Plasma enhanced atomic layer deposition of $SrTiO_3$ thin films with $Sr(tmhd)_2$ and $Ti(i\text{-}OPr)_4$

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$SrTiO_3$ (STO) thin films were deposited in the deposition temperature range of 250–350 °C by plasma enhanced atomic layer deposition (PEALD) with $Sr(tmhd)_2$ (tmhd=tetramethyl heptanedionate) and $Ti(i\text{-}OPr)_4$ (i-OPr=iso-propoxide) as a precursor. Two precursors were dissolved in tetrahydrofuran, delivered into the vaporizer separately by a newly developed pulse injection method, and the vapor mixture was introduced into the reactor. An argon purge was inserted after the precursor injection and afterward, plasma was generated with the oxygen introduction. Deposition rate was saturated at 0.3–0.4 Å/cycle. Despite the poor volatility of $Sr(tmhd)_2$, $SrTiO_3$ thin films were reproducibly deposited and using plasma activated O_2 gas as an oxidant, films could be deposited at low temperature with carbon residue of STO thin films minimized. Step coverage of both SrO and $SrTiO_3$ were above 90% due to the self-limiting growth behavior of atomic layer deposition process. © *2002 American Vacuum Society.*
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The replacement of SiO_2 with high dielectric materials such as TaO_x, Al_2O_3, $SrTiO_3$ (STO), and $(Ba,Sr)TiO_3$, is a major challenge.[1–4] STO thin films are of great interest as a capacitor dielectric material for giga-bit dynamic random access memories because of its high dielectric constant and low leakage current density. Many deposition techniques, such as sputtering,[5] coevaporation,[6] and metalorganic chemical vapor deposition (MOCVD)[7] have been investigated. Among them, MOCVD has many advantages such as good controllability of composition and conformal step coverage. However, even with the MOCVD technique, uniformity of cation composition and thickness in three-dimensional structures could not be obtained due to the different thermal behavior of Sr and Ti precursors.[7] To overcome these problems, the atomic layer deposition (ALD) process was used, which ensures perfect conformality through the self-limiting film deposition mechanism.[8]

Generally, it is more difficult to select Sr and Ti precursors for the ALD process than the chemical vapor deposition (CVD) process. In a conventional CVD process, the thermal stability of precursors is needed during the transport to avoid premature gas-phase reaction. However, in ALD processes, precursors must be decomposed easily at low temperature on the deposition surface where the reactive gas was introduced as well as be stable enough not to decompose during the transport. Some researchers have reported that $SrTiO_3$ thin films were successfully deposited by the ALD method.[9,10] Vehkamaki *et al.*[9] have reported that precursors with diketone ligand do not react with the most common and convenient oxygen sources at temperatures low enough to prevent thermal decomposition. As a solution to this problem, it was suggested that cyclopentadienyl compounds of Sr could be used as an ALD precursor. But those compounds were easily decomposed near or below the sublimation temperature and self-limiting growth behavior was not easily obtained. Wang *et al.*[10] reported that the deposition temperature was higher than 600 °C. At this temperature, precursors such as $Ti(i\text{-}PR)_4$ are self-decomposed as was already reported.[11] In this case, it is not easy to obtain conformal step coverage, which is an advantage of the ALD process.

In this rapid communication, STO thin films were successfully deposited by the ALD method with diketone ligand, tmhd (tmhd-tetramethylheptanedionate) at a low temperature. Figure 1 shows the schematic of a plasma enhanced atomic layer deposition (PEALD) reactor. Plasma was ig-

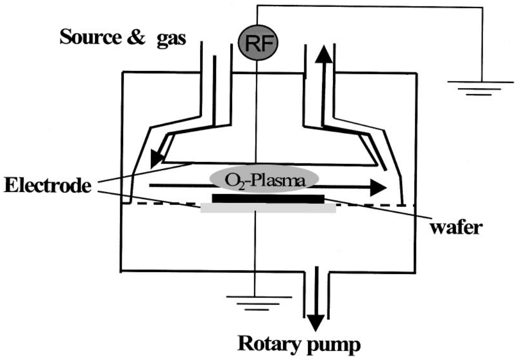

FIG. 1. Schematic of the plasma enhanced atomic layer chemical vapor deposition reactor.

