Flatband Voltage Shift Caused by Dopants Diffused from Poly-Si Gate Electrode in Poly-Si/HfSiO/SiO₂/Si

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1. Introduction

HfSiO(N) is considered to be a prospective high- κ dielectrics material due to its modest dielectric constants and good interface properties [1-4]. However, it was reported that the flatband voltage ($V_{\rm fb}$) for n-MOS and that for p-MOS shifted in the opposite directions [4]. The $V_{\rm fb}$ shift ($\Delta V_{\rm fb}$) for p-MOS was particularly large (>0.4V) [3, 4]. Such large $\Delta V_{\rm fb}$ make LSI design difficult and the reduction of $\Delta V_{\rm fb}$, especially for p-MOS, is a most important issue for practical use of HfSiO(N) in CMOS devices.

In this paper the $\Delta V_{\rm fb}$ of HfSiO with poly-Si gate electrode was investigated in terms of dopants in HfSiO diffused from poly-Si gate electrode. The major charge for the $\Delta V_{\rm fb}$ was localized near poly-Si/HfSiO interface, whose density is estimated to be about 10¹³ cm⁻². It is speculated that the charge is caused by dopants (P, As, B) diffused into HfSiO gate dielectrics from poly-Si.

2. Experimental

4nm-thick SiO₂ was fabricated by the thermal oxidation process on HF-last p-type Si substrate. HfSiO films with Hf/Hf+Si ratio of 30% were deposited by the chemical vapor deposition (CVD) method using TEOS (Si(OC₂H₅)₄) and HTB (Hf[OC(CH₃)]₄) with substrate temperature at 600°C. After the deposition, films were annealed at 750°C in O₂ ambient. 150nm-thick poly-Si films were deposited on Hf-silicate films, followed by dopant implantation and activation process listed in Table I. The point of those experiments is that with the 4nm-thick SiO₂ fabricated under HfSiO there is no need to take into account $\Delta V_{\rm fb}$ by dopant penetration to Si substrate.

3. Results and Discussion

 $\Delta V_{\rm fb}$ of HfSiO with phosphorus implanted (5×10¹⁵ cm⁻²) poly-Si gate is shown in Fig.2. $\Delta V_{\rm fb}$ is defined as $V_{\rm fb}$ of HfSiO minus $V_{\rm fb}$ of SiO₂ control in this paper. $\Delta V_{\rm fb}$ had a good linear relationship with the HfSiO thickness thicker than 4nm for all activation annealing conditions. The slope corresponds to the HfSiO/SiO₂ interface charge. At the limit of the HfSiO thickness to zero, the extrapolated $\Delta V_{\rm fb}$ is explained by the work function difference, the dipole moment or the fixed charge at the poly-Si/HfSiO interface. However, at the thinner thickness that trend changed and $\Delta V_{\rm fb}$ decreased. These results suggest that the extrapolated $\Delta V_{\rm fb}$ corresponds to the charge localized near the poly-Si/HfSiO interface with a finite width approximately 1nm as shown schematically in Fig.5. As the HfSiO thickness is thinner than the width the total charge is decreased. The poly-Si/HfSiO interface charge is dominant for the entire $\Delta V_{\rm fb}$. The results for arsenic (not shown) closely resembled these results. Fig. 3 shows a similar result for boron implantation. The direction of $\Delta V_{\rm fb}$ of boron, however, was different from that of phosphorus and arsenic. The results for the dopant dependence of $\Delta V_{\rm fb}$ indicate that dopants in HfSiO layer cause the charge.

To make sure that the $\Delta V_{\rm fb}$ depend on dopants, specimens with less phosphorus dose were fabricated. Fig.4 shows $\Delta V_{\rm fb}$ for phosphorus implantation with dose of

 2×10^{13} cm⁻². The $\Delta V_{\rm fb}$ corresponding to the poly-Si/HfSiO interface charge decreased.

