Effects of the Interfacial Layer on Electrical Properties of TiO₂-based High-k Dielectric Composite Films

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Effects of interfacial layer on the electrical properties of TiO₂ based dielectric thin films prepared by atomic layer deposition are investigated. It was confirmed from XPS data that the Hf-silicate and La-silicate interfacial layers including SiOₓ were formed in the interface of the HfO₂/TiO₂/Al₂O₃ (HTA) and La₂O₃/TiO₂/Al₂O₃ (LTA) gate stack structures, respectively. In addition, the dielectric constants and leakage currents of HTA and LTA structures were affected by the formation of Hf-silicate and La-silicate layer in the interface and crystallization of TiO₂ thin film, respectively. It was also found that the LTA thin film annealed at 600 °C showed the low equivalent oxide thickness of 0.91 nm and the low leakage current of 4.16×10⁻⁶ A/cm² at 4 MV/cm.

Introduction

High-k dielectric thin films such as HfO₂, ZrO₂, TiO₂, La₂O₃, and Al₂O₃ have been investigated to replace SiO₂ thin film for the gate dielectric layer in the MOSFET (1-5). Among them, many researchers have focused TiO₂ thin film as an attractive candidate to replace SiO₂ thin film because of its high dielectric constant (40-80). However, TiO₂ thin film has a weak point such as relatively large leakage current due to its small bandgap energy and a low band offset with silicon (6). To overcome the demerits of TiO₂ thin film, Al₂O₃/TiO₂/Al₂O₃ (ATA) gate stack structure and nanolaminate structure have been proposed (7-9). The leakage current of TiO₂ thin film was decreased due to Al₂O₃ thin film which has a large energy bandgap (8.8 eV) and high band offset with silicon (7). However, the dielectric constant of ATA structure was reduced compared than TiO₂ thin film, since Al₂O₃ thin film has lower dielectric constant than TiO₂ thin film. Thus, it is essential that the study to increase the dielectric constant and to decrease the leakage current simultaneously. Although the research on ATA structure has been performed, the effects of the interfacial layer on the electrical properties of TiO₂-based dielectric composite thin film have not been studied. In this work, the effects of the interfacial layer on electrical properties in the X/TiO₂/Al₂O₃ (where X represents HfO₂ or La₂O₃) gate stack structure are investigated.

Experiments

HTA structure composed of HfO₂ (2 nm)/TiO₂ (4 nm)/Al₂O₃ (2 nm), and LTA structure composed of La₂O₃ (2 nm)/TiO₂ (4 nm)/Al₂O₃ (2 nm) were deposited on p-type Si (100) via atomic layer deposition (ALD) at a deposition temperature of 250 °C. The native oxide of Si substrate was removed by dipping in buffered oxide etchant solution for 1
min. Al(CH\textsubscript{3})\textsubscript{3}, Ti(NMe\textsubscript{2})\textsubscript{4}, and La(iPrCp)\textsubscript{3} were used as a Al, Ti and La precursor, respectively. H\textsubscript{2}O was also used as a reactant for Al\textsubscript{2}O\textsubscript{3}, TiO\textsubscript{2} and HfO\textsubscript{2} thin films. Especially, O\textsubscript{2} plasma was used as a reactant for La\textsubscript{2}O\textsubscript{3} thin film. After the deposition, the HTA and LTA thin films were annealed for 1 min in the O\textsubscript{2} atmosphere at the temperature varied from 400 to 600 °C. Al was deposited on the dielectric thin films by thermal evaporation through a shadow mask with an area of 3.14×10\textsuperscript{-4} cm\textsuperscript{2} as the gate electrode. The film thicknesses of the HTA and LTA structures were measured by ellipsometer (Rudolph Auto EL II). The high frequency capacitance-voltage (C-V) measurements were performed using the Keithley 590 C-V analyzer at 1 MHz, and the leakage current density-electric field (J-E) characteristics were measured using by Keithley 236 source measure unit. X-ray photoelectron spectroscopy (XPS) was also performed using mono-chromated AlK\textalpha.  

**Results and discussion**

Figure 1 shows the XPS spectra of O 1s at the interfaces of HTA and LTA structures annealed at 600 °C. The binding energies of core levels have been calibrated by setting the C 1s peak to 284.5 eV. The peaks located at 531.0 and 532.5 eV were observed in HTA structure, which is associated with Hf-Si-O bonds and Si-O bonds, respectively (10). It is indicated that an Hf-silicate layer including SiO\textsubscript{x} was formed in the interface of Si/HfO\textsubscript{2} thin film. The peaks located at 530.4, 531.3 and 532.5 eV were observed in LTA structure, which is associated with La rich La-Si-O bonds and La low La-Si-O bonds and Si-O bonds, respectively (4). It is confirmed that La-silicate layer including SiO\textsubscript{x} was formed in the interface of Si/La\textsubscript{2}O\textsubscript{3} thin film. The high composition ratio of Si-O bonds in the LTA structure is due to the effects of O\textsubscript{2} plasma as a reactant of La\textsubscript{2}O\textsubscript{3}.

