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Role of Interfacial Reaction in Atomic Layer Deposition of TiO_2 Thin Films Using $Ti(O\text{-}iPr)_2(tmhd)_2$ on Ru or RuO_2 Substrates

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The role of the interfacial reactions in the atomic layer deposition of TiO_2 films was examined using titanium diisopropoxide bis(tetramethylheptadionate) ($Ti(O\text{-}iPr)_2(tmhd)_2$) as the titanium precursor, and H_2O or O_3 as the oxygen sources when the films were grown on ruthenium (Ru) or ruthenium dioxide (RuO_2) substrate at a growth temperature of 370 °C. Anatase-TiO_2 films with a dielectric constant of 32 were grown on ruthenium substrates when H_2O was used, whereas rutile-TiO_2 films with a much higher dielectric constant (89) were grown when O_3 was used as the oxygen source. The rutile-TiO_2 film was grown with the aid of an in-situ-formed thin RuO_2 layer on the surface by the strong oxidation power of O_3, which has structural similarity to the rutile-TiO_2 film, as has been reported previously with different precursor and growth temperature [S. K. Kim et al. *Appl. Phys. Lett.* **2004**, *85*, 4112]. The initial and steady-state growth rates of the TiO_2 films were strongly dependent on the oxygen source. O_3 induced a substrate-enhanced growth mode at the initial growth step (< 25 cycles), whereas H_2O resulted in a linear growth mode, regardless of the number of cycles, and a lower growth rate at the steady regime, because of its lower reactivity toward tmhd ligands. A substrate-enhanced growth mode was also observed on the RuO_2 substrate, regardless of the oxygen source. Interestingly, RuO_2 was reduced completely to metallic Ru during TiO_2 film growth. Oxygen atoms that come from the reduction of the RuO_2 substrate induced substrate-enhanced growth, and the reduction process was limited kinetically by the growth temperature. Reduction of the RuO_2 substrate occurred at the early stages of TiO_2 film growth. Therefore, it played a key role in determining the phase of the growing TiO_2 films. Reoxidation of the reduced Ru substrate during the O_3 pulse step promoted the formation of rutile TiO_2.

1. Introduction

Titanium dioxide (TiO_2) has a wide range of microelectronics and optical applications, such as high-density capacitors, dye-sensitized solar cells, gas sensors, and photocatalysts, bceause of its promising electrical, chemical, and optical properties.[1−3] Among them, considerable work has been focused on the development of TiO_2 thin films as a capacitor dielectric for aggressively scaled next-generation dynamic random-access memory (DRAM) with sub-30-nm design rules, because of its high dielectric constant (k).[4−6]

TiO_2 exists mainly as three phases: anatase, rutile, and brookite. Among them, the k-values of rutile along the a-and c-axes (90 and 170, respectively) are much higher than those of anatase (30−40) and other comparable simple binary oxides, such as ZrO_2 and HfO_2. Therefore, the development of high-density DRAM capacitors requires the production of rutile-TiO_2 films, which has been achieved on Ru or RuO_2 electrodes.[5−7]

Because the step coverage of chemical vapor deposition (CVD) is insufficient in nanoscale semiconductor devices, atomic layer deposition (ALD), which is characterized by its unique self-limiting deposition mechanism, is expected to be the deposition method of thin films with severe three-dimensional cells with high aspect ratios in DRAM capacitors.[8,9] The growth of TiO_2 films has been studied extensively, and there have been many advances in the growth of TiO_2 films grown by ALD.[10−14] In most cases,

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anatase-TiO_2 films were grown with $Ti(O\text{-}i\text{-}C_3H_7)_4$ (TTIP) as the titanium precursor, and the possible growth temperatures of the ALD process were rather low (< 270 °C), because of the thermal decomposition of TTIP. Anatase is the stable phase of TiO_2 at low temperatures, and it can be transformed to the rutile phase via high-temperature annealing (at > 700 °C).[15] However, Kim et al. reported that the growth of rutile-phase TiO_2 film was possible on ruthenium substrates in the as-deposited state, using O_3 as an oxygen source at low growth temperatures (T_g) of 250 °C.[5] The in-situ-formed thin RuO_2 layer played a key role in the growth of rutile-TiO_2 films. A thin interfacial RuO_2 layer that was formed via the strong oxidation potential of O_3 during TiO_2 film growth induced the rutile structure to grow at a low T_g value, although it is stable at temperature greater than ~700 °C. Note that the RuO_2 has a rutile crystal structure, which is identical in ion arrangement to that of the rutile-TiO_2 structure with a small lattice mismatch. Therefore, local epitaxial growth of TiO_2 films on an in-situ-formed RuO_2 phase occurred, because of the structural compatibility, even at low growth temperatures. The lattice mismatches between rutile TiO_2 (lattice parameter a_{TiO_2} = 0.4593 nm, c_{TiO_2} = 0.2959 nm) and RuO_2 (a_{RuO_2} = 0.4499 nm, c_{RuO_2} = 0.3107 nm) along the *a*- and *c*-axes were only 2.09% and 4.76%, respectively.[5,6]

