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Suppression of Silicidation in ZrO_2/SiOx/Si Structure by Helium Annealing

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1. Introduction

Recently, there have been expectations that ZrO_2 insulator [1-7] with high dielectric constant and sufficient thermodynamic stability on Si substrate [8] will be applied as an alternative gate insulator for sub-100nm CMOS transistor. However, previous experiments have indicated two major problems when applying gate process. One is the interfacial oxide growth due to residual oxygen in annealing ambient which causes the increase of equivalent oxide thickness [1-5]. The other is the silicidation due to high-temperature annealing (over 900℃) under ultrahigh vacuum (UHV) [2,6,7]. Thus, a window of optimal oxygen partial pressure (P_{O2}) is narrow in which the thermal stability of ZrO_2/SiOx/Si structure can be achieved [5]. Regarding silicide formation, many reaction paths of silicidation for ZrO_2/SiOx/Si structure have already been suggested [2,5,6]. In particular, it has been recently found that the trigger of silicidation is the contact of ZrO_2, SiO and Si accompanying disappearance of interfacial SiOx layer due to SiO desorption [7]. The purpose of this study is to suppress the silicidation by control of the SiO desorption, which results in widening the window of optimal P_{O2}. The author found that helium (He) gas physically obstructs SiO removal from the ZrO_2/SiOx layer, thus impeding silicidation effectively.

2. Experimental

Experiments were carried out by using a UHV chamber system (Fig.1) in which ZrO_2/SiOx/Si samples were annealed under UHV($<1\times10^{-9}$ Torr), 1Torr ultra-dry N_2 or He with controlled P_{O2} ranging from 10^{-9} to 10^{-5} Torr. CZ n-type Si(100) substrates were cleaned by RCA treatment, and 1nm chemical oxides were grown on Si substrates. Next, ZrO_2 films (2nm) 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 SiOx thickness (1→3nm). Then, the samples were transferred to the UHV chamber and annealed at 920℃ for 1-10 min in various ambients. Changes of binding states and layered structures of ZrO_2/SiOx/Si system 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.2 shows the changes in Zr3d and Si2p spectra from ZrO_2/SiOx/Si in UHV, N_2 and He ambients. In contrast to UHV and N_2, it is clearly shown that He gas suppresses silicidation. The P_{O2} dependences of silicidation under He and N_2 annealing are indicated in Fig.3, respectively. It can be concluded from Fig.3 that He annealing attained an about 2 orders reduction in P_{O2} without silicidation as compared with N_2 annealing. In Fig.4, changes in expanded Si2p spectra before and after He annealing are plotted. Data analysis revealed that the He annealing changed ZrSiOx into SiO_2, thus causing phase separation but not silicidation at interface region.

Next, the optimal P_{O2} regions where the interfacial SiOx layer does not grow or disappear by He and N_2 annealing, respectively (Fig.5), were investigated. It is shown in Fig.5 that the optimal P_{O2} region in He (over 2 orders) is wider than that in N_2 (just 1 order). This can also be seen in the TEM images shown in Fig.6. ZrO_2/SiOx layered structure was confirmed to remain after He annealing (a). In contrast, the layered structure disappeared, and many silicide grains embedded locally in Si substrate after N_2 annealing (b).

Possible physical origins for the suppression of silicidation by He annealing are as follows. One is the high diffusion rate and high solubility in ZrO_2/SiOx layer, which reflect the small atomic diameter of He, as proposed for SiO_2 in Ref.[9]. He may dynamically occupy the interstices necessary to accommodate SiO thus blocking SiO diffusion. The other is the high thermal conductivity. He atoms adsorbed in interstices may affect (quench) atomic vibrations at the SiOx/Si interface, thus reducing probability of bond-breaking processes [10]. In addition, He atom is inactive and does not cause chemical degradation.

Finally, it is noted that the He anneal has a significant impact on the isothermal degradation of interfacial oxide (Fig.7). It was found that the interfacial oxide thickness slightly decreases due to phase separation and is kept during He annealing, whereas it rapidly decreases during UHV and N_2 annealing. From these results, rapid thermal He annealing is the most effective in suppressing degradation of interface.

4. Conclusions

Suppression of silicidation in ZrO_2/SiOx/Si structure by He anneal was demonstrated for the first time. Interfacial reactions accompanying atomic removal can be controlled using this method. It was found that He gas physically obstructs SiO removal through the quenching of atomic vibration and the occupation of SiO diffusion path in the ZrO_2/SiOx layer, thus impeding silicidation. The range of the operating O_2 pressure was able to be widened successfully.

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References

[1]M. Copel et al., Appl. Phys. Lett. **76**, 436 (2000).
[2]T. S. Jeon et al., Appl. Phys. Lett. **78**, 368 (2001).
[3]Heiji Watanabe, Appl. Phys. Lett. **78**, 3803 (2001).
[4]G. D. Wilk et al., J. Appl. Phys. **89**, 5243 (2001).
[5]J.-P. Maria et al., J. Appl. Phys. **90**, 3476 (2001).
[6]Heiji Watanabe, Appl. Phys. Lett. **80**, 559 (2002).
[7]Kouichi Muraoka, Appl. Phys. Lett. submitted.
[8]K. J. Hubbard et al., J. Mat. Res. **11**, 2757 (1996).
[9]A. Stesmans et al., Appl. Phys. Lett. **74**, 1466 (1999).
[10]V. V. Afanas'ev et al., Appl. Phys. Lett. **74**, 1009 (1999).

