研究

Synthesis and Properties of V-Doped $(\text{Sr,Ca})_2(\text{Nb,Ta})_2\text{O}_7$ Thin Films by Chemical Solution Deposition

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Received July 8, 2005

SYNOPSIS

Ca- and V-codoped $\text{Sr}_2(\text{Nb,Ta})_2\text{O}_7$ thin films have been fabricated by the chemical solution deposition. Homogeneous and stable precursor solutions were prepared by controlling the reaction of starting metal-organic compounds. The improvement of ferroelectric properties of the $\text{Sr}_2(\text{Nb,Ta})_2\text{O}_7$ -based films were achieved through the V doping to the $(\text{Sr}_{0.9}\text{Ca}_{0.1})_2(\text{Nb}_{0.3}\text{Ta}_{0.7})_2\text{O}_7$. In the composition range of $0 \leq x \leq 0.15$, $(\text{Sr}_{0.9}\text{Ca}_{0.1})_2\{(\text{Nb}_{0.3}\text{Ta}_{0.7})_{1-x}\text{V}_x\}_2\text{O}_7$ (SCNTV_x) thin films crystallized in the single-phase of $(\text{Sr,Ca})_2(\text{Nb,Ta})_2\text{O}_7$ without any formation of the second phase. The crystallization temperature of the layered perovskite SCNTV_x thin films on Pt/Ir/Ti/SiO₂/Si substrates was found to be below 700 °C. Synthesized SCNTV_x thin films showed the low dielectric constant with low loss tangent over wide frequency and temperature regions. Furthermore, the SCNTV_x thin films with an optimum amount of V could be crystallized at 650 °C and exhibited the typical ferroelectric hysteresis loop with a Pr of 0.8 μC/cm² and a E_c of 75 kV/cm.

KEY WORDS

$\text{Sr}_2(\text{Nb,Ta})_2\text{O}_7$, thin film, chemical solution deposition, Ca and V doping, ferroelectric properties

1 Introduction

Thin film processing of ferroelectric materials has been receiving considerable attention for the applications in various integrated thin film devices such as nonvolatile memories. In the case of memory devices, low temperature processing of ferroelectric thin films is strongly demanded. Recently, metal/ferroelectric(/metal)/insulator/semiconductor field-effect transistor (MF(M)IS-FET)-type memory devices have been investigated extensively because of their advantages of the miniaturization of memory cells. However, when the dielectric constant of ferroelectrics 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 required instead of well-known $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT)- or Bi-layered perovskite-related materials¹⁾.

$\text{Sr}_2(\text{Nb,Ta})_2\text{O}_7$ (SNT)-based materials are the most suitable candidate ferroelectrics for nonvolatile memory such as an MF(M)IS-FET-type because of their low dielectric constant and high thermal stability²⁾. Several researchers reported the processing and properties of SNT thin films³⁻⁶⁾. The substitution of Nb for Ta site of $\text{Sr}_2\text{Ta}_2\text{O}_7$ has been performed in order to control the Curie temperature

of SNT phase for ferroelectric applications. In this case, 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 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^{3,4,7)}. Therefore, the authors examined the calcium (Ca)-substituted SNT (SCNT) thin films by a chemical solution deposition in order to overcome these problems^{8,9)}. However, further investigation is required on the low temperature fabrication of the SCNT thin films.

This paper describes on the fabrication of Ca- and V-doped $\text{Sr}_2(\text{Nb,Ta})_2\text{O}_7$ (SCNTV) thin films on Pt/Ir/Ti/SiO₂/Si substrates via the chemical solution deposition using metal-organic precursor solutions. The effect of V doping to $(\text{Sr,Ca})_2(\text{Nb,Ta})_2\text{O}_7$ was mainly studied on the low temperature crystallization and electrical properties of chemically derived SCNTV thin films.

