# Effects of GeO<sub>2</sub>-Metal Interaction on V<sub>FB</sub> of GeO<sub>2</sub> MIS Gate Stacks

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## 1. Introduction

The flatband voltage ( $V_{FB}$ ) shift of GeO<sub>2</sub> MIS gate stack is not fully understood, because an unexpected negative shift is often observed and time-dependent shift by the exposure to the air has been also pointed out [1]. We also have to pay attention to the  $V_{FB}$  shift by Fermi-level pinning (FLP) of metals on oxides [2] and dipole layer formation at oxide/oxide interface [3], which are often reported for high-k gate stacks. In this study we clarify the  $V_{FB}$  shift of GeO<sub>2</sub> MIS stacks by metal-GeO<sub>2</sub> interactions.

## 2. Experimental

The GeO<sub>2</sub>films were deposited by rf-sputtering of GeO<sub>2</sub> target, on thermally oxidized p-Si wafers. After annealing in N<sub>2</sub>+ O<sub>2</sub> 0.1% ambient at 600°C, Al, Cu, and Au were evaporated to fabricate metal/GeO<sub>2</sub>/SiO<sub>2</sub>/p-Si MIS capacitors. No annealing was conducted after gate metal deposition. Note that the deposited GeO<sub>2</sub> films on SiO<sub>2</sub> were employed in this study, instead of thermal oxide, to focus our attention to the metal/GeO<sub>2</sub> interface phenomena without the effects of GeO<sub>2</sub>/Ge interface reactions, such as GeO desorption [4]. For comparisons, HfO<sub>2</sub> MIS capacitors were also fabricated on the same substrates.

# 3. Results and Discussions

The 1 MHz C-V characteristics of Au/GeO<sub>2</sub>/SiO<sub>2</sub>/p-Si MIS capacitors with various GeO<sub>2</sub> thicknesses are shown in **Fig. 1**. It is clearly seen that the effects of fixed charges at the interface and those in the bulk on  $V_{FB}$  are negligibly small, because there is no thickness dependence of  $V_{FB}$ . However, it should be noted that the  $V_{FB}$  is always negatively shifted (-0.3V~ -0.4V) from that of the SiO<sub>2</sub> MIS stack without GeO<sub>2</sub> irrespective of GeO<sub>2</sub> thickness.

There are two possible interface phenomena as the origin of the observed  $V_{FB}$  shifts in Fig. 1: the FLP of metals on GeO<sub>2</sub> and the dipole formation at GeO<sub>2</sub>/SiO<sub>2</sub> interface. In order to clarify which phenomena are dominant,  $V_{FB}$  of the capacitors with different gate metals and various GeO<sub>2</sub> film thicknesses were examined. In this experiment, the  $GeO_2$ films were chemically etched in  $H_2O + CH_3OH$  solution to obtain a variety of film thickness before annealing the films at 600°C. As shown in Fig. 2, it is clearly seen that the  $V_{FB}$ difference between the GeO<sub>2</sub> MIS capacitor and the SiO<sub>2</sub> one significantly changes by employing different gate metals. The  $V_{FB}$  on GeO<sub>2</sub> showed a significant negative shift only in the case of Au, whereas almost no  $V_{FB}$  shift or even a slight shift to the opposite direction was observed in the case of Cu and Al. Thus it should be the metal/GeO<sub>2</sub> interface, rather than the bottom interface, that has the dominant role to determine the  $V_{FB}$  shift. In Fig. 3, the  $V_{FB}$ 



**Fig. 1** C-V characteristics of Au/GeO<sub>2</sub>/SiO<sub>2</sub>/p-Si MIS capacitors with various GeO<sub>2</sub> film thickness. The samples were annealed at 600°C in N<sub>2</sub> + 0.1% O<sub>2</sub> ambient before Au deposition. No PMA was applied. A negative  $V_{FB}$  shift (-0.2~ -0.3 V) was clearly observed, even though  $V_{FB}$  does not show any dependence on the GeO<sub>2</sub> film thickness.



**Fig. 2** GeO<sub>2</sub> film thickness dependence of  $V_{FB}$  of GeO<sub>2</sub>/SiO<sub>2</sub>/p-Si MIS capacitors with Au, Cu, and Al as the gate metals. The horizontal axis shows capacitance equivalent thickness (CET) of GeO<sub>2</sub> films, determined from difference between the total CET and that of SiO<sub>2</sub>. Cu gate and Al gate capacitors result in quite a small  $V_{FB}$  shift compared with Au gate ones.

of SiO<sub>2</sub>, GeO<sub>2</sub>/SiO<sub>2</sub>, and HfO<sub>2</sub>/SiO<sub>2</sub> MIS capacitors are plotted as a function of the vacuum work functions of the gate metals [5]. It is obvious that the data of GeO<sub>2</sub> capacitors do not show the linear dependence on the vacuum work function of the metals. On the other hand, the  $V_{FB}$  shift of HfO<sub>2</sub>/SiO<sub>2</sub> stack always shows a constant positive shift around +0.2 ~ +0.3 V, irrespective of the employed gate metals. This behavior is attributable mainly to the dipole effects at HfO<sub>2</sub>/SiO<sub>2</sub> bottom interface, whereas the HfO<sub>2</sub>/metal interaction is suggested to be negligible.



