Impact of nitrogen on effective work function of Metal/Oxide stack: a first-principles study of the Pt/HfO₂ interface

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Abstract

Modulating the effective work function (Φ_{eff}) of metal electrodes is both crucial and challenging in metal-oxide-semiconductor transistors. The introduction of atomic dopants is shown to be an effective method to modify the interface Φ_{eff} . Here we apply the first principles calculations to systematically explore the impact of incorporation of the non-metallic ambient gas element N on the effective work function of a Pt/HfO₂ interface. We find that Φ_{eff} is very closely related to the doped atomic position and concentration of the incorporated N atoms. The incorporation is favored at the interface near HfO₂ side, and it can significantly increase the interface Φ_{eff} for the Pt/HfO₂ stack (making it more *p*-type). Also, the Φ_{eff} increases with the increase of doped N concentration due to the mitigation effect of doped N on interface dipole moment. Our findings will provide guidance in developing the environment annealing approach to modulation of Φ_{eff} of the Metal/Oxide stack.

Key words: A. Metal/Oxide interface; B. N dopant; D. Work function; E. First-principles study;

1. Introduction

Metal/metal oxide interfaces play an important role in several fields of modern science and technology, such as catalysis or coatings, and are central in the complementary metal-oxide-semiconductor (CMOS) process. Propelled by Moore's law, the transistor scaling race continues relentlessly for decades, and innovations in gate stack have been a crucial part of the success of the semiconductor technology [1-2]. In order to continue this development, and orchestrated effort is needed towards battling the leakage current problem, where the replacement of SiO₂ with high dielectric constant gate dielectric and the poly-silicon electrode with a metal gate promises to provide a suitable a solution [3].

As a transition metal with unique properties, platinum has high work function, high chemical stability, and strong catalytic activity. Hf-based oxides (*e.g.*, HfO₂) exhibit the best combination of desired properties and have been successfully introduced into the 45-nm technology node along. Thus, the Pt/HfO₂ stack is generally used as supported

catalysts and as a promising metal gate/high- k dielectric combination in advanced CMOS. The work function of a metal electrode needs to be optimized in such a way that the metal Fermi level lines up with either the valence band maximum or conduction band minimum of the underlying Si substrate. However, it was experimentally shown that the platinum work function is high, varying between 4.6 and 4.9 eV in the p -type CMOS device, different from its vacuum work function (~ 5.6 eV), due to several interfacial effects (such as charge transfer, bond formation, defect accumulation, dipole creation, *etc.*) [4]. Generally speaking, the vacuum level discontinuity across the interface implies that the work function of the metal on the surface may be different from that of the interface. The latter is generally known as the effective work function (Φ_{eff}), which depends on the surface work function of metal (Φ) as well as the additional dipoles generated at the metal and oxide interface [5]. Therefore, the Φ_{eff} is a critical parameter in designing the metal electrodes, and it strongly depends on the processing conditions (*e.g.*, the oxygen and nitrogen partial pressure during annealing) to which the device is subjected.

It has been widely reported that Φ_{eff} of metals is strongly related to the processing conditions, and the Φ_{eff} of many metals is shifted toward the middle of the Si band gap upon high temperature annealing, regardless of the initial value of the vacuum work function [6]. Experiment and theory suggest possible ways of tuning Φ_{eff} by implanting dopants into the gate stack, or by introducing an interfacial “capping” layer either at the Si/HfO₂ interface or at the metal/HfO₂ interface [7]. There are many reported ways of tuning the Φ_{eff} of gate electrodes, for example, by dopants implantation and annealing, which induces the variation of the metal-dielectric interface status, which leads to the modulation of the work function of the gate electrode [8]. For example, such tuning can be achieved by inserting a capping layer with a dipole moment pointing from dielectric to metal at metal/HfO₂ interfaces or pointing from Si to dielectric at Si/HfO₂ interfaces [9], or by implanting Al into TiN electrode by diffusion [10]. The Pt/HfO₂ interface stack is usually annealed in forming gas or ambient atmosphere which contains N₂, especially in the post metallization anneal (PMA) process of gate-first CMOS integration scheme [11]. The role of oxygen at the Pt/HfO₂ interface has been researched extensively [12], but

how nitrogen impacts the metal/metal oxide interface remains unknown.

Here we describe the results of our theoretical exploration of the dependence of the metal/High- k interface properties on the atmosphere treatment conditions. We propose that effective work function adjustment can be obtained this way. In this work, we have adopted the density functional theory calculations to explore the impact of element N on the Φ_{eff} of Pt/HfO₂ stack in an ambient annealing atmosphere, and we have determined the variation in morphology of the Pt/HfO₂ interface with implantation of elemental nitrogen.

