

Fabrication and Evaluation of SrTa₂O₆ Thin Films Using Chemical Solution Deposition Method

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Abstract. SrTa₂O₆ (STA) thin films were fabricated using two Chemical Solution Deposition methods, the Metal-Organic Decomposition (MOD) method and the Sol-Gel method. Electrical properties of STA thin films were investigated with a metal-insulator-metal structure. Both of the STA thin films deposited by the two methods were crystallized at 800 °C. The dielectric constants (ϵ) of crystalline thin films were much higher than those of amorphous thin films. The ϵ of about 150 for crystalline STA thin films fabricated by the Sol-Gel method is lower than that by the MOD method, but its leakage current density was improved markedly from 10^{-3} to 10^{-8} A/cm² at 250 kV/cm. The larger leakage current is regarded as the reason of higher ϵ .

Introduction

Along with the miniaturization of electronic devices high-k materials are needed to replace conventional SiO₂ in a broad range of application areas, such as information storage capacitors for future dynamic random access memories (DRAMs), embedded capacitors, tunable devices and gate oxides for field effect transistors [1, 2]. The research and application of some high-k materials including Al₂O₃, HfO₂, ZrO₂ and Ta₂O₅ have already performed [2-7]. Recently, SrTa₂O₆ (STA) has attracted much attention because of its high dielectric constant and low leakage current density [2, 8-13]. Several deposition methods have been used to investigate its fundamental electrical properties with a metal-insulator-metal (MIM) structure, such as Metal Organic Chemical Vapor Deposition (MOCVD) [2], Plasma-Enhanced Atomic Layer Deposition [9] and Sputtering [8]. However, reports on using the Chemical Solution Deposition (CSD) method are rare in the literature.

The CSD method possesses many advantages in preparing oxide thin films, such as good homogeneity, lower processing temperature, precise control of composition, simplicity and lower equipment cost [14]. However, the fabrication conditions of the CSD method greatly affect the micro-structures [15] and the electrical properties. Therefore, in this study, we investigated the capacitance vs. frequency and leakage current properties of STA thin films by two CSD methods, the Metal-Organic Decomposition (MOD) method and the Sol-Gel method, under various fabrication conditions.

Experimental

In the MOD method, the composition and concentration of the STA precursor was 0.1 mol/L SrO-TaO_{2.5} solution (Kojundo Chemical Lab.). To increase wetness, the solution was diluted with butyl acetate in a 1:1 ratio. In the Sol-Gel method, the composition and concentration of the STA precursor were set at Sr/Ta = 1/2 and 7 wt%, respectively. The prepared precursors were spin-coated on Pt/TiO_x/SiO_x/Si (Pt/Si) substrates at 3000 rpm for 30 sec. Then the MOD-prepared films were dried at 150 °C for 1 min and pyrolyzed at 250 °C for 4 min; the Sol-Gel-prepared films were dried at 100 °C for 5 min and pyrolyzed at 450 °C for 3 min on hot plates in air. This coating and heating treatment was repeated four times, until the thicknesses reached about 150 nm for the MOD method and 200 nm for the Sol-Gel method. After these processes, samples were annealed from 500 to 800 °C for 30 min in air using a tube furnace. Figure 1 shows the fabrication process of STA thin films.

To measure the electrical properties, Pt top electrodes with a diameter of about 0.09 mm were deposited through shadow masks using the rf sputtering method.

The crystal structure and composition of obtained films were evaluated by X-ray Diffractometry (XRD: X'pert MRD, PANalytical) and X-ray fluorescence (XRF: MagiX Pro, PANalytical). Surface morphologies were observed with Atomic Force Microscopy (AFM: SPA400, Seiko Instruments). For accuracy several points were measured on each sample. Deposited film thicknesses were determined by Transmission Electron Microscope (TEM: JEM-3100FEF, JEOL). Leakage currents were measured with Programmable Electrometer (Keithley617, Keithley). A hold time of 30 sec was set for each measuring point to eliminate relaxation process effects. Capacitance vs. frequency and capacitance vs. voltage properties were measured by Impedance Analyzer (HP4149A, Hewlett-Packard). All of the electrical properties were measured at room temperature.

