The preparation of SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film by R.F. magnetron sputtering

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ABSTRACT: The dielectric characteristics of layer structured bismuth material SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ have been well developed. SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ ceramic was used as the target material and SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film was deposited on ITO glass substrate by R.F. magnetron sputtering method at room temperature for 10–40 min. A 200–600nm thin film was obtained by rapid thermal annealing (RTA) process at 600°C with different time in oxygen using the raising temperature rate of 900°C/min. The crystallization and dielectric characteristics of SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film were developed with the aid of X-ray diffraction patterns, SEM, and impedance analyzer.

KEYWORDS: SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$, layer structured, ferroelectric

1. Introduction

Bismuth layered perovskite materials are able to withstand $10^{12}$ erase/rewrite operations and therefore have attracted an increasing attention for NvRAMs application [1]. The layer structured bismuth compound ferroelectric has the general formula: $A_{n-1}B_nO_{3n+3}$, where A is usually a divalent ion, such as Sr, Ba, or Pb, and B is Ti$^{4+}$, Nb$^{5+}$, or Ta$^{5+}$ [2–4]. Within the bismuth family, SrBi$_2$Ta$_2$O$_9$ ceramics had attracted the most attention in the past years [5–7]. Although the polarization of SrBi$_2$Ta$_2$O$_9$ ceramics is less than the competing
PZT-based materials, the bismuth-layer compounds are much stables to polarization fatigue free property, i.e. almost no charge loss will happen when polarization is reversed many cycles.

In the SrBi$_2$Nb$_2$O$_9$ and the SrBi$_2$Ta$_2$O$_9$ compositions, the substitution of Nb$_2$O$_5$ and Ta$_2$O$_5$ by V$_2$O$_5$ will help to lower the sintering temperatures and produce materials with enhanced dielectric properties that are useful in applications [8-10]. In the past, it would be interesting to investigate ceramic material based on SrBi$_2$Ta$_2$O$_9$ composition, V$_2$O$_5$ was used to substitute for Ta$_2$O$_5$ to form the compositions of SrBi$_2$Ta$_{2-x}$V$_x$O$_9$. Bulk SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ materials were sintered at different temperatures and their dielectric characteristics were investigated as a function of sintering temperature and V$_2$O$_5$ content. The dielectric characteristics of SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics were well developed, and the SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ ceramic was chosen as the target material to deposit the ferroelectric thin film. Rapid thermal annealing (RTA) process is used to sinter the deposited thin film, and the characteristics of sintered thin film were developed in this study.

2. Experimental Procedures

Reagent-grade raw materials of SrCO$_3$, Bi$_2$O$_3$, Ta$_2$O$_5$, and V$_2$O$_5$ with higher than 99.5% purity were used as starting materials, mixed according to the composition SrBi$_2$Ta$_{1-x}$V$_x$O$_9$ (where $x=0.1$, 0.2, 0.3, and 0.4) and ball-milled for 5h with deionized water. After drying and ground, then the powder was calcined at 850°C for 3h. After calcinations and ground again, then polyvinylalcohol (PVA) was added as a binder. The calcining powder was uniaxially pressed into pellets in a steel die with the size of 1mm in thick, 15mm in diameter (for dielectric characteristics measured) and 4.5 mm in thick, 56mm in diameter (for
RF sputter used). After debinding, sintering of these pellets was carried out at 1050°C for 4h.

HOYA NA-40 glass coated with Indium-Tin Oxide (ITO) of 0.2µm thickness is chosen as the substrate in this study. Sheet resistance and transmittance of the ITO films was 15Ω/□ and larger than 80%, respectively. ITO glass substrates were ultrasonically cleaned in acetone, 2-Propanal and D.I. water for 20 minutes, dried by pure N₂ and baked in oven at 110°C for 30mins before film deposition. SrBi₂Ta₁.₈₉V₀.₂O₉ thin films were deposited on ITO glass substrate by R.F. magnetron sputtering system, and part area of the ITO glass was covered by glass to form bottom electrode. The deposition conditions are shown in Table1.

Table1. Typical growth condition of Bi₄Ti₃O₁₂ + 4wt% Bi₂O₃ thin film

<table>
<thead>
<tr>
<th>Target</th>
<th>Bi₄Ti₃O₁₂ + 4 wt% Bi₂O₃ (2 inches)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>0.7mm thickness, 15Ω/□ ITO glass</td>
</tr>
<tr>
<td>Substrate temperature</td>
<td>room temperature</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>pure Ar</td>
</tr>
<tr>
<td>Base pressure</td>
<td>5x10⁻⁶ Pa</td>
</tr>
<tr>
<td>Work gas pressure</td>
<td>1.5Pa</td>
</tr>
<tr>
<td>Deposition time</td>
<td>10~60 min</td>
</tr>
</tbody>
</table>

For electrical measured, Al was evaporated on the surface of the thin films under the pressure of 5 x 10⁻³Pa for 30s, forming the top dot electrodes. The crystal structure of the films was identified by (XRD) with Cu-kα wavelength. Surfaces and cross-section microstructures of the thin film were observed using field emission scanning electronic microscopy (FE-SEM).
3. Results and discussion

