The decomposition mechanism of SiO₂ with the deposition of oxygen-deficient M(Hf or Zr)Oₓ films

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Abstract

The dynamic process of the reactions during deposition of M(Hf or Zr)O₂ thin films on SiO₂-covered silicon substrate in oxygen deficient conditions has been investigated. A series of reactions across the interface were identified with thermodynamic arguments and with X-ray Photoelectron Spectroscopy (XPS) and transmission electron microscopy (TEM) analyses. The oxygen deficient MOₓ<2 absorbs the oxygen in the SiO₂ layer to form fully oxidized metal oxide. The SiO₂ can be an oxygen source for the growth of metal oxide in the initial several monolayers. An epitaxial YSZ on silicon without amorphous low-k interfacial layer has been obtained in the experiments. The finding here implies that an oxide/semiconductor interface with excellent physical properties and chemical stability can be built up by applying this dynamic mechanism.

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1. Introduction

Silicon dioxide has been used as the primary gate dielectric materials in field-effect device since the advent of first integrated circuit. However, as device scaling continues, one of the more fundamental limits to the scaling of the gate dielectrics is the exponential increase in tunneling current with decreasing film thickness. For film below 20 Å, the leakage current rise to 1–10 A/cm² [1], which requires significant power dissipation and will alter device performance. To reduce the leakage current while maintaining the same gate capacitance, high-permittivity materials have been proposed as alternative gate dielectrics replacing conventional SiO₂ in silicon-based semiconductor device for sub-100 nm devices. Among them, HfO₂ and ZrO₂ are the potential candidates [1,2]. However, most of these high-k materials are metal oxides; the formation of interfacial oxides, silicates and silicides was often observed during the film deposition or the subsequent rapid thermal annealing [2–6]. Therefore, the thermodynamic stability of high-k metal oxide in contact with silicon is a critical issue for the application of alternative gate dielectrics in silicon-based devices [7–9] and the growth of epitaxial oxide on silicon [10–13]. But until now many reports about this issue are contradictory, and the thermodynamic reactions of these metal oxides with SiO₂ were not yet clear. Furthermore, lack of sufficient thermodynamic data causes more difficulty to determine the stability of the HfO₂ and ZrO₂ on silicon, especially when most of the film depositions and the thermal anneal are operated in oxygen deficiency conditions. In this report, we present experiment results on a dynamic process of the chemical reaction of SiO₂ layer with oxygen deficient HfOₓ<2 and Y-stabilized ZrOₓ (YSZ) films. We found that the SiO₂ layer can be decomposed by the deposition of oxygen deficient metal oxides and the oxygen in the underlying SiO₂ layer can be absorbed to form fully oxidized metal oxides films.

2. Experiment

The ultra-thin HfO₂ and Y-ZrO₂ films were deposited by pulsed laser deposition (PLD) system with a base vacuum of...
formed on the substrate. However, after 5-s HfO2 deposition, the substrate only presents the peak at 533.4 eV, corresponding to the O 1s binding energy of SiO2. After 5-s HfO2 deposition, the peak shifted to 532.3 eV and with the increase of film thickness, this peak keeps on shifting toward lower energy and fixes its position at 530.6 eV after 20–30 s film deposition, corresponding to fully oxidized HfO2. Because the film was deposited in oxygen deficient condition, the full oxidation of Hf oxide can be attributed to the incorporation of oxygen atoms from SiO2 layer, while the SiO2 is decomposed to SiO.

After close inspection the presence of a small shoulder can be observed on the high-energy of the main O 1s peak for 20–30 s films, this may be due to that the upper layer of film cannot absorb enough oxygen atoms when the film become slightly thick. The spikes on the peak for 30s deposition presented in Fig. 1(b) may be due to the oxygen defects at the surface of HfO2 thin film. Well in agreement with the above explanation, the peaks of Hf 4f core-level spectra shifted 0.3 eV for 10–30 s deposition compared with that of 5-s deposition (see Fig. 1(c)), corresponding to HfO2. Therefore, we think the SiO2 layer on the silicon substrate can be an oxygen source for the oxygen deficient Hf oxide until the SiO2 is completely decomposed into evaporated SiO.

