Effect of crystallinity and nonstoichiometric region on dielectric properties of Sr Ti O 3 films formed on Ru

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Effect of crystallinity and nonstoichiometric region on dielectric properties of SrTiO$_3$ films formed on Ru

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The dielectric constant depending on the film thickness for SrTiO$_3$ films formed on Ru was investigated after an annealing step at 600 °C, which shows that the dielectric constant increased abruptly with the film thickness up to 20 nm and then increased slightly, remaining relatively constant at a value of about 65. The abrupt increase was due to the crystallinity of SrTiO$_3$ films. On the other hand, the slight increase was related to the existence of nonstoichiometric region near the interface of SrTiO$_3$ film and Ru, which was intermixed with SrTiO$_3$ and Ti–O phases having an equivalent oxide thickness over 0.32 nm. © 2007 American Institute of Physics.

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As the minimum feature size of semiconductor devices decreases, the dimension of memory cells also decreases. To maintain the required cell capacitance (25–30 fF/cell) in dynamic random access memory (DRAM) with 45 nm or below design rule, multicomponent materials with high dielectric constant have been extensively investigated. SrTiO$_3$ with a perovskite structure as one of the most promising high dielectric materials has attracted much attention because of its high dielectric constant ($k=300$) and good chemical stability. Although SrTiO$_3$ has high dielectric constant, it is obvious that complicated three-dimensional (3D) structures are indispensable for the required cell capacitance in high density memories. Therefore, good conformality is required from the thin film deposition methods. Of the various deposition methods, atomic layer deposition (ALD), which is based on the principle of self-limited reaction mechanism by the chemisorptions of two or more precursors alternately pulsed to the reactor, is currently under widespread development as an attractive deposition method for multicomponent films because it enables precise control of the film thickness at atomic dimensions, easy and accurate control of the film composition, and the conformal deposition for 3D structures. In high density DRAM capacitors fabricated with high dielectric materials, such as SrTiO$_3$ and (Ba,Sr)TiO$_3$, the bottom electrode materials play an important role. Ru is one of the best promising bottom electrode materials for use in high density DRAM capacitors because it has high electrical conductivity and is easily dry etched. Moreover, Ru can block the oxygen diffusion during the deposition and postannealing of the dielectric materials by forming conductive RuO$_2$. For high density DRAM applications, it is expected that SrTiO$_3$ film thickness should be thinner than 50 nm. In general, as the thickness of the perovskite-structured oxide films decreases to a few tens of nanometers, the dielectric properties of the films deviate considerably from those of the bulk materials. It has been reported that the dielectric constant of SrTiO$_3$ films decreases with decreasing SrTiO$_3$ film thickness, especially for the film thickness thinner than 100 nm. In this letter, the dielectric constant depending on the film thickness for SrTiO$_3$ films less than 50 nm formed on Ru by plasma-enhanced atomic layer deposition (PEALD) was investigated after annealing, focusing on the crystallinity of SrTiO$_3$ films and the existence of nonstoichiometric region near the interface of SrTiO$_3$ film and Ru.