2. Method

Our work function calculations were performed using the *Vienna ab initio Simulation Package* (VASP) based on the density functional theory (DFT) [13] and the projector-augmented wave (PAW) pseudo-potential [14]. The exchange-correlation function was treated within the *Perdew, Burke and Ernzerhof* (PBE) [15]. The total energy was converged to within 1 meV with a kinetic energy cutoff of 400eV. *Monkhorst-Pack* k -point meshes are adopted, *i.e.*, $11 \times 11 \times 11$ and $15 \times 15 \times 15$ for interface structure relaxation and static calculation, respectively. All calculations assume no spin polarization and are performed using the 'accurate' setting within VASP to avoid wraparound errors. We choose monoclinic phase (m -) HfO₂ as a model structure, and the calculated lattice constants for bulk m -HfO₂ are $a = 5.136 \text{ \AA}$, $b = 5.195 \text{ \AA}$, $c = 5.307 \text{ \AA}$ and $\beta = 99.76^\circ$, which is about 2% higher than the experimental value of $a = 5.116 \text{ \AA}$, $b = 5.172 \text{ \AA}$, $c = 5.295 \text{ \AA}$ and $\beta = 99.18^\circ$, due to the GGA error [16]. The calculated lattice constant of the bulk Pt is $5.136 \text{ \AA}$, in good agreement with the experimental value of $a = 5.128 \text{ \AA}$ [17]. Next, we choose (1×1) unit cell of HfO₂ (001) surface interfaced with $(2 \times \sqrt{3})$ unit cell of Pt surface (111) surface orientations. To match the lateral periodicity, the requirement of least strain for interface needs to be taken into account. *i.e.*, Pt surface is stretched to match HfO₂ surface, and -5.2% and 8.3% strain emerges along a and b directions of HfO₂, respectively. Such a strain state is considered appropriately, because Pt is to be deposited on a HfO₂ film in the actual production process and the Pt layer is expected to conform to the HfO₂ layer. Our interface model was constructed in a

super-cell that consist of Pt/HfO₂ hetero-structure and a vacuum of 10Å. All atoms were allowed to relax to their equilibrium positions. To determine the preferred configuration of N dopant at the near-interface area, as well as its segregation into the oxide or the metal slab, we calculated the corresponding interface formation energy. The lower interface formation energy means the structure is more thermodynamically stable. The formation energy (E_{form}) is general a function of chemical potential and can be estimated by [18], $E_{\text{form}} = [E_{\text{doped}} - E_{\text{pure}} - n(E_{\text{N}} - E_{\text{M}})]/A$, where E_{doped} is the total energy of the doped super-cell configuration, n is the number of atoms of element N in the super-cell, E_{pure} is the total energy of undoped super-cell, and E_{N} and E_{M} are respective the chemical potential of doping element and the substituted element [19]. Subsequently, the methodology to determine Φ_{eff} is supposed to discuss. The effective work function can be derived by using the interface dipole moment for the structure identified above and the Pt vacuum work function (Φ), which can be expressed as [6],

$$\Phi_{\text{eff}} = \Phi + \Delta\Phi = \Phi + 4\pi\Delta\mu/A \quad (1)$$

where A is the interface area, and $\Delta\mu$ is the extra dipole moment generated at the interface when metal contacts dielectric (oxide). Because Pt surface is stretched to match HfO₂ surface, we should take vacuum work function of strained Pt surface as Φ . The calculated Φ for the strained (111) Pt surface (required to form a coherent interface with HfO₂ as described above) is 5.72 eV in this work and corresponding value for the Pt slab equilibrium is 5.68 eV (consistent with experimental value of 5.65 eV), which is according with the Φ -strain relationship was reported in our previous work [20].

3. Results and Discussions

A. Configurations concerned

To understand energetics of N dopant within the Pt/HfO₂ hetero-structure, we've performed separate calculations for different interface configurations. The relaxed Pt/HfO₂ structure is shown in Figure 1. It's noted that the HfO₂ side for the clean interface in present work is fully O terminated, which is mainly formed by Pt-O bonds with bond lengths ranging from 1.735 angstrom to 2.009 angstrom.

FIG.1. The model Interface of Pt/HfO₂ heterostructure. HfO₂ side layers of O atoms (left) and Pt side layers of Pt atoms (right) substituted by N atoms are noted as L1-L3 and R1-R3, respectively.

