

博士論文（要約）

Process Development of 3-dimensional $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Capacitors in
Ferroelectric Memory using Supercritical Fluid

〔 超臨界流体を利用した $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ 強誘電体メモリ用
三次元キャパシタ形成プロセスの開発 〕

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論文の内容の要旨

論文題目 Process Development of 3-dimensional $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ Capacitors in Ferroelectric
Memory using Supercritical Fluid
(超臨界流体を利用した $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ 強誘電体メモリ用三次元キャパシタ
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This dissertation focused on the deposition process development of 3-dimensional (3D) $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BTO) capacitors for next generation of ferroelectric random access memory (FeRAM). Supercritical CO_2 (scCO_2) was used as the reaction medium, and conformal deposition of TiO_2 , BTO, and RuO_2 (as electrode) films were fabricated on high aspect ratio trenches based on kinetic studies. The work could be separated into 5 steps; (1) fundamental reaction kinetics and diffusivity study in scCO_2 , (2) conformal TiO_2 deposition as a preparation of BTO deposition, (3) stoichiometric and conformal BTO deposition, (4) conformal RuO_2 deposition as the electrode, (5) fabrication of 3D capacitors. By realizing each step, I have demonstrated successful fabrication of $\text{RuO}_2/\text{BTO}/\text{RuO}_2$ 3D capacitors for FeRAM.

FeRAM, which has low power consumption and short access time, is a promising nonvolatile memory and has gained much attention in the past decades. BTO-based ceramics were developed for ferroelectric layers in FeRAM due to their non-volatility, high remanent polarization, and lower coercive field. In recent several years, introduction of 3D structure capacitors has become a trend to decrease the unit size and increase the integration density for memory devices. As for FeRAM, however, according to the international technology roadmap for semiconductors (ITRS), manufacturable solutions for 3D ferroelectric capacitors are still unknown. Conformal thickness

and uniform composition of multi-component oxide (e.g., BTO) are two big issues for conventional deposition techniques. In this work, supercritical fluid deposition (SCFD) was adopted as a novel solution to overcome these issues and fabricate 3D BTO ferroelectric capacitors.

SCFD is a novel deposition technique involving the oxidation/reduction of organic compounds using oxidant/reductant in the liquid-gas-like scCO_2 . SCFD has promising prospects of thin film fabrication on high aspect ratio structures in ultra-large scale integration (ULSI) and micro-electro-mechanical systems (MEMS). Comparing with traditional chemical vapor deposition (CVD) and atomic layer deposition (ALD), SCFD enables highly conformal film deposition on high aspect-ratio (AR) features without compromising the growth rate due to the unique characteristics of the scCO_2 as reaction medium that combines liquid-like properties such as high fluid density and gaseous properties such as high diffusivity. Furthermore, uniform composition of multi-component oxide in trench structure using SCFD was reported. In my subject, SCFD was introduced to fabrication of 3D-BTO capacitors. Starting with fundamental mechanism study in SCFD, kinetics of conformal deposition of TiO_2 films was first investigated as a preparation of BTO fabrication. Then, ferroelectric BTO deposition was enabled by introducing the Bi precursor into the conformal TiO_2 -SCFD. Conformal RuO_2 was deposited as the electrodes on 3D structure. Finally, 3D-capacitor was fabricated for memory devices; $\text{RuO}_2/\text{TiO}_2/\text{RuO}_2$ 3D-capacitors for 3D-dynamic RAM, and $\text{RuO}_2/\text{BTO}/\text{RuO}_2$ 3D-capacitors for the next generation 3D-FeRAM.

As there was few report regarding kinetics study of conformal oxide film deposition in scCO_2 , fundamental study of reaction kinetics and transfer property (diffusivity) was carried out first based on TiO_2 -SCFD, and guidelines of conformal deposition were also summarized. To avoid particle generations and reaction in fluid, a cold-wall flow-type reactor with face-down configuration was designed and used in SCFD. Titanium di(*i*-propoxide) bis(2,2,6,6-tetramethyl-3,5-heptanedionato) [$\text{Ti}(\text{O-}i\text{-Pr})_2(\text{tmhd})_2$] was selected as the precursor due to its good solubility and deposition capability in scCO_2 . Stoichiometric and smooth TiO_2 was deposited from the thermal decomposition of $\text{Ti}(\text{O-}i\text{-Pr})_2(\text{tmhd})_2$ at 250-325°C 10-20 MPa. Linearly increasing growth rate with precursor concentration indicated the first-order reaction kinetics in TiO_2 -SCFD. Regardless of varied pressure, the reaction rate constant (k_s) exponentially increased to the temperature, where the activation energy (E_a) was calculated to be ~50 kJ/mol. A micro-cavity model based on the mass balance was then introduced to analyze the thickness profiles of TiO_2 deposited along trenches, where the ratio of k_s and diffusivity (D), k_s/D , was derived. Therefore, D could be estimated by substituting the obtained k_s . A modified Chapman-Enskog-equation was used to correlate the obtained D . Based on these fundamental studies (reaction kinetics and transfer property), a guideline was summarized to achieve the conformal deposition in SCFD (low

pressure and low temperature to guarantee a small k_s/D).