Results and Discussions

Figure 2(a) and 2(b) show the XRD patterns using the thin film diffraction technique of STA thin films annealed at various temperatures by the MOD method and the Sol-Gel method, respectively. Definite regularity diffraction peaks were observed at 800 °C annealing, and broad peaks in a halo pattern were observed from 500 to 700 °C annealing using the two methods, indicating that STA thin films crystallized at 800 °C and were in amorphous states below this

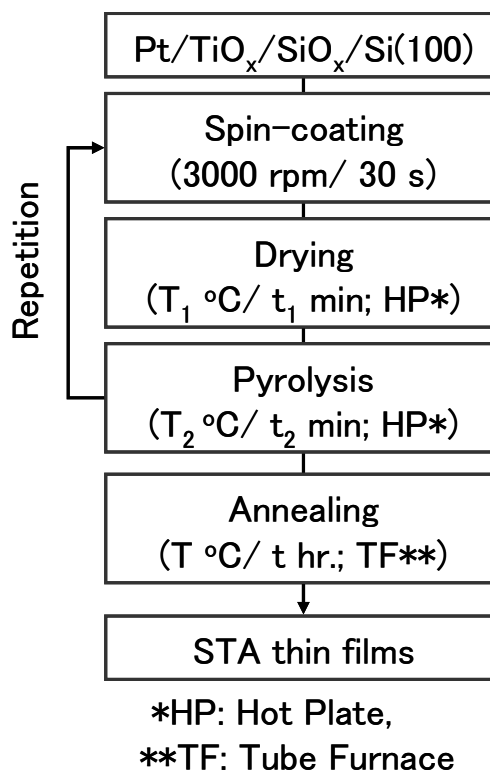


Fig.1: Fabrication process of STA thin films by the MOD and the Sol-Gel method. T₁, T₂ and T are the drying, pyrolysis and annealing temperatures, respectively. t₁, t₂ and t are the drying, pyrolysis and annealing times, respectively.

temperature. This crystallization temperature agrees well with what has been reported in Refs. [2] and [9], but is lower than that reported in Ref. [10]. These two crystalline thin films are polycrystalline and have the same phases, belonging to the orthorhombic tungsten bronze structure [2].

Dielectric constants (ϵ) and loss tangents ($\tan \delta$) at 100 kHz of MOD derived STA thin films are compared in figure 3(a). ϵ increased slightly with increasing annealing temperatures for thin films in amorphous states. However, it increased rapidly to about 260 after crystallization, which is about 3~4 times higher than those of amorphous films. This value is much higher than those reported in Refs. [2] and [9]. Sol-Gel derived STA thin films showed the same characteristic, as shown in figure 3(b). The ϵ value in the crystalline state of about 150 is comparable to that of other reports.

$\tan \delta$ decreased as annealing temperature increased for both methods. In particular, low $\tan \delta$ values of 0.02 were found for two crystalline films which agree with other reports [2, 9] and satisfy the low $\tan \delta$ parameter for capacitor applications. Therefore, dielectric properties of crystalline STA thin films, which possess higher ϵ and lower $\tan \delta$, are more suitable for capacitor applications than amorphous STA thin films.

