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Supercritical Fluid Deposition of Conformal $SrTiO_3$ Films with Composition Uniformity in Nanocontact Holes

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$SrTiO_3$ with a high dielectric constant is considered a promising capacitor dielectric for dynamic random access memory. Until now, a $SrTiO_3$ deposition with compositional uniformity and perfect conformality inside high-aspect nanoscale holes has been difficult by chemical vapor deposition (CVD) and atomic layer deposition (ALD). In this study, we report a supercritical fluid deposition (SCFD) of $SrTiO_3$. Compared to CVD $SrTiO_3$, the SCFD $SrTiO_3$ showed perfect conformality and compositional uniformity inside nanosize holes. From these results, the SCFD is expected to be a solution for the stoichiometry and conformality issues of the CVD and ALD $SrTiO_3$.
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$SrTiO_3$ (STO) is considered as a promising dielectric material for dynamic random access memory capacitors due to its high dielectric constant up to 300, low leakage current, and good chemical stability.[1-7] Moreover, complicated three-dimensional (3D) device structures with device downscaling to sub-40 nm have emerged to increase integration density.[8,9] Hereupon, a highly conformal deposition technique is an essential requirement for nanoscale device fabrications. One widely studied deposition technique for STO thin films is metallorganic chemical vapor deposition (MOCVD).[10-13] Although relatively good composition controllability can be achievable by MOCVD, it is difficult to obtain highly conformal deposition on nanoscale 3D structures. In addition, compositional variation in deep trenches or nanoholes is also a significant problem. For example, energy-dispersive spectroscopy (EDS) analysis exhibited that the Sr/Ti composition ratio of MOCVD STO films continuously decreases from top to bottom of the nanoholes.[10] The nonuniform Sr/Ti ratio of the MOCVD STO films inside nanoholes was attributed to the different deposition characteristics of Ti and Sr precursors, depending on arriving rates and sticking coefficients of the precursors during MOCVD.[10-12]

Atomic layer deposition (ALD) was suggested as an alternative technique for MOCVD STO.[14-17] Generally, ALD enables a deposition with atomic thickness uniformity, high conformality in nanoscale holes and trenches, and large-area uniformity.[18] In spite of these promising aspects, previous studies on ALD of STO reported that various problems exist such as lack of volatile precursors and difficulty in controlling stoichiometry.[14-16] Although ALD STO showed better results in terms of thickness and chemical conformality than MOCVD STO, the Sr/Ti ratio along the 3D contact holes was not uniform and sensitive to growth parameters such as growth temperatures and precursor injection rates.[15,16]

Recently, supercritical fluid deposition (SCFD) emerged as a promising thin-film deposition method for deposition on nanoscale 3D structures due to its excellent conformality and gap-filling properties.[19-21] Especially, SCFD has merits of chemical vapor deposition (CVD) and ALD such as large-area process for mass production, high deposition rate, and high conformality.[19-21] The supercritical fluid CO_2 has liquidlike solubility, enabling much higher precursor concentrations than that of typical CVD, and has gaslike surface tension, diffusivity, and viscosity.[19] These characteristics of supercritical fluid enable precursors to reach the insides of high-aspect nanoholes, resulting in extremely high gap filling and conformality.[20] There have been reports on SCFD of various metals and binary oxides such as Ru, Co, Ni, Pd, Cu, HfO_2, ZrO_2, and TiO_2.[20,21] However, as far as we know, there has been no report on an SCFD of ternary oxides. Because an SCFD does not require high volatility of the precursors, it can be a good alternative to CVD or ALD for STO thin films. Moreover, there is a strong possibility for obtaining chemically uniform and highly conformal films, because the chemicals are transported as a solution in supercritical solvent to deep inside of nanoholes. In this study, we comparatively investigated the SCFD and CVD of STO thin films. The experimental results show that the SCFD is a viable tool for deposition of chemically uniform and conformal complex oxides for nanoscale devices.

