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Ethanol-Assisted Flow-Type Supercritical Fluid Deposition of $SrRuO_3$ for Stoichiometric Film Formation

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We achieved stoichiometric $SrRuO_3$ film formation using a flow-type supercritical fluid deposition (SCFD) reactor with ethanol addition. Ethanol equalized the deposition rates of component materials, SrO and RuO_2 by increasing the Sr precursor solubility in $scCO_2$ and selectively suppressing RuO_2 deposition reactions. The compositional profile of the deposited film on a three-dimensional structure was verified using the macrocavity method. We demonstrated $SrRuO_3$ film formation with compositional uniformity and conformality on high-aspect-ratio features using ethanol-assisted SCFD. The $SrRuO_3$ film formed using this method has potential applications in the fabrication of high-aspect-ratio memory devices.

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$SrRuO_3$ is a promising material for bottom electrodes in memory devices such as dynamic random access memory (DRAM) and ferroelectric random access memory (FeRAM).[1,2] These memories will be monolithically integrated with logic circuits for improved performance (called "embedded memory"); accordingly, the fabrication process temperature should be below 400°C to avoid thermal damage to logic circuits.[3] Conventional technologies, including metal organic chemical vapor deposition (MOCVD), are not feasible in practical applications due to their high process temperature of 400°C. Additionally, considering that FeRAM adopts a three-dimensional (3D) structure similar to DRAM, good step coverage on high-aspect-ratio features is also required for fabrication technologies. Supercritical fluid deposition (SCFD) satisfies these requirements because of the unique properties of supercritical fluid.[4] Many kinds of metal deposition have been reported, such as Cu, Pt, and Ru, at low temperatures, i.e., below 250°C.[4,5] We recently demonstrated that $SrRuO_3$ film deposited in our closed-type reactor exhibited properties sufficient for the bottom electrodes of memory devices: purity, crystallinity, and good step coverage at low deposition temperature.[6] In a closed-type reactor, however, it is difficult to control the temperatures of the substrate and the fluid individually; thus, it is not the best choice of reactor to control a process involving fluid-phase reactions. In most cases of oxide film deposition by SCFD, fluid-phase reactions play an important role by producing active intermediate species for deposition. Therefore, we used a flow-type reactor, which is also beneficial for mass production. In this work, the Sr precursor was supplied by an ethanol solution to ensure a stable supply of less-soluble Sr precursor as well as to increase the Sr precursor solubility (entrainer effect).[7] Ethanol also played a role as a cosolvent that inhibited the RuO_2 growth rate.

All deposition runs were carried out using our in-house flow-type reactor (Figure 1). The substrate or macrocavity structure was placed on the bottom of the reactor. The reactor had an inner volume of 8 mL and was heated by a pedestal heater. The substrate temperature was 250°C for all depositions. In contrast, the substrate temperature was 230°C in our previous work using a closed-type reactor. In the closed-type reactor, the substrate was not heated as high to avoid SrO particle generation via the fluid-phase reaction. The substrate temperature in the flow-type reactor was increased to promote surface reactions without generating SrO particles in the fluid.[6] Bis(2,2,6,6-tetamethyl-3,5-heptanedionato)strontium [$Sr(tmhd)_2$], the Sr precursor, was injected as an ethanol solution via a liquid pump; the concentrations of the Sr precursor and ethanol were controlled by the solution concentration and pumping speed. SrO particle formation occurred readily in a highly concentrated O_2 environment, and thus the O_2 concentration should be lower than 0.1 mol/L. Bis-cyclopentadienyl-ruthenium [ruthenocene, $Ru(cp)_2$] has been used as a new precursor to suppress Sr particle generation by using low O_2 concentration. In our previous work [6], tris(2,2,6,6-tetramethyl-3,5-heptanedionato)ruthenium [$Ru(tmhd)_3$]was used, which required high O_2 concentration to form RuO_2 using ethanol addition. However, Sr precursors were relatively reactive, and easily formed SrO particles with addition of O_2. As a result, Sr particle formation was a serious problem when $SrRuO_3$ was deposited using $Ru(tmhd)_3$ and O_2. Ruthenocene required less O_2 concentration in RuO_2 deposition, and the low O_2 concentration helped to avoid Sr particle generation in $SrRuO_3$ deposition. An excessive amount of solid Ru precursor was filled in a dissolution bottle and dissolved Ru precursor in $scCO_2$ was supplied. O_2 and $scCO_2$ were premixed in a syringe pump and injected. The O_2 concentration was fixed at 7.4×10^{-2} mol/L in all experiments. The total pressure was kept at 15 MPa during deposition.