Meanwhile, the authors previously reported that dense and well-crystallized TiO_2 and $SrTiO_3$ (STO) films could be grown at the as-deposited state via ALD at a higher T_g value (~370 °C).[16] The higher thermal energy made it possible to grow denser ALD films. Denser ALD films generally have better electrical characteristics, compared to the ALD films grown at a lower T_g value. In this case, titanium diisopropoxide bis(tetramethylheptadionate) ($Ti(O\text{-}iPr)_2(tmhd)_2$) was used, because it is a thermally more stable precursor than TTIP. Based on the necessity of the high-temperature ALD process, an understanding of the growth behavior of TiO_2 films is very important at higher T_g values. However, the detailed growth characteristics of TiO_2 films at a high T_g value have not been reported yet. This may not be a trivial task, because the growth of TiO_2 films can be affected by the oxidation and/or reduction of the substrate. The oxidation and reduction processes can occur more severely at this T_g value, particularly on Ru or RuO_2 substrates, because the transformation between Ru and RuO_2 can occur readily. This suggests that the growth characteristics of the TiO_2 films at higher T_g values could be different from typical ALD processes at lower T_g values (~250 °C). Therefore, careful study of the growth of TiO_2 films at a higher T_g value is important.

In the meantime, TiO_2 films have been studied extensively for nonvolatile memory applications, because of the resistive switching behavior of TiO_2 films.[17,18] Most of the resistive switching mechanism is governed by the characteristics of the redox reactions at the interfaces between the electrode material and TiO_2 layer. Therefore, an understanding of the initial growth of TiO_2 films (< 10 nm) on various electrodes is also important.

This study examined the effects of the oxygen sources, such as H_2O and O_3, on the growth characteristics of TiO_2 films grown on Ru and RuO_2 substrates at a higher T_g value of 370 °C, including the growth rate, growth mode, and phase. It was found that the oxidation, reduction, and reoxidation of the Ru and RuO_2 substrates crucially influence the various growth characteristics at this high T_g value.

2. Experimental Procedure

A 4-in.-diameter single wafer traveling-wave-type ALD reactor (CN-1 Co, Plus-100) was used to grow the TiO_2 films. $Ti(O\text{-}iPr)_2(tmhd)_2$ was used as the titanium precursor. The bubbler for the titanium precursor was heated to 130 °C. The precursor was delivered to the ALD chamber with the assistance of an argon carrier gas at a flow rate of 200 sccm. The working pressure was 0.5 Torr. H_2O or O_3 were used as the oxygen sources. H_2O was cooled to 3 °C, to control its high vapor pressure. The O_3 concentration was 320 g/m^3. The ALD process consisted of a titanium-precursor pulse (3 s)−argon purge (5 s)−oxygen source pulse (2 s)−argon purge (5 s). Sputter-deposited Ru(30 nm)/thermally oxidized SiO_2(100 nm)/Si wafers and ALD-grown RuO_2-(40 nm)/thermally oxidized SiO_2(100 nm)/Si wafers were used as substrates. The ALD RuO_2 films were grown using 2,4-(dimethylpentadienyl)(ethylcyclopentadienyl)Ru dissolved in ethylcyclohexane at a concentration of 0.2 M as the ruthenium precursor and O_2 as the reactant at a growth temperature of 250 °C. Background O_2 flow was used during the ruthenium-precursor pulse step to suppress the reduction of RuO_2 to Ru. The TiO_2 film growth temperature (T_g) was varied from 300 °C to 420 °C. The TiO_2 film thickness was estimated by ellipsometry, and the layer density of the deposited Ti atom was determined by X-ray fluorescence spectroscopy (XRF) (Themoscientific, Model ARL Quant'X). The crystal structure of the film was examined by X-ray diffraction in glancing-angle mode (GAXRD), using a Cu Kα X-ray source (PANalytical, X'pert Pro). The incidence angle, scan step size, and time per step during the GAXRD measurement were 2°, 0.01°, and 0.5 s, respectively. The chemical compositions and surface chemical structures of the films were analyzed by Auger electron spectroscopy (AES, Perkin−Elmer, Model 660). The step coverage of the TiO_2 films deposited inside a contact hole structure was confirmed by scanning electron microscopy (SEM) (Hitachi, Model S-4800). Metal−insulator−metal (MIM) capacitors were fabricated to determine the dielectric constant of the TiO_2 films with a top Pt electrode through shadow mask (~80 nm thick and 0.3 mm in diameter) via electron beam evaporation. The capacitance−voltage ($C-V$) characteristics were measured using a Hewlett Packard Model HP 4194A impedance analyzer at 10 kHz.