We deposited STO thin films on Si substrates with nanoscale contact holes with less than 150 nm diameter and higher than 5:1 aspect ratio by MOCVD and SCFD. For both deposition techniques, we used the same precursors, Sr(tetramethyl-heptanedionato)$_2$ [Sr(tmhd)$_2$] and Ti(methylpentanediol)(tetramethylheptanedionate)$_2$ [Ti(mpd)(tmhd)$_2$] as Sr and Ti precursors, respectively. The molecular structures of the two precursors are schematically shown in Fig. 1. For CVD STO, a cold-wall reactor with a liquid injector was used. Single-mixture solution of Sr and Ti precursors was injected via a liquid flowmeter. The single-mixture solution was composed of 1:1 mole ratio between Sr(tmhd)$_2$ and Ti(mpd)(tmhd)$_2$. The mixture solution of the precursors and Ar carrier gas were fed into the vaporizer and then injected through a shower head. Oxygen gas was used as an oxidant with a flow rate of 420 sccm. The substrate temperature was 400°C, and the pressure during deposition was 340 mTorr. For SCFD STO, the Sr and Ti precursors were premixed with 1:1 mole ratio and dissolved in supercritical CO_2 at 150 atm and 80°C in a separate premix cell. After the working pressure of

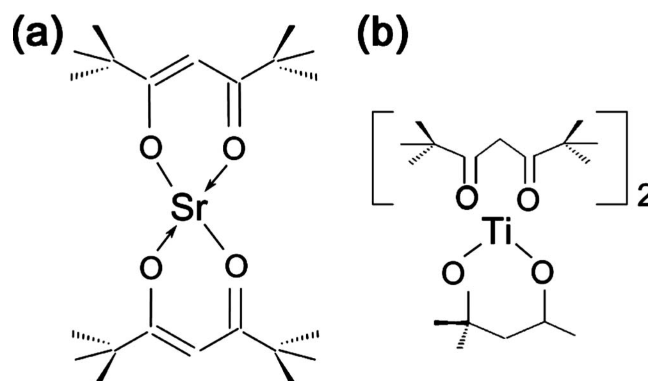

Figure 1. Sr and Ti precursors used for the CVD and SCFD of $SrTiO_3$: (a) Sr(tmhd)$_2$ and (b) Ti(mpd)(tmhd)$_2$.

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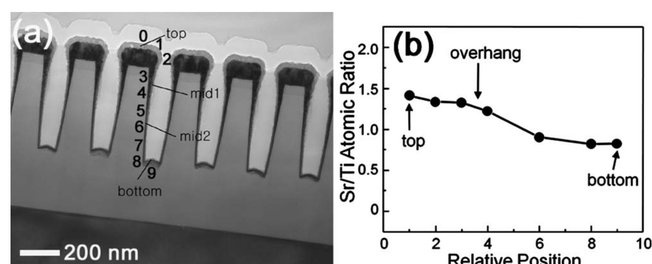

Figure 2. (a) TEM image of the CVD $SrTiO_3$ film on nanoscale contact holes. (b) Sr/Ti atomic ratios of CVD $SrTiO_3$ film depending on the position.

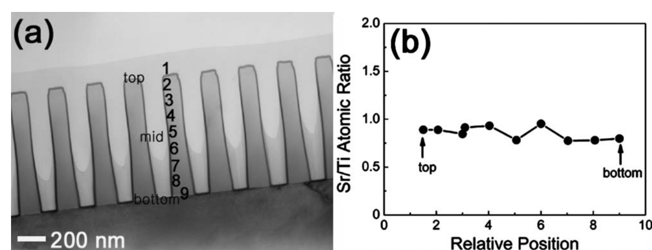

Figure 4. (a) TEM image of the SCFD $SrTiO_3$ film on nanoscale contact holes. (b) Sr/Ti atomic ratios of SCFD $SrTiO_3$ film depending on the position.

