Effects of GeO₂-Metal Interaction on $V_{FB}$ of GeO₂ MIS Gate Stacks

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1. Introduction

The flatband voltage ($V_{FB}$) shift of GeO₂ 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 GeO₂ MIS stacks by metal-GeO₂ interactions.

2. Experimental

The GeO₂ films were deposited by rf-sputtering of GeO₂ target, on thermally oxidized p-Si wafers. After annealing in N₂+ O₂ 0.1% ambient at 600°C, Al, Cu, and Au were evaporated to fabricate metal/GeO₂/SiO₂/p-Si MIS capacitors. No annealing was conducted after gate metal deposition. Note that the deposited GeO₂ films on SiO₂ were employed in this study, instead of thermal oxide, to focus our attention to the metal/GeO₂ interface phenomena without the effects of GeO₂/Ge interface reactions, such as GeO desorption [4]. For comparisons, HfO₂ MIS capacitors were also fabricated on the same substrates.

3. Results and Discussions

The 1 MHz C-V characteristics of Au/GeO₂/SiO₂/p-Si MIS capacitors with various GeO₂ 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 SiO₂ MIS stack without GeO₂ irrespective of GeO₂ thickness.

There are two possible interface phenomena as the origin of the observed $V_{FB}$ shifts in Fig. 1: the FLP of metals on GeO₂ and the dipole formation at GeO₂/SiO₂ interface. In order to clarify which phenomena are dominant, $V_{FB}$ of the capacitors with different gate metals and various GeO₂ film thicknesses were examined. In this experiment, the GeO₂ films were chemically etched in H₂O + CH₃OH 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 GeO₂ MIS capacitor and the SiO₂ one significantly changes by employing different gate metals. The $V_{FB}$ on GeO₂ 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/GeO₂ interface, rather than the bottom interface, that has the dominant role to determine the $V_{FB}$ shift. In Fig. 3, the $V_{FB}$ of SiO₂, GeO₂/SiO₂, and HfO₂/SiO₂ MIS capacitors are plotted as a function of the vacuum work functions of the gate metals [5]. It is obvious that the data of GeO₂ capacitors do not show the linear dependence on the vacuum work function of the metals. On the other hand, the $V_{FB}$ shift of HfO₂/SiO₂ 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 HfO₂/SiO₂ bottom interface, whereas the HfO₂/metal interaction is suggested to be negligible.
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 GeO$_2$, by Ge3d XPS measurements of GeO$_2$/SiO$_2$/Si stacks covered with ultrathin Au, Cu and Al films. As shown in Fig. 4, we found that the reduction of GeO$_2$ into Ge was clearly observed only for Al/GeO$_2$ interface, by the reaction of GeO$_2$/Al$\rightarrow$AlO$_x$/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/GeO$_2$ 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$_2$ often forms neutral oxygen vacancies or divacancies (divalent Ge centers) [6], and we actually detected a photo absorption in GeO$_2$ 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/GeO$_2$ will not allow the atomic transfer but the electron transfer as shown in Fig. 5 (a). On the other hand, Al/GeO$_2$ interface is expected to become Al(+Ge)/AlOx/GeO$_2$ layered structure as the result of interface reaction, as schematically shown in Fig. 5 (b). Thus 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$_2$, 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$_2$ interaction significantly affects the $V_{FB}$ of GeO$_2$ MIS stacks. The negative flatband voltage shift of Au/GeO$_2$/SiO$_2$/Si MIS capacitor will be the result of FLP of Au on GeO$_2$, probably caused by the defects on GeO$_2$ surface, whereas the Al-GeO$_2$ interaction is suppressed because of the interface reaction to passivate the GeO$_2$ surface.

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References