Influence of La-Mn-Al Co-Doping on Dielectric Properties and Structure of BST Thick Film

Mao-Yan Fan and Sheng-Lin Jiang

Abstract—A new sol-gel process is applied to fabricate the BST (Ba, Sr1−x, TiO3) sol and nano-powder of La-Mn-Al co-doping with Ba/Sr ratio 65/35, and the BST thick film is prepared in the Pt/Ti/SiO2/Si substrate. The powder and thick film are characterized by X-ray diffraction and transmission electron microscope. The influence of La-Mn-Al co-doping on the dielectric properties and micro-structure of BST thick film is analyzed. The results show that the La, Mn, and Al ions can take an obvious restraint on the growth of BaSrTiO3 grains. The polycrystalline particles come into being during the crystallization of thick film, which may improve the uniformity and compactness of thick film. The influence of unequal-valence and doping amount on the leakage current, dielectric loss, and dielectric property are mainly discussed. The dielectric constant and dielectric loss of thick film are 1200 and 0.03, respectively, in the case of 1mol% La doping, 2mol% Mn doping, and 1mol% Al doping.

Index Terms—BST thick film, dielectric property, La-Mn-Al co-doping, sol-gel process.

1. Introduction

The Ba,Sr1−x, TiO3, briefly named BST, is a typical ABO3 perovskite structure with many advantages, such as high dielectric constant, low dielectric loss, low leakage current, large dielectric adjustable range, and high pyroelectric coefficient, etc. which may be extensively used for dynamic random access memory (DRAM), integrated microwave devices, and infrared detector, etc. As a typical grain refiner, Al3+ has a smaller semi-diameter than Ti4+. The Mn element of B group, generally exists as K+, Fe2+, Fe3+, Cr3+, Ce3+, Al3+, Mn2+, Mn4+, and Mg2+, may reduce the dielectric loss and leakage current. Otherwise little doping may change the single cubic Ba0.6Sr0.4TiO3 phase. The increasing non-cubic phase causes the reduction of crystal symmetry, the increase of interfaces and the increase of fraction between grains. The doping with large ratio may result in the uneven distribution of grain size, increase of faults and increase of dielectric loss. The moderate doping may cause the decrease of grain size and the uniform distribution of cubic and cuboid BST, which forms the 3D polycrystalline multiphase component. Furthermore, the moderate doping may widen the dielectric peak and increase the dielectric constant and dielectric loss. Also the change rate of dielectric constant near Curie point increases remarkably. The doping of acceptor impurity into BST thin film, such as K+, Fe2+, Fe3+, Cr3+, Ce3+, Al3+, Mn2+, Mn4+, and Mg2+, may reduce the dielectric loss and leakage current. The Mn element of \( \text{VIII} \)B group, generally exists in the form of Mn3+, and its semi-diameter is a bit larger than Ti4+. A little Mn2+ doping may improve the crystallization of BST thin film and increase the dielectric constant. As a typical grain refiner, Al3+ has a smaller volume than Ti4+. Al3+ replaces Ti4+ by Al3+ doping, which reduces the distances between ions at the center of oxygen octahedron, packing the grain structure and reinforcing the system anharmonicity. Thus the BST by Al3+ doping.
conducts can not only lower the leakage current and dielectric loss, but also increase the electric-field modulation.

La$^{3+}$, Mn$^{2+}$, and Al$^{3+}$ are used for Ba$_{0.66}$Sr$_{0.33}$TiO$_3$ co-doping in our tests. There are many reports about the BST doping with one element$^{[12],[13]}$, but few ones about doping with over two elements. The doping with various elements may supply a gap of the single element doping. Thus, the complementary advantages can be exerted.

2. Modification Mechanism by La-Mn-Al Co-Doping

The perovskite structure of BST ceramic is formed by the compact arrangement of oxygen octahedron as skeleton. There is little probability for occurrence of gap ions in materials. The main defects are the cation vacancy and oxygen vacancy. According to the valence state relation between purity ions and in-suit ions, the doping can be divided into three types. The first type is acceptor impurity, meaning that high-valence positive ions are replaced by low-valence positive ions. For example, when Ti$^{4+}$ is substituted by Mn$^{2+}$, Mn$^{3+}$ or Al$^{3+}$, oxygen vacancy will occur to maintain the electroneutrality. The second type is donor impurity, meaning that low-valence positive ions are replaced by high-valence positive ions. For example, when La$^{3+}$ replaces Ba$^{2+}$ and/or Sr$^{2+}$, the donor impurity induces cation vacancy to satisfy electroneutrality. The last type is variable valence impurity$^{[14],[15]}$, also named stable additive, such as Mn$^{2+}$ and Mn$^{3+}$.

