# Influences of annealing in reducing and oxidizing ambients on flatband voltage properties of HfO<sub>2</sub> gate stack structures

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We have applied a combinatorial technique to fabricate work function (WF) tuned Pt-W alloy films and used the films as metal electrodes for  $HfO_2/SiO_2/Si$  capacitors. As the ratio,  $R_{Pt}$ , of Pt to W changes from 0 to 1, the WF value varies continuously from 4.7 to 5.5 eV. This tunability enables us to systematically investigate the effect of WF variation on electrical properties. After a forming gas annealing process, the values of flatband voltage  $(V_{\rm fb})$  from capacitance-voltage properties are almost constant, regardless of the WF variation, because of oxygen vacancy formation that results in Fermi level pinning. On additional oxidizing gas annealing (OGA), the effect of WF value on  $V_{\rm fb}$ becomes dominant. However, the difference in  $V_{\rm fb}$  between W and Pt is 0.34 V, which is much smaller than the observed WF difference of 0.8 eV. We attribute this phenomenon to the lowering of the effective WF due to an electric dipole, induced by oxygen vacancy formation at the metal/  $HfO_2$  interface. Moreover, a decrease in  $V_{fb}$  in W-rich regions was observed following the OGA, suggesting the formation of a W-O bond at the interface. These results clearly indicate that the control of bonding states at the metal/HfO<sub>2</sub> interfaces on an atomic scale is essential for the realization of a combination of metal and high-k dielectric films in future complementary metal-oxide-semiconductor devices. © 2007 American Institute of Physics. [DOI: 10.1063/1.2721384]

### I. INTRODUCTION

Silicon oxinitride (SiON) has been used as a gate dielectric film of metal-oxide-semiconductor field-effect-transistor (MOSFET) and, currently, an equivalent oxide thickness (EOT) of the SiON film is about 1 nm for high-performance devices. The concentration of N in the SiON film is increased to reduce leakage current and penetration of B atoms. In order to achieve further integration and higher performance, the SiON film must be replaced by a high-k dielectric film which permits an increase in the physical thickness of the dielectric film, so that the tunneling current can be dramatically reduced. A number of studies have been reported, seeking an alternative high-*k* dielectric film using HfO<sub>2</sub>, HfSiO(N), HfAIO(N), ZrO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub>, and Y<sub>2</sub>O<sub>3</sub>. Among these, the Hf-based dielectric film is one of the most promising candidates, because its properties include thermal stability, suitable energy barrier heights for electrons and holes, and advantageous electrical properties, due to existence of an ultrathin SiO<sub>2</sub> interfacial layer between the high-*k* film and Si.<sup>1</sup>

However, one of the most formidable issues related to commercial introduction of the Hf-based dielectric film is the controllability of the work function (WF) of gate electrodes that determines the threshold voltage of MOSFETs. In a combination of poly-Si and HfSiON (HfO<sub>2</sub>), a lowering of effective WF ( $\phi_{m,eff}$ ) is observed for B-doped poly-Si gates. Similar phenomena have been reported with metal gates, for example TiN, TaSi, NiSi, W, and Ru, which will be neces-

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sary to be introduced in the near future to avoid an additional increase in EOT due to a depletion layer at the interface of poly-Si and high-k dielectric.

The instability in  $\phi_{m,eff}$  strongly depends on annealing conditions, specifically on annealing ambients, containing oxidizing and reducing gases. Metal-induced gap states (MIGS),<sup>2,3</sup> Hf-Si bonds,<sup>4</sup> B-dopant atoms,<sup>5</sup> oxygen vacancy  $(V_{\rm O})$   $(V_{\rm O}$  formation model)<sup>6,7</sup> at the interfaces of metals and high-k dielectric films have all been proposed as possible mechanisms and origins for the instability in  $\phi_{m,eff}$ . The important point to note is that the  $\phi_{\mathrm{m,eff}}$  instability becomes significant as WF of gate electrode material increases. Therefore, in order to elucidate the origin and mechanism for the instability, we aimed to fabricate continuously WF-tuned metal alloy films, so that the dependence of  $\phi_{m,eff}$  on annealing conditions could be examined systematically. For this reason, we have employed a combinatorial deposition technique which provided wide and precise controllability over the film composition ratios of binary/ternary alloys and compounds. We chose a Pt-W alloy system as a means of tuning WF from the viewpoint of the thermal stability on HfO<sub>2</sub> and the relatively large difference in WF (4.7 and 5.5 eV for W and Pt, respectively) that could be achieved, primarily by changing the number of valence electrons from 6  $(5d^46s^2, W)$  to 10  $(5d^96s^1, Pt)$ .

