Interfacial Reactions of ZrO$_2$/SiO$_2$/Si Layered Structures

Heiji Watanabe

Silicon Systems Research Laboratories, NEC Corporation, 34 Miyukigaoka, Tsukuba, Ibaraki 305-8501, Japan
Phone/Fax: +81-298-50-1512/56-6138, e-mail: h-watanabe@dt.jp.ne.com

1. Introduction

High-k materials such as ZrO$_2$ have recently received considerable attention as alternative gate dielectrics for MOS devices [1], and we need to understand the reactions occurring at ZrO$_2$/Si interfaces because these reactions influence the electrical properties of the gate stack and determine the scaling limit of its equivalent oxide thickness. The thermal stability of the ZrO$_2$/Si system [2] and the relation between the growth of high-k materials on Si wafers and the surface conditions of those wafers (hydrogen-terminated or covered with native oxide) [3] have been studied, but the details of the reaction mechanisms have not been clarified. In addition, insertion of an ultrathin SiO$_2$ layer is expected to improve electrical properties of the interface. The work reported here tried to obtain process guidelines for making a high-k gate stack. Interfacial reactions of ZrO$_2$/SiO$_2$/Si during fabrication and post-annealing, as well as the role of the interfacial SiO$_2$ layer, were investigated systematically by using in-situ x-ray photoelectron spectroscopy (XPS) and cross-sectional transmission electron microscopy (XTEM).

2. In-situ re-oxidation method

Experiments were carried out by using a UHV-based multi-chamber system (Fig. 1) in which ZrO$_2$/SiO$_2$/Si samples were fabricated by oxidizing a thin Zr layer at 550°C under 1x10$^{-4}$Torr oxygen (in-situ re-oxidation method).

Figure 2 shows Si2p spectra obtained before and after re-oxidation. When Zr was deposited on a 0.6-nm-thick chemical oxide, 60 minutes of oxidation caused an interfacial silicate layer to form (as indicated by the hatched area). But because the re-oxidation was performed under a low O$_2$ pressure, the growth of the interfacial SiO$_2$ layer was suppressed and we could control the thickness of the interfacial silicate with atomic-level precision as shown in Fig. 3. This means that a 0.6-nm-thick oxide can be utilized as a blocking layer against interfacial reactions.

3. Thermal stability of ZrO$_2$/SiO$_2$/Si interfaces

Figures 4(a) and (b) show how the thermal stability of ZrO$_2$/SiO$_2$(0.6nm)/Si samples depend on the oxygen pressure (UHV or 1x10$^{-4}$Torr), annealing temperature, and annealing method (UHV system or N$_2$ ambient in a conventional furnace). Figures 4(a) and (b) respectively represent changes in chemical shift peaks originating from the interfacial silicate and from the ZrO$_2$ overlayer. These results indicate that thermal stability of the interfaces depends on oxygen pressure and that the interfacial reaction is due to oxygen diffusion through the ZrO$_2$ overlayer. Thus, a careful control and reduction of residual oxygen will be required for fabrication of sub-10Å gate dielectrics.

4. Silicate formation depending on interfacial SiO$_2$ and Zr overlayer thickness

The role of the ultrathin SiO$_2$ layer was investigated by forming ZrO$_2$ layers on wafers oxidized only two monolayers thick [4]. Figure 5 shows changes in the Si2p spectra during fabrication. Note that the silicate layer formed was thicker than that formed when the Zr was deposited on 0.6-nm-thick SiO$_2$ (see Fig.2). This can also be seen in the XTEM image shown in Fig. 6. These results mean that an interfacial oxide more than two monolayers thick must be used.

The interfacial reaction mechanism was also explored by investigating the dependence of the silicate formation on the thickness of the ZrO$_2$ overlayer. The relation between the thickness of the interfacial silicate layer (estimated by XTEM) formed after re-oxidation and the initial thickness of the Zr layer (deposition time) is shown in Fig. 7. It is clear that the silicate thickness increased with increasing Zr thickness. Considering that there was no difference in the interfacial structure before re-oxidation (after Zr deposition), the change in the interfacial silicate thickness (see Fig. 7) cannot be explained simply by oxygen diffusion through the ZrO$_2$ overlayer. We can therefore conclude that catalytic effects of ZrO$_2$ layers, such as the dissociation of oxygen molecules, play an important role in the interfacial reaction.

5. Conclusions

The results of this experimental investigation showed that oxygen diffusion through ZrO$_2$ causes silicate to form at the interface. This suggests that it is important to control residual oxygen pressure during device fabrication. The dependence of the interfacial reaction on the thickness of the ZrO$_2$ overlayer suggests that this layer has a catalytic effect.

Acknowledgments

I am grateful to Ms. M. Oshida for her technical support and to Drs. K. Watanabe, T. Tatsumi, H. Kamiyama, K. Manabe, T. Yoshihara, H. Ono, and N. Ikarashi for their valuable comments and discussions.

References

Process chamber
(UHV-oxidation, EB-evaporation)

Fig. 1. UHV-based multi-chamber system.

Fig. 2. In-situ XPS analysis before and after oxidation of a thin Zr layer. The hatched area represents the intensity difference between upper and lower spectra (silicate component).

Fig. 3. Change in normalized chemical shift peak intensity ([Si-O-Zr]/[Si-O-Si]) as a function of re-oxidation time.

Fig. 4. Effects of residual oxygen on the interfacial reactions. (a) and (b) show intensities of chemical shift peaks in Si2p and Zr3d spectra. Filled and open circles respectively represent results from annealing in oxygen ambient and in UHV condition.

Fig. 5. Change in Si2p spectra during re-oxidation using a Si wafer covered with a SiO$_2$ layer of two monolayers thick. After the initial hydrogen-terminated surface was oxidized, and a thin Zr layer deposited on the oxide was oxidized.

Fig. 6. XTEM image of a ZrO$_2$/ZrSi$_2$O$_5$/Si layered structure.

Fig. 7. Change in the interfacial silicate thickness as a function of initial Zr thickness.