In order to describe morphology of the Pt/HfO₂ with element N dopant implantation, we consider two basic configurations (see Fig. 1), *e.g.*, substituting N for O atoms on the dielectric side (No) and substituting N for Pt atoms on the metal side (N_{Pt}), and model the various interface morphologies by varying the concentrations and doped positions. In each case the atomic positions were relaxed and the in-plane lattice constants and all angles are kept fixed. Next, we further construct the difference models for each configuration (as illustrated in Fig. 1), *i.e.*, (1) a clean Pt/HfO₂ interface (referred as a clean model), and when the doped layer is (2) the first interface layer (L1 or R1 model), (3) the second layer (L2 or R2 model), and (4) the third layer (L3 or R3 model) of the metal or dielectric side, respectively. In the case of No-L1 model, the N atoms are supposed to be fourfold coordinated and segregate the interface layer, which are bonded to 2 Pt and 2 Hf atoms. Due to the larger atomic radius of N relative to O, the N atoms move slightly closer to the interface deviating from original O position, and the lengths of Pt-N bonds ranging from 1.925 angstrom to 2.313 angstrom.

B. Formation energy of N at the interface

FIG. 2. Formation energy per interface area (in $\text{eV}/\text{\AA}^2$) of N doped Pt/HfO₂ heterostructure as a function of dopant atoms number with respect to undoped system. (a) No configurations concerned with L1-L3 Models. (b) N_{Pt} configurations concerned with R1-R3 Models.

The formation energies for doped hetero-structures (with respect to that of a perfect system) as a function of N dopant atoms number are plotted in Fig. 2. In the case of No configuration (Fig.2a), formation energies are negative and decrease dramatically with the increase of N concentrations. The formation energy of L1 model decreases more significantly in comparison with the other models, which means nitrogen atoms are energetically inclined to segregate into the Pt/HfO₂ interface. However, in the case of N_{Pt} configuration (Fig.2b), formation energy increases firstly then decreases with the increase of N concentrations, and most values of E_{form} are positive. It indicates that N is very difficult to diffuse to Pt side of stack. Therefore, nitrogen atoms prefer to segregate the interface by substituting O atoms in HfO₂ side, which is mostly due to fact that the radius and electro-negativity of nitrogen are much closer to those of oxygen compared with platinum. Then, we will employ the No configuration to investigate the effective work function of N doped Pt/HfO₂ stack in the following sections.

C. Impact of interface N on the effective work function

As discussed above, due to interface effect, the actual work function doesn't always correspond to vacuum work function in experimental observation [21]. This work

function shift ($\Delta\Phi$) can be defined by the difference of the effective work function of stack and the vacuum work function of corresponding metal. We can rewrite equation (1) as, $\Delta\Phi = \Phi_{\text{eff}}(\text{Pt}/\text{HfO}_2) - \Phi(\text{Pt}) = 4\pi\Delta\mu/A$, where $\Phi(\text{Pt}/\text{HfO}_2)$ and $\Phi(\text{Pt})$ are the work function of the interface system and Pt surface slab, respectively.

Considering unstable N_{Pt} configuration, we adopt N_{O} configuration to investigate the work function for HfO_2/Pt system. N dopant induced changes in the work function shift ($\Delta\Phi$) as a function of N atoms number (*i.e.*, N dopant concentration) is shown in Figure 3. We found that $\Delta\Phi$ is strongly correlated with N concentrations and doped positions (doped layers). Firstly, the work function shift for N_{O} configuration for all models (including clean and L1-L3 models) are negative, which indicates Φ_{eff} of stacks is less than Φ of Pt surface, and the absolute value of work function shift ($|\Delta\Phi|$) decreases with the increase of N concentration (*i.e.*, the Φ_{eff} decreases with the increase of N concentration). Specifically, the $\Delta\Phi$ undergoes a drastic increase in comparison to undoped system when one N atom is doped. Next the increasing trend becomes much more smooth and steady when doped N is increased to two, three and four atoms, respectively. Secondly, the presence of N atoms in the L1 model has a significant effect on the work function shift. As seen in the inset in Fig. 3, replacing one O atom by N atom in the L1 model results in a decrease of about 0.2 eV or 75% in the $|\Delta\Phi|$ compared to the clean model. When doped N atoms are gradually far away from the interface (the N is placed in the second L2 or third L3 layer), their value of work function does not show any obvious shifts. Above results will provide experimentalists with some insights in engineering the Φ_{eff} (or $\Delta\Phi$) by controlling the proportion of N_2 and O_2 of the annealing atmosphere. This results are consistent with the prior experimental observations in which Pt/HfO_2 stack after annealing in air or N_2 atmosphere displays a larger Φ_{eff} than that as-deposited state [22], and indicates N is an efficient dopant for *p*-type MOSFETs.

FIG. 3. N dopant induced changes in work function shift ($\Delta\Phi$, in eV) as a function of N concentration. Inset: the $\Delta\Phi$ of the four types of interface models: clean, L1, L2 and L3.

