Mater. Res. Soc. Symp. Proc. Vol. 917 © 2006 Materials Research Society 0917-E04-05

A SYSTEMATIC APPROACH OF UNDERSTANDING AND RETAINING PMOS COMPATIBLE WORK FUNCTION OF METAL ELECTRODES ON HfO2 GATE DIELECTRICS

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ABSTRACT

In this work we have performed Ultraviolet Photoelectron Spectroscopy (UPS) and X-Ray Photoelectron Spectroscopy (XPS) on: (i) 40Å of Ru deposited on 20Å of ALD-HfO_2 (Ru-HfO_2), (ii) 40Å of Re deposited on 20Å of ALD-HfO_2 (Re-HfO_2), and (iii) 40Å of W deposited on 20Å of ALD-HfO_2 (W-HfO_2) in as deposited as well as after 600°C in-situ anneal exposure. The samples with Ru and Re indicated significant reduction in the oxygen content and shift in the Hf peaks towards higher binding energy after anneal as compared to the as deposited state. The loss of oxygen after anneal was associated with the reduction in the surface work function of Ru and Re measured by UPS. However, the sample with W showed a redistribution of oxygen after anneal leading to the formation of multiple oxides of W having a net higher surface work function. The spectroscopic measurements were correlated with the electrical measurements made on MOS capacitors with Ru metal gates on HfO_2 gate dielectric. The results indicated that the oxygen content at metal/high-k interface plays an important role in governing the effective work function of Ru on HfO_2 gate dielectric.

INTRODUCTION

Recently, much attention has been focused on studying HfO_2 as gate dielectric for future generation CMOS devices. The polycrystalline silicon gates have been reported to suffer from Fermi level pinning on HfO_2 which has necessitated the investigation of dual work function metal gate electrodes on HfO_2 gate dielectric [1-2]. Recent reports have shown that the high work function metal gates suffer from a significant reduction in the effective work function on ultra-thin HfO_2 after subsequent anneals, which poses a challenge for the development of candidate metal gates suitable for PMOS applications [3-4]. Furthermore, it has been demonstrated that the starting surface condition of HfO_2 before the metal gate deposition and the oxygen content at metal/HfO_2 interface play an important role in governing the effective work function ($\Phi_{m,eff}$) of high work function metals [5]. In this work, we have performed extensive spectroscopic analysis to understand the origin of the instability in $\Phi_{m,eff}$ after subsequent anneals and proposed routes to retain the high $\Phi_{m,eff}$.

EXPERIMENTAL DETAILS

High-k samples consisting of 20Å of ALD HfO_2 on 10Å of interfacial SiON on p-type silicon substrates were obtained from Sematech. The as-received high-k samples were transferred to RF magnetron sputtering machine with a base pressure of $1x10^{-8}$ torr.

The spectroscopic samples were prepared by depositing 40Å of Ru (Ru-HfO_2), 40Å of Re (Re-HfO_2), and 40Å of W (W-HfO_2) using sputtering in Argon plasma. The samples were then ex-situ transferred to a UPS/XPS chamber and pumped down to $1x10^{-9}$ Torr. The ex-situ transfer of the samples caused the surface of the metal to be oxygen rich. The UPS and XPS measurements were made both for as deposited samples (without any temperature treatment after metal deposition) and after an in-situ anneal in the UPS/XPS chamber at 600˚C anneal for 10 minutes. MOS capacitors were also fabricated on the same high-K films by depositing 400Å of Ru gate (capped with 600Å of W in-situ) on 20-80Å HfO_2 having 10Å SiON on p-silicon substrate. The gates were patterned using wet etch. The capacitance- voltage (CV) curves were measured using HP4284 LCR meter and the flatband voltage (V_{FB}) and effective oxide thickness (EOT) were obtained using NCSU CV model [6]. The $\Phi_{m,eff}$ was extracted using "V_{FB} vs. EOT" method [7].

