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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 epitaxial growth without an interfacial layer [1, 2]. Moreover, the Ge diffusion into HfO_2 and thinning of the interfacial layer beneath HfO_2 were also reported on Ge substrate [3, 4]. Although promising device characteristics of Ge substrate with high-k gate dielectric have been demonstrated, direct comparison of ZrO_2 and HfO_2 on Ge substrate has not been carried out, to our knowledge. In this work, we performed the comparison especially in terms of the interfacial layer thinning, film dielectric constant and leakage current through the film. Remarkable thinning of interfacial layer beneath ZrO_2 as well as higher dielectric constant of ZrGeO makes it easier to realize thin capacitive equivalent thickness (CET), compared to HfO_2 on Ge.

2. Experimental

MIS capacitors with thin gate dielectric were fabricated on the (100) oriented antimony lightly doped n-type Ge substrates (0.2 Ωcm), which were cleaned with DHF and DI water rinse. ZrO_2 or HfO_2 of about 3nm thick was deposited by sputtering. Circular Pt gate electrodes were formed using stencil masks by electron beam evaporation. Subsequently, MIS capacitors were subjected to nitrogen gas anneal at 500°C for 30 min with top Pt gate electrodes.

In order to derivate the dielectric constant (ε_r), thick ZrGeO or HfGeO insulators of 100 nm with varied Ge/(Zr+Ge) or Ge/(Hf+Ge) ratio from 0 to 75% were deposited by sputtering on Si substrate and MIS capacitors were fabricated.

3. Results and Discussion

Figure 1 shows high-resolution cross-sectional transmission electron microscopy (HR-XTEM) images before and after 500°C N_2 annealing. There exist interfacial layers (I. L.s) beneath ZrO_2 and HfO_2 before annealing presumably due to the surface oxidation of Ge substrate prior to the film deposition. After annealing, however, the interfacial layer between ZrO_2 and Ge substrate disappeared and the complete absence of interfacial layer can be confirmed by the fact that crystal lattice of ZrO_2 reaches down to the very surface of the substrate. It should be noted that the interfacial layer was left beneath HfO_2 even after annealing. 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 absorb more Ge atom than HfO_2. Since Gibbs free energy is almost the same for ZrO_2 and HfO_2, we speculate the difference of 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_2 content increase in high-k materials. Figure 3 indicates that the ε_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 ε_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-V_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 ε_r of ZrGeO and larger absorption of interfacial 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

Direct comparison of ZrO_2 and HfO_2 gate dielectric on

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 ZrO_2 and Ge substrate with 500°C N_2 annealing. ZrO_2 is more suitable to realize ultra-thin single layer high-k gate dielectric than HfO_2 on Ge substrate.

References

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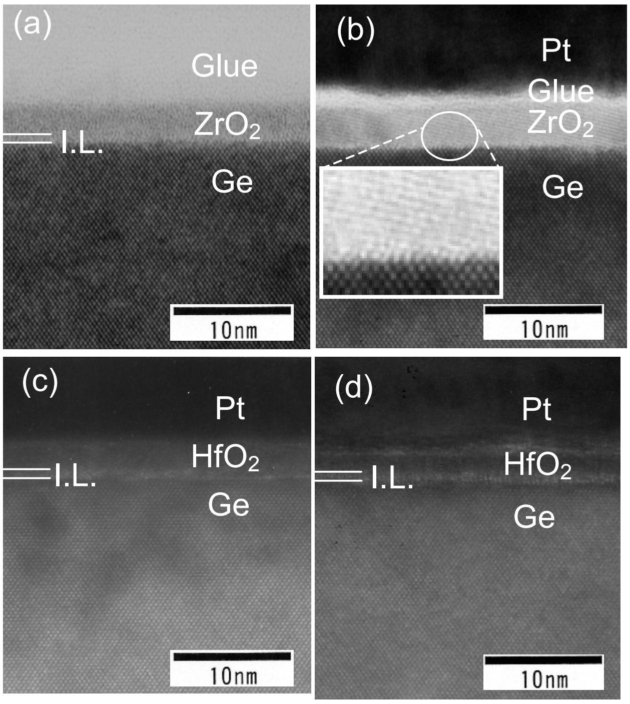

Fig. 1 HR-XTEM images of (a) ZrO_2 as-deposited, (b) ZrO_2 after 500°C N_2 anneal, (c) HfO_2 as-deposited, and (d) HfO_2 after 500°C anneal. For samples (a) and (b), Pt electrodes peeled off during the TEM sample preparation.

