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Citation: *Journal of Applied Physics* **116**, 063707 (2014); doi: 10.1063/1.4892799

View online: <http://dx.doi.org/10.1063/1.4892799>

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Effects of strain on effective work function for Ni/HfO₂ interfaces

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(Received 25 March 2014; accepted 30 July 2014; published online 12 August 2014)

The effective work functions for Ni/HfO₂ interfaces under two strain modes (uniaxial and triaxial strains) were studied by using first-principles methods based on density functional theory. The calculated results indicate that the effective work functions are strongly affected by the type of interface and the strain states (tensile and compressive strains). For the both above strain states, the changed value of the effective work functions linearly increases with increasing strain. Moreover, it is observed that for a certain strain, the variation of the effective work function for triaxial strain state is almost larger than that for uniaxial strain state. Finally, the electrons gas model, the interface dipole, and screening role of HfO₂ were used to analyze and explain the strain and interface effects in metal-oxide interfaces. The evident difference between the effective work functions of Ni-Hf and Ni-O interfaces is found to be attributed to different metallic bondings and ionic bondings via the analysis of the charge density distributions. Our work strongly suggests that controlling the strain and interface structure is a promising way for modulating the work function of Ni/HfO₂ interfaces. © 2014 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4892799>]

I. INTRODUCTION

To satisfy the aggressive downscaling of metal-oxide-semiconductor field-effect transistor (MOSFET), both high dielectric constant “high-k” gate dielectric and metal gate electrode are required to replace the traditional SiO₂ gate dielectric and polycrystalline Si, respectively.^{1,2} For metal gate, work function is one of the most important factors, which determines the threshold voltage and the performance of MOSFET. The suitable metal gates need to satisfy the requirement of having two separate work functions which are near the conduction band minimum and the valence band maximum of the underlying Si substrate, respectively.^{3,4} However, the selection of suitable gate metal is not basically achievable, because the effective work function (EWF, ϕ) of the gate metal depends on the gate dielectric and could differ from its vacuum work function.^{5–7} Therefore, to achieve this goal, many methods have been proposed to tune the work function, including alloying modulation for binary alloys, bilayer metal gate technology, and so on.^{8,9} Due to the actual interface strain effects, such as lattice mismatch or defect accumulation in the interface region, the EWF will deviate from its unstrained value. The strain effect on work function of the gate metal has been investigated experimentally. For example, Levitov *et al.* found the work function of metal aluminum was decreased by applying cyclic stress.^{10,11} Li *et al.* found that the work functions of Al and Cu were changed due to mechanical deformation.¹² To interpret the experimental phenomena and find out the physical origin of the influence of strain on work function, several theoretical studies have been performed. For example, Gong *et al.* used the first-principles calculation to investigate the change of the work function for Nb-W surfaces under the compressive (tensile) strain.¹³ Recently, Wang *et al.* used the similar approach to

systematically investigate the strain-dependent work function on the Pt(100) surface.¹⁴ They found that the compressive (tensile) strain has the work function of Pt(100) surface increase (decrease), and a canonical relationship between the strain and the metal vacuum work function was proposed. However, the study of the effect of strain on the EWF of metal-oxide interfaces is rare. Moreover, the physical origin of the influence of strain on the EWF of metal-oxide interface remains unknown.

It is well known that the vacuum work function of the metal surface can be modulated by the surface dipole layer.^{14–16} A similar phenomenon should exist in the metal-oxide interfaces. Very recently, the interface dipole formed in the metal-oxide interface was believed to strongly affect the EWF of the system.^{17–19} Tse *et al.* studied the electronic and atomic structures of metal-HfO₂ interfaces. It was found that there existed a large interface dipole for O-rich interfaces, which reduced their barrier heights by about 0.9 eV below those of the nonpolar interfaces.¹⁷ Bokdam *et al.* investigated the EWF at TiN/HfO₂ interface consisting of either Ti-O or N-Hf interface bonds. They found that as N-rich interface bonds were replaced by O-rich bonds, the EWF was decreased by up to 0.36 eV, which was attributed to the formation of opposing interface dipoles.¹⁹ However, it is still not very clear how the dipole is formed in the interface and how it affects the EWF of metal-oxide system. HfO₂ is one of the most promising gate dielectrics to replace traditional SiO₂ because of its high dielectric constant and excellent thermal stability, etc. And Ni has become a more ideal gate metal material because of its high work function, thermal stability, and good compatibility with high dielectric constant medium material. Therefore, in this work, we studied the effect of strain on the EWF for the typical metal-oxide (Ni/HfO₂) interface. The electrons gas model,¹⁴ the interface dipole barrier, and screening role of HfO₂ are used to analyze and explain the effect of strain on the EWF of metal-oxide interfaces.

