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Control of Interface Properties of High-k/Ge with GeO_2 Interface Layer

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1. Introduction

High-k/Ge CMOS is considered as one of the promising candidates for beyond scaling devices. For realizing high performance Ge devices, the control of high-k/Ge interface properties is required. However, the controllability of high-k/Ge interface is significantly different from that of high-k/Si, because of the lack of thermodynamic stability of Ge native oxides [1]. In this study, we investigate two reactions, which have crucial effects on high-k/Ge interface properties; the volatilization of GeO, and the intermixing of high-k with Ge.

2. Properties of GeO_2/Ge Interface

It is often observed that almost no GeO_2 interlayer exists at high-k/Ge interface after thermal processes [2], however, the Ge-O bonds inevitably exist at the interface. Thus the controllability of GeO_2/Ge interface is essentially required. The desorption of Ge oxides occurs due to the generation of volatile GeO at GeO_2/Ge interface (GeO_2+Ge→2GeO↑), which severely deteriorate the MIS characteristics [3]. We have found that GeO volatilization rate in the GeO_2/Ge system is limited by the GeO diffusion in the GeO_2 film. As shown in **Fig. 1**, the reduction rate of GeO_2 films during N_2 annealing depends on the film thickness significantly. Those experimental results are well fitted by the calculated curves, assuming that the volatilization rate obeys the equation of the diffusion-limited processes ($dT_{ox}/dt = -\alpha/T_{ox}$). These results suggest that the control of quality of ultrathin GeO_2 film, which is the case of interlayer, would be more challenging.

We have found that the defects generation in GeO_2 films by thermal annealing is detectable as an increase of sub-bandgap photo absorption. **Fig. 2** shows the extinction factor (k) of 100 nm-thick sputtered GeO_2 films on Ge, determined by spectroscopic ellipsometery. Before annealing, a sharp increase of k was observed at 6 eV, which corresponds to the bandgap of GeO_2. After annealing in N_2 at 600°C, a broad increase of k from around 5 eV was clearly observed, in addition to the sharp increase at 6 eV. The sub-gap absorption from ~ 5 eV suggests the generation of significant amount of gap-states, which will be caused by the GeO volatilization. Note that the sub-gap absorption is also seen for the film annealed in O_2, probably because the GeO volatilization proceeds even in O_2, simultaneously with the GeO_2 growth at the interface. From thermodynamic considerations, it is suggested that O_2 with a much higher pressure is required to suppress the GeO volatilization [4]. Thus the GeO volatilization is not so easy to suppress that specially engineered processes would be required to achieve a high quality GeO_2/Ge interface.

3. Control of High-k/Ge Interface

Since there is almost no GeO_2 interlayer, the high-k/Ge interface properties strongly depend on the employed high-k materials, in addition to the interlayer quality. The C-V characteristics of high-k/Ge MIS capacitors with Y_2O_3 and La_2O_3 show relatively good characteristics even after N_2 annealing at 600°C, whereas those with HfO_2 shows severely deteriorated ones [5]. These results clearly indicate the importance of high-k material selection. During the annealing, a reaction layer is formed at the interface by the diffusion of Ge into high-k films. We found that the crystallinity of high-k films was significantly altered when Ge was included in the film, as shown in **Fig. 3**. HfO_2 changes its crystal phase whereas Y_2O_3 is amorphized by Ge doping. The amorphized layer at the interface would be beneficial for the interface properties. Thus the ability to form amorphous interface reaction layer would determine the intimacy of high-k materials with Ge, as long as almost no interface GeO_2 layer exists. It is reasonable that amorphous high-k materials including LaLuOx [6] show

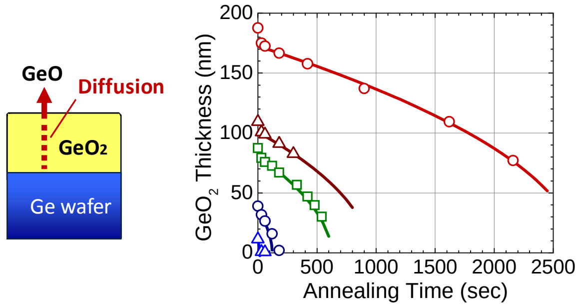

Fig. 1 Change of sputtered GeO_2 film thickness by annealing at 600°C in N_2 on Ge (100) substrates. The solid curves are calculated by assuming the equation; $dT_{ox}/dt = -\alpha/T_{ox}$ (α = 5.4 nm²/s). The good agreement of calculation with experimental data indicates that desorption rate is controlled by the GeO diffusion process in the GeO_2 film.

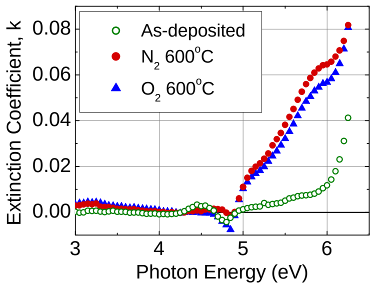

Fig. 2 Extinction coefficient (k) of 100 nm-thick sputtered GeO_2 films on Ge (100), before and after annealing in N_2, O_2 at 600°C. The sharp increase of k at ~6 eV is corresponding to the bandgap of GeO_2, whereas increase ~5 eV suggests the sub-gap absorption.

