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Suppression of Silicidation in Poly-Si/ZrO_2/SiO_2/Si Structure by Helium Through Process

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1. Introduction

Recently, there have been expectations that high-k insulators including Zr or Hf atom, for example ZrO_2, HfO_2, Zr and Hf silicate, will be applied as an alternative gate insulator for sub-100nm CMOS transistor [1]. However, the thermal degradation problem of these high-k insulators remains unsolved. In particular, the interface reaction control with poly-Si gate electrode is indispensable [2,3]. Regarding ZrO_2, previous experiments have indicated two main occasions of silicidation when applying gate process. One is Si deposition by SiH_4 gas [4,8]. The other is high-temperature annealing (over 900℃) after the Si deposition [2,4-8]. The purpose of this study is to find ways of suppressing these silicidation reactions by controlling the deposition and the post-annealing conditions. The author found that helium (He) through process of SiH_4 flow diluted by He at low temperature and high pressure He annealing is the most effective means of suppressing the silicidation in not only ZrO_2/SiO_2/Si interface but also poly-Si/ZrO_2 interface.

2. Experimental

CZ n-type Si(100) substrates were cleaned by RCA treatment, and 1nm chemical oxides were grown on Si substrates. Next, ZrO_2 films (2, 20nm) were formed on the chemical oxides by ZrO_2 target sputtering (Ar/O_2 RF plasma 400W) at room temperature. This sputtering process causes increase of interfacial oxide thickness (1→3nm). Then, the samples were transferred to the CVD chamber, and Si films (2, 20nm) were formed on the ZrO_2 films using SiH_4 1Torr diluted by N_2 or He 2Torr at 500～650℃. After the deposition, the samples were annealed at 920℃ for 1min in N_2 or He ranging from 0.1 to 300Torr. Changes of bonding states and layered structures of poly-Si/ZrO_2/SiO_2/Si system between before and after annealing were measured by *in-situ* x-ray photoelectron spectroscopy (*in-situ* XPS) and transmission electron microscopy (TEM), respectively.

3. Results and Discussion

Fig.1 shows the changes in Zr3d spectra from ZrO_2 (20nm) surface between before and after SiH_4/N_2. In contrast to 500℃, it is clearly shown that 600℃ deposition causes surface silicidation. The temperature dependences of silicidation under SiH_4/N_2 and SiH_4/He are indicated in Fig.2. This result means that the silicidation does not depend on dilution gas and can be suppressed by lowering of initial deposition temperature below 600℃. In the Si2p spectra from ZrO_2 (20nm) surface after SiH_4/He (500℃) shown in Fig.3, *in-situ* angle-resolved XPS analysis revealed that thin SiO_2 film (0.7nm) is formed between Si cap (1.6nm) and ZrO_2 surface. This did not occur when Si cap was deposited on clean Si surface (not shown). Thus, it is suggested that the SiO_2 growth and the creation of oxygen vacancy at ZrO_2 surface are simultaneously caused by SiH_4 flow.

Next, to investigate the effect of ambient gas during post-annealing, we prepared the initial structure of Si cap (1.6nm)/ SiO_2 (0.7nm)/ ZrO_2 (2nm)/ SiO_2 (3nm)/ Si formed by 500℃ deposition. It is shown in Fig.4 that He through process (SiH_4/He and He annealing) can completely suppress the silicidation whereas N_2 through process cannot. Fig.5 shows the ambient gas and pressure dependences of silicidation. This result reveals two important points. One is that higher pressure He annealing tends to suppress the silicidation. The other is that SiH_4/He is more effective in the case of He annealing. These results can also be seen in the TEM images shown in Fig.6. Lower interfacial oxides disappeared locally, and large silicide grains embedded in poly-Si after N_2 annealing (a)(b). In contrast, the oxides were confirmed to remain after He annealing (c)(d). It is noted that SiH_4/N_2 creates small silicide grains in poly-Si (c), whereas SiH_4/He does not (d).

Possible physical origin for the suppression of silicidation at lower interface by He annealing is the dissipation of vibration energy of damage-prone site in SiO_2/Si interface by multiple collisions of dissolved He atoms [9]. We have already found that He gas physically obstructs SiO creation through the quenching of atomic vibration at the ZrO_2/SiO_2/Si interface [10], thus impeding the trigger reaction of silicidation [5]. However, the combination of SiH_4/N_2 and He annealing cannot suppress the silicidation at upper poly-Si/SiO_2/ZrO_2 interface. This result suggests that higher concentration He atoms incorporated by He through process are indispensable for sufficiently quenching the upper atomic vibration, because the upper thin SiO_2 film rather than the lower thick SiO_2 film is easily degraded by SiO creation.