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II. METHOD

We consider the fcc-Ni(001)/cubic-HfO₂(001) interfaces, as fcc-Ni(001) has very good lattice match to cubic-HfO₂(001) after relative 45° rotation. In this paper, two types of Ni(001)/HfO₂(001) interface were considered, including HfO₂ terminated with Hf atom layer (Hf-Ni interface) and HfO₂ terminated with O atom layer (O-Ni interface), as shown in Figs. 1(a) and 1(b), respectively. The EWF calculations were performed using first-principles calculation. All calculations were carried out by Vienna *ab initio* simulation package (VASP) using projector augmented wave (PAW) potentials.^{20–23} The exchange correlation energy was treated within PW91 generalized gradient approximation (GGA).²⁰ In all calculations, spin polarization was included. The plane-wave basis cutoff of 400 eV was used. For Hf-Ni (O-Ni) interfaces, we used (1 × 1) interface supercells with nine layers of Ni, seven layers of Hf, and six (or eight) layers of O, and no vacuum. The half supercells for two types of interfaces were shown in Fig. 1. Monkhorst-Pack *k* mesh was adopted for the calculations, and we used 8 × 8 × 1 *k*-point mesh. In the present study, the EWF of Hf-Ni interfaces and O-Ni interfaces under uniaxial and triaxial strains with different strain amount (<5%) was investigated. The schematics for uniaxial and triaxial strains are shown in Figs. 1(c) and 1(d), respectively. Moreover, for convenience, we call the interface without strain as static state, and one with uniaxial (triaxial) strain as uniaxial (triaxial) strain state. Our calculated lattice constant for bulk cubic-HfO₂ is $a_{\text{HfO}_2} = 5.025 \text{ \AA}$, which is slightly lower than the experimental value of 5.08 Å.²⁴ To find the equilibrium structures of Hf-Ni and O-Ni interfaces under their static states, during the relaxation, the lateral lattice parameters were set to be the value of bulk ($a_{\text{HfO}_2}/\sqrt{2} = 3.553 \text{ \AA}$), and the internal atomic coordinates and the vertical lattice vector were allowed to relax to minimize the DFT total energy. For the interfaces under various strain states, the lattice deformation

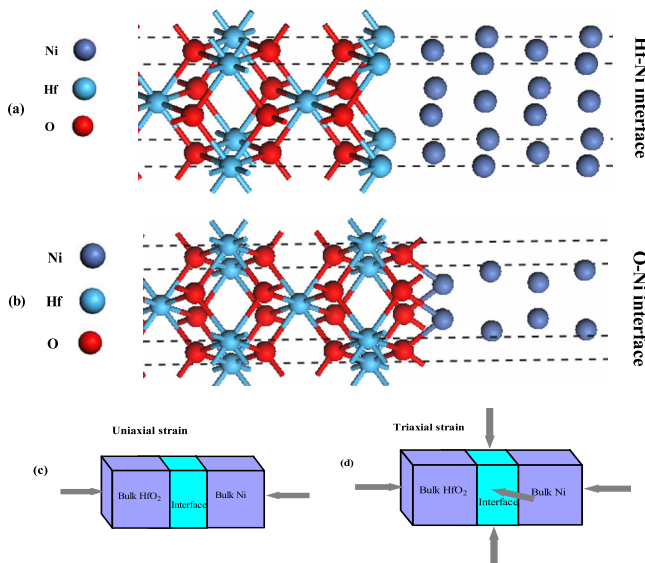


FIG. 1. Schematic of the supercell structures for (a) Hf-Ni and (b) O-Ni interfaces and the schematic illustration of (c) uniaxial and (d) triaxial strain states. The arrows in (c) and (d) mean the directions of the strain.

