

Phase shifters 응용을 위한 Sol-gel 법으로 제작된 BST 박막의 Ce 첨가에 따른 구조적, 유전적 특성

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Dielectric and Structural of BST Thin Films with Ce-doped prepared by Sol-gel method for Phase shifters

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Abstract

The dielectric and electrical characteristics of Ce doped ($Ba_{0.6}Sr_{0.4}TiO_3$ (BST) thin films were investigated as a function of Ce content. Both atomic force microscopy (AFM) and x-ray diffraction (XRD) analysis showed that increasing the Ce doping ratio causes the decrease in grain size while the surface remains smooth and crack-free. The dielectric properties of the Ce doped BST films were found to be strongly dependent on the Ce contents. The dielectric constant and dielectric loss of the BST films decreased with increasing Ce content. However, it was also found that, compared with undoped films, the increase of Ce content improves the leakage-current characteristics. The improvement of the electrical properties of Ce-doped BST films may be related to the decrease in the concentration of oxygen vacancies. The figure of merit (FOM) reached the maximum value of 48.9 at the 1 mol % of Ce doping. The dielectric constant, loss factor, and tunability of the 1 mol% Ce doped $Ba_{0.6}Sr_{0.4}TiO_3$ thin films were 320, 0.011, and 46.3%, respectively.

Key Words : Dielectric properties; Sol-gel, Tunable,

1. 서론

Recently, ferroelectric materials are of great interest for the application in the ferroelectric and paraelectric thin film capacitors for dynamic random access memory (DRAM) devices and tunable microwave devices, such as electrically tunable mixers, delay lines, filters, capacitors, oscillators, resonators and phase shifters [1-2]. For tunable device applications mentioned above, dielectric thin films have the set of properties to be satisfied: a moderate-to-low dielectric constant at microwave frequencies, low dielectric loss factor, large-scale variations of the dielectric constant by direct current (dc) biasing field and low leakage-current

density [3].

The $SrTiO_3$, and $(Ba,Sr)TiO_3$ (BST) films have been intensively investigated due to their high dielectric constant and good thermal stability [4-6]. Among them, BST thin films are characterized by a lower loss tangent and higher tunability. Therefore, BST thin films may be considered as the preferable candidates for applications in tunable microwave devices. According to the results of previous investigations, the electrical properties such as dielectric constant, dielectric loss, and leakage current of BST thin films depend on the deposition method, composition, dopant, electrode, microstructure, interfacial quality, and thickness of the films [3-4]. Many researches have studied

the undoped BST thin films, which offer tunability upward of 50% at bias voltage of less than 10 V. However, high tunability of undoped BST thin films is escorted by high loss tangents, which is much larger than 0.02. It is well known that dopants can significantly modify the dielectric and electrical properties of ferroelectric materials such as BST. It has been explored that a donor for the A site of the perovskite structure, which have been known to lower leakage current and dielectric loss [7-8].

In this paper, we report on the influence of the cationic substitution of Ce in A site such as Ba or Sr site of the ABO perovskite structure on electrical and dielectric properties of BST thin films.

2. 실험

The precursor solutions for both undoped and Ce-doped $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ were prepared by the sol-gel method using barium acetate, strontium acetate, cerium acetate, and Ti-isopropoxide as the starting materials. The solid-state barium acetate, and strontium acetate were initially dissolved in acetic acid to obtain a (Ba, Sr) stock solution. Then, cerium acetate (as a dopant precursor) with concentrations ranging from 0.1 to 10 mol % was added to the (Ba, Sr) stock solution. Titanium iso-propoxide was dissolved in 2-methoxyethanol under a N_2 atmosphere. Finally, both stock solutions were mixed to prepare the stoichiometric, transparent, and stable Ce-doped BST precursor. For the fabrication of undoped and Ce-doped BST thin films, the Ce-doped BST precursor solution was syringed through a 0.2 m syringe filter on the Pt(120 nm)/Ti(30 nm)/ SiO_2 /Si substrate. The BST films were deposited by the spin-coating technique at 4000 rpm for 30 s. After the spin-coating procedure, the BST films were kept on hot plate at 400 C for 10 min to remove the organic contaminations. Then, the pre-baked films were annealed at 700 C for 1 h in oxygen atmosphere for crystallization. The final thickness of Ce-doped BST thin film was about 200 nm.

