論文の内容の要旨

A Kinetic Study on Multicomponent Oxide Film Formation Process using Supercritical Fluid

(超臨界流体を利用した複合酸化物薄膜形成プロセスの速度論に関する研究)

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This dissertation focused on multicomponent oxide deposition such as $SrRuO_3$ and $SrTiO_3$ that can be used for memory devices using supercritical fluid based on its kinetic studies. To achieve multicomponent oxide deposition, I have set 4 steps; (1) kinetic studies on SrO and RuO_2, (2) stoichiometric $SrRuO_3$ deposition, (3) kinetic study and potential-step-coverage evaluation for TiO_2 supercritical fluid deposition (SCFD), and (4) process development of stoichiometric $SrTiO_3$ film formation. By realizing each step, I have demonstrated successful multicomponent oxide of $SrRuO_3$ and $SrTiO_3$ SCFD based on the kinetics studies.

$SrRuO_3$ and $SrTiO_3$ were selected as representative materials of multicomponent oxides, because it will be used and promising for dynamic random access memory (DRAM). According to the international technology roadmap for semiconductors (ITRS) 2011, DRAM will adapt three-dimensional structure with aspect ratio of about 70 after 2017. In addition, the memory device will be integrated with a preformed logic circuit to decrease total energy consumption. Thus, there are two requirements for memory capacitor fabrication process; (1) conformal deposition on high-aspect-ratio features, and (2) low process temperature to avoid thermal damage to logic circuit. In these senses, process development of $SrRuO_3$ and $SrTiO_3$ is necessary for the next-generation

memory fabrication. SCFD, which will be discussed in detail, is the most promising method, since it allows to overcome these challenges owing to its unique properties of its reaction medium, supercritical CO_2 ($scCO_2$).

In the SCFD, the system possesses both liquid- and gas-like properties. The SCFD, where oxidation/reduction of organic compounds takes place on a heated substrate to fabricate thin film, enables low temperature process and conformal film deposition. Unlike conventional vacuum based deposition methods, the precursor dissolved into $scCO_2$ achieves high concentration because of liquid-like property of $scCO_2$. The dissolved precursors and $scCO_2$ molecules form "clusters" and decrease the activation energy of reaction, resulting in low process temperature. Gas-like high diffusivity of $scCO_2$ and high precursor concentration contribute to conformation deposition. Taking these two advantages, I have employed the SCFD to form $SrRuO_3$ and $SrTiO_3$.

As there is no report on $SrRuO_3$-SCFD, a simple closed type SCFD system was used to examine the feasibility of $SrRuO_3$ deposition using $Sr(tmhd)_2$ and $Ru(tmhd)_3$. Before deposition of $SrRuO_3$, individual deposition of SrO and RuO_2 was done. It was found that the deposition rate of RuO_2 was much faster than that of SrO. Deposition rate of SrO and RuO_2 was balanced under a Sr-/Ru- precursor concentration ratio of 6 at the temperature of 230°C with the O_2 concentration of 0.3 mol/L. XRD results showed the presence of a crystallized $SrRuO_3$ phase in the deposited film despite a thin film with thickness of 30 nm. The electrical resistivity of the film was measured to be 300 μΩ-cm, and step coverage in Si trenches having an aspect ratio of 10 was measured to be 0.84. The results showed the potential of $SrRuO_3$-SCFD.

For the in-depth study of $SrRuO_3$-SCFD, an in-house flow-type reactor of SCFD was used. Ruthenocene was tested to replace $Ru(tmhd)_3$ to suppress particle generation, where the phenomenon can be accelerated by high O_2 concentration, because ruthenocene formed RuO_2 with less O_2. A series of tests of SrO and RuO_2 deposition revealed that deposition reaction is attributed to intermediate species form by fluid phase reaction of precursor. Ethanol was used to deliver higher concentration

of Sr precursor due to the used Sr precursor's extremely low solubility in $scCO_2$. Ethanol also played a role as a co-solvent that inhibited the RuO_2 growth rate due to the lower deposition rate of SrO compared with RuO_2. Although RuO_2 deposition rate was suppressed by addition of ethanol, it still showed higher deposition rate. When the precursor molar ratio of Sr and Ru precursors was 2.2, a Sr/Ru atomic ratio of 0.95 in film was achieved. Ethanol addition did not induce contamination in the fabricated film, and the crystalline of the formed film was same to the closed type SCFD results. Macrocavity method was utilized to verify compositional profile of the deposited film on the 3D structures. In spite of serous film thickness variation within macrocavity, compositional profile was almost uniform around the stoichiometric ratio. Conformal deposition onto nanoscale trenches covered by thermal SiO_2 with an aspect ratio of 12.5 was then confirmed, and its step coverage was measured to be 0.90.

