Direct comparison of ZrO$_2$ and HfO$_2$ on Ge substrate in terms of the realization of ultra-thin high-k gate stacks

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1. Introduction

Ge is one of the attractive materials as the substrate of MISFET due to its higher mobility compared to Si. However, the lack of thermally stable Ge oxide impedes the usage of the material. On the other hand, as the aggressive scaling of MIS devices leads to the fundamental limit of SiO$_2$ as the gate dielectrics, high-quality deposited high-k materials have been developing for the replacement of SiO$_2$. Recently, it has been reported that ultra-thin gate insulator has been fabricated with the combination of ZrO$_2$ and Ge substrate [1]. They also said that ZrO$_2$ film showed locally interfacial layer beneath HfO$_2$ were also reported on Ge substrate [2]. Moreover, they also said that ZrO$_2$ film showed locally interfacial layer beneath HfO$_2$ without an interfacial layer [1,2]. In order to confirm Ge diffusion into the high-k dielectric, we checked XPS spectra of samples before and after 500°C N$_2$ annealing (Fig. 2). Significant increase of Ge oxide peak observed in the annealed samples of both ZrO$_2$ and HfO$_2$ clearly indicates that the interfacial Ge oxide diffused into high-k dielectrics. We believe that most Ge, which diffused into the films, came from the interfacial layers, because the total dielectric film thickness remained almost the same. It should be noted that the Ge peak in Fig. 2 (b) results from the substrate: this peak was absent in the grazing angle XPS (not shown). The number of detected photoelectron of Ge oxide is higher in the annealed ZrO$_2$ sample than that in annealed HfO$_2$ sample. It may indicate that ZrO$_2$ absorbs more Ge atom than HfO$_2$. Since Gibbs free energy is almost the same for ZrO$_2$ and HfO$_2$, we speculate the difference in the thinning of the interfacial layer after annealing originates from other material properties such as the difference in the activation energy of interdiffusion of GeO$_x$/ZrO$_2$ and GeO$_x$/HfO$_2$.

This interdiffusion phenomenon results in GeO$_x$ content increase in high-k materials. Figure 3 indicates that the $\varepsilon_r$ of ZrO$_2$ and HfO$_2$ containing Ge decrease by the increase of Ge content and are reaching to the reported value of GeO$_2$ [5]. It also reveals that the $\varepsilon_r$ of ZrGeO are larger than those of HfGeO for wide range of GeO$_2$ ratio, especially at low GeO$_2$ concentration.

Figure 4 shows $C_g$, $V_g$ and $J_g$ characteristics of ZrO$_2$ samples shown in Fig. 1. 500°C N$_2$ annealing resulted in the large increase in the capacitance and CET of 1.2 nm (including accumulation layer thickness) was obtained. $J_g$ hardly changed with this interdiffusion phenomenon.

Finally we compared CET as well as $J_g$ for ZrO$_2$ and HfO$_2$ samples shown in Fig. 1. Figure 5 shows that 500°C N$_2$ annealing causes CET reduction of ZrO$_2$ samples without $J_g$ increase, on the contrary, HfO$_2$ samples showed drastic increase in $J_g$, although this reason is not clear yet.

Thanks to higher $\varepsilon_r$ of ZrGeO and larger absorption of interface layer without large increase in $J_g$, ZrO$_2$ on Ge is preferable to HfO$_2$ in terms of the realization of very thin CET gate stacks.

4. Conclusion

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Ge substrate was performed. We indicated that ultra-thin (CET 1.2 nm) single layer high-k gate dielectric could be obtained using the combination of ZrO₂ and Ge substrate with 500°C N₂ annealing. ZrO₂ is more suitable to realize ultra-thin single layer high-k gate dielectric than HfO₂ on Ge substrate.

References
[5] CRC Handbook of Chemistry and Physics, 12-47, ed. 75th

Fig. 1 HR-XTEM images of (a) ZrO₂ as-deposited, (b) ZrO₂ after 500°C N₂ anneal, (c) HfO₂ as-deposited, and (d) HfO₂ after 500°C anneal. For samples (a) and (b), Pt electrodes peeled off during the TEM sample preparation.

Fig. 2 XPS of samples: (a) ZrO₂ and (b) HfO₂ before and after 500°C annealing. XPS detector was set at the normal position to the surface.

Fig. 3 Dielectric constants of (a) ZrGeO and (b) HfGeO with different N₂ anneal temperatures (400°C and 800°C).

Fig. 4 (a) CV, (b) Jg on ZrO₂ before and after 500°C N₂ annealing

Fig. 5 CET-Jg of samples: ZrO₂ and HfO₂ before and after 500°C N₂ annealing