can be realized by decreasing or increasing their lattice constants on the basis of their static states, corresponding to compressive and tensile strains. To find the equilibrium structures of the interfaces with a certain strain state, the internal atomic coordinates were allowed to relax. Here, all deformation scales were less than 5%. The interface EWF (ϕ) can be estimated as^{25–27}

$$\phi = \chi_{\text{HfO}_2} + E_g^{\text{HfO}_2} - VBO, \quad (1)$$

where χ_{HfO_2} and $E_g^{\text{HfO}_2}$ denote the electron affinity and band gap of HfO₂, respectively. The valence band offset (VBO) denotes the difference between Ni Fermi energy and the oxide valence band maximum. The VBO for interface can be obtained by using the standard “bulk-plus-lineup” procedure.^{15,28,29} And it is usually split into two terms:

$$VBO = (E_F^{\text{Ni}} - E_{\text{VBM}}^{\text{HfO}_2}) + \Delta V, \quad (2)$$

where the first term is the energy difference between the metal Fermi energy and the oxide valence band maximum which are measured relative to the respective average of electrostatic potential ($V_{\text{ref},\text{Ni}}$ and $V_{\text{ref},\text{HfO}_2}$). They can be obtained from two independent bulk calculations. As considering the role of $V_{\text{ref},\text{Ni}}$ and $V_{\text{ref},\text{HfO}_2}$, Eq. (2) is rewritten as

$$VBO = (E_F^{\text{Ni}} - V_{\text{ref},\text{Ni}}) - (E_{\text{VBM}}^{\text{HfO}_2} - V_{\text{ref},\text{HfO}_2}) + \Delta V. \quad (3)$$

The third term ΔV is the difference between the double macroscopic average of the electrostatic potential residing in Ni and HfO₂ bulk-like-regions, respectively, which can be obtained using the double macroscopic average technique.³⁰ Combining Eq. (3) with Eq. (1), the EWF can be evaluated through the equation

$$\phi = \chi_{\text{HfO}_2} + E_g^{\text{HfO}_2} - [(E_F^{\text{Ni}} - V_{\text{ref},\text{Ni}}) - (E_{\text{VBM}}^{\text{HfO}_2} - V_{\text{ref},\text{HfO}_2}) + \Delta V]. \quad (4)$$

The third term in Eq. (4) is well known as *p*-type Schottky-barrier height (SBH). The first and second terms are the electron affinity and the band gap of HfO₂, respectively. In the calculation, the experimental values with $\chi_{\text{HfO}_2} = 5.7$ and $E_g^{\text{HfO}_2} = 2.5$ eV were used.⁷ As the oxide gap can be underestimated by DFT, a GW correction of 1.23 eV for HfO₂ valence band maximum has been considered.^{7,25} And for Ni, a correction of 0.29 eV was added by comparing our DFT calculation value (4.93 eV) and the experimental value (5.22 eV) for the work function of Ni(001) surface. The overall corrections, −0.94 eV, are used in the following EWF calculation. Here, the negative sign means the corrections will decrease the EWF. Our calculations of *p*-type SBH for Hf-Ni and O-Ni interfaces of Ni(001)/HfO₂(001) are 4.00 and 2.06 eV, respectively, which are close to the results of Ni(001)/ZrO₂(001) (3.80 and 2.13 eV), indicating that our calculations are reliable for the EWF of interfaces.

III. RESULTS AND DISCUSSION

Figs. 2(a) and 2(b) show the EWFs ϕ and their variations $\Delta\phi$ [$\Delta\phi = \phi(\alpha) - \phi(0)$] of Hf-Ni and O-Ni interfaces