3. Results and Discussions

Figure 1a shows the change in the growth per cycle (GPC) of the TiO_2 films grown on a ruthenium substrate, depending on the T_g value and the oxygen source type. The GPC increased slowly as the T_g value increased, up to 390 °C, and more rapidly at higher T_g values for both oxygen sources. The GPC of TiO_2 films using O_3 was higher than that of H_2O at all T_g values, but the difference

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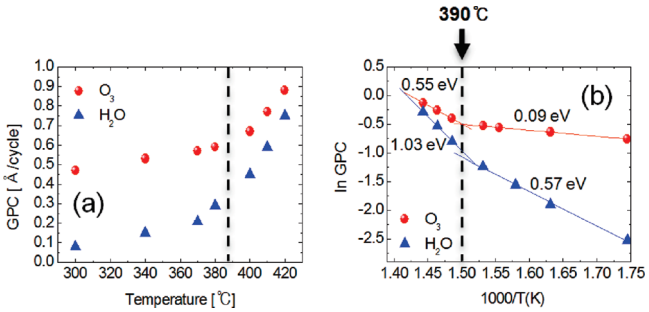

Figure 1. Change in the growth per cycle (GPC) of TiO_2 film grown on a ruthenium substrate, depending on the T_g value and the oxygen source: (a) regular plot and (b) plotted in Arrhenius form.

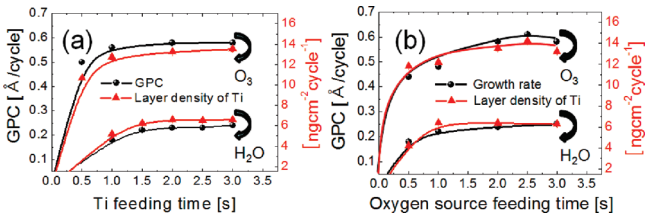

Figure 2. Change in the growth rate of TiO_2 film as a function of (a) the titanium precursor and (b) the oxygen source feeding time with 100 cycles on a ruthenium substrate. The growth rate was plotted in GPC form.

decreased as the T_g value increased. The drastic increase in the GPC of TiO_2 above 390 °C suggests that thermal decomposition of the titanium precursor occurs. Therefore, the ALD regime of TiO_2 could be defined as occurring below this temperature (< 390 °C). The Arrhenius plot indicates more clearly that the transition from an ALD process to a CVD process begins at 390 °C, as shown in Figure 1b. The apparent activation energies in the ALD and CVD regions for O_3 were 0.09 and 0.55, respectively, and the apparent activation energies in the ALD and CVD regions for H_2O were 0.57 and 1.03 eV, respectively.

The effects of the oxygen source on the GPC of TiO_2 thin films were examined at T_g = 370 °C, which is lower than the thermal decomposition temperature (390 °C). Figures 2a and 2b show the change in the GPC of TiO_2 films grown on a ruthenium substrate, as a function of the titanium precursor and oxygen source feeding time, respectively, where the titanium precursor and oxygen source purge time was 5 and 5 s, respectively. Here, ALD sequences were repeated for 100 cycles on a ruthenium substrate and the GPC was calculated by dividing the film thickness by 100. The GPC of TiO_2 film using H_2O was saturated at 0.24 Å/cycle, irrespective of the titanium-precursor input time (t_{Ti}) > 2 s. The change in Ti layer density also showed saturation growth behavior. The Ti layer density increased as the feeding time increased and was saturated at 7 ng/cm^2 per cycle at t_{Ti} > 2 s. Interestingly, the GPC of TiO_2 film using O_3 was saturated at 0.58 Å/cycle, irrespective of the titanium-precursor input time (t_{Ti}) > 2 s, which is more than double that using H_2O, as shown in Figure 2a. The Ti layer density increased as the feeding time increased and became saturated at 14 ng/cm^2 per cycle at t_{Ti} > 2 s. Figure 2b shows similar saturation behaviors of the film growth rate, with respect to the oxygen source feeding time. The higher GPC

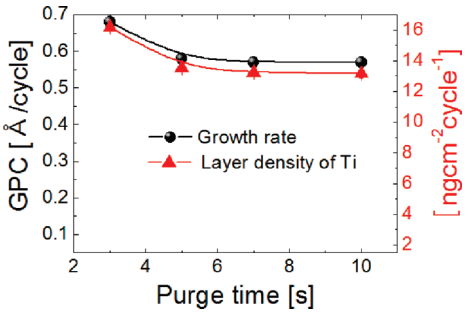

Figure 3. Saturated GPC, with respect to the precursor purging time, which was achieved at T_g = 370 °C on a ruthenium substrate. The higher GPC using O_3 was not due to the incomplete purging of the residual precursor.

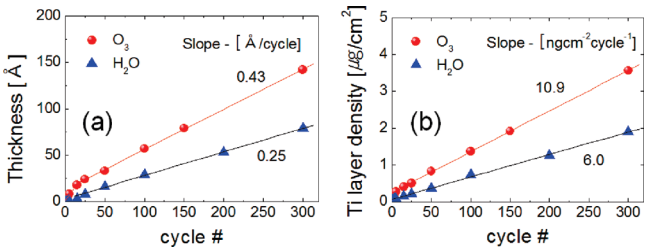

Figure 4. (a) Film thickness and (b) Ti layer density of the TiO_2 thin films grown on a ruthenium substrate, as a function of the deposition cycle number at 370 °C. The film thickness increased linearly as the cycle number increased, which is characteristic of layer-by-layer growth in the ALD process, and the steady-state GPC of the TiO_2 films using H_2O and O_3 were 0.25 and 0.43 Å/cycle, respectively.

using O_3 was not due to the incomplete purging of the residual precursor. Figure 3 shows the changes in the GPC as a function of the titanium-precursor purge time when O_3 was used. Five seconds was long enough to achieve a saturated growth rate. The origin of such a different saturated growth rate for the two oxygen sources was assigned to the limited reaction between the titanium precursor and H_2O, because of the strong bond energy between the tmhd ligand and the Ti ion. The residual ligand will hinder the adsorption of the precursor during the next precursor pulse step, because of steric hindrance, which can induce a decrease in the GPC.[19] The higher oxidation potential of O_3 seemed to remove the tmhd ligands more efficiently than H_2O and a higher GPC could be achieved from O_3.