DISCUSSIONS

Figure 1(a) shows the UPS spectrum of Ru-HfO_2, Re-HfO_2 and W-HfO_2 in an as-deposited state. The width of the spectrum (E_f-E_{cutoff}) indicated that the surface work function ($\Phi_{m,surf}$) of Ru is higher than Re which in turn is higher than W ($\Phi_{m,surf}$(Ru)> $\Phi_{m,surf}$(Re)> $\Phi_{m,surf}$(W)). However, the UPS spectrum after an in-situ anneal in the UPS chamber, shown in figure 1(b), indicated that the $\Phi_{m,surf}$ of Ru and Re decreased while the $\Phi_{m,surf}$ of W increased as compared to the as deposited state. In fact, the $\Phi_{m,surf}$ of W was observed to be higher than Ru and Re ($\Phi_{m,surf}$(W)> $\Phi_{m,surf}$(Ru)> $\Phi_{m,surf}$(Re)) after anneal.

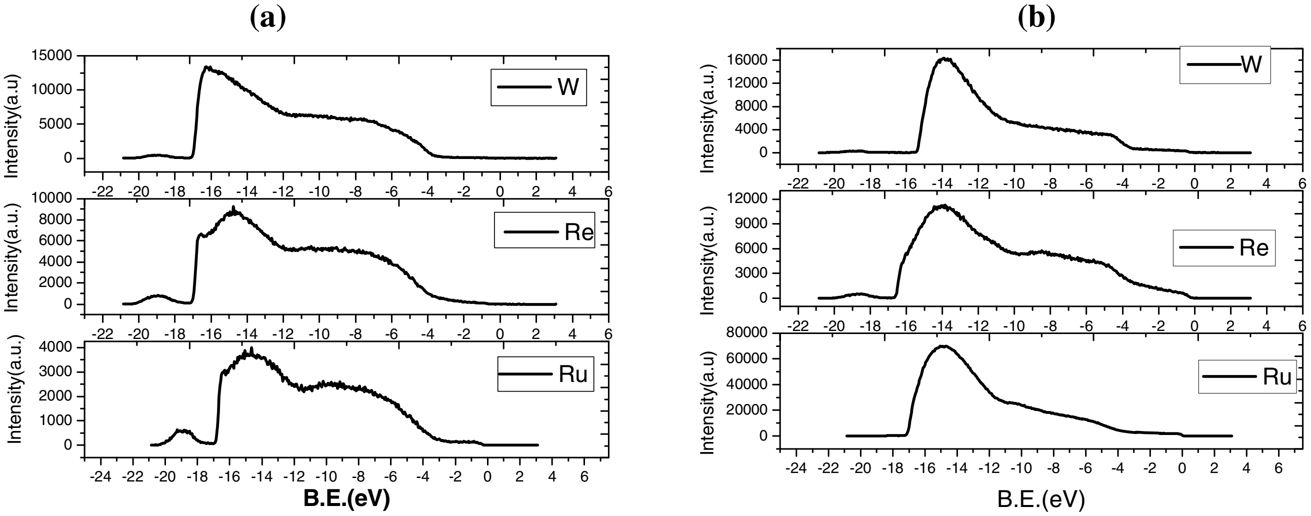

(a) **(b)**

Figure 1. The UPS spectrum of Ru-HfO_2, Re-HfO_2, and W-HfO_2 in as deposited state (a) and after 600˚C for 10 minutes in-situ anneal in the UPS chamber (b).

The XPS spectrums of the above samples are shown in figure 2. Peaks for Ru and Re corresponded to Ru-O and Re-O bonding in as deposited state which shifted towards lower binding energy corresponding to Ru and Re after anneal as shown in figure 2(a) and (b). However, as shown in figure 2(c), the peaks corresponding to W showed clear peaks of W and WO_3 in as deposited state. After anneal, the peaks for W shifted towards higher binding energy while the peaks corresponding to WO_3 showed broadening. This indicated a redistribution of oxygen in W after anneal leading to the formation of the multiple oxides of W (WO_x). It should be noted that the surface of these samples were expected to be rich in oxygen due to ex-situ transfer from the metal deposition chamber to the XPS/UPS chamber in as deposited state. However, the shift in peaks after in-situ anneal indicated that Ru and Re lose the adsorbed oxygen from the surface after anneal. The reduction in the surface work function of Ru and Re after anneal can be attributed to the loss of oxygen from the surface. On the other hand, W retained its oxygen after the anneal and redistribution of oxygen in W resulted in the formation of the multiple oxides of W. The formation of WO_x after anneal could be responsible for an increase in the surface work function of W after anneal [8]. It is also known that the properties of WO_x can vary from metallic to semi-metallic depending upon the oxygen content.