To examine the origin of this shift, we try to establish the relationship between the work function shift and interface dipole moment as well as electron density distribution. According to equation 1, the $\Delta\Phi$ is proportional to interface normal component of extra dipole moment ($\Delta\mu$) induced by interface effect, and the $\Delta\mu$ of interface system $\mu(\text{Pt}/\text{HfO}_2)$ can be given as [21], $\Delta\mu = \mu(\text{Pt}/\text{HfO}_2) - \mu(\text{HfO}_2) - \mu(\text{Pt})$, where $\mu(\text{Pt}/\text{HfO}_2)$, $\mu(\text{HfO}_2)$ and $\mu(\text{Pt})$ are surface normal components of dipole moments of interface, HfO_2 substate, and Pt layer respectively. The $\Delta\mu$ of doped system is determined by the electronic interaction between N and other atoms in Pt/HfO₂ interface, which can be derived as [23], $\Delta\mu = -\int_{z_0}^{z_0+l/2} z\Delta\rho(z)dz$, where z direction is perpendicular to the interface plane, z_0 is chosen to be at the center of HfO₂-substrate side, and l is the length of the stack in the z direction. The $\Delta\rho$ is the charge density difference averaged over the plane parallel the surface at some position z , described by, $\Delta\rho(z) = \rho(z)_{\text{Pt}/\text{HfO}_2} - \rho(z)_{\text{Pt}} - \rho(z)_{\text{HfO}_2}$, where $\rho(z)_{\text{Pt}/\text{HfO}_2}$ is the charge density of the interface system. $\rho(z)_{\text{Pt}}$ and $\rho(z)_{\text{HfO}_2}$ are the charge densities of the isolated clean Pt layer and HfO₂ substrate respectively, both of which are in the precise positions adopted at their corresponding interface system [24].

FIG. 4. Charge density difference of No-L1 configuration with different concentrations as a function of the direction perpendicular z to the interface. The positions of atoms are listed by circles in the bottom, and doped area in HfO₂ side is drawn by yellow.

By analyzing the charge density difference (Eq. 7), we can explain the mechanism of $\Delta\Phi_{\text{eff}}$ shifts in terms of extra dipole moment at the interface. For a given metal/dielectric stack, extra interface dipoles are formed in the interface region due to electron transferring from Pt side to dielectric (HfO₂) side. Figure 4 displays the distributions of $\Delta\rho$ for No-L1 model with different concentrations as a function of the direction perpendicular z to the interface. Clearly, the interaction of N with Pt/HfO₂ is noticeable. Firstly, the interface dipole is mainly due to the contribution of the first atom layer (L1), while the second layer (L2) has a very small contribution to the interface dipole and the effects of the third (L3) as well as farther layers are negligible. This result explains that L1 model exhibits most significant effect on the work function shift in the L1-L3 models. Furthermore, it is evident from Fig. 4 that the amplitude of $\Delta\rho$ decreases when doped-N concentration increases, *i.e.*, diffusion of N element into the interface mitigates the electrons transfer to some extent. It may be attributed to the element electro-negativity difference. We found the electronegativity of N, O, Hf and Pt by Pauling scale are 3.04, 3.44, 1.3 and 2.28, respectively, and electronegativity of N locates between O and Pt [17]. The electron charges transfer from Pt to O when Pt layer contacts HfO₂ layer and forms an interface, while the electrons transferring will be weakened when O atoms are

gradually replaced by N atoms, which is much less electronegative than O. As a result, the N incorporation can deplete the electron charge transfer in Pt/HfO₂ interface, and interface dipole moment decreases correspondingly, thereby the value effective work function (or work function shift) would be raised.

4. Summary

In summary, we have investigated the impact of gas ambient element N on the Pt/HfO₂ interface effective work function (Φ_{eff}) as well as work function shift ($\Delta\Phi$) using density functional theory calculations. First, we have found that doped ambient gas element N tends to be favored at the interface and near the dielectric side, the system stability decreases with increasing dopant concentration. Second, work function shift of Pt/HfO₂ stack is strongly correlated to doped N position and concentration, *i.e.*, the modulation of Φ_{eff} and $\Delta\Phi$ is most effective when the first atom layer in HfO₂ side is doped, and the work function shift decreases (more *p*-type) with an increase of doped concentration. Third, the N-induced change of work function is originated from interface charge redistribution, resulting in additional interface dipole moment. Our work shows a scheme to modulate the interface structure by changing the annealing gas N composition so as to adjust the interface effective work function, which should provide experimentalists with some insights in their effort in atomic-level chemical design of Metal/Oxide stack.

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