The GPC estimated by dividing the thickness of a single film by the number of cycles can be subject to error, because of the possible presence of nucleation retardation or enhancement during the initial growth stage. Therefore, a more-accurate saturated GPC, which is free of the influence of the substrate, was estimated as follows.

The TiO_2 thin films were grown on a ruthenium substrate with increasing deposition cycle number at T_g = 370 °C, as shown in Figure 4. The film thickness increased linearly as the cycle number increased, which is a characteristic of layer-by-layer growth in the ALD process, except for the very early stages of film growth, and the steady-state GPC of the TiO_2 films using H_2O and O_3 were 0.25 and 0.43 Å/cycle, respectively. The steady-state

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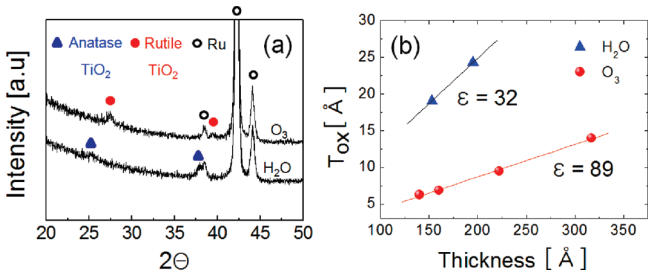

Figure 5. (a) GAXRD patterns of the as-deposited TiO_2 films grown on a ruthenium substrate using H_2O and O_3 (incident glancing angle = 2°), (b) typical plot of the equivalent oxide thickness (T_{ox}) versus film thickness. The dielectric constants of the TiO_2 film using H_2O and O_3 were 32 and 89, respectively, which are close to the reported values for anatase and rutile, respectively.

GPC of the TiO_2 film using O_3 was 1.7 times higher than that of H_2O. The changes in the Ti layer density were 6.0 ng/cm^2 per cycle and 10.9 ng/cm^2 per cycle, respectively. The ratio between the rate of increase in the Ti layer density using H_2O and O_3 was also ~1.7, which is consistent with the GPC ratio shown in Figure 4a. This suggests that both films have similar bulk density. However, the ratio was slightly lower than that in Figure 2, because the GPC in Figure 2 was calculated from a single sample when the sequence was repeated for 100 cycles. In this case, the growth acceleration effect at the initial growth step was included when O_3 was used. The accelerated GPC occurred at the initial growth step below 25 cycles when O_3 was used, whereas no accelerated growth was observed when H_2O was used. More details of the mechanism of initial growth are discussed later.

The crystal structures of the TiO_2 films grown on the ruthenium substrate with the two types of oxygen sources were examined. TiO_2 films 38 nm thick and 26 nm thick were grown using H_2O and O_3, respectively. Figure 5a shows GAXRD patterns of the as-deposited TiO_2 films on a ruthenium substrate at an incident glancing angle of 2°. Anatase-TiO_2 films were grown using H_2O, as indicated by the XRD peaks at 25.3° and 37.8°, which are assigned to the anatase (101) and (004) planes. However, the rutile-TiO_2 films were grown using O_3, as illustrated by the peaks at 27.4° and 39.2° for the rutile (110) and (200) planes. This suggests that selection of the oxygen source is a key factor for the phase control of TiO_2 films, which is consistent with the results reported by Kim et al.[5] They showed that the in-situ-formed thin RuO_2 layer made it possible to grow TiO_2 films as a rutile structure when O_3 was used as the oxygen source at T_g = 250 °C.

$C-V$ analysis was conducted to confirm the structure with the dielectric constant of the films. Figure 5b shows a typical plot of the equivalent oxide thickness (T_{ox}), as a function of physical thickness of the film (T_{phy}). T_{ox} decreased linearly as the film thickness decreased. The dielectric constant (ε) of the TiO_2 film grown on a ruthenium substrate that was extracted from the slopes of the linear fitted lines using the equation $T_{ox} = (3.9/\varepsilon)T_{phy}$, using H_2O and O_3, were 32 and 89, respectively, which are similar to the reported values for anatase and rutile.[5,20] The measured dielectric constants of the TiO_2 films, depending on the oxygen source type are consistent with the XRD data in Figure 5a. Therefore, the phase evolution behavior of the TiO_2 film on the Ru electrode, depending on the type of oxygen source, is identical to that reported previously using TTIP at T_g = 250 °C,[5,20] although the precursors and T_g values were different.

Figures 6a and 6b show the AES depth profiles of the TiO_2 films grown on a ruthenium substrate when H_2O and O_3 were used, respectively. The carbon concentrations at the TiO_2/Ru interface were slightly higher in both cases, because of overlap of the C and Ru Auger peaks. Therefore, the data in regions other than the Ru layer should be compared. The impurity level of carbon is negligible in bulk TiO_2 films in both cases, which suggests that pure TiO_2 films were grown by this ALD process.