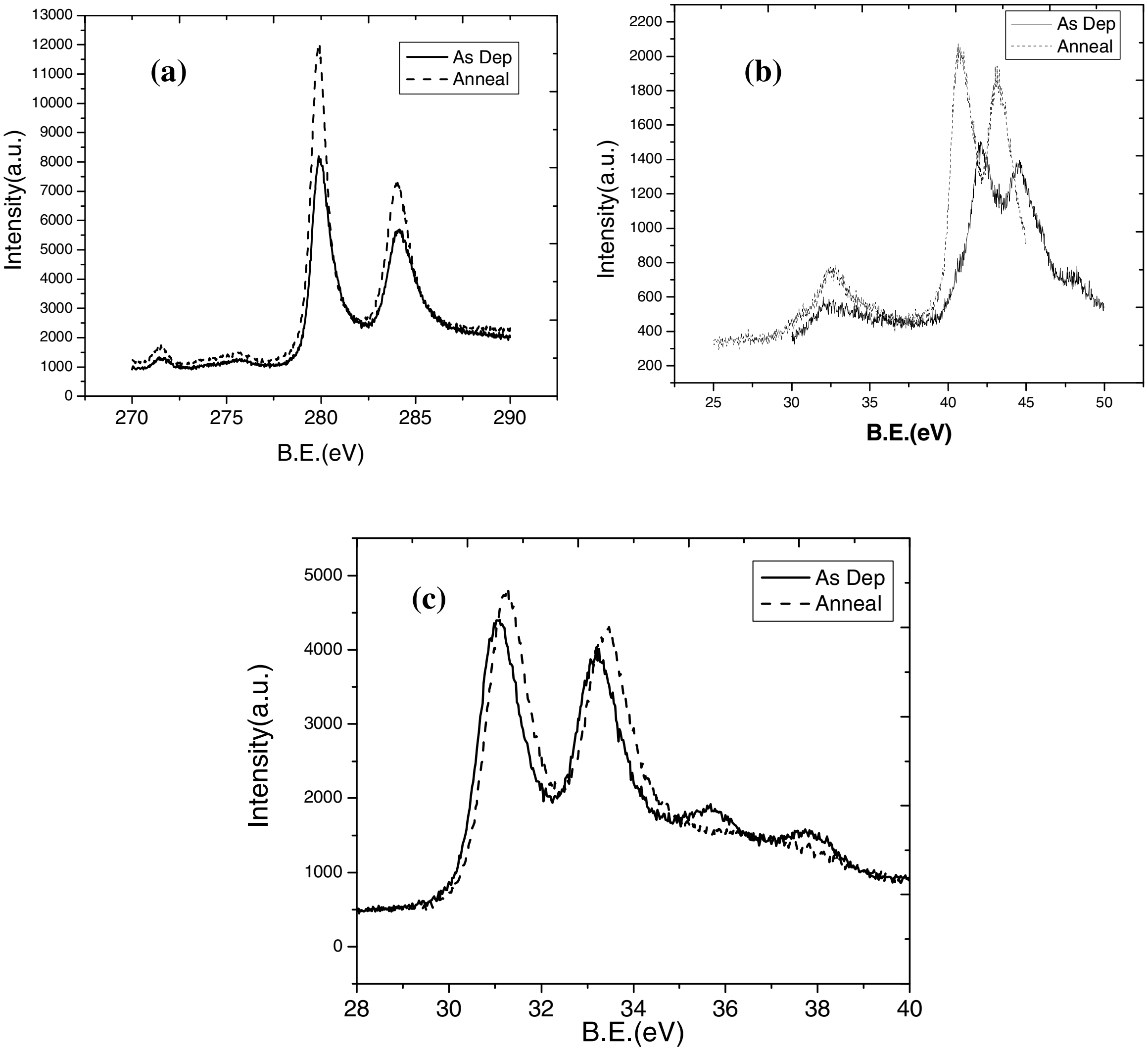
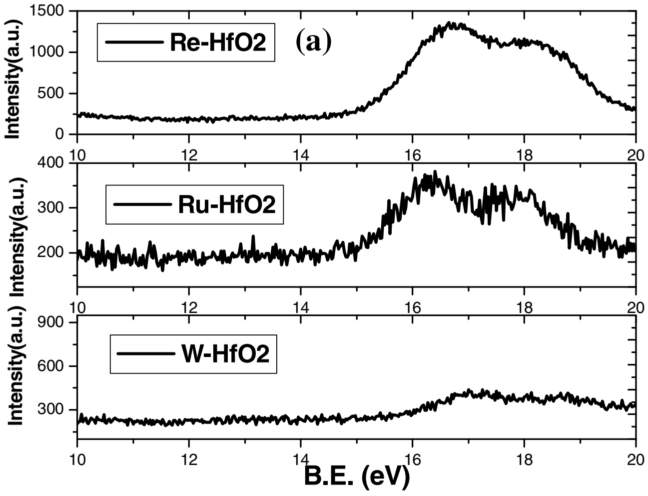
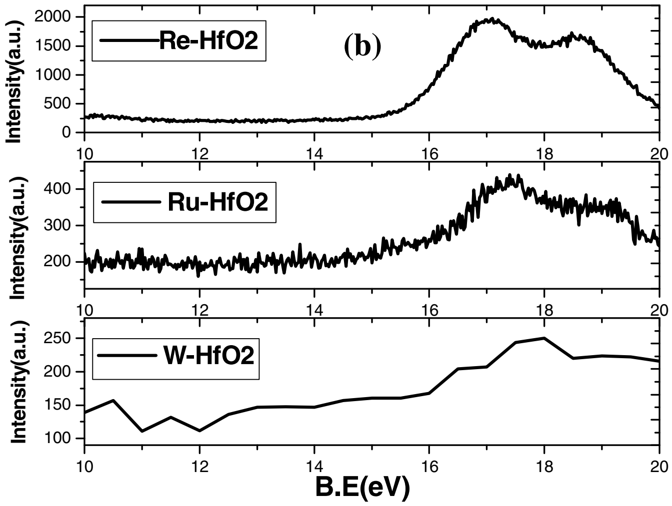