In this article, we report on the dependence of  $\phi_{m,eff}$  on annealing conditions by using the WF-tuned Pt-W alloys as metal gate electrodes of metal/HfO<sub>2</sub>/SiO<sub>2</sub>/Si capacitors. It has been clearly demonstrated that the effective WF is strongly correlated with the vacuum WF, while the local electronic/bonding states at the metal/HfO<sub>2</sub> interface play an important role. Consideration of three types of mechanism, i.e., the catalytic effect of Pt, the V<sub>O</sub> formation model, and a generalized charge neutrality level (GCNL) theory, are required to understand the observed changes in V<sub>fb</sub>, depending on WF values and annealing conditions.

# **II. EXPERIMENTAL**

We used high-k dielectric films with a 6-nm-thick  $HfO_2/1$ -nm thick SiO\_2/p-type Si structure as substrates. The HfO<sub>2</sub> film was deposited using a metal-organic chemical vapor deposition method. The resistivity of the *p*-type Si is  $0.01-0.02 \ \Omega \ cm$ . A combinatorial ion-sputter system was utilized to deposit a composition-spread film of Pt-W alloy on to the substrates. The details of the ion sputtering system are described in Refs. 8 and 9. As schematically shown in Fig. 1(a), we vary the deposition rate of each target across the sample surface by moving a mask with a 7-mm-side square hole, located between a sample and the targets. Hence, the Pt composition ratio to W of deposited film,  $R_{\rm Pt}$  $=N_{\rm Pt}/(N_{\rm Pt}+N_{\rm W})$ , could be controlled in a layer-by-layer fashion, where  $N_{\text{Pt}}$  and  $N_{\text{W}}$  are the numerical densities of Pt and W atoms, respectively. Typically, a set of alternating depositions of Pt and W with a thickness of 0.2 nm is repeated for approximately a few hundred cycles until a target thickness is obtained. Consequently, we obtain a Pt-W composition-spread film with a size of  $\sim 7 \times 9 \text{ mm}^2$ , in which the  $R_{\text{Pt}}$  ranges from 0 to 1 along the 9 mm side. Two



FIG. 1. (Color online) (a) Schematic diagram of a combinatorial deposition system. It consists of a moving mask with a 7 mm wide square hole between targets and the sample to control the composition ratio of Pt to W. (b) Capacitor structure, using composition-controlled Pt-W alloy electrodes, deposited by the combinatorial method. The diameter of the capacitors was 100  $\mu$ m.

types of Pt-W composition-spread film were fabricated on the HfO<sub>2</sub> substrates: (1) continuous films for x-ray photoelectron spectroscopy (XPS)/x-ray diffraction (XRD) measurements, and (2) capacitor electrodes with a diameter of ~100  $\mu$ m, using a stencil mask [Fig. 1(b)]. The latter structure enables us to fabricate about 40 variations of capacitor with  $R_{\rm Pt}$  ranging from 0 to 1 on a single specimen. The Pt-W alloy films were deposited at room temperature, with a thickness of 60 nm.

XPS was used to characterize the composition ratios, together with the values of vacuum WF,  $\phi_{m,vac}$ , as a function of lateral position in the continuous films. The surfaces of Pt-W alloy films were carefully cleaned by *in-situ* sputtering in order to reduce the surface contamination which would alter the offset energy of secondary electrons. For crystal structure characterization, we have carried out XRD measurements using a Bruker D8 system which was equipped with a two-dimensional x-ray detector. Therefore, we could obtain diffraction spectra, simultaneously, along  $\theta$  and  $\chi$  directions. In order to map the structural changes as a function of  $R_{\rm Pt}$ , we used an aperture for x-ray collimation with a dimension of 300  $\mu$ m. CV properties were characterized in order to examine the effect of the WF variation and annealing conditions on the electrical properties. The area of each capacitor was calibrated by scanning electron microscopy to obtain an accurate capacitance and a dielectric constant. The capacitors were located every 200  $\mu$ m using a contact mask, so that we could obtain 45 capacitors within the 9 mm wide composition-spread region. The values of  $V_{\rm fb}$ , maximum oxide capacitance  $(C_{\text{max}})$ , and minimum capacitance  $(C_{\text{min}})$  in an inversion region were extracted, using the NCSU-CVC program.<sup>10</sup> We employed annealing in forming gas  $(N_2/H_2, 5\% H_2)$ and slightly oxidizing gas