For the deposition of ultrathin YSZ films on SiO2-covered silicon substrate, similar phenomenon as that of HfO2 also can be observed XPS spectra in Fig. 2. Therefore, we suggest that the above process can be described by the following chemical reaction

\[
\text{SiO}_2 + M(\text{Hf or Zr}) \rightarrow \text{MO}_2(\text{HfO}_2 \text{ or ZrO}_2) + \text{SiO} \uparrow
\]
Tromp et al. [14] found that the critical oxygen partial pressure above which the silicon oxide layer remains stable at 730 °C is about 7 × 10⁻⁵ mbar. Thus SiO desorption is expected for lower growth partial pressure 2.0–6.0 × 10⁻⁶ mbar during the initial deposition process. As a result, the thickness of native amorphous SiO₂ layer will be reduced or evenly eliminated in lower partial pressure deposition process.

As to the formation of silicate, we think it will take place during the initial stage before SiO₂ is completely decomposed. This can be observed from the O 1s and Si 2p XPS spectra for 5-s deposition. But with the deposition continuing, we think it will be decomposed when more oxygen deficient MOₓ<2 film was deposited on the substrates.

\[
\text{SiO}_2 + \text{MO}_2 \rightarrow \text{MSiO}_4
\]  
(2)

\[
\text{M} + \text{MSiO}_4 \rightarrow 2\text{MO}_2 + \text{Si}
\]  
(3)

This conclusion is further supported by our XPS depth profiling and cross-section high resolution TEM results of thicker films below.

Fig. 2 shows a typical XRD pattern of YSZ film on Si substrate. It can be seen that the film is uniformly [100] oriented. It suggests that the epitaxial relationship between YSZ and Si is cube-on-cube heterostructure. Fig. 3 shows the cross-sectional TEM image of 12.5 nm YSZ films on silicon substrate. The YSZ films are found to grow epitaxially on (100) Si substrate. From the film surface to the interface, the films show uniform atomic pattern. The electron diffraction pattern of the YSZ/Si interface and the X-ray diffraction pattern of the films indicate that the crystal orientation relationship between YSZ and silicon is YSZ(001)∥Si(001) and YSZ(100)∥Si(100). From Fig. 4, it can be clearly seen that there is no amorphous interfacial oxide at the interface. The YSZ–Si interface is atomically sharp, within the region of our image. Although we did not conduct any acid-etching...
process on the natively oxidized Si substrate, no amorphous SiO$_x$ layer was observed at the YSZ/Si interface in the cross-sectional TEM image. This phenomenon is considered as the result of the reaction of metallic ions with SiO$_2$ on the surface of Si wafer under lower oxygen pressure and high temperature conditions, which has been described above.

4. Conclusion

In summary, the dynamic process of the reactions during deposition of M(Hf or Zr)O$_2$ thin films on SiO$_2$-covered silicon substrate in oxygen deficient conditions has been investigated. A series of reactions across the interface were identified with thermodynamic arguments and with XPS and TEM analyses. The oxygen deficient MO$_{x-2}$ absorbs the oxygen in the SiO$_2$ layer to form fully oxidized metal oxide. The SiO$_2$ can be an oxygen source for the growth of metal oxide in the initial several monolayers. The finding here implies that an oxide/semiconductor interface with excellent physical properties and chemical stability can be built up with this dynamic mechanism. The realization of commensurate oxide/semiconductor heterostructure could fundamentally change the scaling laws for conventional silicon-based technology and would introduce the possibility for entirely new device physics based on the utilization of the anisotropy response of crystalline oxides grown commensurately on semiconductor [20].

References