Effect of crystallinity and nonstoichiometric region on dielectric properties of SrTiO₃ films formed on Ru

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The dielectric constant depending on the film thickness for SrTiO₃ 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 SrTiO₃ films. On the other hand, the slight increase was related to the existence of nonstoichiometric region near the interface of SrTiO₃ film and Ru, which was intermixed with SrTiO₃ 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.¹ SrTiO₃ 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.² Although SrTiO₃ has high dielectric constant, it is obvious that complicated three-dimensional (3D) structures are indispensable for the required cell capacitance in high density memories.^{3,4} 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.^{4–7} In high density DRAM capacitors fabricated with high dielectric materials, such as SrTiO₃ and (Ba,Sr)TiO₃, the bottom electrode materials play an important role.⁸ Ru is one of the most promising bottom electrode materials for use in high density DRAM capacitors because it has high electrical conductivity and is easily dry etched.⁹ Moreover, Ru can block the oxygen diffusion during the deposition and postannealing of the dielectric materials by forming conductive RuO₂.¹⁰ For high density DRAM applications, it is expected that SrTiO₃ film thickness should be thinner than 50 nm.¹¹ 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.^{12,13} It has been reported that the dielectric constant of SrTiO₃ films decreases with decreasing SrTiO₃ film thickness, especially for

the film thickness thinner than 100 nm.^{14,15} In this letter, the dielectric constant depending on the film thickness for SrTiO₃ films less than 50 nm formed on Ru by plasma-enhanced atomic layer deposition (PEALD) was investigated after annealing, focusing on the crystallinity of SrTiO₃ films and the existence of nonstoichiometric region near the interface of SrTiO₃ film and Ru.

SrTiO₃ 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(dipivaloylmetanato) 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 supercycle⁶ that consisted of two groups of subcycle dedicated to SrO and TiO₂, respectively. Each subcycle consisted of several unit cycles, and four consecutive pulses were supplied in a unit cycle. One unit cycle for SrO or TiO₂ 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 TiO₂ films. The as-deposited films were annealed by rapid thermal annealing at 600 °C for 10 min under N₂ ambient. To examine the dielectric properties, Pt/SrTiO₃/Ru metal-oxide-metal structures were fabricated. 100-nm-thick Pt dots with a diameter of 160 μm were deposited on SrTiO₃ 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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FIG. 1. (a) Dependence of Sr composition ratio $[Sr/(Sr+Ti)]$ in STO films on SrO unit-cycle ratio $[SrO/(SrO+TiO_2)]$ in one STO supercycle. 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, $SrTiO_3$ films were slightly Ti rich with Sr:Ti ratio of 1:1.03, and carbon content in $SrTiO_3$ films was less than the detection limit (<1 at. %). From Rutherford backscattering spectroscopy analysis, the density of $SrTiO_3$ films was 4.74 g/cm³, approaching that of bulk $SrTiO_3$ (4.81 g/cm³).

Figure 1(b) shows the dielectric constant depending on the film thickness after annealing for $SrTiO_3$ films less than 50 nm formed on Ru. As illustrated in Fig. 1(b), 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.

To explain for the abrupt increase in the dielectric constant with increasing the film thickness under 20 nm, the effect of the film thickness on the film crystallinity was investigated using XRD analysis. Figure 2(a) shows the XRD patterns of $SrTiO_3$ films with various film thicknesses after annealing. 10-nm-thick $SrTiO_3$ film had an amorphous structure. $SrTiO_3$ films over 15 nm were crystallized, but 15-nm-thick $SrTiO_3$ film had lower peak intensity with a broad full width at half maximum (FWHM) compared to $SrTiO_3$ films over 20 nm. Therefore, it is thought that the abrupt increase in the dielectric constant with increasing the film thickness under 20 nm is attributed to the improved film crystallinity.

FIG. 2. (a) XRD patterns of $SrTiO_3$ films with various film thicknesses after annealing. (b) Dependence of the equivalent oxide thickness on the film thickness after annealing.

FIG. 3. (Color online) XPS analyses for Ti 2p peak of (a) 15-nm-thick $SrTiO_3$ film measured at a take-off angle of 75° and 2.8-nm-thick $SrTiO_3$ film measured at take-off angles of (b) 15°, (c) 45°, and (d) 75° after annealing.

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:¹⁶

$$EOT = \frac{k_{SiO_2}}{k_{SrTiO_3}} d_{tot} + \left(EOT_{IL} - \frac{k_{SiO_2}}{k_{SrTiO_3}} d_{IL} \right), \quad (1)$$

where k_{SiO_2} and k_{SrTiO_3} are relative dielectric constants of SiO_2 and $SrTiO_3$ films, respectively, d_{tot} is the sum of the physical thickness of $SrTiO_3$ film and the physical thickness of the interfacial layer, EOT_{IL} is the EOT of the interfacial layer, and d_{IL} is the physical thickness of the interfacial layer. As illustrated in Fig. 2(b), the y-axis intercept obtained from the extrapolation indicates that the EOT_{IL} is over 0.32 nm. Therefore, it was confirmed that the interfacial layer having the EOT over 0.32 nm between $SrTiO_3$ film and Ru existed.

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 angle resolved XPS analysis. Figure 3(a) shows the result for 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

FIG. 4. (Color online) XPS analyses for Sr 3d peak of 2.8-nm-thick SrTiO₃ film measured at take-off angles of (a) 15° and (b) 75° after annealing.

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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