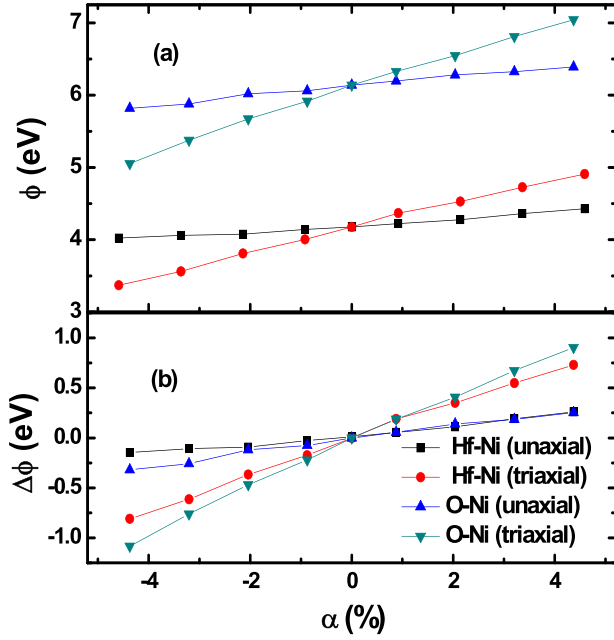


FIG. 2. (a) EWF ϕ , (b) the variations ($\Delta\phi$) as a function of the strain α for Hf-Ni and O-Ni interfaces with uniaxial and triaxial strain states.

as a function of strain α (%) for uniaxial and triaxial strain states. The negative and positive signs mean the compressive and tensile strains, respectively. From Figs. 2(a) and 2(b), we can find that (1) the work functions depend quite strongly on the type of interface, the EWFs of O-Ni interfaces are about 2 eV higher than those of Hf-Ni interfaces, (2) the EWF increases (decreases) with increasing tensile (compressive) strain, which is contrary to the previous prediction for metal surface.¹⁴ This illustrates the different effects of the strain between the metal surface and metal-oxide interface. And for all strain states, the changed value of ϕ linearly increases with enhancing magnitude of strain, (3) for a certain strain, the value of $\Delta\phi$ for triaxial strain state is always larger than that for uniaxial strain state. Moreover, the change rate of ϕ on the strain for O-Ni interfaces is essentially larger than that for Hf-Ni interfaces.

To further understand the physical mechanism for the changes of EWF that are induced by the strain for the Ni/HfO₂ interfaces, we can rewrite EWF in Eq. (4)^{14,31} as follows:

$$\begin{aligned} \phi = & -(E_F^{Ni} - V_{ref,Ni}) \\ & + [\chi_{HfO_2} + E_g^{HfO_2} + (E_{VBM}^{HfO_2} - V_{ref,HfO_2}) - \Delta V] = -\mu_{Ni} + D, \end{aligned} \quad (5)$$

where μ_{Ni} is the bulk chemical potential of the electrons related to the intrinsic metal bulk electronic structure and D characterizes the effect of the dipole barrier in the interface. Thus, the effects of strain on the EWF of the interface can be split into two terms: the effect of the intrinsic bulk electronic structure and the effect of the dipole barrier in the interface, as shown in Figs. 3(a) and 3(b). From the figures, it is clearly seen that for two kinds of interfaces, the absolute values of $\Delta\mu_{Ni}$ and ΔD increase linearly as the absolute value of α increases for both compressive and

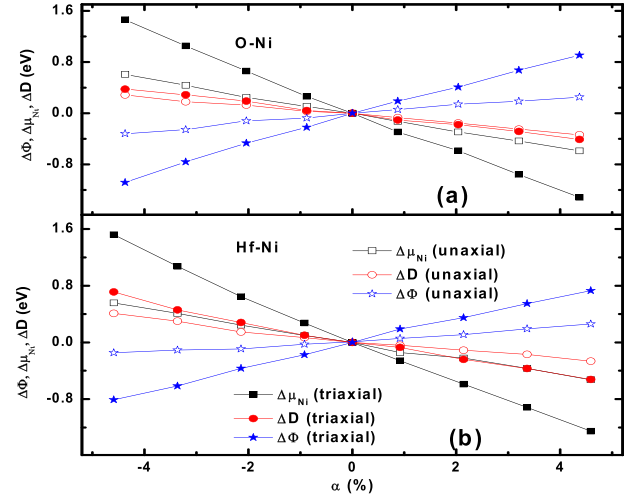


FIG. 3. The changed values of the intrinsic bulk electronic structure μ_{Ni} and the interface dipole barrier D and the EWF as a function of the strain α for (a) O-Ni interfaces and (b) Hf-Ni interfaces.

tensile strains. However, the absolute values of ΔD are always less than those of $\Delta\mu_{Ni}$.