**Fig. 3** Relationship between flatband volatage ( $V_{FB}$ ) and vacuum work function of the employed gate metals for GeO<sub>2</sub>/SiO<sub>2</sub>/p-Si, SiO<sub>2</sub>/p-Si, and HfO<sub>2</sub>/SiO<sub>2</sub>/p-Si MIS capacitors. The thickness of SiO<sub>2</sub> (~6nm) is identical to all the samples, although that of both GeO<sub>2</sub> and HfO<sub>2</sub> films are ~ 2.5 nm. Note that the film thickness dependence of  $V_{FB}$  is small enough for all the samples to extract the  $V_{FB}$  to discuss the effective work functions of metals

Thus the pronounced metal-dielectric interaction is a unique phenomenon only observed for  $GeO_2$  gate stacks.

Next we investigated the interface reactions between the metal and GeO2, by Ge3d XPS measurements of GeO<sub>2</sub>/SiO<sub>2</sub>/Si stacks covered with ultrathin Au, Cu and Al films. As shown in Fig. 4, we found that the reduction of GeO<sub>2</sub> into Ge was clearly observed only for Al/GeO<sub>2</sub> interface, by the reaction of  $GeO_2+Al \rightarrow Al_2O_3+Ge$ , even though we did not employ any annealing after metal deposition. On the other hand, no reaction was detectable by XPS at the Au/GeO2 interface. This is because such red-ox reaction should be pronounced more for the lower work function metals. Based on these results, we consider a possible model to explain what we observed in this study as follows. It is well known that the oxygen-deficient GeO<sub>2</sub> often forms neutral oxygen vacancies or divacancies (divalent Ge centers) [6], and we actually detected a photo absorption in GeO<sub>2</sub> films corresponding to the formation of those defects [7]. Those defects existing at the  $GeO_2$ surface can be the origin of the electron transfer from  $GeO_2$ to Au, by taking account of the model to explain the FLP of poly-Si on  $HfO_2$  with oxygen vacancies [8]. Note that chemically non-reactive interface of Au/GeO2 will not allow the atomic transfer but the electron transfer as shown in Fig.5 (a). On the other hand, Al/GeO<sub>2</sub> interface is expected to become Al(+Ge)/AlOx/GeO<sub>2</sub> layered structure as the result of interface reaction, as schematically shown in Fig. 5 (b). Then the  $GeO_2$  surface is passivated by ultrathin AlOx layer, which will be the reason for the quite small  $V_{FB}$  shifts of Al-gate capacitors. Based on these considerations, the significant  $V_{FB}$  shift for the Au gate capacitors is possibly attributed to FLP of Au caused by the oxygen-deficient type defects on the surface of GeO<sub>2</sub>, whereas the FLP is not significant for the low work function metals like Al because of the interface red-ox reactions to form an interface layer.

#### 4. Conclusions

The metal-GeO<sub>2</sub> interaction significantly affects the  $V_{FB}$  of GeO<sub>2</sub> MIS stacks. The negative flatband voltage shift of Au/GeO<sub>2</sub>/SiO<sub>2</sub>/Si MIS capacitor will be the result of FLP of Au on GeO<sub>2</sub>, probably caused by the defects on GeO<sub>2</sub> surface, whereas the Al-GeO<sub>2</sub> interaction is suppressed because of the interface reaction to passivate the GeO<sub>2</sub> surface.

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**Fig. 4** Ge3d XPS of GeO<sub>2</sub> covered with ultrathin (~ a few nm) Au, Cu, and Al films. The signal intensity is normalized by Ge<sup>4+</sup>. The reaction between the metals and GeO<sub>2</sub> results in the reduction of Ge at the interface even without PMA, which will be more pronounced for metals with lower work functions. Especially, in the case of Al, the reduction of Ge<sup>4+</sup> results in the formation of significant amount of Ge<sup>0</sup>

(a) Au/GeO2	(b) Al/GeO <sub>2</sub>
e <sup>-</sup> Au	Al (+Ge)
V.	AlOx
GeO2	GeO <sub>2</sub> Ge
SiO <sub>2</sub>	SiO2
Si	Si

**Fig. 5** Schematics of the interactions between metal and GeO<sub>2</sub> film for (a)Au/GeO<sub>2</sub> and (b)Al/GeO<sub>2</sub>. In the case of Au/GeO<sub>2</sub>, electron transfer occurs since there is no passivation layer to suppress the interaction between the defects states in GeO<sub>2</sub> and Au. On the other hand, the reaction of GeO<sub>2</sub>+Al $\rightarrow$ Al<sub>2</sub>O<sub>3</sub>+Ge will reduce GeO<sub>2</sub> and extract Ge to form Al-Ge alloy which was detected in Fig. 5, accompanied with the formation of AlO<sub>x</sub> ultrathin layer to passivate the GeO<sub>2</sub>-metal interactions.