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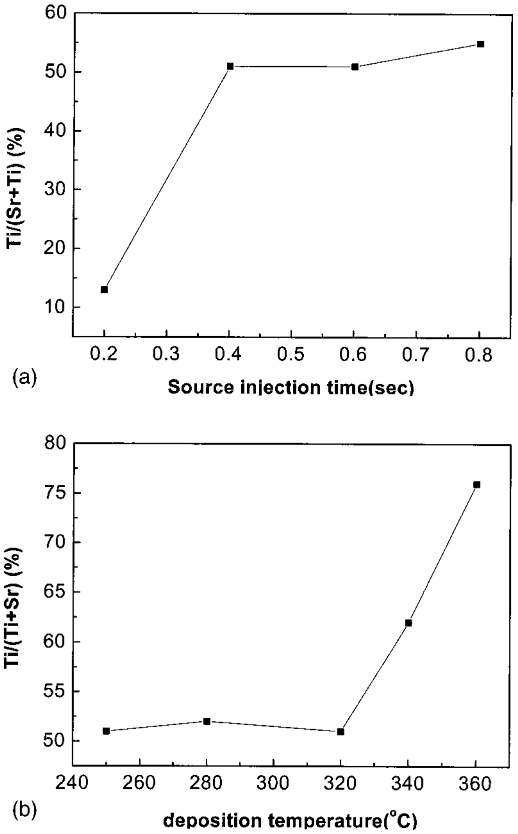

FIG. 2. Variation of Sr and Ti cation composition as a function of: (a) the source injection time (deposition temperature at 300 °C) and (b) deposition temperature (injection time at 0.4 s).

nited directly on the wafer whenever O_2 gas was introduced. The deposition temperature was in the range of 250–350 °C and reactor pressure was 1 Torr. STO thin films were deposited on the Ru/SiO_2/Si wafer with a supply of $Sr(tmhd)_2$ and $Ti(i\text{-}OPr)_4$ (iso-propoxide), argon purge, O_2 plasma, and argon purge. $Sr(tmhd)_2$ 0.1 M solution and $Ti(i\text{-}OPr)_4$ 0.1 M solution were prepared with tetrahydrofuran solvent. Two solutions were injected separately into the evaporator at the same time with two pulsed liquid injectors and vaporized mixtures were introduced into the deposition reactor. Injection time of the precursor was varied from 0.2 to 0.8 s. After the precursor injection, argon was used as a purge gas for 3 s. Right after the purge, plasma was generated with the oxygen introduction and another argon purge was done before the next injection of the precursor. Deposition rate was saturated at 0.3–0.4 Å/cycle.

Figure 2 shows the chemical composition of STO thin films as a function of the precursor injection time at the deposition temperature of 300 °C. The cation incorporation rate was dependent on the increase of the precursor pulse duration, and then saturated above 0.4 s. Also at the fixed source pulse length, temperature-independent self-limiting growth rate of 0.032 nm/cycle was obtained at the deposition temperature of 250–325 °C, and in this temperature range, film composition was about the same with the injection rate of the two precursors, i.e., Ti/(Ti+Sr)=0.5. Above that range, the Ti incorporation rate was rapidly increased, which may be due to the self-decomposition of $Ti(i\text{-}OPr)_4$.