The change of the intrinsic bulk electronic structure on strain can be understood by free-electron gas model approximation (FGM).¹⁴ It is well known that the change in chemical potential depends on the density of electrons. In the framework of FGM, the Fermi energy levels $E_f(n)$ are described by

$$E_f(n) = \hbar^2(3n\pi^2)^{2/3}/2m, \quad (6)$$

where n is the average free density of electrons for the bulk, \hbar is the reduced Planck constant, and m is the electron mass. The change of $E_f(n)$ can be derived as

$$\Delta E_f(n) = \frac{\hbar^2}{3m} (3\pi^2)^{2/3} (n)^{-1/3} \Delta n. \quad (7)$$

If we define the average density of electrons for the unstrained and strained bulks as n_0 and $n = n_0 + \Delta n$, respectively, where Δn is the slight change of the density of electrons and $\Delta n/n_0 \approx \alpha \leq \pm 5\%$. Therefore, Eq. (7) can be rewritten as

$$\Delta E_f(n_0 + \Delta n) = \frac{\hbar^2}{3m} (3\pi^2)^{2/3} (n_0 + \Delta n)^{-1/3} \cdot \Delta n. \quad (8)$$

Based on the Taylor series expansion, Eq. (8) can be expressed as

$$\Delta E_f(n_0 + \Delta n) = \frac{\hbar^2}{3m} (3\pi^2)^{2/3} \cdot (n_0)^{-1/3} \cdot \Delta n \cdot \left(1 - \frac{1}{3} \frac{\Delta n}{n_0}\right). \quad (9)$$

Since the slight change of density of electrons Δn satisfies $\Delta n \ll n_0$, thus all the contributions from the second and the higher-order terms can be neglected, so the change of the $E_f(n)$ can be approximately expressed as

$$\Delta E_f(n_0 + \Delta n) = \frac{\hbar^2}{3m} (3\pi^2)^{2/3} \cdot n_0^{-1/3} \cdot \Delta n. \quad (10)$$

Equation (10) reveals that the change of the Fermi energy levels $\Delta E_f(n)$ is nearly linear with the change of density of electrons Δn . As found in Fig. 4, our calculated results indicate that the change of density of electrons for Ni bulk almost increases linearly with increasing strain α , which is consistent to the theoretical results in Eq. (10). These results explain well the changing relationship for the intrinsic bulk electronic structure μ_{Ni} on the strain, as shown in Fig. 3.

The interface dipole barrier D which is the second contribution for EWF in Eq. (5) reflects the interface dipole density P . The electronic displacement and dipole formation in the interface can be observed by looking at the electron density of the entire interface minus the electron densities of the two separate constituent materials. Since only the component perpendicular to the interface is relevant, it is convenient to work with plane averaged charge density of the valence electron density $n(z) = \frac{1}{A} \int n(x, y, z) dx dy$. The interface dipole barrier is proportional to the dipole density p and can be given as^{19,32}

$$D = k \cdot p = k \left[e \left(- \int_{z_0}^{c/2} \Delta n_{inter}(z) \cdot z \cdot dz + \frac{1}{A} \sum_i a_i \cdot \Delta z_i \Big|_{z_0}^{c/2} \right) \right], \quad (11)$$

where the electron displacement in the formation of the interface is defined as $\Delta n_{inter}(z) = n_{inter}(z) - n_{Ni}(z) - n_{HfO_2}(z)$. Here, $n_{inter}(z)$ is the electron density of the interface; $n_{Ni}(z)$ and $n_{HfO_2}(z)$ are the electron densities of the clean metal and oxide layers, respectively. i indexes the ion; a_i is the net atomic number of ion i ; e is the electronic charge; k is the proportionality coefficient; Δz_i is the displacement of z coordinate for ion i ; A is the area of the surface unit cell. The center of metal Ni is chosen to be at z_0 , and $c/2$ corresponds to the center of oxide. Fig. 5(a) shows the change of the dipole density Δp as a function of the strain. For Hf-Ni and O-Ni interfaces with uniaxial and triaxial strains, the changes of dipole densities almost increase linearly with increasing strain α , which is consistent to the change of the interface dipole barrier D on the strain, as shown in Fig. 3. We plot the changed value of the interface