2 Experimental Procedure

For the synthesis of V-doped $(\text{Sr,Ca})_2(\text{Nb,Ta})_2\text{O}_7$ thin films, $\text{Sr}(\text{OEt})_2$, $\text{Ca}(\text{OEt})_2$, $\text{Nb}(\text{OEt})_5$, $\text{Ta}(\text{OEt})_5$ and

$\text{VO}(\text{OEt})_3$ [Kojundo Chemical, Japan] were selected as starting materials. All procedures were conducted in a dry N_2 atmosphere for preparing precursor solutions and films. $\text{Sr}(\text{OEt})_2$ and $\text{Ca}(\text{OEt})_2$ corresponding to the $(\text{Sr}_{0.9}\text{Ca}_{0.1})_2\{(\text{Nb}_{0.3}\text{Ta}_{0.7})_{1-x}\text{V}_x\}_2\text{O}_7$ [SCNTV_x, $x=0.0, 0.05, 0.1$ and 0.15] compositions were dissolved in absolute ethanol. 2-Ethoxyethanol was added to the solution as a stabilizing agent. The molar ratio of 2-ethoxyethanol to $(\text{Sr,Ca})_2(\text{Nb,Ta,V})_2\text{O}_7$ (SCNTV) precursor was set at 14. The solution was refluxed at 80°C for 1 h, and then mixed with an ethanol solution of $\text{Nb}(\text{OEt})_5$, $\text{Ta}(\text{OEt})_5$ and $\text{VO}(\text{OEt})_3$. The mixed solution was refluxed again for 18 h yielding a 0.1 M precursor solution.

Films were fabricated using the SCNTV precursor solutions by spin-coating on Pt/Ir/Ti/SiO₂/Si substrates. The deposited films were calcined at 500°C for 1 h at a heating rate of $10^\circ\text{C}/\text{min}$, and then heated to crystallization temperatures by a rapid thermal heating ($200^\circ\text{C}/\text{min}$) in an O_2 flow. The coating-crystallization process was repeated several times in order to increase the film thickness.

The prepared films were characterized by X-ray diffraction (XRD) [Rigaku, RINT2100/PC] analysis using $\text{CuK}\alpha$ 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 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 various temperatures. The ferroelectric, leakage current and fatigue properties of the films were evaluated with ferroelectric test systems [Radiant Technology, RT66A and Aix ACCT. Inc., TFA-ANALYZER 2000].

3 Results and Discussion

3.1 Synthesis of V-doped $(\text{Sr,Ca})_2(\text{Nb,Ta})_2\text{O}_7$ thin films

The authors have already reported that Ca substitution for Sr site in $\text{Sr}_2(\text{Nb}_{0.3}\text{Ta}_{0.7})_2\text{O}_7$ accelerates the low temperature crystallization and improves the ferroelectric properties of resultant films^{8,9}. The Ca substitution to $\text{Sr}_2(\text{Nb}_{0.3}\text{Ta}_{0.7})_2\text{O}_7$ was considered to enhance the stability of layered perovskite $\text{Sr}_2(\text{Nb,Ta})_2\text{O}_7$ structure and induce to increase the distortion of Nb–O octahedra in $\text{Sr}_2(\text{Nb,Ta})_2\text{O}_7$ structure. As a result, crystallinity and ferroelectricity could be improved as compared with non-substituted $\text{Sr}_2(\text{Nb}_{0.3}\text{Ta}_{0.7})_2\text{O}_7$ films. The fabrication temperature of ferroelectric SCNT films was lowered to 750°C . In this study, further investigations of lower processing temperature

were carried out. In this case, the optimum amount of Ca substitution to $\text{Sr}_2(\text{Nb}_{0.3}\text{Ta}_{0.7})_2\text{O}_7$ was determined on the basis of the previous work⁹.

Fig. 1 illustrates XRD pattern and P–E hysteresis loop of $(\text{Sr}_{0.9}\text{Ca}_{0.1})_2(\text{Nb}_{0.3}\text{Ta}_{0.7})_2\text{O}_7$ (SCNT) thin film on Pt/Ir/Ti/SiO₂/Si substrate heat-treated at 700°C . Although SCNT thin film crystallized in the layered perovskite SCNT phase at 700°C , the crystallinity of the film was found to be poor (Fig. 1 (a)). The SCNT thin films crystallized with high crystallinity at 750°C ^{8,9}. Also, it revealed from Fig. 1 (b) that the SCNT thin films did not show any ferroelectric P–E hysteresis loop at room temperature. This result is due to the poor crystallinity of the 700°C -processed SCNT thin film. Therefore, further improvement of processing conditions was required. In this case, vanadium (V) is selected as a dopant, because the effect of V doping on the grain growth behavior and electrical properties of $\text{Sr}_2\text{Nb}_2\text{O}_7$ was reported by S.Seraji et al¹⁰.