Figure 2: The XPS spectrum of Ru-HfO_2 (a), Re-HfO_2 (b), and W-HfO_2 (c) in as deposited and after 600°C for 10 minutes in-situ anneal.

These observations indicated that the oxygen content in Ru, Re and W plays an important role in governing their work function. The adsorption of oxygen in these metals followed by subsequent charge transfer from metal to oxygen results in an increase in the work function.

These findings can be translated to understand the factors governing the metal/high-k interface in a MOS device. Figure 3 shows the XPS spectrum corresponding to Hf 4f core level in HfO_2. The binding energy corresponding to Hf 4f core in HfO_2 is dependent on the metal gate contacting HfO_2 in the as-deposited state as evident from figure 3(a) where it was observed that the Hf 4f binding energy is lower for Ru (16.32 eV) compared to Re (16.74 eV) and W (17.07eV). Since the possibility of chemical reaction associated with metal gate deposition is unlikely in the as-deposited state; the differences in the binding energy could be arising as a result of dipoles at metal/HfO_2 interface due to metal-oxygen charge transfer or difference in sputtering damage to HfO_2 caused during metal deposition process. However, this differences in Hf 4f core level binding energy between different metal gates decreased after annealing and shifted towards higher binding energy (~17.2-17.4 eV) as shown in figure 3(b). The shift in binding energy due to chemical reactions at such low annealing temperatures is not clear. Therefore, the change in the binding energy can be attributed to the alteration of dipoles at metal/HfO_2 or HfO_2/IL/Si interfaces [9]. Shown in figure 3(c) is the XPS spectrum of Hf 4f core in 20Å HfO_2/IL/ p-Si in as received state without any metal on top of HfO_2. The peaks corresponding to Hf-O as well as Hf-Si can be observed. It is reported that Hf-Si creation at HfO_2/Si interface is accompanied with the creation of oxygen vacancies acting as a source of positive charge at Hf-Si interface [10]. However during anneal, the oxygen from HfO_2 can move to the Si interface which can change the charge profile in the gate dielectric stack.





