system is in equilibrium with the surrounding gas reservoir of interest, we replace \( \mu_{\text{O}} \) with one half of the chemical potential of an oxygen molecule, \( \mu_{\text{O}_2} \), which
is a function of temperature and oxygen pressure. $\mu_{O_2}$ can be obtained from statistical thermodynamics or JANAF thermodynamic tables [27]. Finally, we get

$$\gamma'_{\theta_0} = \left[ E_{\theta_0:HfO_2} - E_{\theta_0:HfO_2}^{0.5} - kT \ln \frac{\Omega_{\theta_0}}{\Omega_{\theta_0:0.5}} - (n_{O}/2-n_{Hf})\mu_{O_2}(T,P_{O_2}) \right]/A \quad (10)$$

Based on Eq. (10), one can compute the interface energy of various interface structures at a given $(T,P_{O_2})$. The interface phase diagram could be obtained by identifying the most stable interface for given $T$ and $P_{O_2}$.

The computed interface phase diagram for Pt: $\theta_{O}:HfO_2$ is shown in Fig. 7. As we can see, the oxidation of the Pt-HfO$_2$ interface occurs at a high oxygen pressure and low temperature. In the normal or most expected processing condition (i.e., $300 < T < 1500$ K and $10^{-12} < P_{O_2} < 1$ atm), the stable interfacial O coverage between Pt and HfO$_2$ is most likely to be $\sim 0.75$ ML. In view that the experimental data for the Pt-HfO$_2$ interface morphologies are sparse, we compared our calculated phase diagram with the experimental data for Pt surface oxidation. Since 0.5 ML O at the Pt-HfO$_2$ interface passivates the HfO$_2$ and has little interaction with Pt, the net interfacial O strongly bonded to Pt is actually $\theta_{O} = 0.5$. For example, the interfacial Pt in Pt:0.5: HfO$_2$ behaves like a clean Pt interface. In Fig. 7, the open and solid circles stand for the $(T,P_{O_2})$ combinations at which a 0.25 ML O-adsorbed (111) Pt surface and a clean (111) Pt surface are observed in experiment, respectively, consistent with our phase diagram. Another interesting finding of this work is that the oxidation of Pt at the interface is similar to that of a free (111) Pt surface. The saturation coverage of the chemically adsorbed O on (111) Pt surface is 0.25-0.3 ML, after which a layer of PtO$_2$ forms
immediately on the surface. Here, we find that the corresponding $\theta_0 = 0.5$ ML value beyond which interfacial PtO$_2$ is formed is 0.25.

3.3 Effective work function for Pt-HfO$_2$ [29]

Based on the equation $(EWF = WF + 4\pi D_{i,\text{net}}/A)$ and the values of $D_{i,\text{net}}$ obtained from DFT calculations, we determined the EWF for each Pt: $\theta_0$: HfO$_2$ interface structure considered [cf. Fig. 8 (a)]. The important features of the plot could be summarized as follows. (1) The interface dipole moment (or EWF) is dependent on the interfacial O content. (2) The EWFs of the most expected interfaces [red filled squares in Fig. 8 (a)] increase from 3.71 eV to 5.45 eV with $\theta_0$ increasing from 0 to 0.75 ML. (3) Further oxidation of Pt: 0.75: HfO$_2$ to Pt: 2: HfO$_2$ only decreases EWF by $\sim 0.09$ eV. Hence, the saturation EWF for Pt-HfO$_2$ is $\sim 5.45$ eV.

By combining EWF results and the interface stability, we next portray the averaged effective work function ($\overline{EWF}$) in Fig. 8 (b), which is defined as

$$\overline{EWF} = \sum_{\theta_0=0}^{2} EWF_{\theta_0} \times P_{\theta_0} = \sum_{\theta_0=0}^{2} EWF_{\theta_0} \times \frac{\exp(-\gamma_{\theta_0}/kT)}{\sum_{\theta_0=0}^{2} \exp(-\gamma_{\theta_0}/kT)}.$$  

(11)

where $EWF_{\theta_0}$ and $P_{\theta_0}$ are the EWF and the probability of $\theta_0$ coverage.