The ALD reaction is affected by the substrate and the growing surface.[21] The ALD film growth behavior can be classified into four groups, based on how the GPC varies with the number of deposition cycles. The first is the linear-growth mode, where the GPC is constant from the first cycle to all the deposition cycles. Film growth was always in the steady-state growth regime. The second is a substrate-enhanced growth mode, where the GPC is higher at the initial growth step than the steady-state growth regime. The third and fourth are the substrate-inhibited growth of Types 1 and 2, respectively. In Type 1 substrate-inhibited growth, the GPC is lower at the initial growth step than at the steady-state growth regime. In Type 2 substrate-inhibited growth, the GPC additionally reaches a maximum after the very first inhibited-growth behavior and the GPC approaches the steady-state GPC, which is lower than the maximum.

Figures 4a and 4b showed the typical linear-growth mode and substrate-enhanced growth mode when TiO_2 films were grown on the ruthenium substrate, using H_2O and O_3, respectively. It has been regarded that the substrate-enhanced growth mode can occur when the number of reaction sites on the substrate is higher than that on the ALD-grown material, provided that the reactive sites present on the surface are the dominant factor in the ALD reaction. However, the origin of substrate-enhanced growth can be different in this case. To find the origin of the accelerated growth during TiO_2 film growth using O_3, the TiO_2 films were also grown on a RuO_2 substrate, assuming that oxygen may play an important role in substrate-enhanced growth.

Figures 7a and 7b show the changes in the Ti layer density of TiO_2 films grown on Ru and RuO_2 substrates, as a function of the deposition cycle number, using H_2O and O_3, respectively. Figures 7c and 7d show respective enlargements of Figures 7a and 7b at the initial growth step below 30 cycles. Accelerated growth was not observed on the ruthenium substrate but was clearly observed on the RuO_2 substrate at the initial growth stage (< 25 cycles) when H_2O was used, even though the variation rates in Ti layer density

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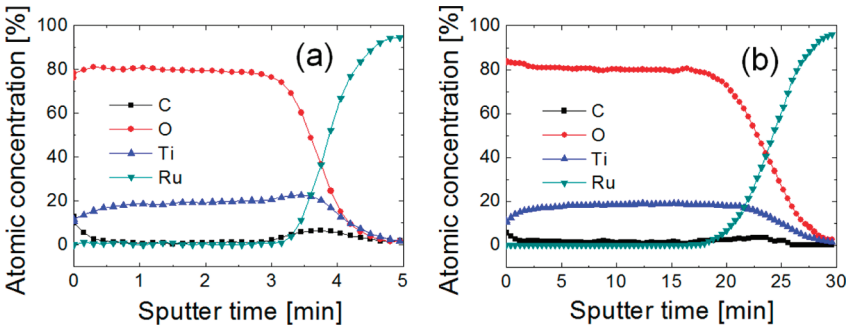

Figure 6. AES depth profiles of the TiO_2 films grown on the ruthenium substrate at 370 °C, using (a) H_2O and (b) O_3, respectively.

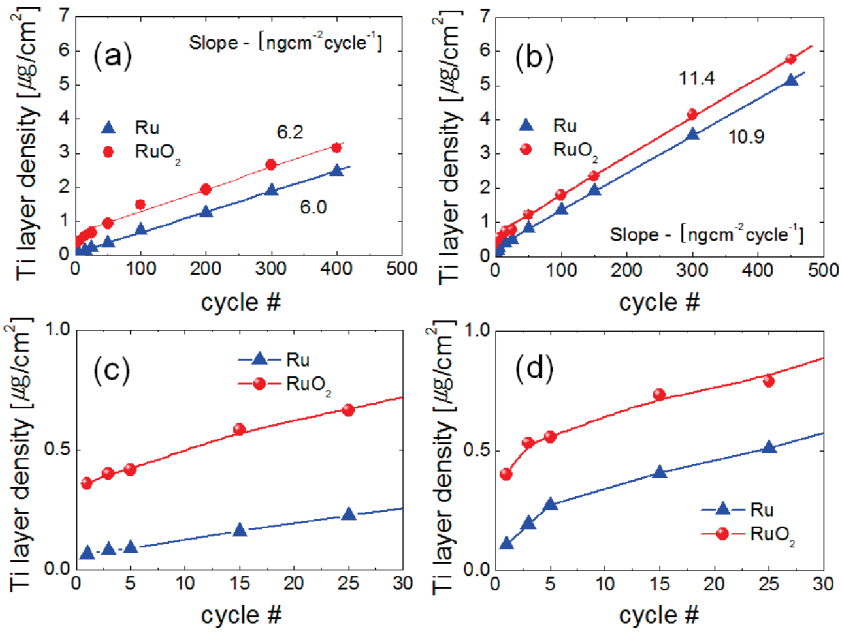

Figure 7. Variations in the Ti layer density of TiO_2 films on the ruthenium and RuO_2 substrates, depending on the deposition cycle number, using (a) H_2O and (b) O_3. Panels (c) and (d) respectively show enlargements of Figures 7a and 7b at the initial growth step below 30 cycles.

at a steady state (>25 cycles) were identical in both cases (6.0−6.2 ng/cm^2 per cycle). Interestingly, the Ti layer density using H_2O was quite excessive (358 ng/cm^2) after the first one-cycle deposition on the RuO_2 substrate than that of the ruthenium substrate (65 ng/cm^2), and an almost-linear-growth mode was maintained over one cycle.