Conformal TiO_2 was then deposited as a preparation for BTO fabrication, since there was no literatures regarding TiO_2 - nor Bi_2O_3 - SCFD. The guideline obtained from fundamental study (low temperature and low pressure to guarantee a small k_s/D) was applied on TiO_2 -SCFD for conformal deposition, where the effect of temperature on film impurities was also taken into account. Conformal TiO_2 with low carbon impurity (<1 atom%) was deposited on 50 AR trenches at 300°C and 10 MPa. On another hand, as a further study, addition of alcohols was introduced to SCFD to promote the growth rate and precursor concentration simultaneously. Comparing with ethanol and iso-propanol, methanol was found to have the most significant effect on the deposition. The relatively high dielectric constant of methanol was believed to be the reason, since the solvent effect in SCFD could be promoted by high dielectric constant of the fluid, which was confirmed by the decreased activation energy.

Based on the conformal TiO_2 -SCFD, BTO was fabricated by introducing Bi precursor. Mechanism of BTO-SCFD was also studied, where the total growth rate of BTO-SCFD was found to be determined by the concentration of Ti precursor. Considering that the composition was affected by the Ti/Bi precursor ratio, stoichiometric composition of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was then required by tuning the precursor ratio. Based on the conformal TiO_2 -SCFD, conformal BTO was also deposited on 10 aspect ratio trenches. Uniform composition along the depth was also confirmed by Auger electron spectroscopy (AES). Furthermore, after annealing at 400°C, the amorphous as-deposited BTO was successfully crystallized, and a (117) orientation was observed. The conformal crystallized BTO is expected to be the ferroelectrics of the 3D ferroelectric capacitor.

Conformal RuO_2 was prepared as underlayer and bottom electrodes for BTO. RuO_2 was selected due to its good lattice matching with TiO_2 and BTO, while the high work function of RuO_2 (~5 eV) could also guarantee a high barrier height and suppress the leakage from TiO_2 and BTO (work function of ~4.2 eV). Ruthenium tri(2,2,6,6-tetramethyl-3,5-heptanedionato) [$\text{Ru}(\text{tmhd})_3$] was selected for RuO_2 -SCFD. Basic reaction kinetics and conformal deposition were checked at 250°C 10MPa. Despite that the as-deposited RuO_2 was amorphous, crystalline RuO_2 with a preferring (110) orientation was obtained after post annealing in O_2 ambient at 400-700°C. As the bottom electrode in 3D capacitors, the well-crystallized conformal RuO_2 was expected to promote crystallinity and electric properties of TiO_2 and BTO on it, which had been reported in references regarding 2D capacitor fabrication.

Finally, TiO_2 and BTO were stacked with RuO_2 to form 3D capacitors. 2D capacitors were also fabricated for characterization of electric properties, which was promoted by modification of the

post annealing process. I-V, C-V, and hysteresis loop measurements were employed to estimate the leakage density, dielectric constant of TiO₂, and ferroelectric properties of BTO, respectively. The dielectric capacitors using SCFD-TiO₂ as insulator showed low leakage of $\sim 10^{-6}$ A/cm² and relatively high dielectric constant of ~ 70 , which has promising prospects on the dynamic RAM. The ferroelectric RuO₂/BTO/RuO₂ capacitor had remanent polarization of ~ 4 μ C/cm² and coercive field of ~ 50 kV/cm, which is expected to be applied in 3D-FeRAM. 3D capacitors using TiO₂ and BTO were enabled in the end of this work. Doped Si with >10 AR trenches was used as the substrate and enabled the bottom contact with SCFD-RuO₂ during electric characterization. Top electrodes were also fabricated by the conformal SCFD-RuO₂. Superiority of the 3D configuration was expected.

In this dissertation, 3D capacitors were successfully composed with RuO₂/TiO₂/RuO₂ and RuO₂/BTO/RuO₂ structure using SCFD. It is expected to be the first solution to achieve conformality of both thickness and composition for multi-component 3D capacitors. First, conformal TiO₂-SCFD and its reaction kinetics / diffusivity were studied as a preliminary research of BTO-SCFD. Deposition mechanism was investigated to optimize reaction conditions to achieve conformal films on high AR trenches. Then, BTO was fabricated by introducing Bi precursor into the conformal TiO₂-SCFD process. Stoichiometric and conformal BTO-SCFD was achieved via mechanism study, where Ti precursor determined the thickness profiles along trenches. Finally, after obtaining conformal SCFD-RuO₂ as the electrode material, 3D capacitors using TiO₂ and BTO were fabricated, which has promising prospects on 3D memory devices.