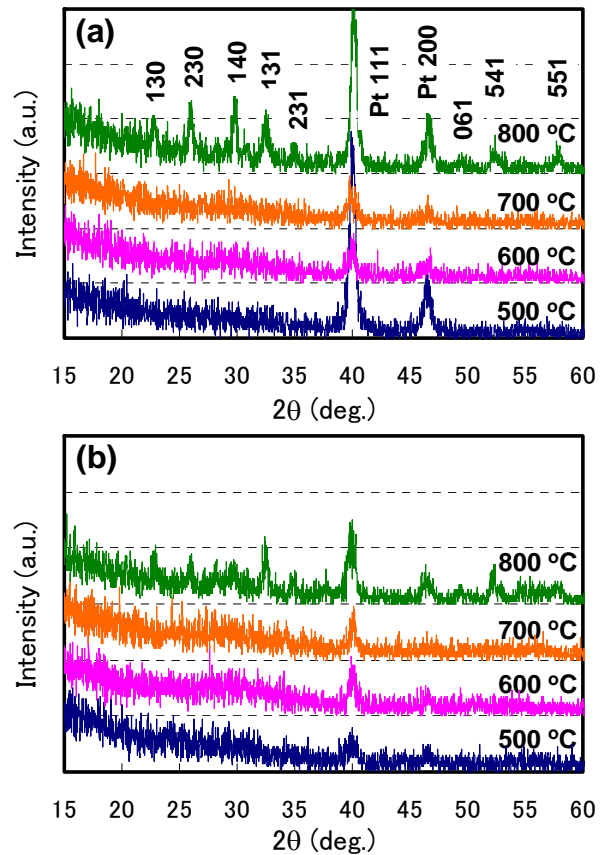


Fig.2: XRD patterns by the thin film diffraction technique of STA thin films annealed at various temperatures by (a) the MOD method and (b) the Sol-Gel method.

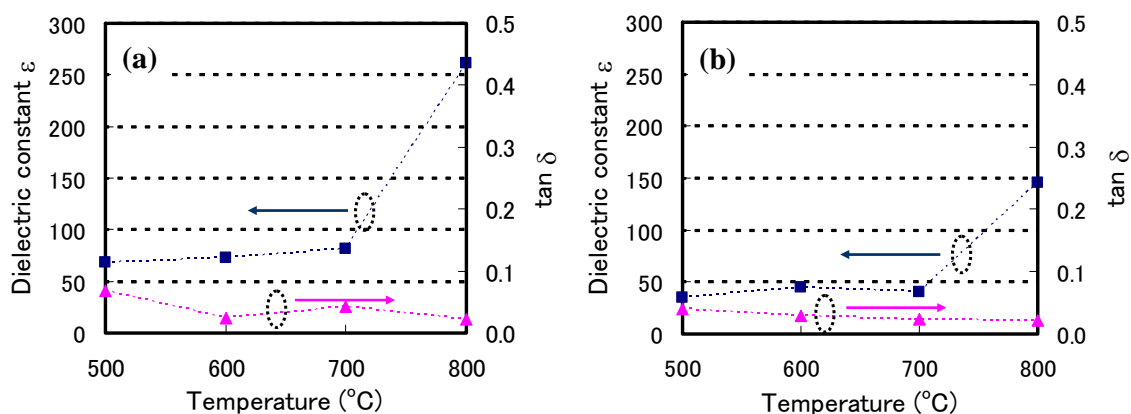


Fig.3: Dielectric constants (ϵ) and loss tangents ($\tan \delta$) at 100 kHz of STA thin films by (a) the MOD method and (b) the Sol-Gel method as a function of temperature.

Leakage currents of MOD derived STA thin films are shown in figure 4(a) indicating that

leakage currents of amorphous films are lower than that of the crystalline film. The lowest value of about 10^{-7} A/cm² at 250 kV/cm was obtained by the 700 °C annealed film, which was degraded up to 10^{-3} A/cm² at 800 °C annealing. The leakage current of the crystalline STA thin film is much larger than that reported by Regnery et al. [2] and is too large to fabricate actual devices. Leakage currents of Sol-Gel derived STA thin films are shown in figure 4(b). As in the amorphous state, the leakage current of the film annealed at 700 °C is lower than those annealed at 500 and 600 °C. However, a considerable difference between thin films by the two methods was observed at crystallization. The leakage current of the Sol-Gel derived thin film was improved after crystallization, which is even lower than that of the 700 °C-annealed thin film. The value of about 10^{-8} A/cm² at 250 kV/cm is comparable to that by the MOCVD method [2].