We demonstrated first the effect of ethanol on the deposition of RuO_2 and SrO on planar SiO_2/Si structure. The deposition period was 30–60 min, and the thickness of the deposited film was measured using a field-emission scanning electron microscope (FE-SEM, JEOL 6340F). The deposition rate of RuO_2 without ethanol addition was faster than the SrO deposition rate (Figure 2). Ethanol addition effectively decreased the deposition rate of RuO_2, whereas the SrO deposition rate was independent of the ethanol concentration. Ethanol decreased the RuO_2 deposition rate for all three ruthenocene concentrations examined, which can be explained by the interaction between the precursor and ethanol. Alcohol molecules are likely to surround precursor molecules,[8,9] ethanol surrounded the precursor, hindering O_2 contact to the precursor molecules, which suppressed the fluid-phase reaction that contributes to deposition. This hindrance should have been observed for SrO deposition; however, a simultaneous reaction involving ethanol neutralized the hindrance, counteracting the effect of ethanol on the deposition rate. Ethanol addition increases the dielectric constant of a solvent and thereby enhances the solvent effect.[10] This enhanced solvent effect promotes the pyrolysis of a thermally decomposable precursor in $scCO_2$, resulting in increased deposition rates. This effect is valid for SrO deposition, not RuO_2 deposition, because only the Sr precursor is thermally decomposed in $SuRuO_3$-SCFD.[11]

Although ethanol decreased the RuO_2 deposition rate, the Sr/Ru atomic ratio in the $SrRu_xO_y$ film fabricated using equal Sr and Ru precursor concentrations was about 0.18 (cf. ideal ratio is 1), as measured by an X-ray photoemission spectroscope (XPS, ULVAC-Φ XPS model 1600C). We introduced more Sr precursor to increase Sr incorporation. When the precursor molar ratio of Sr and Ru precursors was 2.2, a Sr/Ru atomic ratio of 0.95 was achieved. Thus, 7.3×10^{-4} mol/L Ru precursor, 1.6×10^{-3} mol/L Sr precursor, and 0.086 mol/L ethanol were used to evaluate the quality of the deposited $SrRuO_3$ film. In contrast to our previous work,[6] the Sr/Ru precursor molar ratio decreased with ethanol addition. The crystal orientation of the film was analyzed by X-ray diffraction (XRD, Rigaku, Smart Lab) using the 2θ ω mode. XRD measurements revealed that the fabricated

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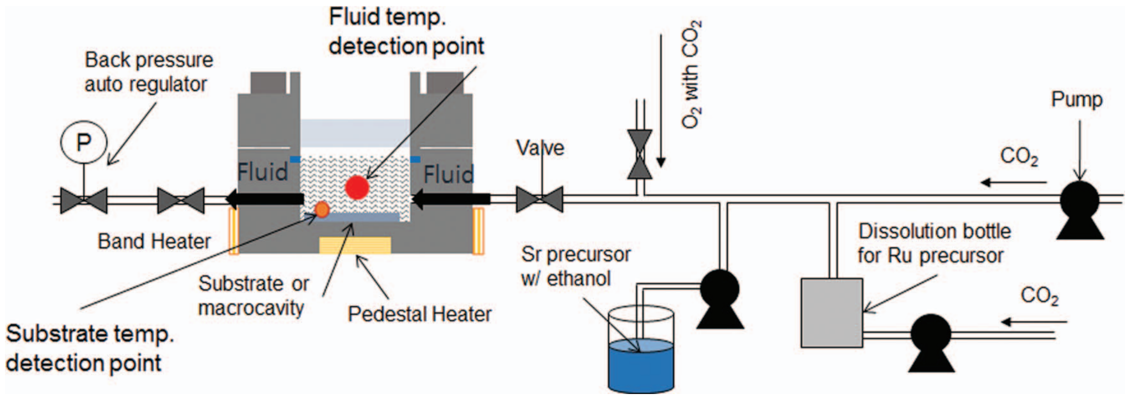

Figure 1. Schematic of the in-house flow-type SCFD setup.

$SrRuO_3$ film had crystalline peaks at (121) and (123) (data not shown here) and agreed with our previous work.[6] Ethanol addition did not affect the purity of the fabricated film, and the films did not contain detectable carbon impurities. Consequently, the electrical resistivity was measured to be about 480 $\mu\Omega\cdot$cm, similar to that of the sample without ethanol.[6] These results indicated that ethanol does not significantly influence the deposited film properties.

The compositional uniformity of the film deposited on the nanoscale trenches is required; however it is rather difficult to be analyzed by XPS due to its large detection area of over 10 μm. We therefore analyzed the compositional profile of the film deposited on the microscale 3D structure called macrocavity, consisting of two facing substrates with 200-μm spacing (Figure 3).[12] Deposition was carried out for 3 h. We analyzed the compositional profile of the film deposited on the microscale 3D structure. Figure 4 shows the compositional profile and film thickness as functions of the distance from the inlets. The film thicknesses decreased with increasing distance from each inlet, whereas the compositional profile was almost uniform around the stoichiometric ratio, even with decreasing film thickness. The stoichiometric ratio ranged from 0.89 to 1.07. Compositional uniformity of $SrRuO_3$ film on the microscale cavity guaranteed a similar uniformity on nanoscale trenches. Lee et al. reported similar results for $SrTiO_3$-SCFD on the nanoscale via holes using transmission electron microscopy combined with energy dispersive X-ray spectroscopy (TEM-EDX).[13] Film thickness uniformity is also an important factor for memory devices, and conformal deposition onto nanoscale trenches covered by thermal SiO_2 with an aspect ratio of 12.5 was confirmed. Figure 5 shows the $SrRuO_3$ film deposited on the trenches whose step coverage was measured to be 0.90. This result also agreed well with the closed-type reactor experiments.