FIG. 2. (Color online) (a) Composition ratio of the Pt-W alloy, evaluated by XPS core spectra, as a function of position. (b) Work function dependence on the Pt composition ratio,  $R_{\rm Pt}=N_{\rm Pt}/(N_{\rm Pt}+N_{\rm W})$ , measured by the offset energies of the secondary electrons.

 $(N_2/O_2, 0.1\% O_2)$  ambients at temperatures ranging from 400–500 °C and 250–400 °C, respectively.

### **III. RESULTS AND DISCUSSION**

The composition ratio of the Pt-W alloy film was evaluated as a function of lateral position, using the intensities of XPS core spectra (Pt 4*f* and W 4*f*). As designed by movement of the combinatorial mask during the deposition, the  $R_{\rm Pt}$  is linearly controlled from 0 (W) to 1 (Pt) [Fig. 2(a)]. At both edges of the composition spread region (6 mm), pure W and Pt regions were located, ~1.5 mm in width. In Fig. 2(b), the WF values evaluated from the offset energies of the XPS secondary electrons are shown as a function of  $R_{\rm Pt}$ . By controlling  $R_{\rm Pt}$  from 0 to 1, the vacuum WF was successfully tuned from 4.7 to 5.5 eV. The controllability of work function difference between Pt and W is about 0.8 eV, consistent with reported values.<sup>11</sup> Note that the slope of WF changes at around  $R_{\rm Pt}$ =0.5.

We examined the structural changes from W [bodycentered cubic (bcc),  $a_L=0.3165$  nm] to Pt [face-centered cubic (fcc),  $a_L=0.3924$  nm] as a function of  $R_{Pt}$  using XRD, where  $a_L$  is the lattice constant. Figure 3(a) shows XRD spectra along the  $2\theta$  direction for steps of 0.05 in  $R_{Pt}$  In a pure W region ( $R_{Pt}=0$ ), a W(110) peak is observed. As the  $R_{Pt}$  increases, peak intensities related to a bcc-based A15  $\beta$ -W structure are elevated, the effect of which is reported as



FIG. 3. XRD spectra from the as-deposited Pt-W alloy film, with  $R_{\rm Pt}$  ranging from 0 to 1. (a)  $2\theta$  plot which represents the crystal structures. (b)  $\chi$  plot showing a degree of oriented crystallization for each peak observed in the  $2\theta$  plot. No significant changes were observed after FGA and OGA processes.

being attributed to the metastable structure of W under tensile strain.<sup>12,13</sup> The peak energy from the  $\beta$ -W structure is constant in the  $R_{\rm Pt}$  range from 0.05 to 0.30. An amorphous structure region exists at  $R_{\rm Pt}=0.35$  (very narrow range of  $R_{\rm Pt}$ ). At  $R_{\rm Pt}$ =0.40, the Pt(111) phase appears, with a slightly larger lattice constant and, as  $R_{\rm Pt}$  increases to 1, the lattice constant becomes that of a bulk Pt(111). The Pt-W alloy exhibits a solid solubility system in the  $R_{\rm Pt}$  range from 0.6 to 1, consistent with the gradual shift in Pt(111).<sup>14</sup> Note that the crystalline peaks from W and Pt do not coexist. This implies that the interface of the metal alloy/HfO<sub>2</sub> is likely to be composed of a uniform structure at any given composition ratio,  $R_{\rm Pt}$ . Figure 3(b) shows XRD spectra along the  $\chi$  direction, which mainly reflect crystalline orientation. The broad W(110) and sharp Pt(111) peaks indicate that the W(110) is a randomly oriented polycrystal, while the Pt-rich regions have a highly (111)-oriented fcc structure. At the onset of the appearance of the Pt(111) phase ( $R_{Pt}=0.40$ ), the Pt(111) peak splits, indicating that the Pt(111) film forms a twin structure in the course of the transformation from the  $\beta$ -W structure to fcc. These crystal structures do not change following forming gas annealing (FGA) and/or oxidizing gas annealing (OGA). No tungsten oxide phase was observed.