For the micro-mechanism of doping, the internal bias field theory is can well interpreted. The acceptor ions and oxygen vacancy form the compound with electric dipole moment. The compound may adjust slowly its orientation in the electric field caused by spontaneous polarization, then form the internal bias field. The internal bias field parallel to the direction of spontaneous polarization can stabilize the spontaneous polarization and harden the material performance, which makes dielectric constant decrease and frequency constant and aging rate increase. But the donor plays an inverse role in contrast to the acceptor. The addition of donor causes cation vacancy and the domain walls move readily by electric field or external force, softening the material performance. Thus the dielectric constant increases, and mechanical quality factor and aging rate decrease. Due to its variable valence, the transition metal ions make the modified ferroelectric have some soft and hard doping characteristic. Thus the transition metal ions are called stable additive.

The substitution position of doping ion in the normal lattice may be estimated by the electroneutrality principle and tolerance coefficient. According to electroneutrality principle, the electrovalence should change little. Furthermore, the tolerance index of solid solution theory shows that the closer the radius of two ions is, the bigger the substitution change is. Generally speaking, the ion with large radius and low valence enters into position A, the ion with small radius and high valence into position B. The radius of common doping ions and the substitution position in BST are listed in Table 1. The ions radius difference is expressed as a percentage.

3. Tests

3.1 La-Mn-Al Co-Doping and Fabrication of BST Thick Film

The BST co-doping gel and nano-powder with Ba/Sr ratio of 65/35 are made with Ba(CH$_3$COO)$_2$, Sr(CH$_3$COO)$_2$, C$_6$H$_6$LaO$_6$, C$_8$H$_8$MnO$_4$·4H$_2$O, C$_6$H$_8$AlO$_4$·2H$_2$O, and Ti(OC$_3$H$_7$)$_4$ as primary raw materials, CH$_3$COOH and C$_2$H$_5$OH as solvent, and (CH$_2$OH)$_3$ as stabilizer. The concentration of La-Mn-Al co-doping is 0.4mol/L with La: Mn: Al of 0.5%-1%-0.5% mol, 1%-2%-1% mol and 2%-4%-2% mol, respectively. The results show that the BST nano-powder with average grain size less than 100 nm is obtained by sintering the dry gel at 900 °C and then by 12 h grinding. The BST nano-powder and BST gel are mixed with quality ratio of 2:5, and then the powder is dissolved uniformly into gel by a period of grinding and ultrasonic. Then the BST thick film is fabricated by spin-coating method with 10 s spinning speed of 350 rpm, 20 s coating speed of 3000 rpm, Pt/Ti/SiO$_2$/Si as substrate. The pretreatment of each film is conducted in the rapid heat-treatment furnace (RTA-300), with 10 min heat preservation at 180 °C and then 15 min heat preservation at 350 °C. This spin-coating process is repeated six times. Thus the BST thick film with La-Mn-Al co-doping is approximately 4 μm to 5 μm. The sample is placed in the quartz watch glass after the completion of pretreatment, then is heated to 750 °C in the muffle furnace for annealing. The annealing needs to last two hours.

3.2 Analysis and Measurement Methods

The phase structure of BST thick film is analyzed by X-ray diffraction analyzer (D8-Advance). The microstructure of BST thick film is measured by XL30FEG SEM. The relative dielectric constant and dielectric loss of BST interlining thick film under different frequencies and electrical fields are measured by the HP4284LCR meter.

Table 1: Substitution position of some common doping ions

<table>
<thead>
<tr>
<th>Introduced ion</th>
<th>Radius (nm)</th>
<th>Ba$^{2+}$ (%)</th>
<th>Sr$^{2+}$ (%)</th>
<th>Ti$^{4+}$ (%)</th>
<th>Substitution position</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn$^{2+}$</td>
<td>0.080</td>
<td>40.741</td>
<td>29.203</td>
<td>-17.647</td>
<td>B</td>
</tr>
<tr>
<td>Mn$^{3+}$</td>
<td>0.062</td>
<td>54.074</td>
<td>45.132</td>
<td>8.82353</td>
<td>B</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>0.050</td>
<td>62.963</td>
<td>55.752</td>
<td>26.4705</td>
<td>B</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>0.115</td>
<td>14.815</td>
<td>-1.7699</td>
<td>-69.117</td>
<td>A</td>
</tr>
</tbody>
</table>

Notice: Ba$^{2+}$: r=0.135nm; Sr$^{2+}$: r=0.113nm; Ti$^{4+}$: r=0.068nm
4. Results and Discussions

4.1 XRD and SEM Analysis of BST Powder

Fig. 1 shows the XRD spectrum of BST sample with Ba/Sr ratio of 65/35 prepared by 2h sintering of dry gel at 950°C. The La-Mn-Al concentrations of (a), (b), and (c) are 0.5%-1%-0.5% mol, 1%-2%-1% mol, and 2%-4%-2% mol, respectively. The acute characteristic peaks of BST perovskite structure with high diffraction intensity occur in the crystal faces of (100), (110), (111), (200), (210), (211), and (220). The powder has pure perovskite structure.