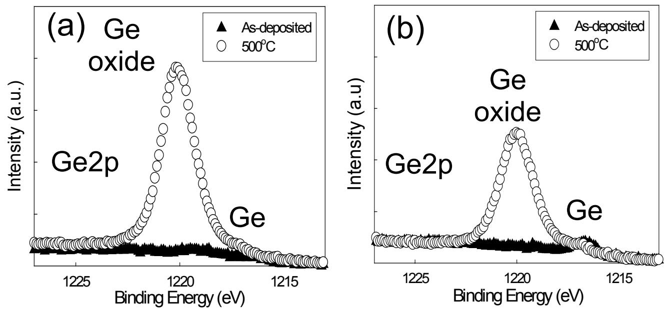

Fig. 2 XPS of samples: (a) ZrO_2 and (b) HfO_2 before and after 500°C annealing. XPS detector was set at the normal position to the surface.

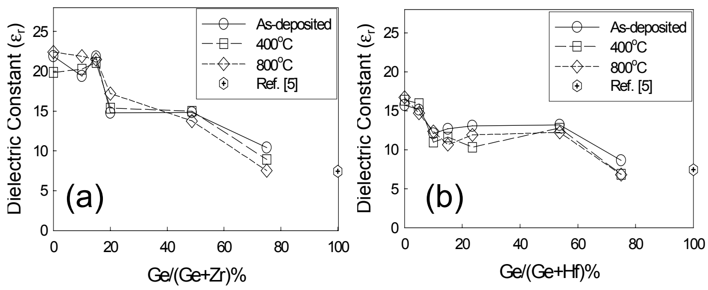

Fig. 3 Dielectric constants of (a) ZrGeO and (b) HfGeO with different N_2 anneal temperatures (400°C and 800°C).

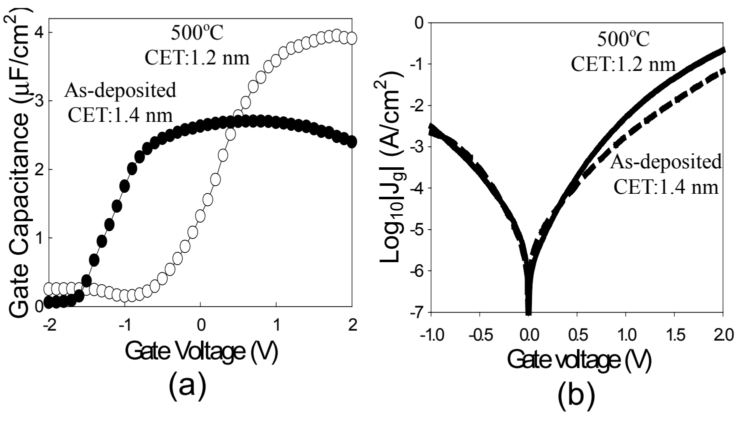

Fig. 4 (a) CV, (b) J_g on ZrO_2 before and after 500°C N_2 annealing

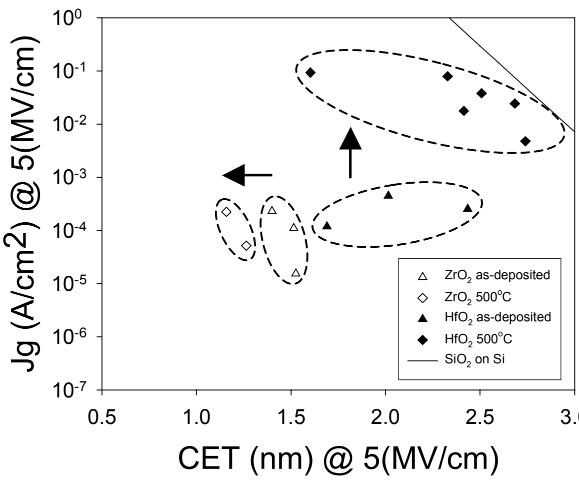

Fig. 5 CET-J_g of samples: ZrO_2 and HfO_2 before and after 500°C N_2 annealing