We have applied the WF-tuned Pt-W films as capacitor electrodes on  $HfO_2$  dielectric films. Figure 4(a) shows a plot of CV curves obtained from the capacitors after FGA at 450 °C for 30 min. The CV curves were normalized by  $C_{\text{max}}$ , extrapolated by the CVC program. The estimated  $C_{\text{max}}$  is  $\sim 1.5 \times 10^{-6}$  (F/cm<sup>2</sup>), from which is derived a dielectric constant  $\varepsilon_r$  of 18.0 for HfO<sub>2</sub>. We obtain a capacitance ratio  $C_{\min}/C_{\max}$  of 0.19. This translates into a substrate impurity concentration of  $1.4 \times 10^{18}$  (cm<sup>-3</sup>), which is consistent with the substrates used. The 40 CV curves from samples with various  $R_{\rm Pt}$  values approximately overlap, regardless of the WF difference of  $\sim 0.8$  eV. This result shows that, in a combination of a metal electrode and a Hf-based high-k dielectric film, the  $V_{\rm fb}$  is highly uncontrollable after FGA. With additional OGA at 300 °C, subsequent to the FGA at 450 °C, CV curves show voltage shifts reflecting the WFs of the metal electrodes [Fig. 4(b)]. However, the difference in  $V_{\rm fb}$  be-



FIG. 4. (Color online) (a) CV curves after FGA, obtained from Pt-W/HfO<sub>2</sub>/SiO<sub>2</sub>/Si capacitors. The CV curves almost overlap, regardless of WF variation. (b) CV curves after OGA at 300 °C for 30 min, subsequent to FGA at 450 C for 30 min. The CV curves shift toward the right as  $R_{\rm Pt}$  increases, corresponding to an increase in WF.

tween the W and Pt electrodes is 0.34 V, still smaller than the observed WF difference of 0.8 eV in the XPS measurements.

Figure 5 demonstrates the changes in  $V_{\rm fb}$  value as a function of  $R_{\rm Pt}$  after three types of annealing process: (1) FGA at 450 °C, (2) FGA at 450 °C + OGA at 250 °C (with OGA annealing times of 10 min, 2 and 24 h), and (3) FGA at 450 °C + OGA at 300 °C + FGA at 450 °C. FGA was performed for 30 min. Following the FGA process shown with open squares, the difference in  $V_{\rm fb}$  between Pt and W regions ( $\Delta V_{\rm fb}$ ) is less than 0.05 V, corresponding to an overlapping



FIG. 5. (Color online)  $V_{\rm fb}$  dependence on annealing ambients as a function of  $R_{\rm Pt}$ , extracted using the CVC program. The  $V_{\rm fb}$  curves for all annealing conditions cross over at  $R_{\rm Pt}$ =0.46.



FIG. 6. Differences in  $V_{\rm fb}$  between Pt and W electrodes as a function of annealing temperature in an oxidizing ambient for 30 min. The values in  $V_{\rm fb}$  after FGA only are indicated by open symbols for reference.

of the CV curves in Fig. 4(a). A broad peak in  $V_{\rm fb}$  is observed at  $R_{\rm Pt} \approx 0.5$ . With the additional OGA at 250 °C, the values of  $V_{\rm fb}$  in the W-rich ( $0 \le R_{\rm Pt} \le 0.5$ ) regions decrease. On the other hand, those in Pt-rich regions ( $0.5 \le R_{\rm Pt} \le 1.0$ ) shift upwards. This tendency is commonly observed after OGA processes at annealing temperatures from 250 to 400 °C. The magnitude of  $\Delta V_{\rm fb}$  increases as the OGA process time increases, being 0.34 V after a 24 h anneal. As shown by the open circles, the changes in  $V_{\rm fb}$  due to the OGA annealing are reversible with an additional FGA, suggesting that dramatic mass transport/diffusion through the metal/high $k/SiO_2$  structure does not occur with FGA and OGA under these annealing conditions.