150 atm was reached in the main deposition chamber, the substrate heater was heated to growth temperature. Then, the Sr/Ti precursors dissolved in supercritical CO_2 fluid were injected into the main chamber simultaneously with H_2O_2 (30%) solution. The compositions of CVD and STO SFCD were analyzed by inductively coupled plasma-mass spectroscopy (ICP-MS). The microstructure and conformality on nanoscale contact holes were analyzed by cross-sectional transmission electron microscope (TEM) and position-depending compositional analysis by EDS equipped with a TEM.

First, we deposited STO thin film by MOCVD for a comparative study. Figure 2a shows the TEM image of the CVD STO at a growth temperature of 400°C on deep-trench structures. The step coverage of the CVD STO is about 35%, which is defined as the thickness ratio of the STO thin film from the top area to bottom area in the holes. A large overhang was observed with significantly small thickness at the bottom and the side wall in the holes, which is a typical example of the poor conformality of CVD STO.[11] Even though we used a liquid-injection system to compensate for the difference in volatility of the two precursors, the Sr/Ti ratio in the films was not uniform in the contact holes. Figure 2b shows the Sr/Ti atomic ratio in the CVD STO measured by EDS equipped with a TEM. Excess Sr content with a Sr/Ti ratio >1.4 is observed at the top of the holes, while Sr content is slightly deficient at the bottom of holes with Sr/Ti = 0.8. Hwang et al. reported similar results about poor conformality and compositional variation along the 3D contact holes, largely dependent on the solution flow rate.[10]

Next, we investigated the STO SCFD using the same $Sr(tmhd)_2$ and $Ti(mpd)(tmhd)_2$ precursors and H_2O_2 (30% in water) as an oxidant.[22-25] Generally, H_2O is immiscible with supercritical fluid CO_2.[21,24] Previously, various oxides, including ZrO_2, MnO_x, RuO_x, and Al_2O_3, were deposited using H_2O_2 as an oxidant.[25] Thus, in the current experiments, H_2O_2 was used as an oxidant for the STO growth. The STO thin films were deposited at growth temperature (Ts) range from 80 to 380°C and pressure range from 70 to 280 atm. Figure 3a shows that the growth occurs between 180 and 280°C with an almost constant growth rate of ~230 Å/min. The growth rate significantly decreased at temperatures below 130°C and above 330°C. The low growth rate below 130°C originated from the reduction of reaction rate of Sr and Ti precursors with H_2O_2 oxidant for the formation of $SrTiO_3$ phase.[12,16] The growth rate was not changed significantly between 75 and 200 atm, while it decreased abruptly above 200 atm (Fig. 3b). High growth rates were obtained for the SCFD of ZrO_2, MnO_x, and RuO_x thin films, which showed good solubilities under a narrow growth temperature range.[24] Thus, a solubility of Sr and Ti precursors and H_2O oxidant is a key parameter for the growth rate of the SCFD STO. We suggest that the low growth rate of the SCFD STO is due to a poor solubility of the SCFD STO under a growth condition of a high pressure above 200 atm and a high temperature above 330°C.

Figure 4a shows the cross-sectional TEM image of SCFD STO deposited at 200°C and 150 atm for 40 s. STO film (15 nm thick) with excellent conformality was obtained on the nanoholes as shown in the figure. Figure 4b shows the Sr/Ti ratio of the SCFD STO thin film measured by EDS. The Sr/Ti ratio remains almost constant from the top to the bottom of the contact holes at Sr/Ti = 0.86 ± 0.07. In addition, the average Sr/Ti ratios in the STO films deposited at 150 atm were analyzed by ICP-MS as a function of growth temperatures. As Fig. 5 shows, the Sr/Ti ratio remained almost constant at 0.82 ± 0.09 for all the samples grown between 130 and 330°C. This result indicates that the cation composition of the SCFD STO thin films is insensitive for large variation in growth temperature. On the contrary, Sr/Ti ratio was largely changed from 1.1 to 0.6 by changing the growth temperature from 250 to 290°C in the previous report of the ALD STO.[15] This is an additional benefit of SCFD, because the process window to achieve relatively good compositional uniformity is large.