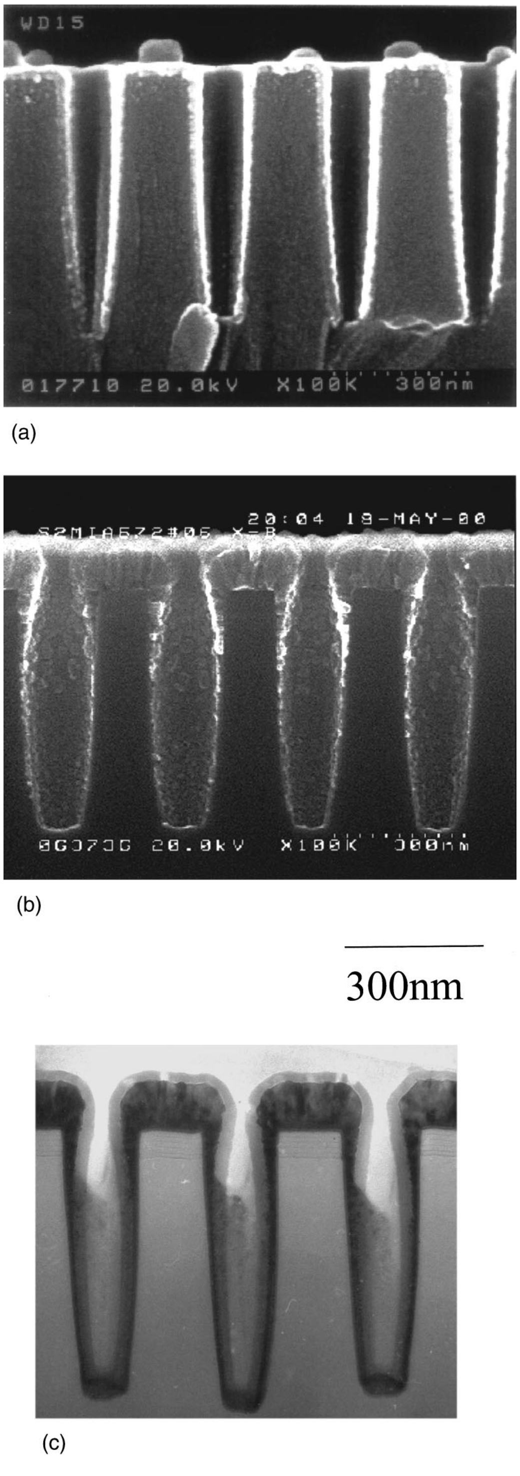

FIG. 3. Comparison of step coverage of SrO films deposited with: (a) PEALD and (b) CVD, and (c) STO films using PEALD at the deposition temperature of 280 °C.

There was an improvement in step coverage using an ALD process due to its self-limiting growth behavior. Figure 3 shows a comparison of the step coverage of SrO films using: (a) PEALD and (b) CVD methods with $Sr(tmhd)_2$ as a precursor at an aspect ratio of about 4 on the Ru/SiO_2/Si

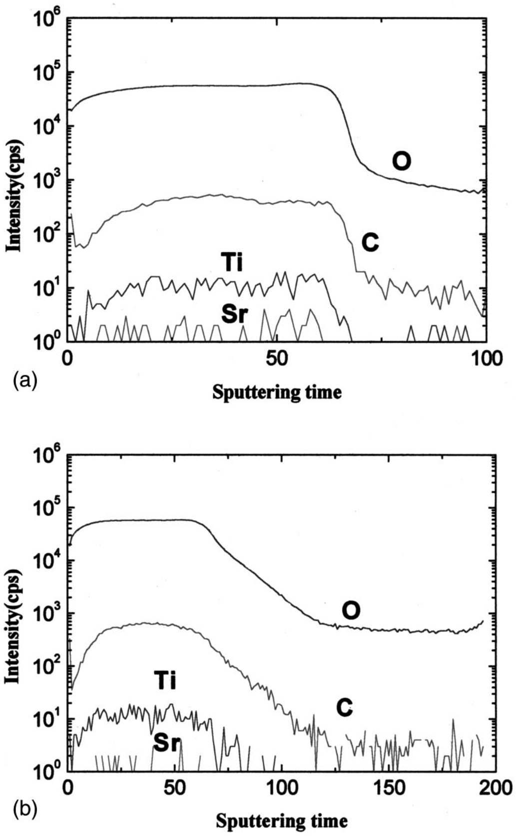

FIG. 4. Comparison of carbon contamination of STO thin films deposited with: (a) PEALD at the deposition temperature of 280 °C and (b) CVD at 460 °C.

steps. Compared with SrO films deposited by a MOCVD method with a step coverage of $d_{\min}/d_{\max}$, where $d_{\min}$ and $d_{\max}$ refers to the thickness on the sidewall near the bottom and on the top surface, respectively, below 20%, excellent step coverage above 90% was obtained with the PEALD method. Also, the $d_{\min}/d_{\max}$ ratio of STO films was above 90% without overhang on the top surface, as shown in Fig. 3(c). This result was mainly due to the ALD process where the deposition was determined by the surface reaction and the chemisorption of the precursor.

Based on the above facts, it is believed that when an oxidant is properly selected such as O_2 gas activated by plasma, diketone compounds can be used as an ALD precursor for metal–oxide thin films at a low deposition temperature. At lower deposition temperatures with organometallic sources, carbon contamination is a major concern. Carbon contamination of STO thin films deposited by the ALD method was monitored by secondary ion mass spectrometry analysis. As shown in Fig. 4, the carbon content of STO thin films deposited at 280 °C by the ALD method was equal to or smaller than that of the film deposited by the optimized CVD method at 460 °C.

Some crystallinity of STO thin films was detected at the deposition temperature of 280 °C. Electrical properties of STO thin films were measured after annealing in O_2 atmosphere at 450 °C for 10 min. SiO_2 equivalent oxide thickness of 17.6 nm STO films was about 1.2 nm and leakage current was 2×10^{-6} A/cm^2 at 1 V. Further study is needed to improve the electrical properties of STO films.

In this Rapid Communication, it was shown that STO films can be deposited using the ALD method with Sr(tmhd)$_2$. With O_2 plasma, Sr(tmhd)$_2$ was successfully used as an ALD precursor and good step coverage and low carbon level were obtained.

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