In Fig. 6, the controllable ranges of  $V_{\rm fb}$  between Pt and W electrodes after a 30 min OGA process, subsequent to FGA, are summarized as a function of OGA temperature. The FGA temperature used was 450 °C for all samples and the values in  $V_{\rm fb}$  after the FGA process are shown with open symbols for reference. Although the difference in  $V_{\rm fb}$  between Pt and W electrodes,  $\Delta V_{\rm fb}$ , is widened by the OGA processes, the maximum difference is 0.34 V at an OGA temperature of 350 °C. The pinning factor, *S*, defined as  $q\Delta V_{\rm fb} \equiv S \Delta WF$ , is 0.43 (0.34/0.80), where *q* and  $\Delta WF$  correspond to the elementary charge and the differences in WF between Pt and W electrodes, respectively. The calculated *S* value for HfO<sub>2</sub> is 0.53.<sup>15</sup> An OGA temperature above 450 °C yields a significant increase in EOT values.

Here, we consider the dominant origins of the  $V_{\rm fb}$  changes due to the FGA and OGA processes. The flatband voltage is expressed as

$$V_{\rm fb} = \phi_{\rm m,eff} - \phi_{\rm s} - Q_{\rm f}/C_{\rm i},\tag{1}$$

where  $\phi_{m,eff}$ ,  $\phi_s$ ,  $Q_f$ , and  $C_i$  are the effective metal WF, semiconductor WF, fixed charges in a dielectric film, and capacitance of a dielectric film, respectively. The dependences of  $C_i$  on the annealing conditions and  $R_{Pt}$  have a less than 10% deviation. In addition, the  $V_{fb}$  curves for all annealing conditions intersect at  $R_{Pt}$ =0.46 (Fig. 5), indicating that the density of  $V_0$  in the HfO<sub>2</sub> film does not change significantly with the FGA and OGA processes because a change in  $Q_f$  should cause a parallel shift in  $V_{fb}$ . Therefore, we attribute the  $V_{fb}$ instability to the change in  $\phi_{m,eff}$ . The observed changes in

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 $V_{\rm fb}$  as a function of  $R_{\rm Pt}$  can be classified by three phenomena: (1) the constant  $V_{\rm fb}$  observed after FGA; (2) the decrease in  $V_{\rm fb}$  after OGA in the W-rich regions; and (3) the increase in  $V_{\rm fb}$  after OGA in the Pt-rich regions. We consider that the constant values of  $V_{\rm fb}$  result from a catalytic effect of Pt that induces significant  $V_{\rm O}$  formation at the metal/high-*k* interface as the  $R_{\rm Pt}$  increases. In addition, this reaction occurs until it reaches an equilibrium, so that the energy gain due to electron transfer balances the elevation of  $E_{\rm fb}^{-6.7}$ 

Next we focus on the decrease in  $V_{\rm fb}$  after OGA in the W-rich regions. This corresponds to decrease in  $\phi_{m,eff}$ . After OGA, both metallic and oxide tungsten peaks were observed by XPS. However, as we mentioned earlier, we have limited the OGA temperature to below 400 °C, so that no tungsten oxide phase was detected by XRD. We consider that the values of WF in W-rich electrodes are not determined by tungsten oxide. In fact, oxidation of the W electrodes does not explain the observed change, because the work function of tungsten oxide is 6.24 eV,<sup>16</sup> which is greater than that of tungsten. Besides this, neither the Hf-Si bond model<sup>4</sup> nor the  $V_{\rm O}$  formation model<sup>7</sup> accounts for the phenomenon, because the OGA process usually diminishes these effects, compared to the FGA process. In order to elucidate the anomalous negative shift observed in the W-rich region, we employed the GCNL theory that describes charge transfer in metallic and high-k dielectric films in contact.<sup>17</sup> In the previous charge neutrality level (CNL) model,<sup>15,18</sup> the charge neutrality level is determined by the high-k dielectric film itself. On the other hand, in the GCNL theory, the bonding configuration at the metal high-k interface and the density of states of the metal are essential for the determination of the generalized charge neutrality level on which the effective WF of metals depends. Here, we consider the possible bonding structures at the interface of Pt-W alloy/HfO<sub>2</sub>, based on the enthalpies of formation. According to Refs. 19-21, the enthalpies of formation for W-Hf, W-O, Pt-Hf, and Pt-O are -10 (WHf), -589.5 (WO<sub>2</sub>), -134 (PtHf), and -71.2 (PtO), respectively, in kJ/mol. This suggests that, at the interface of W/HfO<sub>2</sub>, the W-O bond is preferential, so that electron transfer occurs from O2p occupied states which form the valence band of  $HfO_2$ , into unoccupied 5d states of W, because the O2p states are fully preoccupied by an ionic bond between Hf and O. This lowers the effective WF. Therefore, we consider that the change in bonding configuration, such as oxygen atom insertion at the W/HfO<sub>2</sub> interface, can account for the negative  $V_{\rm fb}$  shift in the W-rich regions after the OGA process.

