Preparation and Dielectric Properties of Ca-Doped Sr$_2$(Nb$_{0.3}$Ta$_{0.7}$)$_2$O$_7$ Thin Films by Chemical Solution Deposition Method

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Ca-doped Sr$_2$(Nb, Ta)$_2$O$_7$ thin films have been synthesized by the chemical solution deposition. Homogeneous and stable precursor solutions were prepared by controlling the reaction of starting metal alkoxides. The improvement of ferroelectric properties of the Sr$_2$(Nb, Ta)$_2$O$_7$-based films were achieved through the Ca-substitution for Sr sites in the Sr$_2$(Nb$_{0.3}$Ta$_{0.7}$)$_2$O$_7$ structure. (Sr$_{1-x}$Ca$_x$)$_2$(Nb$_{0.3}$Ta$_{0.7}$)$_2$O$_7$ crystallized in the single-phase of (Sr, Ca)$_2$(Nb$_{0.3}$Ta$_{0.7}$)$_2$O$_7$ in the case of x < 0.15 without any formation of the second phase such as CaTa$_2$O$_7$. The crystallization temperature of the layered perovskite Sr$_2$(Ca$_{1-x}$)$_2$(Nb$_{0.3}$Ta$_{0.7}$)$_2$O$_7$ thin films on Pt/Ir/Ti/SiO$_2$/Si substrates was found to be below 700°C. (Sr$_{0.7}$Ca$_{0.1}$)$_2$(Nb$_{0.3}$Ta$_{0.7}$)$_2$O$_7$ thin films crystallized at 750°C exhibited the typical ferroelectric hysteresis loop with $P_C$ of 0.58 µC/cm$^2$ and Ec of 80 kV/cm.

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1. Introduction

Ferroelectric thin films have been receiving great attention for the applications in various integrated thin film devices such as nonvolatile memories. In the case of memories, ferroelectric thin films with high quality are strongly required. Recently, metal/ferroelectric/metal/insulator/semiconductor field-effect transistor (MFMIS-FET) type memory devices have been investigated extensively because of their advantages of the miniaturization of memory cells. However, when the dielectric constant of ferroelectric in its structure is high, only a small portion of the working voltage is applied on the ferroelectric layer in such devices. Therefore, a new ferroelectric material with low dielectric constant is strongly demanded instead of well-known Pb(Zr, Ti)O$_3$ (PZT) or SrBi$_2$Ta$_2$O$_9$ (SBT)-related materials. Sr$_2$(Nb, Ta)$_2$O$_7$ (SNT)-based materials are the most suitable candidate ferroelectrics for nonvolatile memory such as an MF(M)IS-FET type because of the low dielectric constant and high thermal stability. Several researchers reported the processing and properties of SNT thin films. The substitution of Nb for Ta site of Sr$_2$TaO$_6$ has been carried out in order to control the Curie temperature of SNT phase for ferroelectric applications. The increase in Nb/Ta ratio is effective to decrease the crystallization temperature of desired ferroelectric SNT phase. However, the fabrication of SNT thin film with good ferroelectric properties at low temperatures is known to be still difficult. Also, the Nb-rich SNT films tend to crystallize into the b-axis oriented film, which is perpendicular to the direction of polarization for SNT crystals. Therefore, the authors examined the calcium (Ca)-substituted SNT (SCNT) thin films by a chemical solution deposition in order to overcome these problems. Further investigation is required on the optimum amount of Ca-substitution into the SNT thin films.

This paper focuses on the synthesis of Ca-substituted Sr$_2$(Nb, Ta)$_2$O$_7$ (SCNT) thin films on Pt/Ir/Ti/SiO$_2$/Si substrates via the chemical solution deposition using metal alkoxide precursor solutions. The effect of Ca-substitution into Sr$_2$(Nb, Ta)$_2$O$_7$ with a Ta rich composition was mainly studied on the crystallization behavior, microstructure and ferroelectric properties of alkoxo-derived SCNT thin films.