4. Conclusions

Suppression of silicidation in poly-Si/ZrO_2/SiO_2/Si structure by He through process was demonstrated for the first time. In Si deposition on ZrO_2 by SiH_4 flow, surface silicidation can be suppressed by lowering of initial deposition temperature below 600℃, and thin SiO_2 film is formed between Si film and ZrO_2 surface. Moreover, He through process of SiH_4 flow diluted by He at low temperature and high pressure He annealing is the most

effective means of suppressing the silicidation in not only $ZrO_2/SiO_2/Si$ interface but also poly-$Si/SiO_2/ZrO_2$ interface. These results mean that high concentration He atoms are indispensable for upper and lower SiO_2/Si interfaces. It is supposed that many He atoms physically obstruct SiO creation through the quenching of atomic vibration in both SiO_2/Si interfaces, thus impeding the trigger reaction of silicidation.

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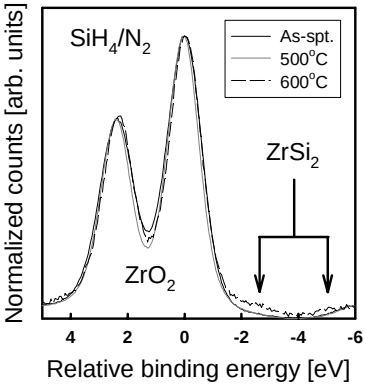

Fig. 1 Changes in Zr3d spectra from ZrO_2 (20nm) surface before and after SiH_4/N_2 (500, 600℃).

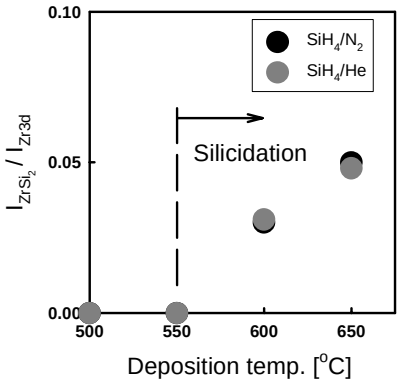

Fig. 2 Temperature dependences of silicidation under SiH_4/N_2 and SiH_4/He. Vertical axis means the ratio of $ZrSi_2$ and total Zr3d intensities (shown in Fig.1).

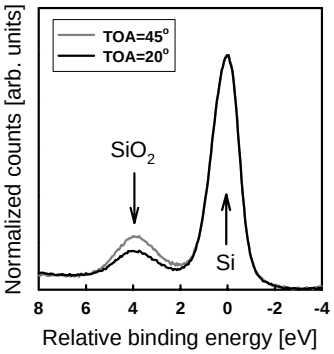

Fig. 3 Si2p spectra from ZrO_2 (20nm) surface after SiH_4/He (500℃) as a function of photoelectron take-off angle (TOA).

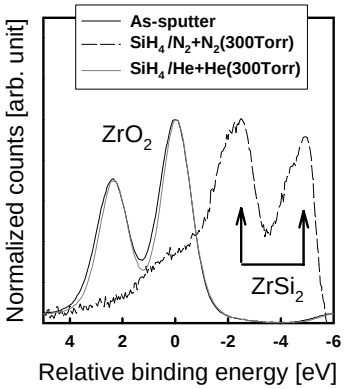

Fig. 4 Changes in Zr3d spectra from ZrO_2 (2nm) surface after N_2 and He through processes.

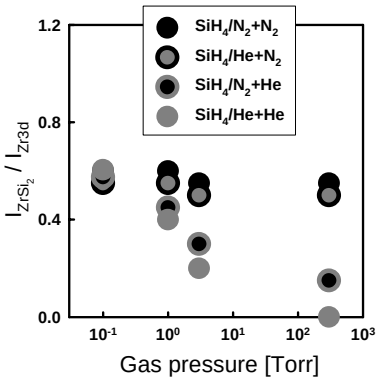

Fig. 5 Ambient gas and pressure dependences of silicidation.

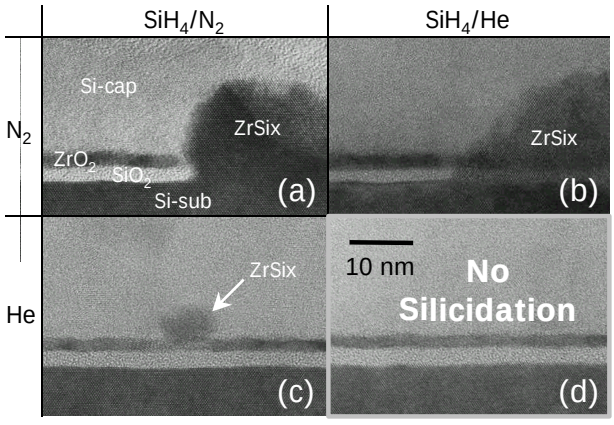

Fig. 6 Cross-sectional TEM images of poly-Si (20nm)/ZrO_2/SiO_2/Si after 500℃ deposition and 300Torr post-annealing.