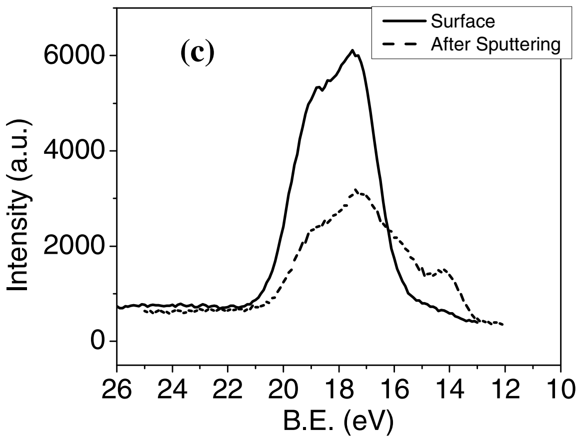


Figure 3. The Hf 4f core level binding energy in (a) as deposited state (b) in-situ anneal for Ru-HfO$_2$, Re-HfO$_2$, and W-HfO$_2$ samples (c) Surface HfO$_2$ and after removing 10Å of surface HfO$_2$ from HfO$_2$/IL/p-Si in as deposited state.

In order to study the implications of dipole modulation on the device properties, capacitance – voltage curves of MOS capacitors with Ru metal gate on HfO$_2$ gate dielectrics were measured. The figure 4 shows V_{FB} vs. EOT for these capacitors in as deposited and after anneals. A high effective work function ($\Phi_{m,eff}$) of Ru was observed from the intercept on the V_{FB} axis in as deposited state. However, the $\Phi_{m,eff}$ of Ru reduced significantly after anneal accompanied by the change in the charge profile at HfO$_2$/IL/Si interface. The high $\Phi_{m,eff}$ of Ru in as deposited state can be attributed to Ru-O charge transfer and subsequent dipole creation at metal/HfO$_2$ interface which resulted in a high $\Phi_{m,eff}$. However, it is also believed that oxygen from Ru/HfO$_2$ interface moves towards HfO$_2$/IL/Si interface after anneal and manifest itself in the form of negative charges as can be seen from the positive slope of V_{FB} vs. EOT plots after anneal. The movement of oxygen from Ru/HfO$_2$ interface to HfO$_2$/IL/Si interface can allow Ru-Hf or Ru-V$_o$ charge transfer at Ru/HfO$_2$ interface which resulted in a lower $\Phi_{m,eff}$ [3,4]. Therefore, in order to retain a high $\Phi_{m,eff}$ of PMOS metals on HfO$_2$, it is important to stop the movement of oxygen from metal/HfO$_2$ interface.

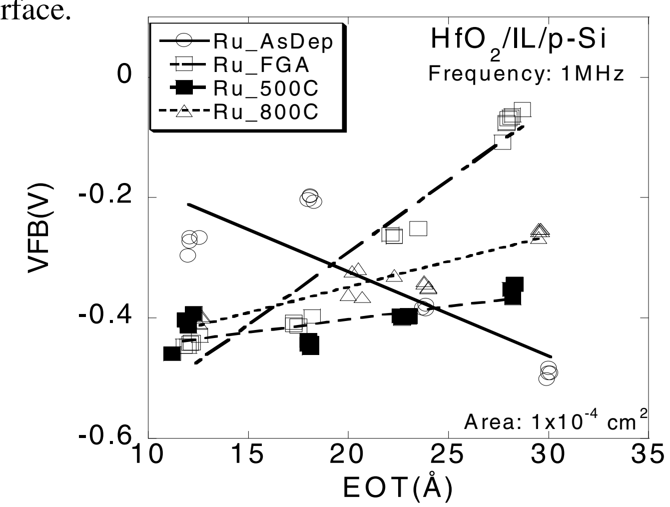


Figure 4: Flatband Voltage vs. EOT plot for Ru/HfO$_2$/pSi capacitors in as deposited state and after anneal.

CONCLUSION

In this paper, we have shown that the oxygen content in metal gates and at metal/HfO_2 interface plays an important role in governing the effective work function of the high work function metal gates. Any subsequent annealing causes the movement of oxygen from metal/HfO_2 interface to HfO_2/IL/Si interface. The movement of oxygen changes the dipoles at metal/HfO_2 and HfO_2/IL/Si interfaces leading to a net reduction in the effective work function of metal gates. Therefore, it is important to stabilize the oxygen content on the surface of high-k in order to achieve the high effective work function of metals suitable for PMOS applications.

ACKNOWLEDGEMENTS

We would like to acknowledge Dr. Prashant Majhi of Sematech for providing the samples used in this work. We would also like to acknowledge SRC/SEMATECH, Intel, Applied Materials, and NSF for their support.

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