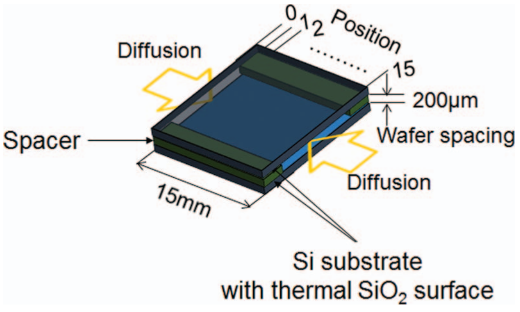

Figure 3. The details of the used macrocavity structure.

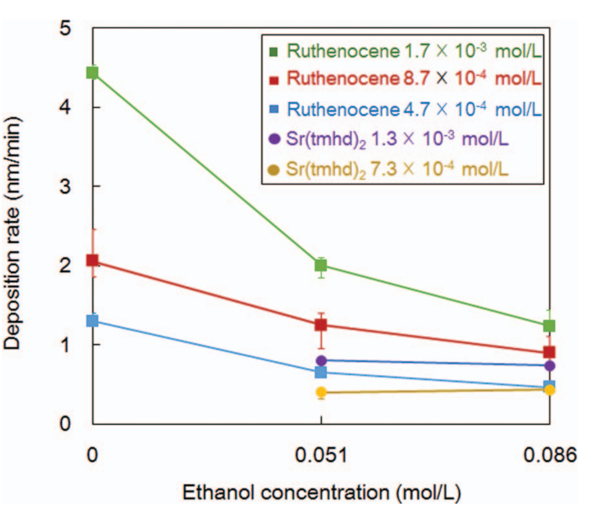

Figure 2. Deposition rate dependence of RuO_2 and SrO on ethanol concentration.

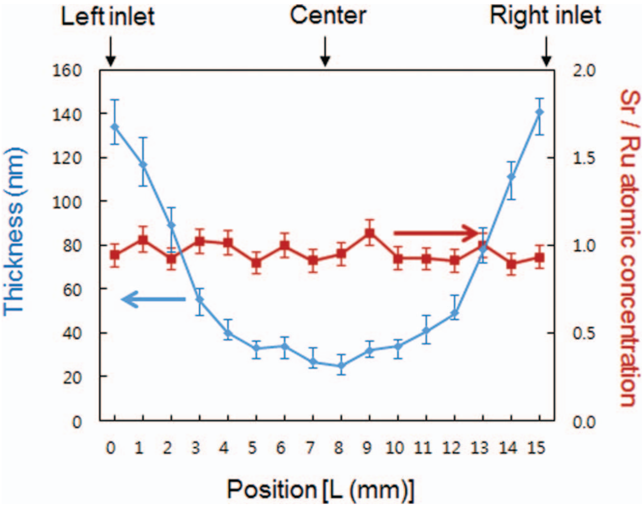

Figure 4. Profiles of $SrRuO_3$ film thickness and composition in the macrocavity.

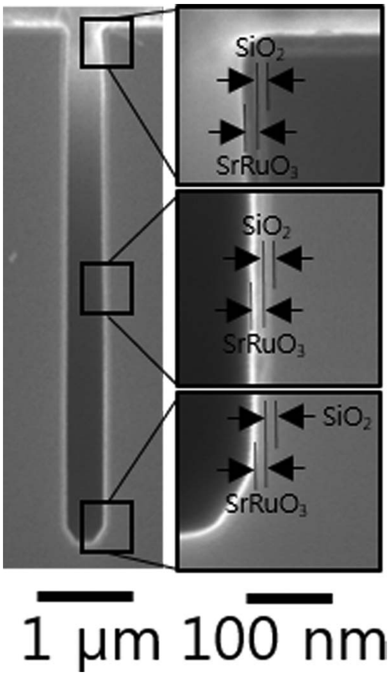

Figure 5. Cross-sectional SEM images of $SrRuO_3$ deposited on 12.5 aspect ratio trenches.

In summary, ethanol addition to $SrRuO_3$-SCFD achieved stoichiometric film formation and supplied high concentrations of Sr precursor using a flow-type reactor. We demonstrated stoichiometric $SrRuO_3$ film formation with compositional uniformity and conformality on high-aspect-ratio features using ethanol-assisted SCFD. The ethanol-assisted $SuRuO_3$-SCFD process has potential applications in the fabrication of high-aspect-ratio memory devices.

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