For the fabrication of V-doped SCNT thin films, homogeneous and stable $(\text{Sr,Ca})_2(\text{Nb,Ta,V})_2\text{O}_7$ precursor

Fig.1 (a) XRD pattern and (b) P–E hysteresis loop of $(\text{Sr}_{0.9}\text{Ca}_{0.1})_2(\text{Nb}_{0.3}\text{Ta}_{0.7})_2\text{O}_7$ (SCNT) thin film prepared at 700°C on Pt/Ir/Ti/SiO₂/Si substrate.

solutions were prepared by optimizing the V concentration and the processing conditions. Fig. 2 illustrates XRD profiles of $(\text{Sr}_{0.9}\text{Ca}_{0.1})_2\{(\text{Nb}_{0.3}\text{Ta}_{0.7})_{1-x}\text{V}_x\}_2\text{O}_7$ (SCNTV_x) thin films on Pt/Ir/Ti/SiO₂/Si substrates heat-treated at 700 °C for 5 min. V-doped SCNT films were found to exhibit high crystallinity compared with that of non-doped SCNT thin films prepared under the same conditions. Also, the crystallinity was improved with increasing the V content. These films didn't show the b-axis preferred orientation compared with the SNT films with Nb-rich composition^{3,4}. However, when the V content (x) was above 0.15, SCNTV_x thin films could not be synthesized because of the poor stability of the SCNTV_x precursor solutions.

3.2 Electrical properties of V-doped $(\text{Sr,Ca})_2(\text{Nb,Ta})_2\text{O}_7$ thin films

Fig. 3 shows P-E hysteresis loops of SCNTV_x thin films on Pt/Ir/Ti/SiO₂/Si substrates. The thickness of the films was approximately 300 nm confirmed by the SEM observation. The SCNTV_x thin films showed typical P-E hysteresis loops at room temperature as shown in Fig. 3. This result indicates that the synthesized SCNTV_x films are ferroelectric at room temperature. The SCNTV_x films showed the remanent polarization of around 1.0 $\mu\text{C}/\text{cm}^2$. This value is appropriate for MF(M)IS-FET applications. V doping to SCNT enhanced the crystallinity and grain growth of resultant films confirmed by XRD and AFM analyses and as a result, remnant polarization could be improved as compared with non-doped SCNT thin films.

Fig. 4 shows the frequency dependences of dielectric constant and $\tan\delta$ for SCNTV_x thin films prepared at 700 °C on Pt/Ir/Ti/SiO₂/Si substrates. The SCNTV_x thin films had low dielectric constants below 50 with small values of $\tan\delta$

over wide frequency range between 100 Hz and 1 MHz. It can be seen from Fig. 4 that V-doped SCNT thin films showed relatively high dielectric constants compared to non-doped SCNT thin films. However, these values were low enough for applying in a ferroelectric layer of MF(M)IS-FET.

Fig. 5 shows the temperature dependences of dielectric constant and $\tan\delta$ for SCNTV_{0.1} thin film prepared at 700 °C on Pt/Ir/Ti/SiO₂/Si substrate. The 700 °C-annealed SCNTV_{0.1} thin film exhibited dielectric constant of around 45 and $\tan\delta$ of less than 0.03 over wide temperature region. This temperature stability is also important for MF(M)IS-FET-type memory device applications.

Fig. 6 shows the leakage current property of SCNTV_{0.1} thin film prepared at 700 °C on Pt/Ir/Ti/SiO₂/Si substrate.

Fig. 2 XRD profiles of $(\text{Sr}_{0.9}\text{Ca}_{0.1})_2\{(\text{Nb}_{0.3}\text{Ta}_{0.7})_{1-x}\text{V}_x\}_2\text{O}_7$ (SCNTV_x) thin films prepared at 700 °C on Pt/Ir/Ti/SiO₂/Si substrates [V content: (a) x=0, (b) x=0.05, (c) x=0.1, (d) x=0.15].