However, accelerated initial growth was observed for both ruthenium and RuO_2 substrates below 5 cycles with a lower extent of excess on the ruthenium substrate when O_3 was used (see Figure 7d). The Ti layer densities on the RuO_2 and ruthenium substrates were 400 and 107 ng/cm^2, respectively, after the first one-cycle deposition, which are higher than that using H_2O. The Ti layer density increased rapidly up to 5 cycles, and the rapid growth was slowed over that cycle. However, the Ti layer density increase rate was still higher than the steady-state growth rate, which can be observed after ~30 cycles, up to 25 cycles. The steady-state growth rates in the Ti layer density on ruthenium and RuO_2 substrates were also identical (10.9−11.4 ng/cm^2 per cycle).

The above phenomena can be understood by the oxygen supply model via reduction of the RuO_2 substrate. Figure 8a shows the GAXRD spectra of the RuO_2 substrate after the deposition of TiO_2 films using H_2O by 1, 5, 25, and 1500 cycles. The peaks at 28.0°, 35.1°, and 40.1° were assigned to the diffraction from RuO_2(110), RuO_2(101), and RuO_2-(200) planes, and 38.4°, 42.2°, and 44.0° were from the Ru(100), Ru(002), and Ru(101) planes. Up to 25 cycles, no peak for TiO_2 was observed, because of the very thin film thickness. TiO_2 films grown with 1500 cycles showed an XRD peak corresponding to anatase-TiO_2. Interestingly, all the RuO_2 peaks disappeared completely and strong Ru peaks were generated, even after only 1 cycle of the ALD process. This suggests that the RuO_2 substrate film was reduced almost completely to ruthenium from the very first cycle of TiO_2 growth, which justifies the evolution of the TiO_2 film to anatase. The possible reduction of RuO_2 to ruthenium via high-temperature (370 °C) treatment under the ALD environment was excluded, because the RuO_2 sample in the chamber without the ALD cycles showed no changes in the XRD pattern of the RuO_2 layer. The oxygen supplied by the substrate during the reduction of RuO_2 can induce a CVD-type reaction with titanium-precursor molecules at the initial growth step. The oxygen atoms supplied from the RuO_2 substrate can react with the adsorbed precursors and produce a TiO_2 layer that is much thicker than the one layer formed at a normal ALD step at the

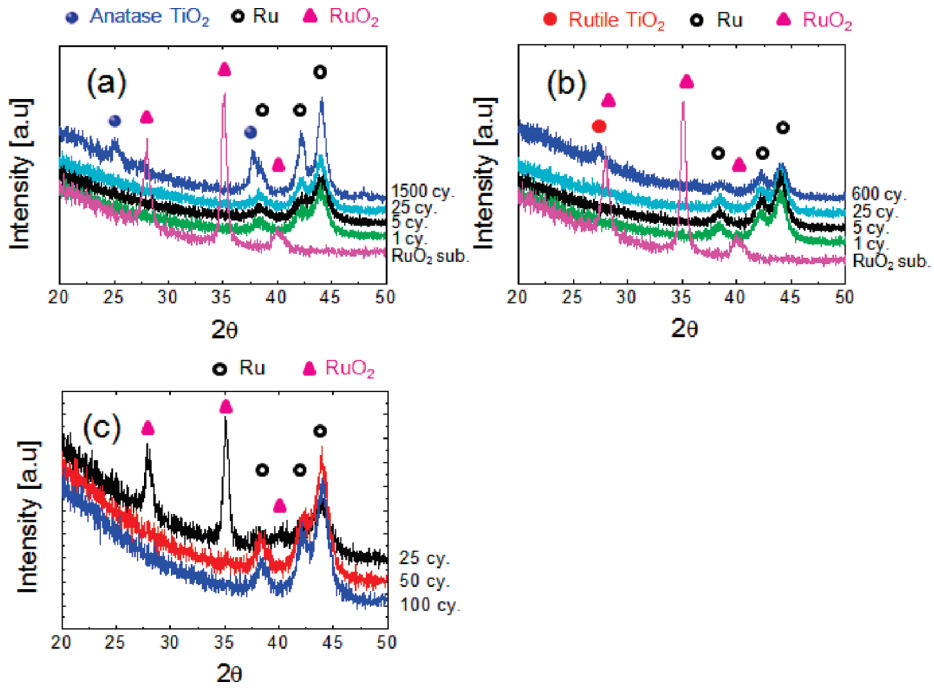

Figure 8. GAXRD patterns of the as-deposited TiO_2 films grown on the RuO_2 substrate, using (a) H_2O and (b) O_3, and (c) with H_2O at $T_g = 250$ °C.

precursor pulse step. This corresponds to the initially high GPC of the TiO_2 film on the RuO_2 substrate when TiO_2 film was grown with H_2O, as shown in Figure 7c.