Fig. 2 shows the SEM photos of powder sample. The grain size is less than 100 nm with uniform distribution. The powder has an uneven dispersion, and the particles take on various shapes in the case of high-concentration doping. In addition, most of particles are polygonal, and few spherical.

4.2 Structure Analysis of BST Thick Film

Fig. 3 and Fig. 4 show the XRD spectrum and SEM photos of BST thick film (single layer) with Ba/Sr of 65/35 and La-Mn-Al co-doping by annealing. The La-Mn-Al concentrations of Fig. 4 (a), (b), and (c) are 0.5%-1%-0.5% mol, 1%-2%-1% mol, and 2%-4%-2% mol, respectively. Fig. 3 shows that the thick film has been crystallized into complete polycrystalline perovskite structure by 2 h annealing at 750 °C. The BST (110) crystal face of perovskite structure has a low surface energy, and the thin film basically grows in the BST (110) crystal face during crystallization. Thus the BST (110) peak of BST thick film is more intensive than other peaks in XRD spectrum. Fig. 4 shows that the grain size is larger in low doping concentration (Fig. 4 (a)) than that in high doping concentration (Fig. 4 (c)). As the doping concentration increases, the FWHM also increases, especially for the BST(110) peak, which shows that the grain size decreases and crystallization quality improves.

Fig. 5 shows the SEM photo of BST thick film with La-Mn-Al co-doping. The BST (110) peak of BST thick film is more intensive than other peaks in XRD spectrum. Fig. 4 shows that the grain size is larger in low doping concentration (Fig. 4 (a)) than that in high doping concentration (Fig. 4 (c)). As the doping concentration increases, the FWHM also increases, especially for the BST(110) peak, which shows that the grain size decreases and crystallization quality improves.

Fig. 5 shows the SEM photo of BST thick film with La-Mn-Al co-doping. The BST (110) peak of BST thick film is more intensive than other peaks in XRD spectrum. Fig. 4 shows that the grain size is larger in low doping concentration (Fig. 4 (a)) than that in high doping concentration (Fig. 4 (c)). As the doping concentration increases, the FWHM also increases, especially for the BST(110) peak, which shows that the grain size decreases and crystallization quality improves.
4.3 I-V curve

The thin film is around 4 μm thick measured by step profiler. The top electrode of BST thick film is prepared by dc magnetron sputtering. The Pt array electrode with 2 mm×2 mm is made by mask method. The I-V curve of BST thick film is measured by Keithley6487 picoammeter at 25°C, as shown in Fig. 6. The leakage current of BST thick film with low doping (sample (a)) increases rapidly in the case of over 0.5 V bias. As the doping concentration increases, the Fermi energy level decreases, which causes the increase of Schottky barrier and gradual reduction of leakage current. In the work voltage range (above 1.5 V), the BST thick film with high-concentration (sample (c)) has a larger leakage current than that with moderate-concentration (sample (b)).

4.4 Dielectric Characteristics

Fig. 7 shows the relationship between relative dielectric constant, dielectric loss and temperature of BST thick film with La-Mn-Al co-doping (sample (b)) in the case of room temperature 25°C, with work voltage of 3 V DC and 1 kHz frequency. The dielectric properties of BST thick film are measured by HP4192A meter. The results show that the Curie temperature of BST interlining thick film exists near 15°C with dielectric constant equal to 1200 and dielectric loss equal to 0.03. The dielectric-temperature change rate is over 1.2%/°C within a wide range near 25°C. The Curie temperature shifts to low temperature, and the dielectric peak widens. Two reasons result in the decrease of Curie temperature. One is that the substitution of Ti⁴⁺ by Al³⁺ and Mn²⁺ causes the gradual reduction of crystal axis c/a toward 1. Thus the material readily transforms from cubic phase to cubic phase, causing the decrease of Curie temperature and performing the characteristic of diffuse phase transition. The other reason is that the doping substitution changes the Ba/Sr ratio and polycrystalline components occur in the BST thick film.

5. Conclusions

The test results show that the La, Mn and Al ions can obviously restrain the growth of BaSrTiO₃ grains and improve the uniformity and compactness of thick film. The donor doping increases the dielectric constant, leakage and change rate of dielectric constant with temperature near Curie point. The acceptor doping conducts an inverse effect in contrast to the donor doping. To improve the dielectric performance, the amount of acceptor doping should be controlled within a suitable range to compensate the redundant electrons of BST. The dielectric constant and dielectric loss of thick film are 1200 and 0.03 respectively, in the case of 1mol% La doping, 2mol% Mn doping, and 1mol% Al doping. The improved BST thick film may be used to produce the uncooled focal plane array (UFPA). The doping BST is a well ferroelectric, and great advancement has been achieved in doping modification. However, there is still much work to do for the breakthrough of its application in infrared detector array, especially for simplification of process and reduction of production cost.

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References


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