The obvious changes in  $V_{\rm fb}$  due to FGA and OGA processes appear in the Pt-rich regions. Shiraishi *et al.* have proposed a  $V_{\rm O}$  formation model at the metal/high-*k* interface, in which created oxygen vacancies cause subsequent electron charge transfer from a HfO<sub>2</sub> film to a poly Si (or metal) gate electrode.<sup>6,7</sup> The dipole lowers the effective WF of the electrode because, in this model, electron charge transfer always occurs from the HfO<sub>2</sub> film to the electrode. In addition, this phenomenon is more dominantly observed for metal electrodes with large WFs, since the energy gain due to the electron transfer is roughly proportional to the difference between the Fermi level of the metal and the energy level of



FIG. 7. Change in  $\phi_{m,eff}$  as a function of  $\phi_{m,vac}$ . The values of  $\phi_{m,eff}$  were evaluated by a combination of XPS and CV measurements.

 $V_{\rm O}$ , which is located at ~0.4 eV above the conduction band bottom of Si.<sup>22</sup> In fact, the  $V_{\rm fb}$  changes reported are mainly on the large WF metals such as Pt, Re, and Ru.<sup>23,24</sup>

We have successfully extracted the effect due to the  $V_{\rm O}$  formation model using the combinatorial WF-tuning approach. The changed values of  $\phi_{\rm m,eff}$  are shown in Fig. 7 as a function of WF, using the  $V_{\rm fb}$  values after a 24 h OGA process (Fig. 5, solid squares). The  $\phi_{\rm m,vac}$ , measured by XPS, was interpolated in order to estimate the difference between  $\phi_{\rm m,eff}$  and  $\phi_{\rm m,vac}$ . We assume that  $\phi_{\rm m,eff}$  is equal to  $\phi_{\rm m,vac}$  at  $R_{\rm Pt}$ =0.46, where the values of  $\Delta V_{\rm fb}$  remain constant after FGA and/or OGA processes, based on the resistance to annealing conditions. This is probably due to the WF value of the metal (4.9 eV) that can accommodate  $\phi_{\rm s}$ . A linear decrease in  $\phi_{\rm m,eff}$  is observed for WF larger than 4.9 eV. This clearly demonstrates that the effect of  $V_{\rm O}$  formation on Fermi level pinning is proportional to the WF value, particularly for the high WF metals.

#### **IV. CONCLUSION**

We have systematically investigated the effect of WF tuning on electric properties of high-*k* dielectric capacitors using a combinatorial deposition technique. The WF of the Pt-W alloy ranges from 4.7 to 5.5 eV as the  $R_{\rm Pt}$  increases. From XRD measurements, the alloy film exhibits W(110),  $\beta$ -W, amorphous-like, and Pt(111) structures, depending on  $R_{\rm Pt}$ . The Pt-W alloy has a solid solubility system.

The extracted values of  $V_{\rm fb}$  as a function of  $R_{\rm Pt}$  in capacitor electrodes strongly depend on the annealing ambients. With a FGA process, the values of  $V_{\rm fb}$  are almost constant, regardless of the difference in WF, mainly due to  $V_{\rm O}$ formation at metal/HfO<sub>2</sub> interfaces, resulting in a complete Fermi level pinning. After an additional OGA process, the largest  $\Delta V_{\rm fb}$  observed in a temperature range of 250–400 °C is 0.34 V, which is smaller than the WF difference of 0.8 eV. We observed an anomalous negative shift of  $\Delta V_{\rm fb}$  in W-rich regions after an OGA process, indicating that the formation of dipoles are due to W-O bonding, as described by the GCNL theory. The linear relationship between the effective and vacuum WF values has been clearly demonstrated for the first time for Pt-rich (high WF) regions, using a combinatorial materials approach.

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