The almost-complete reduction of the RuO_2 substrate can be understood from its smaller Gibbs free energy of formation.[22] The standard formation energy of TiO_2 (−833.972 kJ/mol) is much higher than that of RuO_2 (−201.190 kJ/mol). Therefore, reduction of the RuO_2 substrate can occur readily during growth of the TiO_2 film. This actually coincides with the circumstance that a large amount of active oxygen atoms are supplied to the growing surface during the precursor pulse step, even though no O_3 or H_2O gas was supplied.

On the other hand, the ruthenium substrate is difficult to oxidize with H_2O,[5] and extra oxygen-induced substrate-enhanced growth is not expected. Therefore, a linear-growth mode that occurred from the first cycle on ruthenium when H_2O was used.

Figure 8b shows the GAXRD spectrum of the RuO_2 substrate, as well as spectra obtained after deposition of the TiO_2 film using O_3 after 1, 5, 25, and 600 cycles. The diffraction peaks from the RuO_2 phase had also disappeared and Ru peaks appeared, even after just 1 cycle of deposition. This suggests that the just one titanium-precursor pulse completely reduced the RuO_2 to ruthenium and the resulting oxygen supply largely enhanced TiO_2 growth. This enhancement effect results in the growth of a TiO_2 layer with a layer density of ~400 ng/cm^2 after one ALD cycle, as shown in Figures 7c and 7d. It was confirmed that this thick TiO_2 layer formation was already accomplished before the first supply of the oxygen source for both H_2O and O_3; a Ti layer density of ~450 ng/cm^2 was achieved after only the first titanium-precursor pulse/purge step without an oxygen source supply.

(22) Barin, I. *Thermochemical Data of Pure Substances*, Part II; VCH: Weinheim, Germany, 1989; pp 1254 and 1433.

Figure 7d shows that, in addition to the initial large enhancement at the first cycle on the RuO_2 substrate for O_3, there is additional fast deposition up to ~3 cycles, which was not observed for H_2O (Figure 7c). Because the oxygen supply from the RuO_2 substrate is not feasible from the second cycle for both process sequences, the additional rapid growth using O_3 must originate from the in situ oxidation of the as-formed Ru substrate during the O_3-pulse step and reduction of this newly formed thin RuO_2 layer during the subsequent titanium-precursor pulse step. The limited amount of oxygen released from this in-situ-formed RuO_2, which is believed to be much thinner than the initial RuO_2 substrate, induced a smaller growth enhancement effect than the RuO_2 substrate itself. Therefore, there is further growth enhancement, to a limited extent, up to 3 cycles. The Ti layer density of 400−450 ng/cm^2 corresponds to the 2 −3 unit-cell thickness of TiO_2. Therefore, it is probable that the substrate surface is already fully covered with the TiO_2 after the first cycle. However, the reoxidation of ruthenium during the next O_3 pulse step, and diffusion out of the oxygen from the reoxidized ruthenium to the growing film surface during the subsequent Ti-pulse step, are still probable, because of the thin thickness of the TiO_2 layer. After ~3 cycles, the inward and outward diffusion of oxygen through the TiO_2 layer begins to be blocked and the substrate-enhanced growth behavior was suppressed almost completely after ~25 cycles. A similar enhancement effect by the in situ oxidation and reduction of the Ru layer are expected for the ruthenium substrate when O_3 was used, even though the initial large enhancement at the first titanium-precursor pulse/purge cycle is not expected. This was actually observed as shown in Figure 7d, up to ~5 cycles. This strongly suggests that O_3 oxidizes the Ru surface to RuO_2 in situ, which induced the rutile structure of TiO_2 layer at the initial growth stage. After the first Ti-pulse/purge step, the surface is composed of

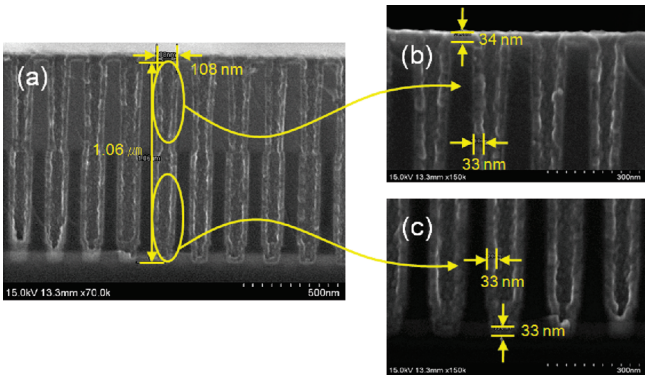

Figure 9. Cross-sectional SEM image of the TiO_2 film using O_3 grown at 370 °C inside a contact hole structure; the deposition cycle was repeated 900 times.

chemisorbed titanium precursors on mainly ruthenium (not RuO_2) substrates. Therefore, the structural arrangement of these Ti atoms (or partially decomposed titanium-precursor molecules) may not resemble the rutile structure, because of a lack of sufficient oxygen atoms. When the subsequent O_3 pulse was made, the remaining ligands are removed completely, and the surface adsorbed Ti atoms oxidize sufficiently. The underlying ruthenium is oxidized to RuO_2 concurrently, which induces the crystallization of the TiO_2 layer into the rutile structure. The thicker TiO_2 layers follow the crystal structures of these thin layers. Figure 8b confirms that this is actually the case. The phase of the thicker TiO_2 film (600 cycles) using O_3 is rutile.