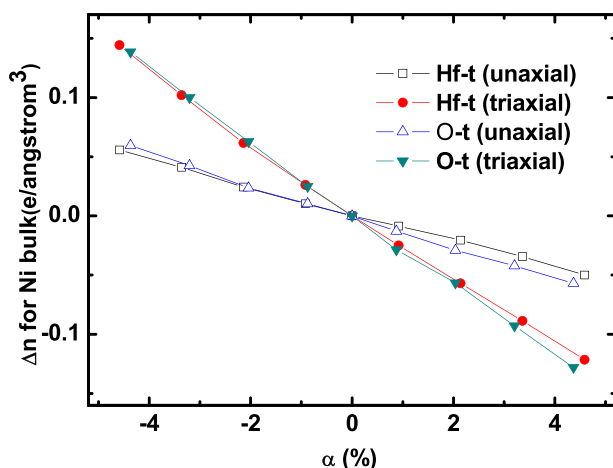


FIG. 4. The change of density of electrons Δn for Ni bulk with respect to the strain α .

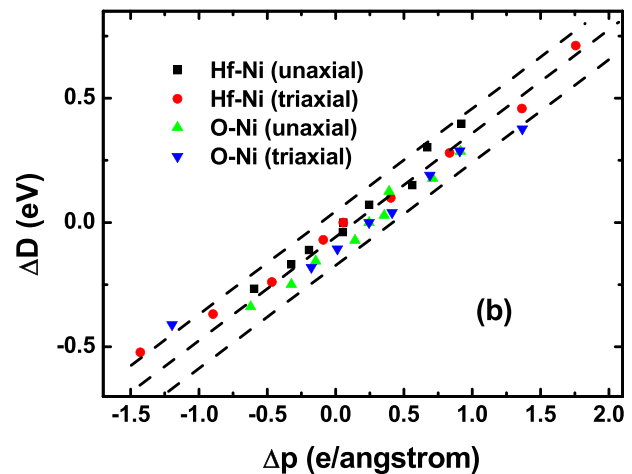
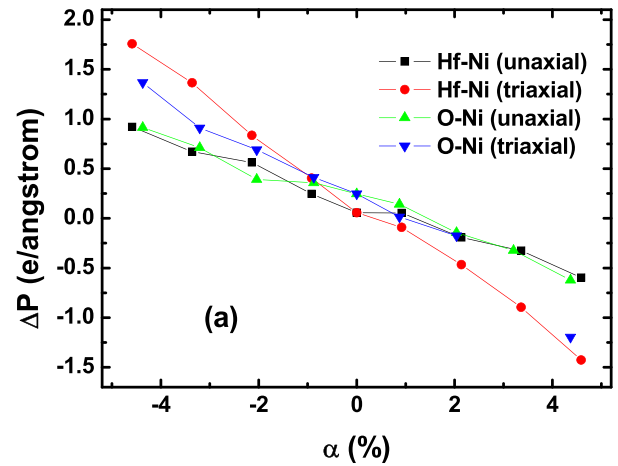


FIG. 5. (a) The changed value of the dipole density Δp with respect to the strain α and (b) the changed value of interface dipole barrier ΔD versus that of dipole densities ΔP .

dipole barrier ΔD as a function of variation of the dipole density ΔP , as seen in Fig. 5(b). From the figure, a linear relationship between ΔD and ΔP can be found, which agrees well with the theoretical prediction in Eq. (11).

Now, we turn to investigate the interface dipoles formed in Hf-Ni and O-Ni interfaces. The different types of chemical bonds exist in O-Ni and Hf-Ni interfaces, respectively. Figs. 6(a) and 6(b) show the charge density changes of the atoms $\Delta \rho$ in Hf-Ni and O-Ni interfaces along the direction perpendicular to interface, respectively. From the figures, it is found that the ionic bonding between O and Ni atoms exists in the interface region for O-Ni interface, while the metallic bonding between Hf and Ni atoms does in the interface region for Hf-Ni interface. In the region of O-Ni interface, the interface dipoles are formed due to the loss of electrons of Ni atoms and the gaining of electrons of O atoms. In contrast, for Hf-Ni interface, the Ni and Hf atoms in the interface lose all the electrons, and the lost electrons are aggregated in the intermediate zone between Ni and Hf atoms in the interface, which gives rise to different interface dipoles with respect to the ionic bonding. It is because of those interface dipole difference that we can explain the changed value of the EWF as high as 2 eV between O-Ni and