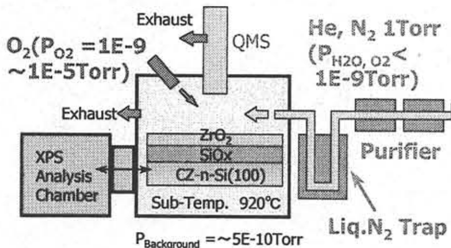

Fig. 1 Schematic diagram of ultra-high vacuum chamber. Residual gas in annealing ambients was monitored by quadrupole mass spectrometry.

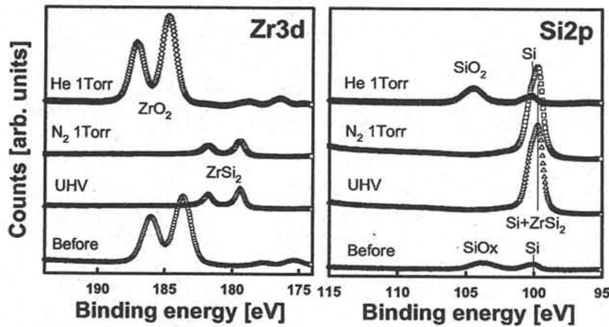

Fig. 2 Changes in Zr3d and Si2p spectra from ZrO_2/SiOx/Si in various ambients (920℃10min, $P_{O2}=1\times10^{-7}$ Torr).

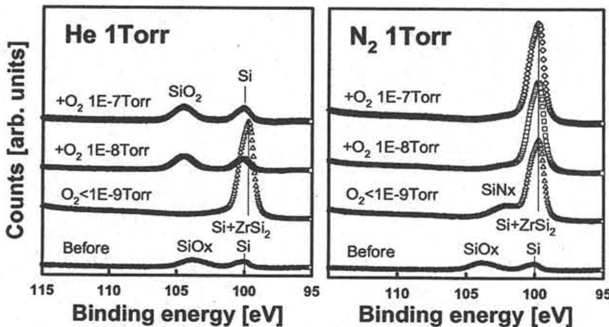

Fig. 3 Changes in Si2p spectra from ZrO_2/SiOx/Si in various P_{O2} (920℃10min, He, N_2 1Torr).

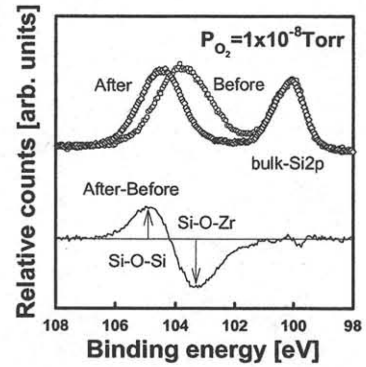

Fig. 4 Changes in Si2p spectra from ZrO_2/SiOx/Si before and after annealing (920℃10min, He 1Torr, $P_{O2}=1\times10^{-8}$ Torr).

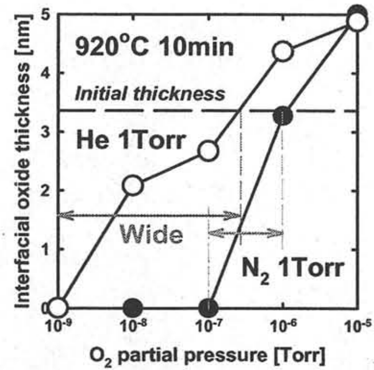

Fig. 5 Interfacial oxide thickness as a function of P_{O2}.

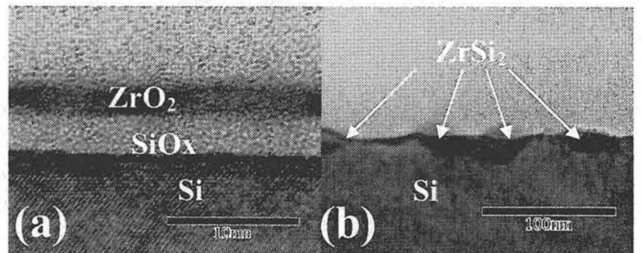

Fig. 6 Cross-sectional TEM images of ZrO_2/SiOx/Si (920℃ 10min (a)He, (b)N_2 1Torr, $P_{O2}=1\times10^{-7}$ Torr).

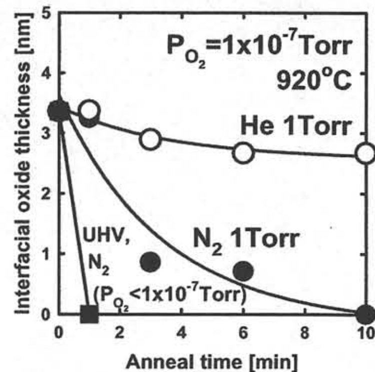

Fig. 7 Isothermal degradation of interfacial oxide in various ambients.