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 $\rightarrow$ GeO), 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 ellipsometry. 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$_2$O$_3$ and La$_2$O$_3$ 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$_2$O$_3$ 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 LaLuO$_x$ [6] show good C-V characteristics, whereas those with GeO$_2$ interlayer severely deteriorated [5].

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; $dT_{ox}/dt = -\alpha T_{ox}$ ($\alpha = 5.4$ nm$^2$/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.
tors, by an additional O2 annealing at 600°C [7]. Up to ~ 1.5 nm GeO2 interlayer is formed as the O2 concentration in-
volatilization is also crucial to avoid the deterioration of the interface. In addition, the suppression of GeO2 by the properties of the Ge-high-k mixed oxides formed at the interlayer. The GeO2 volatilization will occur through (or into) high-k films, simultaneously with GeO2 growth.

In Fig. 5, the decrease of the thickness of GeO2 films covered with or without 10 nm-thick high-k film is shown as a function of annealing time at 600°C in N2. Both HfO2 and Y2O3 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 HfO2 cap seems coming simply from the increase of GeO diffusion layer thickness, whereas Y2O3 works more efficiently to retard the desorption, probably because of the stronger interaction between Y2O3 and GeO. We have also found that Si cap layer can suppress the GeO volatilization much more efficiently than those high-k caps. Thus one of the possible ways to improve GeO2 interlayer quality is to introduce Si or NiSiX cap layer on top of the films before annealing. Actually, by employing a FUSI process at 600°C, the GeO2/Ge MIS characteristics are dramatically improved as shown in Fig. 6, compared to the conventionally processed ones where the Au electrode was deposited after N2 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 GeO2 interlayer. Control of those reactions is the key to realize high-quality high-k/Ge interfaces.

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References

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[6] T.Tabata et al., to be presented in this meeting.