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

In this paper the ΔVfb 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 ΔVfb 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(OCH₃)₄) and HTB (H₂O(OH(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 1. The point of those experiments is that with the 4nm-thick SiO₂ fabricated under HfSiO there is no need to take into account ΔVfb by dopant penetration to Si substrate.

3. Results and Discussion

ΔVfb of HfSiO with phosphorus implanted (5x10¹⁵ cm⁻²) poly-Si gate is shown in Fig 2. ΔVfb is defined as Vfb of HfSiO minus Vfb of SiO₂ control in this paper. ΔVfb 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 ΔVfb 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 ΔVfb decreased. These results suggest that the extrapolated ΔVfb 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 ΔVfb. The results for arsenic (not shown) closely resembled these results. Fig. 3 shows a similar result for boron implantation. The direction of ΔVfb of boron, however, was different from that of phosphorus and arsenic. The results for the dopant dependence of ΔVfb indicate that dopants in HfSiO layer cause the charge.

To make sure that the ΔVfb depend on dopants, specimens with less phosphorus dose were fabricated. Fig.4 shows ΔVfb for phosphorus implantation with dose of 2x10¹³ cm⁻². The ΔVfb 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 10¹³ 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 ΔVfb (<0.1V, data not shown). It is suggested that Hf is related to the defects in a certain way. However, Vfb shifted in the opposite directions each other for n-MOS and p-MOS and a similar ΔVfb 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 ΔVfb. The charge is localized near poly-Si/HfSiO interface and HfSiO/SiO₂ interface. The former is dominant for ΔVfb. 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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References
Implantation

P  $5 \times 10^{15}$ cm$^{-2}$
2$ \times 10^{13}$ cm$^{-2}$
As $5 \times 10^{15}$ cm$^{-2}$
B  $3 \times 10^{13}$ cm$^{-2}$

Activation annealing
800°C, 30min
1000°C, 20sec
1000°C, 3min

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

![Image of Table I](image)

Fig.1 Schematic of samples.

![Image of Fig.1](image)

Fig.2 HfSiO thickness dependence of $\Delta V_{fb}$ for phosphorus implantation ($5 \times 10^{15}$ cm$^{-2}$). $\Delta V_{fb}$ is defined as $V_{fb}$ of HfSiO minus $V_{fb}$ of SiO$_2$ control.

![Image of Fig.2](image)

Fig.3 HfSiO thickness dependence of $\Delta V_{fb}$ for boron implantation ($5 \times 10^{15}$ cm$^{-2}$). $\Delta V_{fb}$ is defined as $V_{fb}$ of HfSiO minus $V_{fb}$ of SiO$_2$ control.

![Image of Fig.3](image)

Fig.4 Dose dependence of $\Delta V_{fb}$ for phosphorus implantation. $\Delta V_{fb}$ is defined as $V_{fb}$ of HfSiO minus $V_{fb}$ of SiO$_2$ control.

![Image of Fig.4](image)

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

![Image of Fig.5](image)

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

![Image of Fig.6](image)

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.

![Image of Fig.7](image)

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

![Image of Fig.8](image)