![Figure 1. XPS spectra of O 1s at the interface of (a) HTA and (b) LTA structure annealed at 600 °C](image)

Figure 2 shows the C-V characteristics of HTA structure for various annealing temperatures. When the HTA thin film was annealed at 400 °C, the dielectric constant and N\textsubscript{ot} were 18.0 and 3.94×10\textsuperscript{12} cm\textsuperscript{-2}, respectively. When the annealing temperature was increased to 500 °C, the dielectric constant and N\textsubscript{ot} were decreased. It is due to the increase of the Hf-silicate layer including SiO\textsubscript{x} in the interface of Si and HfO\textsubscript{2} thin film. The dielectric constant and N\textsubscript{ot} were re-increased to 19.3 and 5.00×10\textsuperscript{12} cm\textsuperscript{-2}, respectively, as the annealing temperature was increased to 600 °C. The increase of dielectric constant can be explained by the transformation of TiO\textsubscript{2} film structure and the densification of the film structure. It is known that crystal structure content of TiO\textsubscript{2} thin film was increased
and the densification of the film structure was formed depending on annealing temperature (3). The increase of crystal structure content at the relatively high temperature above 600 °C is due to the effects of the stack structure.

Figure 2. The high frequency (1MHz) C-V characteristics of HTA structure for various annealing temperature.

Figure 3(a) shows the C-V characteristics of LTA structure depending on the various annealing temperatures. When the annealing temperature was 400 °C, the dielectric constant and N_{ox} of LTA thin film was annealed at were 27.7 and 3.89×10^{11} cm^{-2}, respectively. When the LTA thin film was annealed at 500 °C, the dielectric constant was decreased and re-increased to 34.1 at annealing temperature of 600 °C. The LTA thin film annealed at 600 °C had the low equivalent oxide thickness (EOT) of 0.91 nm. The tendency of dielectric constant of LTA thin film on annealing temperature was similar to that of HTA thin film. The formation of La-silicate layer in the interface of Si and La_{2}O_{3} thin film and the crystallization of TiO_{2} thin film affect the dielectric constant of LTA thin film. The LTA structure has higher dielectric constant than HTA structure, since the dielectric constant of La_{2}O_{3} is higher than HfO_{2} and La-silicate is formed at the interface of Si/La_{2}O_{3} thin film in the LTA structure.

Figure 3. (a) The high frequency (1MHz) C-V characteristics of LTA structure for various annealing temperature and (b) the J-E characteristics of LTA structure for various annealing temperature.

The J-E characteristics of LTA structure for various annealing temperatures are shown in the Fig. 3 (b). When the LTA thin film was annealed at 400 °C, the leakage current density at 4 MV/cm was 2.72×10^{-6} A/cm^{2}. As the annealing temperature was increased to
500 °C, the leakage current density was reduced to $2.53 \times 10^{-6}$ A/cm$^2$ at 4 MV/cm. The decrease of leakage current density in the LTA thin film annealed at 500 °C is explained by the increase of La-silicate interfacial layer in the interface of Si and La$_2$O$_3$ thin film. When the annealing temperature was increased above 600 °C, the leakage current was increased to $4.16 \times 10^{-6}$ A/cm$^2$ at 4 MV/cm due to the crystallization of TiO$_2$ thin film. The low leakage current density of LTA structure than HTA structure is explained by the higher bandgap of La$_2$O$_3$ than HfO$_2$ and the formation of the La-silicate interfacial layer at the interface of Si/La$_2$O$_3$ thin film in the LTA structure.

**Conclusion**

In this study, the effects of interfacial layer have been investigated on the electrical properties in the TiO$_2$ based dielectric thin film. HTA and LTA thin films were deposited via ALD and annealed at various temperatures in the O$_2$ atmosphere. The interfacial layer including SiO$_x$ was formed in the interfaces of the HTA and LTA structures, which were confirmed from XPS data. The formation of Hf-silicate and La-silicate layer including SiO$_x$ in the interfaces and the crystallization of TiO$_2$ thin film affect the dielectric constants and J-E characteristics of HTA and LTA structure, respectively. The LTA thin film annealed at 600 °C showed the low EOT of 0.91 nm and the low leakage current of $4.16 \times 10^{-6}$ A/cm$^2$ at 4 MV/cm, which indicates the possibility of LTA thin film for the gate dielectric applications.

**References**