SrTiO$_3$ films were deposited on Ru (20 nm)/Ti (25 nm)/p-type Si substrates by PEALD at a deposition temperature of 225 °C and a deposition pressure of 3 Torr using bis(dipivaloylmethanato) strontium (Sr(DPM)$_2$) and titanium tetraisopropoxide (TTIP) as precursors and oxygen plasma as an oxidant. 0.2M Sr(DPM)$_2$ dissolved in butyl acetate was injected to the vaporizer using a liquid delivery system, and argon was used as the carrier gas leading a vaporized precursor to the reactor. TTIP, sustained at 60 °C, was delivered from the bubbler to the reactor with argon carrier gas. Sr–Ti–O (STO) films were deposited by repeating a supercycle that consisted of two groups of subcycle dedicated to SrO and TiO$_2$, respectively. Each subcycle consisted of several unit cycles, and four consecutive pulses were supplied in a unit cycle. One unit cycle for SrO or TiO$_2$ consisted of a precursor vapor pulse, a purge pulse, a pulse for an exposure to oxygen plasma, and another purge pulse. The plasma power was kept at 150 W. The thickness per cycle obtained from the saturation region was 0.054 nm/cycle for SrO films and 0.036 nm/cycle for TiO$_2$ films. The as-deposited films were annealed by rapid thermal annealing at 600 °C for 10 min under N$_2$ ambient. To examine the dielectric properties, Pt/SrTiO$_3$/Ru metal-oxide-metal structures were fabricated. 100-nm-thick Pt dots with a diameter of 160 µm were deposited on SrTiO$_3$ films by sputtering. The film thickness was measured at a wavelength of 632.5 nm using an ellipsometer (Gaertner L116C) and by transmission electron microscopy. The crystal structure of the films was investigated using x-ray diffractometer (XRD) (Rigaku) with Cu Kα radiation at 1.5405 Å. The chemical binding state of components in the films was investigated using x-ray photoelectron spectroscopy (XPS) with Mg Kα radiation. The capacitance-

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The number of SrO and TiO$_2$ unit cycles in one STO supercycle is denoted by \((M,N)\). (b) Dependence of the dielectric constant on the film thickness after annealing.

Voltage (C-V) measurement was determined using C-V analyzer (Keithley 590) at a frequency of 1 MHz.

Figure 1(a) shows Sr composition ratio in STO films depending on SrO unit-cycle ratio in one STO supercycle. The number of SrO and TiO$_2$ unit cycles in one STO supercycle is denoted by \((M,N)\). The composition of STO films was controlled by changing the number of SrO and TiO$_2$ unit cycles in one STO supercycle. Stoichiometric SrTiO$_3$ films were obtained when one STO supercycle consisted of seven SrO unit cycles and six TiO$_2$ unit cycles. From Auger electron spectroscopy analysis, the density of SrTiO$_3$ films over 20 nm was less than the detection limit.

To explain for the abrupt increase in the dielectric constant with increasing the film thickness under 20 nm, the equivalent oxide thickness (EOT) was plotted as a function of the film thickness. When the interfacial layer exists, the relationship between the EOT and the film thickness can be written as follows:

\[
EOT = \frac{k_{\text{SiO}_2}}{k_{\text{SrTiO}_3}}d_{\text{ox}} + \left( EOT_{\text{IL}} - \frac{k_{\text{SiO}_2}}{k_{\text{SrTiO}_3}}d_{\text{IL}} \right).
\]

where \(k_{\text{SiO}_2}\) and \(k_{\text{SrTiO}_3}\) are relative dielectric constants of SiO$_2$ and SrTiO$_3$ films, respectively, \(d_{\text{ox}}\) is the sum of the physical thickness of SrTiO$_3$ film and the physical thickness of the interfacial layer, \(EOT_{\text{IL}}\) is the EOT of the interfacial layer, and \(d_{\text{IL}}\) is the physical thickness of the interfacial layer.

To confirm the existence of the interfacial layer between SrTiO$_3$ film and Ru, the equivalent oxide thickness (EOT) was plotted as a function of the film thickness. When the interfacial layer exists, the relationship between the EOT and the film thickness can be written as follows:

\[
EOT = \frac{k_{\text{SiO}_2}}{k_{\text{SrTiO}_3}}d_{\text{ox}} + \left( EOT_{\text{IL}} - \frac{k_{\text{SiO}_2}}{k_{\text{SrTiO}_3}}d_{\text{IL}} \right).
\]

where \(k_{\text{SiO}_2}\) and \(k_{\text{SrTiO}_3}\) are relative dielectric constants of SiO$_2$ and SrTiO$_3$ films, respectively, \(d_{\text{ox}}\) is the sum of the physical thickness of SrTiO$_3$ film and the physical thickness of the interfacial layer, \(EOT_{\text{IL}}\) is the EOT of the interfacial layer, and \(d_{\text{IL}}\) is the physical thickness of the interfacial layer.