The reduction process of RuO_2 is retarded with decreasing T_g. Figure 8c shows the GAXRD patterns of the as-deposited TiO_2 films grown on RuO_2 substrates when H_2O was used at T_g = 250 °C. The RuO_2 phase can be sustained until 25 cycles, suggesting that the reduction process was limited kinetically by the reduced oxygen-scavenging tendency of the titanium-precursor molecules with decreasing T_g. Kim et al. reported that rutile TiO_2 films can be grown even with H_2O at 250 °C when the ruthenium substrate is pretreated with O_3 gas, which must form a thin surface RuO_2 layer.[23] This corresponds to the results shown in Figure 8c, where the RuO_2 phase could be maintained up to 25 cycles, which is large enough to induce rutile TiO_2 formation. RuO_2 is eventually reduced to ruthenium (Figure 8c), even though the reduction is retarded at this temperature. However, this does not affect the formation of rutile-TiO_2, because the initial TiO_2 layer was grown with a rutile structure on the still-intact RuO_2 layer and the subsequent TiO_2 growth just adopts the rutile-TiO_2 structure, regardless of what occurred in the underlying RuO_2 layer. However, at 370 °C, the very fast reduction of RuO_2 to ruthenium after the first ALD cycle using H_2O results in anatase-TiO_2. For O_3, the reduction of RuO_2 occurs similarly after the first cycle, but the subsequent reoxidation of ruthenium by the O_3 pulse results in the formation of rutile.

Figures 9a−c show a cross-sectional SEM image of TiO_2 films grown at 370 °C inside a contact hole structure for 900 deposition cycles. The rutile structure of the TiO_2 film is favorable in the application of DRAM capacitors, because its dielectric constant is considerably higher than that of anatase-TiO_2. Therefore, the TiO_2 films grown using O_3 are of interest. The opening diameter and hole depth was 108 nm and 1.06 μm, respectively, giving an aspect ratio of 10. The step coverage (t_{min}/t_{max}, where t_{min} and t_{max} respectively refer to the thickness on the sidewall near the bottom and top surface) was excellent (> 95%) without overhang on the top surface. This confirms that the developed ALD process is a self-limiting surface reaction, even at T_g = 370 °C.

4. Conclusions

The atomic layer deposition (ALD) growth behavior of TiO_2 films was examined using $Ti(O\text{-}i\text{-}C_3H_7)_2(C_{11}H_{19}O_2)_2$ and H_2O or O_3 as the titanium-precursor and oxygen sources, respectively, at a growth temperature of 370 °C. The selection of the oxygen source is important for determination of the growth rate, the growth mode, and the crystalline structure of the resulting TiO_2 films. The growth characteristics of the TiO_2 film, depending on the substrate (i.e., ruthenium or RuO_2), were also analyzed.

The ALD temperature window was achieved up to 390 °C for both oxygen sources, and O_3 results in generally lower apparent activation energy for film growth. This means that O_3 results in a higher saturated growth rate (0.43 Å/cycle) than that of H_2O (0.25 Å/cycle). The TiO_2 films grown by O_3 and H_2O had crystalline phases of rutile and anatase, respectively, on both ruthenium and RuO_2 substrates, as confirmed by the electrical properties and X-ray diffraction (XRD).

Interestingly, the first pulse cycle of the titanium precursor at 370 °C reduced the RuO_2 substrate to ruthenium, resulting in the formation of a TiO_2 layer, which was much thicker than the layer thickness achieved after one normal ALD cycle, even before any oxygen source pulse step. This results in very strong growth enhancement after the very first ALD step for both oxygen sources. During the subsequent O_3 pulse step, the reduced ruthenium reoxidizes, which further enhances TiO_2 deposition during the next titanium-precursor pulse step by the reduction of RuO_2 again. This also results in the formation of a rutile-TiO_2 film. Even on a ruthenium substrate, the O_3 oxygen source induced the same in situ oxidation and reduction of ruthenium during the O_3- and titanium-precursor injection steps, respectively, which initially enhanced growth without involving the very large enhancement at the first cycle. The reduction process of in-situ-formed RuO_2 seems to be kinetically limited, allowing it to induce the growth of rutile-TiO_2 film. However, in situ oxidation of ruthenium was not expected from the H_2O oxygen source. Consequently, the ALD process with H_2O just exhibited saturated linear-growth behavior from the first cycle on the ruthenium substrate. Therefore, in this case, the TiO_2 film grows almost always as anatase on ruthenium.

(23) Kim, S. K.; Hwang, G. W.; Kim, W. D.; Hwang, C. S. *Electrochem. Solid State Lett.* **2006**, *9*, F5.

Promising step coverage of the TiO_2 film on the capacitor hole structure with an aspect ratio of ~10 was achieved.

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