The poly-Si/HfSiO and the HfSiO/SiO₂ interface charge are summarized in Fig.6. The former was estimated by assuming that the charge is localized at region 1nm from the interface and was of the order of 10^{13} cm⁻². For phosphorus and arsenic the charge was negative and for boron it was positive.

Fig. 7 shows XPS spectra of HfSiO directly deposited on Si substrate. Hf atoms in HfSiO were fully oxidized and no sign of Hf-Si bonding was recognized. After poly-Si deposition, annealing at 1000°C and removing Si substrate, XPS measurement was demonstrated from backside to observe the poly-Si/HfSiO interface in the state as it is. Hf-Si bonding was also not found. The reaction with poly-Si can be considered to be one of the possible causes for the charge creation. However, the absence of Hf-Si bonds means negligible reaction at the poly-Si/HfSiO interface.

Fig. 8 represents the depth profile of boron in HfSiO layer obtained by SIMS analysis from backside. In contrast to the above-mentioned charge distribution, boron distribution is almost uniform. These results indicate that the charge is not caused by boron itself directly. The poly-Si/TEOS (Hf/Hf+Si=0%) samples didn't have such large $\Delta V_{\rm fb}$ (<0.1V, data not shown). It is suggested that Hf is related to the defects in a certain way. However, $V_{\rm fb}$ shifted in the opposite directions each other for n-MOS and p-MOS and a similar $\Delta V_{\rm fb}$ behavior for HfO₂ was reported [5], which cannot also be explained by the charge of Hf itself. Thus, the charge is considered to be caused by the complex defects of dopant and HfSiO.

4. Conclusion

The extra-charge formation in CVD-prepared HfSiO films with poly-Si gate electrodes was systematically studied in terms of the dopant diffusion into the film. Regardless of whether or not penetration of dopants to substrate is controlled, diffusion of dopants in HfSiO leads to $\Delta V_{\rm fb}$. The charge is localized near poly-Si/HfSiO interface and HfSiO/SiO₂ interface. The former is dominant for $\Delta V_{\rm fb}$. It is suggested that the complex defects of dopants and HfSiO defects cause the charge. It is required to decrease those defects or reduce dopants diffusing into HfSiO layer to apply HfSiO to LSI as a gate dielectric.

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Table I Split table for the dopant implantation and the activation annealing.



Fig.4 Dose dependence of $\Delta V_{\rm fb}$ for phosphorus implantation. $\Delta V_{\rm fb}$ is defined as $V_{\rm fb}$ of HfSiO minus $V_{\rm fb}$ of SiO₂ control.

HfSiO thickness(nm)



Fig.2 HfSiO thickness dependence of $\Delta V_{\rm fb}$ for phosphorus implantation (5×10¹⁵cm⁻²). $\Delta V_{\rm fb}$ is defined as $V_{\rm fb}$ of HfSiO minus $V_{\rm fb}$ of SiO₂ control.



Fig.5 Model of charge distribution for (a) phosphorus and (b) boron implantation.





Fig.3 HfSiO thickness dependence of $\Delta V_{\rm fb}$ for boron implantation $(5 \times 10^{15} {\rm cm}^{-2})$. $\Delta V_{\rm fb}$ is defined as $V_{\rm fb}$ of HfSiO minus $V_{\rm fb}$ of SiO₂ control. 10^{14}



30min 20sec 3min Fig.6 Fixed charge density. The charge near poly-Si/HfSiO interface is assumed to be localized at region 1nm from the interface.



Fig.7 (a)XPS spectra of HfSiO (Hf/Hf+Si=30%) directly deposited on Si substrate and (b) schematics of samples. Hf atoms in HfSiO are fully oxidized and no sign of Hf-Si bonding is recognized even after poly-Si deposition and 1000°C annealing.

Fig.8 Depth profile of boron in HfSiO layer obtained by SIMS analysis from backside.