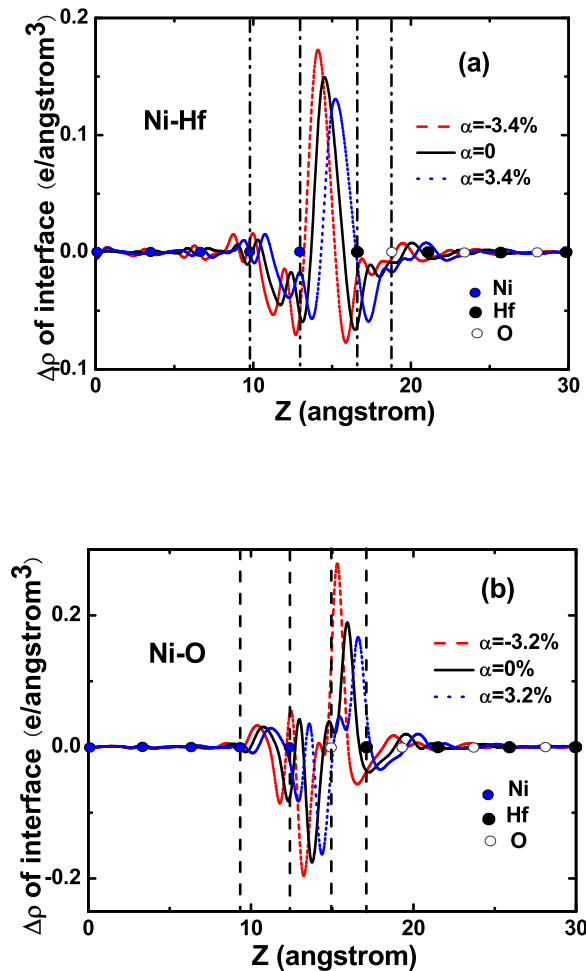


FIG. 6. The charge density changes of the atoms $\Delta\rho$ in (a) Hf-Ni and (b) O-Ni interfaces under triaxial strain. The atomic positions labeled by the dotted lines are for the case of $\alpha = 0$. For simplicity, the atomic positions for $\alpha = -3.2\%$ and 3.2% are not labeled.

Hf-Ni interfaces, as shown in Fig. 2. Moreover, it can be seen from Fig. 6 that for O-Ni and Hf-Ni interface, the interface dipoles are all due primarily to the contributions of the interface layer atoms, while the contributions of the second layer with respect to the interface layer are rather small, and that of the farther layers are negligible. The above studied results strongly suggest that controlling the interface defects (especially Hf or O interface) can modulate the interface dipole distributions that may change from metallic to ionic. As a result, the EWF can be drastically modulated by the control of the interface defects for the metal-oxide gate, which is significant for the metal gate technology and application.

Next, to further interpret the difference noted above in strain effects on work function between metal-oxide interface and metal surface, we shall discuss the change of work function $\Delta\Phi$. According to Eq. (5), the change of the work function can be written as $\Delta\phi = -\Delta\mu_M + \Delta D$. Wang *et al.* studied the strain α dependence of bulk chemical potential μ_M and surface dipole barrier D for Cu(100).³³ It is found that μ_M and D increase or decrease with an increase in compressive or tensile strain, and their change values $\Delta\mu_M$ and ΔD [$\Delta\mu_M = \mu_M(\alpha) - \mu_M(0)$, $\Delta D = D(\alpha) - D(0)$] are nearly

equal. In addition, their absolute values satisfy $|\Delta D| > |\Delta\mu_M|$. As a result, $\Delta\phi = -\Delta\mu_M + \Delta D$ should be small. Thus, the change of work function with 5% biaxial strain for Cu(100) is about 0.25 eV.³³ Similar results can be found in the other metals. It is observed that the value of $\Delta\phi$ with 4% biaxial strain for Pt(100) is about 0.1 eV.¹⁴ For AlCu₃ surface, the value of $\Delta\phi$ with 5% biaxial strain for (001) was found to be about 0.35 eV, but for (111) and (110) plane, it is only about 0.15 eV.³⁴ To further prove this viewpoint, we calculated also the work functions of Ni(001) surface with 4% biaxial strain. The small value of $\Delta\phi$ with about 0.15 eV was also observed, which is similar to that for Pt(100) surface in Ref. 14. Therefore, the small value of $\Delta\phi$ for the metal surfaces should mainly result from the small difference between the values of $\Delta\mu_M$ and ΔD .