Although the exact reason for the cation compositional variation of MOCVD STO inside nanoscale contact holes is not precisely known, the deficiency of Sr at the bottom of holes was attributed to the poorer conformality of Sr component than Ti component, which is related to the difference in arriving rate and sticking coefficient of

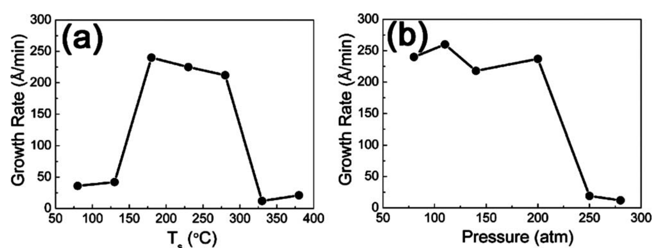

Figure 3. (a) Temperature dependence of growth rate and (b) pressure dependence of growth rate of SCFD $SrTiO_3$ film.

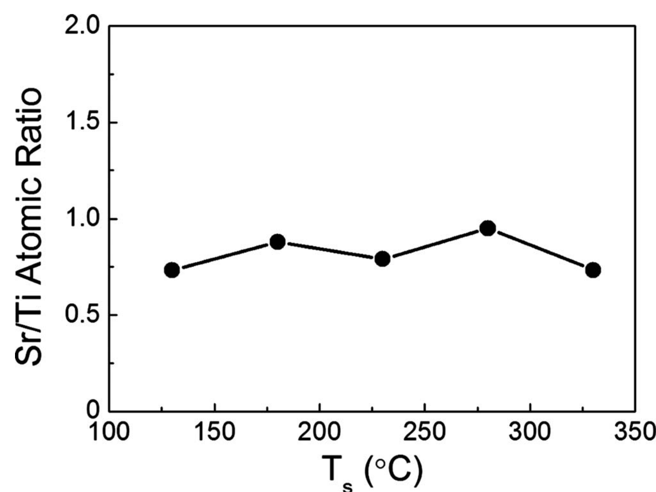

Figure 5. Sr/Ti atomic ratios of SCFD $SrTiO_3$ film depending on growth temperature.

each precursor.[12] Thus, to obtain chemically uniform STO films, the conformality of each component (TiO_2 and SrO) should be achieved. In fact, by using ALD, much improved chemical uniformity along the 3D contact hole was obtained.[15,17]

The SCFD in the current condition resulted in slightly Ti-rich films. Because we have used a 1:1 mole ratio of precursors, we can conclude that the deposition rate of Ti component is higher, which can be controlled by using an optimized mole ratio. In any case, due to the inherently excellent conformality of SCFD, each TiO_2 and SrO are both conformally deposited inside of the nanocontact holes, leading to the observed uniform chemical composition profile. Generally, the good conformality of SCFD is attributed to low viscosity, high diffusivity, zero surface tension, and high pressure in supercritical fluid state.[19,20] Especially, the arrival rate of Sr and Ti precursors is not strongly dependent on the geometry of the substrate compared to CVD or ALD, leading to good delivery of precursor molecules even to the bottom of holes. This perfect transportation of the stoichiometric $SrTiO_3$ precursor enabled compositional uniformity of the SCFD STO with excellent step coverage on the contact holes. Also, as Fig. 5 shows, the composition of SCFD STO is not strongly dependent on the growth temperature, which is an additional benefit of STO SCFD. Thus, SCFD STO is a viable deposition technique for solving stoichiometry and conformality issues of the CVD and ALD STO.

In summary, we developed the SCFD process of a STO thin film as a ternary oxide SCFD process. We obtained perfect conformality and compositional uniformity of the SCFD STO thin film for nanoscale contact holes. The SCFD can be a solution for the stoichiometry and conformality issues of the CVD STO and ALD STO.

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