Reliable High-k TiO₂ Gate Insulator Formed by Ultrathin TiN Deposition and Low Temperature Oxidation

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1. Introduction
As MOSFET gate lengths are scaled down to the 0.1μm regime or beyond, gate oxide thickness is desired to be thinned to below 3nm. High-K gate insulators are attractive materials, since physical thickness can be greater than that of SiO₂, thereby preventing gate leakage current due to direct tunneling through ultrathin SiO₂. Among the various high-K dielectrics, TiO₂ is reported to have a dielectric constant larger than 30, and therefore, physical thickness of TiO₂ can be 8 times larger than that of SiO₂. According to the literature, TiO₂ is usually formed by TiO, CVD or reactive sputtering [1] and the reliability of the film is not sufficient for gate dielectrics. On the other hand, Ti deposition and oxidation process result in slight interfacial reaction between Ti and the underlying layer such as Si, SiO₂, or Si₃N₄.

In this paper, a new TiO₂ formation method is proposed for ultrathin gate dielectrics. In this process, ultrathin TiN deposition and low temperature oxidation are used in order to avoid Si oxidation during TiO₂ formation and to improve the film quality of the TiO₂.

2. Experimental
Figure 1 illustrates the MOS capacitor process flow. First, 1-2.5 nm thermal SiO₂ films were deposited on p-type (100)Si substrates. Secondly, 3-10 nm TiN films were formed by reactive sputtering or CVD. Then, TiN films were oxidized at 350-800°C to form TiO₂ films in dry oxygen. Finally, TiN gate electrodes were formed by depositing 50nm TiN film and wet etching. After gate electrode formation, sintering was carried out at 450°C for 30min in a gas mixture of H₂ and N₂. X-ray diffraction (XRD), transmission electron microscope (TEM), atomic force microscope (AFM), X-ray photoemission spectroscopy (XPS). TiO₂ films were characterized by X-ray diffraction (XRD), transmission electron microscope (TEM), atomic force microscope (AFM), X-ray photoemission spectroscopy (XPS).

MOSFETs were fabricated by using TiO₂/SiO₂ bilayer as a gate insulator. Al/TiN gate electrodes were formed by using the Damascene gate method[2].

3. Results and Discussion
Figure 2 shows an Arrhenius plot of oxidation rate of reactively sputtered TiN films in dry O₂. The oxidation rate was measured by the sheet resistivity changes of TiN films. An activation energy was found to be about 1.8eV, which is almost equal to the previously reported value for thick TiN films [3]. The oxidation rate (consumed TiN thickness in one hour) was 40nm/hour at 500°C. Figure 3 shows XRD spectra of oxidized TiN films at 500-800°C. The spectra indicate that TiN is transformed to rutile type TiO₂ above 700°C. But below 600°C, neither the peak of TiO₂ nor that of TiN was detected. Therefore, amorphous or microcrystalline TiO₂ was considered to be formed below 600°C.

In order to examine residual nitrogen in TiO₂ films after TiN oxidation, XPS analysis was carried out. Figure 4 shows XPS spectra of N1s. The spectra indicate that about 2-3 at% nitrogen is remaining in TiO₂ film when TiN is thick (17nm) and TiN oxidation temperature is as low as 500°C. This result suggests that thicker TiO₂ films block nitrogen outdiffusion through TiO₂ films.

Figures 5(a) and 5(b) show TEM bright field images of MOS capacitors of TiN/TiO₂/SiO₂/(100)Si structures. Here, TiO₂ was formed by 700°C oxidation and TiO₂ thicknesses of Fig. 5(a) and 5(b) are 6nm and 17nm, respectively. The interface between TiO₂ and SiO₂ was found to be extremely smooth and sharp, that is, interfacial reaction was not observed.

