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Invited

Low-Temperature Processing Using Triple Alkoxides Precursors for Non-volatile Ferroelectric Memories

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1. Introduction

Thin films of $SrBi_2Ta_2O_9$ (SBT) and $SrBi_2(Ta, Nb)_2O_9$ (SBTN) are promising materials for nonvolatile ferroelectric memory applications because of their excellent ferroelectric properties, especially with respect to fatigue performance. However, the processing temperatures of the thin films have not been satisfied for the complementary metal oxide semiconductor (CMOS) technology. For the higher integration of the thin films to get higher memory cell densities, the processing temperature of the thin films should be lowered enough for preventing thermal damages which may be introduced to the semiconductor.

The sol-gel method is one of the chemical solution deposition methods and is particularly desirable for synthesis of thin films with complicated chemical compositions. Especially for metal alkoxides as starting materials, the coordination states of the metals and the formation of complexes are controllable [1]. Thereby, after addition of water to the alkoxides, the hydrolysis and polycondensation reactions proceed to produce homogeneous and amorphous gel films [2]. It should be noted that the alkoxide structures before the addition of water must affect the amorphous gel film structures and then the crystallization of oxide thin films.

In this study, the preparation and the molecular structure of triple alkoxides precursors for SBT thin films were described. The effects of the organic functional groups of the alkoxides and the calcination condition such as a mixture of water vapor and oxygen flow on the crystallization of the triple-alkoxy-derived gel films were discussed. The ferroelectric and fatigue properties of the triple-alkoxy-derived SBT thin films were evaluated.

2. Experimental

Preparation of Triple Alkoxides Precursors

A typical flow diagram for preparation of a triple alkoxide (methoxyethoxide) precursor for SBT thin films is shown in Fig. 1. The concentration of the hydrolyzed, triple alkoxide precursor solution containing strontium, bismuth and tantalum in the molar ratio of 1:2:2 was 0.05M. ^{1}H- and ^{13}C-NMR spectroscopy and Fourier-transform infrared spectroscopy measurements were performed to determine the molecular structure of the triple alkoxide precursor. Other than the triple methoxyethoxide, a triple ethoxide was also prepared through the similar route.

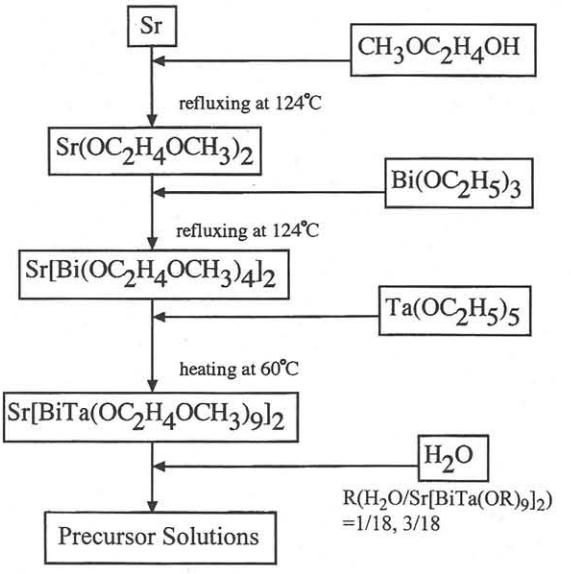

Fig. 1 Flow diagram for preparation of triple alkoxide precursor.

Deposition of SBT Thin Films

Gel films were prepared on platinum-passivated silicon ($Pt/Ti/SiO_2/Si(100)$, $Pt/TiO_x/SiO_2/Si(100)$) substrates by spinning the triple alkoxides precursors. Each layer was dried at 150°C, calcined at 350°C in air or at 250°C in a mixture of water vapor and oxygen flow (WVOF), and then heat-treated at various temperatures for 10 min in oxygen flow by using a rapid thermal annealing apparatus. The thickness of the film increased to about 120-130 nm by repeating the aforementioned treatments several times.

Characterization of SBT Thin Films

The crystal structure and crystallinity of the thin films were determined by XRD and FT-IR method. The microstructure and the surface morphology were observed by using FE-SEM, TEM and AFM. The ferroelectric hysteresis and fatigue properties were measured by using a Sawer-Tower circuit and digital signal analyzer (Models DSA602 and AFG2020, Tektronix, Inc.) or RT6000S instrument (Radiant Technologies Inc.). Before the electrical measurements, top electrodes as platinum or gold were deposited.