2. Experimental procedure

Figure 1 shows a flow diagram for the synthesis of (Sr, Ca)$_2$(Nb$_{0.3}$Ta$_{0.7}$)$_2$O$_7$ thin films. Sr(OC$_3$H$_7$)$_2$, Ca(OC$_3$H$_7$)$_2$, Nb(OC$_3$H$_7$)$_5$, and Ta(OC$_3$H$_7$)$_5$ [Kojundo Chemical, Japan] were selected as starting materials. All procedures were conducted in a dry N$_2$ atmosphere for preparing precursor solutions and films. Sr(OC$_3$H$_7$)$_2$ and Ca(OC$_3$H$_7$)$_2$ corresponding to $(Sr_{1-x}Ca_x)$_2$(Nb$_{0.3}$Ta$_{0.7}$)$_2$O$_7$ (SCNT) (x = 0.0, 0.05, 0.1, 0.15, 0.25 and 0.5) compositions were dissolved in absolute ethanol of 0.1 mol/L. 2-Ethoxyethanol was added to the solution as a stabilizing agent. The molar ratio of 2-ethoxyethanol to (Sr, Ca)$_2$(Nb, Ta)$_2$O$_7$ (SCNT) precursor was set at 14. The solution was refluxed at 80°C for 1 h, and then mixed with an ethanol solution of Nb(OC$_3$H$_7$)$_5$ and Ta(OC$_3$H$_7$)$_5$. The mixed solution was refluxed again for 18 h yielding a 0.1 mol/l precursor solution.

Films were fabricated using the SCNT precursor solutions by spin-coating at 3000 rpm for 30 s on Pt/Ir/Ti/SiO$_2$/Si substrates. The deposited films were calcined at 500°C for 1 h at a heating rate of 10°C/min, and then heated to crystallization temperatures by a rapid thermal heating (200°C/min) in an O$_2$ flow. The coating-crystallization process was repeated several times in order to increase the film thickness.

![Fig. 1. A flow diagram for the synthesis of (Sr, Ca)$_2$(Nb$_{0.3}$Ta$_{0.7}$)$_2$O$_7$ thin films.][1]

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The prepared films were characterized by X-ray diffraction (XRD) [Rigaku, RINT2100/PC] analysis using Cu Kα radiation with a monochromator. Synthesized films were observed by scanning electron microscopy (SEM) [JEOL, JSM-6100]. The surface topography of the films was observed by an atomic force microscope [OLYMPUS NV2000]. Pt electrodes of 0.20 mm diameter were deposited by sputtering on the film as a top electrode. The dielectric measurement was conducted on the thin films using an impedance gain-phase analyzer [HP, 4194A] at 1-1000 kHz. The ferroelectric and fatigue properties of films were evaluated with ferroelectric test systems [Radiant Technology, RT66A and Aix ACCT, Inc., TFA-ANALYZER 2000] at 100 Hz. The applied voltage was 1-20 V.

3. Results and discussion

Figure 2 illustrates XRD profiles of \( \text{Sr}_{x} \text{Ca}_{1-x} \text{Ti}_{2-x} \text{Nb}_{3} \text{Ta}_{0.7} \text{O}_{12} \) (SCNT(0.1)) thin films on Pt/Ir/Ti/SiO\(_2\)/Si substrates heat-treated at various temperatures for 5 min. Pt/Ir/

Ti/SiO\(_2\)/Si substrate is used for the current synthesis, because the Ir layer was found to be effective to improve the thermal stability of Pt layer. The rapid thermal heating was able to achieve the high crystallinity and suppress the diffusion of elements between films and layered substrates. The films began to crystallize in the layered perovskite SCNT phase below 700°C. The crystallinity improved with increasing annealing temperature. It turned out from Fig. 2 that SCNT (0.1) thin films crystallized with high crystallinity above 750°C. These films didn’t show the b-axis preferred orientation compared with the SNT films with Nb-rich composition.\(^3\,A\)

Figure 3 illustrates XRD profiles of \( \text{Sr}_{x} \text{Ca}_{1-x} \text{Ti}_{2-x} \text{Nb}_{3} \text{Ta}_{0.7} \text{O}_{12} \) (SCNT(x)) thin films on Pt/Ir/Ti/SiO\(_2\)/Si substrates heat-treated at 750°C for 5 min. Ca-substituted films were found to exhibit high crystallinity compared with that of non-substituted \( \text{Sr}_{x} \text{Ti}_{2-x} \text{Nb}_{3} \text{Ta}_{0.7} \text{O}_{12} \) film prepared under the same conditions. Also, the crystallinity was improved with increasing Ca-substituted content. However, in the case of \( x \geq \)

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**Fig. 2.** XRD profiles of SCNT(0.1) thin films prepared on Pt/Ir/Ti/SiO\(_2\)/Si substrates at (a) 700°C, (b) 750°C, (c) 800°C and (d) 900°C.