Figure 6 shows gate leakage characteristics with or without TiO₂ films on 2.5 nm thermal oxide. Leakage current was found to be improved in the case with TiO₂ film as compared with that of SiO₂ alone. And thinner TiO₂ (6nm) suppresses gate leakage current better than does thicker TiO₂ (17nm). Figure 7 shows the TiN oxidation temperature dependence of TiO₂ surface roughness and TiO₂ grain size. The roughness was measured by AFM. It is clear that TiO₂ surface roughness becomes larger with increasing TiO₂ thickness and with increasing TiN oxidation temperature.

Figure 8 shows gate leakage characteristics of TiN/TiO₂ (6nm)/SiO₂ structures. It was found that TiN/TiO₂/SiO₂ structure shows lower leakage current density than that of poly Si/SiO₂ structure even at smaller effective oxide thickness. Highest temperature oxidation case was found to show the lowest leakage current.

In order to clarify the reason for these results, C-V characteristics were obtained. Figure 9 shows C-V curves of these samples. Clearly, effective oxide thickness is thicker with increasing oxidation temperature. This indicates that SiO₂ thickness is increased by TiN oxidation process. And the reason for lower gate leakage current in higher TiN oxidation temperature as shown in Fig. 8 was found to be thickening of the interfacial SiO₂ film.

For studying the relationship among the gate leakage current, TiN oxidation temperature and TiO₂ thickness, various kinds of samples were measured. Figure 10 shows TiN oxidation temperature dependence of leakage current density. Initial SiO₂ thickness, namely SiO₂ thickness prior to TiN oxidation, is 2.5nm. TiO₂ thicknesses are 6, 12, 17 and 24 nm. It was found that the leakage current density could be decreased in the case of oxidation below at around 500°C, since TiO₂ was amorphous or microcrystalline structure. The effective dielectric constant of TiO₂ was estimated to be about 80 by comparing the effective oxide thickness and physical thickness of TiO₂/SiO₂ bilayer. In the case of oxidation above around 700°C, interfacial SiO₂ thickness increased.

Figure 11 shows Id-Vd characteristics of Damascene metal gate MOSFETs where TiO₂(6nm)/SiO₂(2.5nm) gate insulator (Teff=3nm) and Al/TiN gate electrode were applied. Good transistor characteristics were obtained by using the TiO₂ formation process.

4. Conclusion
A new TiO₂ gate insulator formation method is proposed. Low leakage TiO₂ films were found to be reproducibly formed by ultrathin TiN deposition and low temperature thermal oxidation. It is considered that better electrical characteristics were obtained as a result of the smoother surface due to microcrystalline structure of the TiO₂ film and the smoother TiO₂/SiO₂ interface without interfacial reaction with an underlying SiO₂ film.

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References
Thermal oxidation
TIN sputtering
TIN oxidation
TIN gate electrode formation

Temperaturc
(°C)
50 / 10
350

Fig. 1: Illustration of MOS capacitor process flow.

Fig. 2: Temperature dependence of oxidation rate of reactively sputtered TIN films.

Fig. 3: XRD spectra of oxidized TIN films at 500-800°C for 10min. TIN thickness is 10nm.

Fig. 4: N1s XPS spectra for TiOx films formed by oxidation at 500°C and 700°C.

Fig. 5: TEM bright field image of TiN/TiOx/SiOx/(100)Si structures. (a)TiOx 6nm. (b)TiOx 17nm.

Fig. 6: Gate leakage characteristics for various TiOx thicknesses.

Fig. 7: The TiOx surface roughness and grain size as a function of TIN oxidation temperature measured by AFM. TiOx thickness is 6nm and 17nm.

Fig. 8: Gate leakage characteristics of TIN/ TiOx(6nm)/SiOx/(100)Si structures. TIN oxidation temperature is ranged from 500 to 800°C.

Fig. 9: C-V characteristics of TIN/ TiOx(6nm)/SiOx/(100)Si structure.

Fig. 10: TIN oxidation temperature dependence of gate leakage current density at 1V.

Fig. 11: Id - Vd characteristics of Al/ TIN Damascene gate transistor with TiOx/SiOx gate insulator.