3. Results and Discussion

Proposed Structure of Triple Alkoxides Precursors

By spectroscopic analysis, the triple alkoxide ($Sr[BiTa(OC_2H_4OCH_3)_9]_2$) was found to be formed and contain Sr-O-Ta bond comprised of two TaO_6 octahedra connected by a strontium atom, and Sr-O-Bi links. A possible molecular structure of the triple alkoxide should be noticed, as the arrangement of metals and oxygen in the triple alkoxide is identical to the sublattice of SBT crystal [3]. Also, the structure was found to preserve upon the hydrolysis using water in the molar ratio to the triple alkoxide of 1:6. $Sr[BiTa(OC_2H_5)_9]_2$ was considered to have the same arrangement as $Sr[BiTa(OC_2H_4OCH_3)_9]_2$.

Crystallization of SBT Thin Films

The $Sr[BiTa(OC_2H_4OCH_3)_9]_2$–derived gel films crystallized at around 550°C, however, the $Sr[BiTa(OC_2H_5)_9]_2$–derived gel films crystallized at lower temperatures below 500°C. As the speed of the hydrolysis reaction for $Sr[BiTa(OC_2H_5)_9]_2$ is higher than that for $Sr[BiTa(OC_2H_4OCH_3)_9]_2$, the $Sr[BiTa(OC_2H_5)_9]_2$-derived gel film may have rather well-developed structure which contains links of the SBT sublattice. The calcination in the mixture (WVOF) was effective for the decomposition and elimination of organic compounds which remained in the gel films and disturbed the crystallization. Therefore, the $Sr[BiTa(OC_2H_5)_9]_2$-derived gel film which underwent the calcination in the mixture (WVOF) crystallized at lower temperatures below 500°C and showed relatively good crystallinity. Also, the calcination in the mixture (WVOF) increased the degree of the c-axis orientation of the SBT thin film [4]. The crystallinity of the SBT thin films improved with the annealing temperatures.

Ferroelectric Hysteresis and Fatigue Properties

Figure 2 shows the P-E hysteresis loops for the $Sr[BiTa(OC_2H_4OCH_3)_9]_2$–derived SBT thin films annealed at various temperatures. The switching polarization ($2P_r$) and coercive electric field (E_c) at 5 V for the 650°C, 700°C, 800°C-annealed SBT thin films were 2.50 μC/cm^2 and 40 kV/cm, 8.85 μC/cm^2 and 36 kV/cm, 15.0 μC/cm^2 and 45 kV/cm, respectively. Although the 650°C-annealed SBT thin film which was prepared from $Sr[BiTa(OC_2H_5)_9]_2$ and underwent the calcination in the mixture (WVOF) showed relatively higher degree of c-axis orientaion, it exhibited improved ferroelectric properties. The $2P_r$ and E_c at 5 V were 7.7 μC/cm^2 and 55 kV/cm, respectively. It was found that the remarkable development of the grain structure in the film introduced the improvement. The polarization did not change after switching of 10^9 cycles for the film [4].

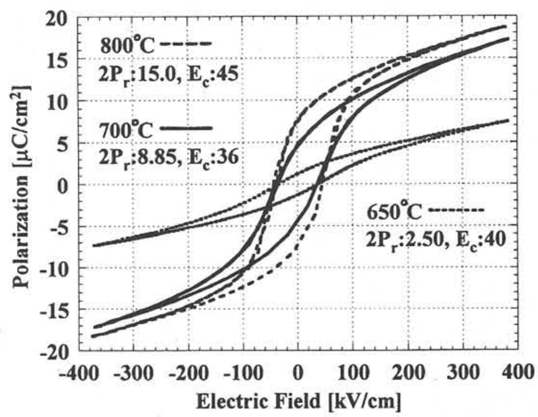

Fig. 2 P-E hysteresis loops for the SBT thin films.

4. Summary

Triple alkoxides precursors such as $Sr[BiTa(OC_2H_4OCH_3)_9]_2$ and $Sr[BiTa(OC_2H_5)_9]_2$ were prepared by controlled reactions of the starting metal alkoxides. The precursors were appropriate for the low-temperature processing of SBT thin films. Additionally, the calcination atmosphere such as the mixture of water vapor and oxygen flow was found to be effective for the low-temperature crystallization of the SBT thin films. The processing using the triple alkoxides precursors for the SBT thin films would be greatly useful for development of non-volatile ferroelectric memories.

References

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