Figure 1 shows the $\varepsilon_{Tc}$ values (the dielectric constants revealed at Curie temperatures) and Curie temperatures of SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics as a function of sintering temperature and V$_2$O$_5$ content. As Fig.1 shows, even only 900°C is used as the sintering temperature, the $\varepsilon_{Tc}$ values of SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics is about 443–485. The $\varepsilon_{Tc}$ values of SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics increase from 900°C to 1000°C. The decrease in pores will account for the results. As the sintering temperatures increase from 1000°C to 1100°C, the $\varepsilon_{Tc}$ values of SrBi$_2$Ta$_{1.9}$V$_{0.1}$O$_9$ ceramics critically decrease, the $\varepsilon_{Tc}$ values of SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ ceramics slightly decrease, and the $\varepsilon_{Tc}$ values of SrBi$_2$Ta$_{1.7}$V$_{0.3}$O$_9$ and SrBi$_2$Ta$_{1.6}$V$_{0.4}$O$_9$ ceramics are almost unchanged. The Curie temperatures of SrBi$_2$Ta$_{2-x}$V$_x$O$_9$ ceramics decrease with the increase of sintering temperatures.

As the Fig.1 shows, as the sintering temperatures are higher than 1050°C, the $\varepsilon_{Tc}$ values of SrBi$_2$Ta$_{1.9}$V$_{0.1}$O$_9$ ceramics critically decrease. This may be caused by that the Curie temperatures are shifted to lower temperatures and in turn to cause the decrease of polarizabilities. As the sintering temperatures are higher than 1050°C, the $\varepsilon_{Tc}$ values of SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$, SrBi$_2$Ta$_{1.7}$V$_{0.3}$O$_9$, and SrBi$_2$Ta$_{1.6}$V$_{0.4}$O$_9$ ceramics are slightly decreased or almost unchanged with the increase of sintering temperature. The curie temperatures are almost unchanged is the reason. Because the SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ ceramic has the stable dielectric characteristics, it is chosen as the target material for deposition.

Fig.2 shows the micrographs of SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film as a function of deposited time and annealing time, and the annealing temperature is 600°C. For short deposited time, 10 min and 20 min, the annealing surface reveals a non-uniform surface, as Figs.2(a), 2(b), and 2(d) are compared. This may be caused by that short deposited time, the thickness of deposited SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$
material is not enough for shrinkage and crystallization. For longer deposited time, 40 min, the annealed SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film shows a uniform grain growth. This result suggests that the deposited time is important factor will influence the characteristics of deposited SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film and at least 40 min deposited time is needed. When Figs.2(b) and 2(c) are compared or Figs.2 (d), (e), and (f) are compared, for longer annealing time, the annealing surface also reveals a non-uniform surface. These results also show that the annealing time is another important effect that will influence the crystallization of SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film.

Fig.3 shows the cross section observation of the deposited SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film, the deposited time is 40 min, and annealed at 600°C for 10 min. As Fig.3 shows, the thickness of the deposited SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film is about 0.6µm, and the annealed film shows a densified structure. Typical X-ray diffraction (XRD) patterns of the deposited SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin films are shown in Fig.3, as a function of deposited time (Fig.3(a), annealing at 550°C for 10min) and annealing temperature (Fig.3(b), deposited time =40min and annealing time =10min). The crystal intensities of (0,0,6) and (0,0,8) planes (14, and 2θ values are at around 21.4° and 28.6°) increase with the increase of annealing time and annealing temperature.

The variations of the relative dielectric constant and dielectric loss of deposited SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film by different annealing temperatures are shown in Fig.4, the annealing time is 10 min. The dielectric constant increases with the increase of annealing temperature and reaches a maximum at 600°C annealing SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film. The dielectric loss increases with the increase of annealing temperature and ranged 4.5~12.3 x 10$^{-3}$. Even the
dielectric loss increase with the increase of annealing temperature, but the fabricated film is enough for real use.

4. Conclusions

SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film was deposited on ITO glass substrate by the combination of R.F. magnetron sputtering and rapid anneal process. The crystal intensities of SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film depends on the deposited time and annealing temperatures. The deposited SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film has the dielectric characteristics of dielectric constant 122~245 and dielectric loss 4.5~12.3 $\times$ 10$^{-3}$. In this study, the optimum deposited and annealing condition are: deposited time =40min, annealing temperature =600$^\circ$C, and annealing time 10 min.

References


Fig.1 The Curie temperatures and the maximum dielectric constants of SrBi$_2$Ta$_{1-x}$V$_x$O$_9$ ceramics.
Fig. 2 The micrographs of SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film, annealing at 600°C, and as a function of deposited time (Dt) and annealing time (At). (a) Dt= 10min and At= 10min, (b) Dt= 20min and At= 5min, (c) Dt= 20min and At= 10min, (d) Dt= 40min and At= 10min, (e) Dt= 40min and At= 15min, and (f) Dt= 40min and At= 20min.

Fig. 3 The cross section of the deposited SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film.
Fig. 4 The X-ray patterns of deposited SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film. Deposited time = 40 min, (a) annealing at 550°C for different annealing time and (b) annealing for 10 min for different temperature.

Fig. 5 The dielectric constant and dielectric loss of deposited SrBi$_2$Ta$_{1.8}$V$_{0.2}$O$_9$ thin film. The deposited time = 40 min, and the annealing time = 10 min.