**Fig. 3.** XRD profiles of SCNT(x) thin films prepared on Pt/Ir/Ti/SiO\(_2\)/Si substrates at 750°C. [Ca content: (a) \( x = 0 \), (b) \( x = 0.05 \), (c) \( x = 0.1 \), (d) \( x = 0.15 \), (e) \( x = 0.25 \) and (f) \( x = 0.5 \)]

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**Fig. 4.** P-E hysteresis loops of SCNT(x) thin films prepared on Pt/Ir/Ti/SiO\(_2\)/Si substrates at 750°C. [Ca content: (a) \( x = 0 \), (b) \( x = 0.05 \), (c) \( x = 0.1 \) and (d) \( x = 0.15 \)]
0.15 compositions, the formation of Ca$_2$Ta$_2$O$_7$ was observed as a second phase.

Figure 4 shows P–E hysteresis loops of (Sr$_{1-x}$Ca$_x$)$_2$Nb$_{0.3}$Ta$_{0.7}$O$_7$ (SCNT(x)) thin films on Pt/Ir/Ti/SiO$_2$/Si substrates. The thickness of the films was approximately 300 nm. The SCNT(x) thin films showed typical P–E hysteresis loops at room temperature as shown in Fig. 3. This result indicates that the synthesized SCNT film is ferroelectric at room temperature. The SCNT(0.1) films showed the highest remnant polarization of 0.58 μC/cm$^2$. It was considered that Ca-substitution induced to increase the distortion of Nb-O octahedra in Sr$_2$(Nb, Ta)$_2$O$_7$ structure and as a result, remnant polarization could be improved as compared with non-substituted Sr$_2$(Nb$_{0.3}$Ta$_{0.7}$)O$_7$ films. In the case of x ≥ 0.15, Ca$_2$Ta$_2$O$_7$, phase, which is a paraelectric with pyrochlore structure as mentioned above, was formed as a second phase. Since the dielectric constant of Ca$_2$Ta$_2$O$_7$ is lower than that of SCNT, the effective applied voltage on SCNT film becomes actually smaller, resulting in the decrease of remnant polarization.

Figure 5 shows the temperature dependence of dielectric constant and tan δ for SCNT(0.1) thin films prepared at 750°C on Pt/Ir/Ti/SiO$_2$/Si substrate. The 750°C-anealed thin film had dielectric constant of about 40 and tan δ of less than 0.04. These values are very suitable for MF(M)IS-FET-type memory devices.

Figure 6 shows the fatigue properties of SCNT(0.1) thin film on Pt/Ir/Ti/SiO$_2$/Si substrate. This film shows very good fatigue endurance until 109 switching cycles. A slight decrease in remnant polarization about 10% was observed at 10$^8$ cycles with no dielectric breakdown.

4. Conclusions

(Sr, Ca)$_2$(Nb, Ta)$_2$O$_7$ precursor solutions with high homogeneity and stability could be prepared by the reaction of metal alkoxides in ethanol-2-ethoxyethanol mixed solvent system. The optimum Ca-substitution for Sr sites in the SNT structure was found to be effective not only in the improvement of ferroelectric properties, but also in achieving the high crystallinity of the resultant films. The SCNT(0.1) thin film prepared at 750°C showed the highest remnant polarization of 0.58 μC/cm$^2$. The dielectric constant of the SCNT(0.1) thin films on Pt/Ir/Ti/SiO$_2$/Si was about 40 with low tan δ over wide temperature region. The (Sr, Ca)$_2$(Nb, Ta)$_2$O$_7$ films synthesized in this study are expected to be a promising ferroelectric layer of MFIS-FETs or MFMIS–FETs.

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References


![Graph](image1)

Fig. 5. Temperature dependence of dielectric constant and tand at 1 MHz for SCNT(0.1) thin film prepared on Pt/Ir/Ti/SiO$_2$/Si substrate at 750°C.

![Graph](image2)

Fig. 6. (a) Fatigue property and (b) P–E hysteresis loops of SCNT(0.1) thin film prepared on Pt/Ir/Ti/SiO$_2$/Si substrate at 750°C.