Previously, despite TiO_2 deposition using $scCO_2$ was reported several times, kinetics of TiO_2-SCFD has not been well understood, and the step coverage of TiO_2 in high-aspect-ratio structures has not been discussed in detail. In this dissertation, I studied the kinetics of TiO_2-SCFD, after successful deposition of TiO_2 without any oxidizer from $Ti(O\text{-}iPr)_2(tmhd)_2$. The kinetic study using macrocavity was carried out in a flow channel reactor, where residence time of precursor was short enough to ignore intermediated species formation in the reactor. I have estimated the surface reaction rate constant of precursor (k_{sp}) and gas phase reaction rate constant (k_g) by using assumed diffusion coefficient (D) of 5×10^{-8} m^2/s. The k_{sp} was calculated to be 3.6×10^{-8} m^2/s, and the low value of k_{sp} indicated that precursor itself did not contribute to thin film deposition directly. The k_g was about 6.0×10^{-3} /s, and it resulted in thin film thickness gradient in the macrocavity. Microcavity method using very-high-aspect-ratio features of (A) 50 (2 μm width and 100 μm depth), (B) 80 (1 μm width, 80 μm depth), and (C) 100 (0.6 μm width, 60 μm depth) was performed to evaluate potential step coverage. Dimensionless number (ϕ) determines the step coverage, and lower ϕ means better step coverage. ϕ

has proportional relationship with square roots of surface reaction rate constant of intermediate species divided by diffusion coefficient ($\frac{k_{si}}{D}$). I extracted $\frac{k_{si}}{D}$ value from microcavity results, and it was calculated to be about 8×10^{1} m^{-1}. The k_{si} was calculated to be about 4.0×10^{-6} m^2/s using the assumed D of 5×10^{-8} m^2/s. The capability of conformal film deposition was evaluated by numerical simulation using the calculated $\frac{k_{si}}{D}$ value. Aspect ratio achieving conformal film deposition by TiO_2-SCFD showed higher value for narrower trenches. The ability of conformal film deposition of SCFD was comparable to atomic layer deposition (ALD).

Finally, I have fabricated a stoichiometric by overcoming two serious problems. First problem of particle generation was solved using a flow channel type reactor. To make the flow channel type reactor, a part to reduce reactor volume called "volume reducer" was fabricated. The flow channel type reactor had short residence time for precursor, so fluid phase reaction, which results in particle generation, was effectively reduced. The other problem, extremely low Sr incorporation, was overcome by using new Sr precursor of $Sr(Cp^*)_2$ and optimizing deposition condition. The using of reactive $Sr(Cp^*)_2$ increased Sr incorporation. However, Sr/Ti atomic concentration in the formed film was still low. Thus, much more Sr precursor than Ti one was used using O_2 concentration of 0.06mol/L. When a Sr-/Ti- precursor molar ratio was 5, a stoichiometric $SrTiO_3$ film was formed. The $SrTiO_3$ film was highly pure, which was successfully deposited on the underlayer of $SrRuO_3$.

In this dissertation, the deposition processes for multicomponent oxides including $SrRuO_3$ and $SrTiO_3$ were established by kinetic studies. The formed $SrRuO_3$ film had high purity, crystallinity, low electrical resistivity and good step coverage. Numerical simulation based on kinetics study for potential step coverage of TiO_2-SCFD demonstrated that SCFD had unrivaled performance of conformal film deposition. Finally, the stoichiometric $SrTiO_3$ was also successfully deposited at low temperature of 250ºC. The results of this dissertation revealed that SCFD has a high potential for multicomponent oxide deposition.