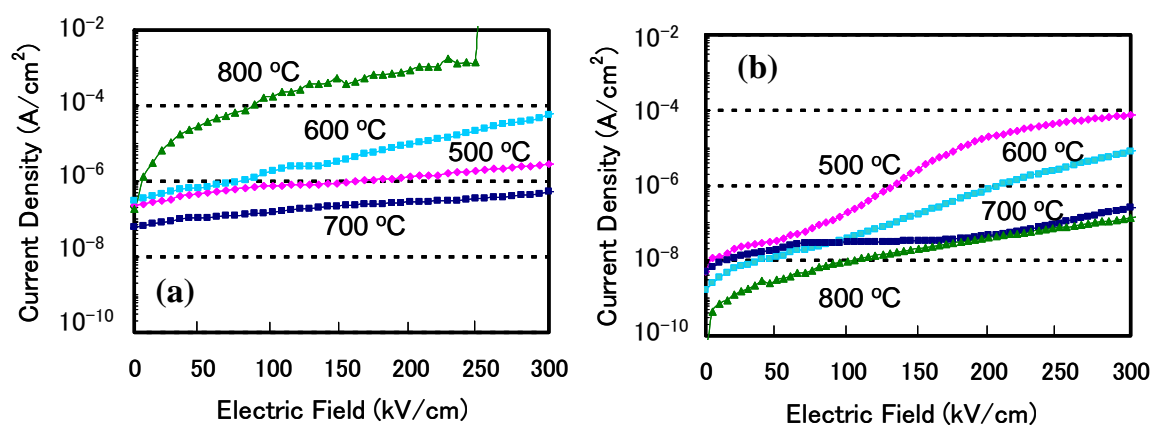


Fig.4: Leakage currents of STA thin films fabricated by (a) the MOD method and (b) the Sol-Gel method as a function of temperature.

For the requirements of application such as high ϵ , low $\tan \delta$ and low leakage current, the crystalline STA thin films by the Sol-Gel method (hereinafter: C-SG) is a promising candidate. Although the crystalline STA thin film by the MOD method (hereinafter: C-MOD) has a higher ϵ , its leakage current is very large. To gain a deeper understanding, the cause of leakage currents of C-MOD and C-SG was investigated.

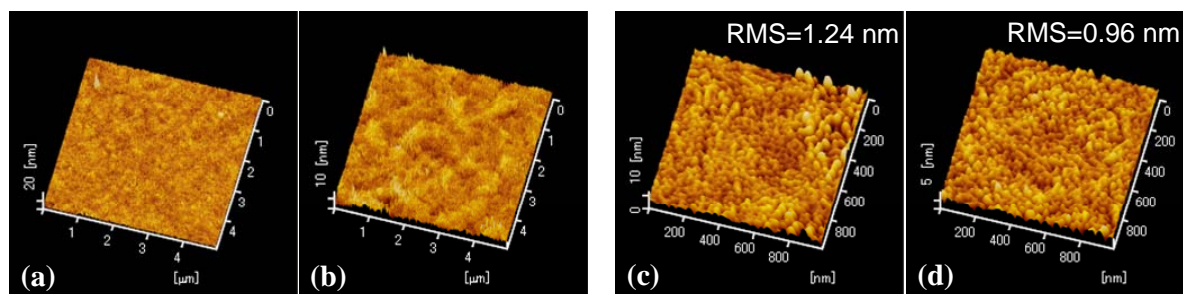


Fig.5: Surface morphologies of crystalline STA thin films by (a) the MOD method, (b) the Sol-Gel method at an area of $5 \times 5 \mu\text{m}^2$ and (c) the MOD method, (b) the Sol-Gel method at an area of $1 \times 1 \mu\text{m}^2$.

The difference in crystalline structure can be excluded because both of them are polycrystalline and no secondary phase was observed, as shown in figure 2. The composition ratios of Sr to Ta were also evaluated by XRF and were found to be about 1 to 2. Hence, the influence of nonstoichiometry could be excluded, too.

Surface morphologies with the scan area of $5 \times 5 \mu\text{m}^2$ for C-MOD and C-SG were shown in figure 5(a) and 5(b), respectively. Almost the same surface morphologies were observed. Then the scan area of $1 \times 1 \mu\text{m}^2$ were also carried out for detailed observation, as shown in figure 5(c): C-MOD and 5(d): C-SG. The surface root mean square (RMS) roughness of C-MOD and C-SG were 1.24 nm and 0.96 nm, respectively. The lower RMS indicates the surface of C-SG is smoother than that of C-MOD. Thus, we attribute the larger leakage current of C-MOD to the worse surface morphology and the enormous high ϵ is presumed to be the result of the leaky property and not a real value.

Summary

SrTa_2O_6 thin films were fabricated on Pt/TiO_x/SiO_x/Si substrates using the Metal-Organic Decomposition method and the Sol-Gel method. They were crystallized at the annealing temperature of 800 °C in air by both methods. The crystalline SrTa_2O_6 thin film by the Sol-Gel method showed a high ϵ of about 150 and a low leakage current density of about 10^{-8} A/cm^2 at 250 kV/cm, both of which are comparable to those reported on the MOCVD derived thin film.

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