Fig. 3 P-E hysteresis loops of SCNTV_x thin films prepared at 700 °C on Pt/Ir/Ti/SiO₂/Si substrates [V content: (a) x=0.05, (b) x=0.1 and (c) x=0.15].

Fig.4 Frequency dependences of dielectric constant and $\tan\delta$ of SCNTV_x thin films prepared at 700 °C on Pt/Ir/Ti/SiO₂/Si substrates [V content: x = 0, 0.05, 0.10 and 0.15].

Fig.5 Temperature dependences of dielectric constant and $\tan\delta$ at 100 KHz for SCNTV_{0.1} thin film prepared at 700 °C on Pt/Ir/Ti/SiO₂/Si substrate.

Leakage current densities were found to be less than 10^{-6} A/cm² to an electric field of 200 kV/cm. Since the fatigue endurance is also important for the practical use, further investigation about ferroelectric fatigue behavior was carried out. As a result, the SCNTV_{0.1} thin film showed good fatigue endurance until 10^{10} switching cycles. Although a slight decrease in remnant polarization about a few percent was observed at 10^{10} cycles with no dielectric

Fig.6 Leakage current property of SCNTV_{0.1} thin film prepared at 700 °C on Pt/Ir/Ti/SiO₂/Si substrate.

Fig.7 P-E hysteresis loop of SCNTV_{0.15} thin film prepared at 650 °C on Pt/Ir/Ti/SiO₂/Si substrate.

breakdown, the P_r value and the shape of the P-E hysteresis loop did not change after 10^{10} cycles.

Form the data described above, it turns out that V doping to SCNT is effective to achieve the low temperature fabrication and improve the ferroelectric properties. However, fabrication temperature of ferroelectric SCNTV_x thin films was not low enough, further optimization of the V content was examined. Fig. 7 shows P-E hysteresis loop of SCNTV_{0.15} thin film prepared at 650 °C. The SCNTV_{0.15} thin film exhibited the typical ferroelectric hysteresis loop with a P_r of $0.8 \mu\text{C}/\text{cm}^2$ and a E_c of 75 kV/cm. The P_r value of the film was as large as that for SCNTV_{0.15} thin film prepared at 700 °C shown in Fig. 3. Of course, the SCNT_{0.15} thin film crystallized in the SCNT single-phase at 650 °C and the crystallinity was as high as 700 °C-processed film. This fact is important for

fabricating the SNT-based thin films combining with the silicon semiconductor device processes.

4 Conclusions

$(\text{Sr,Ca})_2(\text{Nb,Ta,V})_2\text{O}_7$ precursor solutions with high homogeneity and stability could be prepared by optimizing the V concentration and the processing conditions. The V doping to the SCNT was found to be effective not only in improving the ferroelectric properties, but also in achieving the high crystallinity of the resultant films. The SCNTV_{0.1} thin film prepared at 700 °C showed the remanent polarization of 1.0 $\mu\text{C}/\text{cm}^2$. The dielectric constant of the SCNTV_{0.1} thin films on Pt/Ir/Ti/SiO₂/Si was below 50 with low $\tan\delta$ over wide frequency and temperature regions. Also, the SCNTV_{0.1} thin films exhibited good leakage current and ferroelectric fatigue properties. Low temperature fabrication of the SCNTV_x thin films was achieved by optimizing the V doping to SCNT. The $(\text{Sr,Ca})_2(\text{Nb,Ta,V})_2\text{O}_7$ films synthesized in this study are expected to be a promising the ferroelectric layer of MFIS-FETs or MFMIS-FETs.

Acknowledgement

This work was supported by a Grant-in-Aid for Scientific Research on Priority Areas (B), No. 12134203 from the Ministry of Education, Culture, Sports, Science and Technology, Japan and by The Kurata Memorial Hitachi Technology Foundation.

The authors would like to thank Prof. Hayashi of Shonan Institute of Technology for collaborating on the measurement of fatigue properties in this study.

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