As we can see, depending on the temperature and pressure, the probability of each interface structure we considered and hence $\overline{EWF}$ could vary. The predicted $\overline{EWF}$ at the

![Fig. 8: (a) EWFs of Pt: $\theta_0$: HfO$_2$. The data corresponding to most expected interfaces is indicated by red filled squares. Black circles are the prior experimental values for Pt-HfO$_2$ interface. The vacuum work function is represented by “⋆”. (b) EWF as a function of T and O$_2$ pressure. The most expected annealing condition is indicated in the figure.](image-url)
most expected annealing condition (4.4-5.5 eV) is in excellent agreement with the reported experimental values (4.6-5.51 eV) [11, 30]. Although Fig. 8 (a) informs us the potential of Pt as an n-type metal with a low EWF (~ 4 eV), in fact, it can be only achieved at extremely high temperature and low O₂ pressure [cf. Fig. 8 (b)]. In sum, our work theoretically proves the prior presumption that the interfacial O coverage is responsible for the instability of EWF with annealing [11-13].

4. Proposed Work

So far, we have identified factors that control the vacuum WFs of several metals, developed a procedure to compute the interface phase diagrams and correlated the atoms level interface structure to the EWF. Specifically, using Pt-HfO₂ as an example, we have shown that the interfacial O concentration is responsible for the EWF shift during the high temperature annealing. In future work, we would focus on engineering the interface structure to tune the interface dipole moment and hence the EWF by incorporating dopants or molecular nanolayers at the metal-oxide interface (cf. Fig. 3).

4.1 Dopants at Pt-HfO₂ interfaces and TiN-HfO₂ interfaces

Building on prior experience of pure Pt-HfO₂ interfaces, we would apply a similar approach to study the Pt-DL-HfO₂ interfaces [see Fig. 3(b)], where DL (doping layer) is a monolayer of an oxide different from HfO₂. Appropriate doping elements across the periodic table would be selected. For example, La, Al, Y, etc., would be considered because their oxides are thermodynamically stable and have high dielectric constants and large band gaps. The interface stability, EWF and EWF of each Pt-DL-HfO₂ interface considered would be analyzed to determine the most promising dopants for NMOS and PMOS devices, respectively. The appropriate dopants identified would be next applied to the more complicated TiN-HfO₂ interfaces for further analysis, as TiN is expected to be used in the semiconductor industry.

4.2 Molecular nanolayer at Pt-HfO₂ interfaces

Finally, an attempt will be made to create atomic level models of Pt-MNL-HfO₂ [see Fig. 3(c)]. The MNLs will be composed of short organic chains (-CH₂-) and terminated by different species (e.g., S, Si, Hf, etc.). The adhesion of various MNLs to both Pt and HfO₂ would be studied. The ability of MNLs to modify the interface dipole moment and hence the EWF by varying MNL the length and termination will also be explored.
5. Impact of work

The procedures to create the interface phase diagrams, the methodology to compute EWFs and the steps to correlate EWFs to \((T, P_{O_2})\) developed here are broadly applicable to other systems as well. Using Pt-HfO\(_2\) as an example, we have demonstrated that the interfacial O coverage variation is the underlying reason for the widely observed EWF shift during annealing. Finally, the insights on the appropriate way to tune EWFs obtained in this work may help the optimization of the current metal/high-k/Si based MOS devices and the designing of the next generation transistors (e.g., using germanium or gallium nitride as substrate in which case the desirable EWF is no longer ~ 4 eV or 5 eV). The approach of using interfacial dopants or molecular layers for work function tuning has the potential to significantly impact the design and fabrication of sub-50-nm transistors.

7. References