For Ni/HfO₂ interface, the strain α dependence of $\Delta\mu_{Ni}$ and ΔD is consistent with that for the metal surface. However, the contrasts with the metal surface in Refs. 14, 33, and 34 are the evident difference between the values of $\Delta\mu_M$ and ΔD , and their absolute values satisfy $|\Delta\mu_M| > |\Delta D|$. For example, for Hf-Ni interface with triaxial strain state, as $\alpha = -4.6\%$, $\Delta\mu_{Ni} = 1.5$ eV and $\Delta D = 0.7$ eV. The value of ΔD is only about one half of $\Delta\mu_{Ni}$. As a result, the absolute value of $\Delta\phi = -\Delta\mu_{Ni} + \Delta D$ should become bigger.

The smaller change of D in interface can be qualitatively explained as a result of the screening role^{35,36} coming from dielectric HfO₂ in the following way. When Ni and HfO₂ are brought in contact, the charge transfer between them takes place, leading to a dipole formation across the interface. The change of dipole barrier ΔD is directly reflected by the change of dipole density ΔP . And ΔP is determined by the amount of charge transfer and spatial distribution of charges. Moreover, we calculated the charge transfer and spatial distribution of charges for Ni/HfO₂ interface. The calculated results indicate that the amount of charge transfer plays a major role in the change of dipole density P . For example, for Ni-O interface, the changed value for the thickness of the dipolar layer between Ni and Hf atomic planes in interface is about 2.4% under the compressive strain with $\alpha = -3.2\%$. However, the amount of charge transfer with about 15.8% is much larger. The large amount of charge transfer indicates that charge transfer easily happen. Moreover, the ease or complexity of the charge transfer may be reflected by the screening role of HfO₂ which can be weighed by the dielectric constant. Thus, the screening role of HfO₂ is the main factor affecting the change of dipole density P . So the screening role of HfO₂ can directly affect the change of D . For compressive strain, the smaller dielectric constant indicates the larger screening role. As a result, it makes charge easier to transfer, which leads to a smaller D comparing with that of metal surface without dielectric HfO₂. On the contrary, for tensile strain, the bigger dielectric constant indicates the smaller screening role, which leads to a larger interface dipole barrier D . Thus, for Ni(001)/HfO₂(001) interface under a certain strain, the interface dipole is then partially screened by HfO₂, which minimizes the total dipole effect. Therefore, interface dipole barrier D changes less than that in metal surface without oxide, also much less than the change of bulk chemical potential μ_{Ni} , as shown in

Fig. 3. As a result, the change of work function for interface with respect to the strain is much more than that for metal surface. This predicts that strain could become an effective means to modulate the EWF of metal-oxide gate, which is important for the EWF engineering in the high- k /metal gate stack of next generations of CMOS technologies.

IV. CONCLUSION

In conclusion, the effective work functions of Hf-Ni and O-Ni interfaces for Ni/HfO₂ systems under two strain modes (uniaxial and triaxial strains) were calculated by the first-principles calculation. The results reveal that the effective work functions (ϕ_{eff}) strongly depend on the type of interface, and the EWF of O-Ni interfaces are as higher as 2 eV than that of Hf-Ni interfaces. The tensile (compressive) strain increases (decreases) the EWF. For all strain states, the changed value of ϕ linearly increases as the strain increases. For a certain strain, the variation of the $\Delta\phi$ for triaxial strain states is always larger than that for uniaxial strain states. The electrons gas model, the interface dipole, and screening role of HfO₂ are used to analyze and explain the strain effect. Our work strongly suggests that the EWF can be drastically modulated by controlling the strain and the interface defects, which is significant for the metal gate technology and application.

ACKNOWLEDGMENTS

This work is supported by the National Science Foundation of China (11004039, 11204038), National Key Project for Basic Research of China under Grant No. 2011CBA00200.

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