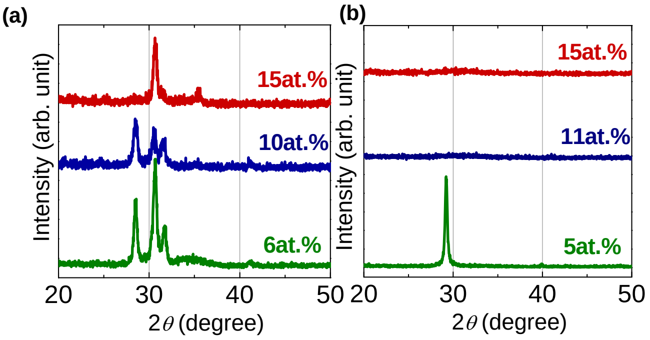

Fig. 3 XRD patterns of **(a)** HfGeOx and **(b)** YGeOX films with various Ge contents, after annealing in N_2 at 600°C. The film thickness was ~20 nm. The YGeOx films are amorphized by increasing the Ge content, while the HfGeOX films crystallize in the monoclinic or the cubic (or tetragonal) phase.

relatively good characteristics on Ge substrates.

When an interface GeO_2 layer is intentionally inserted between high-k and Ge, the interface properties are rather controlled by the quality of the interlayer. **Fig. 4** shows the change of the C-V characteristics of Y_2O_3/Ge MIS capacitors, by an additional O_2 annealing at 600°C [7]. Up to ~ 1.5 nm GeO_2 interlayer is formed as the O_2 concentration increases in the annealing ambient. The growth of interlayer efficiently suppresses the hump in the C-V curves in the depletion region, suggesting a less defective interface states density. Instead, growth of interlayer induces a hysteresis. The origin of the hysteresis would be the defective GeO_2 interlayer. The GeO volatilization will occur through (or into) high-k films, simultaneously with GeO_2 growth.

In **Fig. 5**, the decrease of the thickness of GeO_2 films covered with or without 10 nm-thick high-k film is shown as a function of annealing time at 600°C in N_2. Both HfO_2 and Y_2O_3 cap layers do not block the GeO volatilization completely. However, it is interesting to see that those two cap materials show significantly different effects. A slight retardation by HfO_2 cap seems coming simply from the increase of GeO diffusion layer thickness, whereas Y_2O_3 works more efficiently to retard the desorption, probably because of the stronger interaction between Y_2O_3 and GeO. We have also found that Si cap layer can suppress the GeO volatilization much more efficiently [3,8] than those high-k caps. Thus one of the possible ways to improve GeO_2 interlayer quality is to introduce Si or $NiSi_x$ cap layer on top of the films before annealing. Actually, by employing a FUSI process at 600°C, the GeO_2/Ge MIS characteristics are dramatically improved as shown in **Fig. 6**, compared to the conventionally processed ones where the Au electrode was deposited after N_2 annealing without the cap layer.

4. Conclusion

The high-k/Ge interface quality is controllable by the selection of high-k materials because it is strongly affected by the properties of the Ge-high-k mixed oxides formed at the interface. In addition, the suppression of GeO volatilization is also crucial to avoid the deterioration of GeO_2 interlayer. Control of those reactions is the key to realize high-quality high-k/Ge interfaces.

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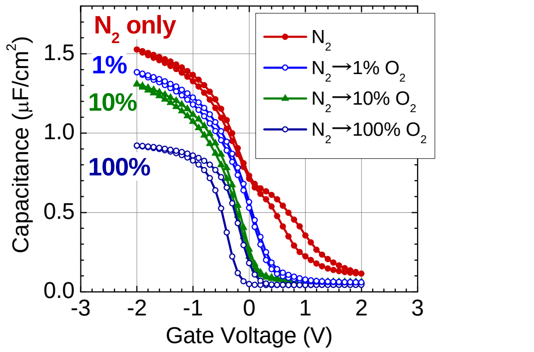

Fig. 4 Bidirectional 1 MHz C-V characteristics of Au/Y_2O_3(/GeO_2)/Ge (100) MIS capacitors fabricated by two-step annealing, consisting of N_2 annealing followed by O_2 annealing. The higher the O_2 concentration in the second anneal ambient, the less interface defects density is observed, but the larger hysteresis appears.

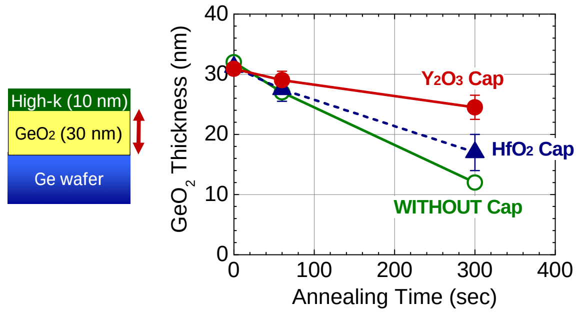

Fig. 5 Changes of GeO_2 film thickness (initially 30nm-thick) by N_2 annealing at 600°C, with or without HfO_2 and Y_2O_3 layers (10 nm-thick) on top of GeO_2 films. The film thickness was determined by x-ray reflectivity measurements. The desorption rate of GeO is retarded, but not blocked by covering with the high-k layers.

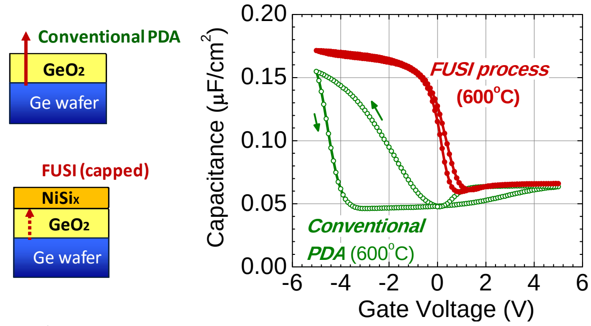

Fig. 6 C-V characteristics of GeO_2(25 nm-thick)/Ge MIS capacitors fabricated with NiSix cap layer (solid) and without cap layer (open). The Ni FUSI process (600°C) was applied as the capped annealing process.

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