To clarify the interfacial layer between SrTiO$_3$ film and Ru, the chemical binding states of SrTiO$_3$ film and the interface between SrTiO$_3$ film and Ru for annealed 15-nm-thick and 2.8-nm-thick SrTiO$_3$ films were investigated using XPS analysis. Figure 3(a) shows the Ti 2p peak of annealed 15-nm-thick SrTiO$_3$ film, which consists of a unique 2p$_{3/2}$-2p$_{1/2}$ component at 458.4 eV binding energy (BE) with spin-orbit splitting value of 5.6 eV. Also, from XRD analysis in Fig. 2(a), in the case of annealed 15-nm-thick SrTiO$_3$ film, crystalline SrTiO$_3$ phase was obtained. These results mean that, although SrO and TiO$_2$ films were sequentially deposited, annealed SrTiO$_3$ film had only SrTiO$_3$ binding state without the phase separation of SrO and TiO$_2$. Figures 3(b)–3(d) show the results for Ti 2p peak of annealed 2.8-nm-thick SrTiO$_3$ film using three different take-off angles of 15°, 45°, and 75° to change the probing depth. Thus, only information of the upper SrTiO$_3$ film is obtained at a take-off angle of 15° whereas the chemical binding states of the interface between SrTiO$_3$ film and Ru are attained at take-off angles of 45° and 75°. In Fig. 3(b), only SrTiO$_3$ peak was displayed, which is the same as Fig. 3(a). However, an optimized fit in Figs. 3(c) and 3(d) required additional...
components with 0.3, 2.3, and 3.5 eV shifts to lower BE indicating TiO₂, Ti₂O₃, and TiO phase, respectively. These results mean that an excess Ti existed, so that Ti–O phases existed in addition to SrTiO₃ phase at the interface between SrTiO₃ film and Ru. Therefore, it is thought that nonstoichiometric region being intermixed with SrTiO₃ and Ti–O phases near the interface of SrTiO₃ film and Ru existed, so that the dielectric constant increased slightly with the film thickness over 20 nm.

The reason for the existence of an excess Ti at the SrTiO₃/Ru interface could be thought that Sr–Ru–O phase at the interface was formed during the deposition and postannealing of SrTiO₃ films. Figures 4(a) and 4(b) show the results for Sr 3d peak of annealed 2.8-nm-thick SrTiO₃ film using two different take-off angles of 15° and 75°. In Fig. 4(a), only SrTiO₃ peak was displayed. However, in the case of a take-off angle of 75°, it was shown that Sr 3d peak seems to be composed of two BE components located at BE of 134.3 eV, which is BE of SrTiO₃, and 133.7 eV, which might be related to Sr–Ru–O. An alternative explanation is that the amount of chemisorbed Sr(DPM)₂ (or TTIP) on Ru differs from that on SrO and TiO₂. During the initial stage of ALD, the outermost surface is gradually converted from the predeposited substrate into an actual film as the deposition proceeds. Thus, the transient region should exist, which causes nonstoichiometric region at the interface because the characteristics of the chemisorption of precursors are dependent on the exposed film surface.

In summary, stoichiometric SrTiO₃ films were deposited on Ru by PEALD at a deposition temperature of 225 °C. For SrTiO₃ films less than 50 nm, the dielectric constant increased abruptly with the film thickness up to 20 nm and then increased slightly, remaining relatively constant at a value of about 65. SrTiO₃ films over 15 nm were crystallized, but a 15-nm-thick SrTiO₃ film had lower peak intensity with a broad FWHM compared to SrTiO₃ films over 20 nm. Furthermore, it was confirmed that nonstoichiometric region near the interface of SrTiO₃ film and Ru existed, which was intermixed with SrTiO₃ and Ti–O phases having the EOT over 0.32 nm.

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