Dielectric measurements were carried out using the metal-insulator-metal (MIM) capacitor configuration. For these purposes, top Pt electrodes with the diameter of 200 m were deposited on the Ce-doped BST films by the dc sputtering method. Pt electrodes having a diameter of 200 m were then dc sputter-deposited on the BST film to form the

top electrode. To investigate the crystallinity, phase formation parameters, and orientation of the Ce-doped BST thin films, XRD profiles were obtained using a CuK radiation source at 30 kV and 60 mA (Rigaku-D/MAX). Surface morphology of Ce-doped BST films was analyzed and quantified using an atomic force microscope (Digital Instrument NanoScope IIIa). Capacitance-voltage characteristics, as well as dielectric constant and dielectric loss, were measured using a HP 4192 impedance analyzer. The leakage-current densities of Ce-doped BST thin films were measured using a semiconductor parameter analyzer (Agilent 4146C) at 0.1-V step voltage and delay time of 1 s. Leakage current densities were measured by using a semiconductor parameter analyzer (Agilent 4146C) in the Pt/BST/Pt capacitors. A staircase shared dc bias voltages, with a 0.2V and delay time of 20 s at each voltage step, were applied to the top electrodes while the bottom electrode were grounded. Time dependent leakage current density was measured at different voltages, for periods of 1 s up to 2000 s.

3. 결과 및 고찰

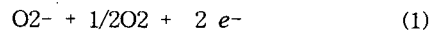
Figure 1 shows the XRD patterns of BST thin films with various Ce doping ratios in the range of 0 - 10 mol %. It can be seen that (100), (110), (111), (200), (210), and (211) peaks corresponding to the BST perovskite structure are obtained in all the films. Additionally, all the films possessed a non-textured polycrystalline structure with no evidence of secondary phase formation. However, when the Ce doping ratio exceeds 10 mol %, an undefined diffraction peak appears at $2\theta = 28.5$. Considering the joint committee of powder diffraction standard (JCPDS) data, this peak may be attributed to the formation of the CeO_2 secondary phase due to the excess of Ce content. As a result, we expect that the formation of the secondary phase can cause the decrease of the dielectric constant and the increase of leakage-current density compared with undoped BST films. The peak intensities of Ce-doped BST thin films decreased and the full widths at half maximum (FWHM) increased with increasing Ce content. The peak broadening effects mentioned in our experiments may be connected with the decrease in grain size with increasing Ce content [2].

The average grain size and the surface roughness of the undoped and doped BST thin

films were analyzed with AFM in tapping mode with amplitude modulation. The AFM images was obtained using an area of 1.4 μm × 1.4 μm. The surface AFM micrographs for the undoped and Ce-doped BST thin films are shown in Fig. 2. All the AFM images show smooth surface morphology and the absence of both cracks and pinholes. However, we have found that the surface morphologies are strongly influenced by the Ce content. As the Ce content increases, both grain size and root mean square roughness (RMS) of the films decreases. This result is in good agreement with data of Fig.1 showed the corresponding decrease in both intensities and peak sharpness. The average grain size of the undoped BST and Ce-doped BST thin films were 4080 nm.

The dielectric and electrical measurements of the undoped and Ce-doped BST thin films were carried out at room temperature on MIM capacitors. Table 1 summarizes the dielectric constant (ε'), dielectric loss (tan δ), figure of merit (FOM), tunability, and leakage current densities values for the undoped and Ce-doped BST thin films as a function of the Ce content at a frequency of 100 kHz. Meanwhile, these data are rather predictable and may be explained on the base of Fig.1 and Fig.2 analyses. It is well known that the value of the dielectric constant of dielectric thin film is strongly affected by microstructure, grain structure, and the grain size. As for the last factor, the larger grain size usually results in larger polarization and therefore gives higher value of dielectric constant. The data represented in Table 1 show that the dielectric constant and dielectric loss factor decreased with increasing Ce content in the BST thin films. The decreasing dielectric constant of the sample with a small grain size may be attributed to the increasing amounts of low dielectric constant grain boundaries. Many researchers have reported that was the grain size effect on dielectric properties in BST films [9]. The dielectric constant and dielectric loss factor of the 1 mol% Ce- doped BST thin films were 320 and 0.011, respectively. The tunability was determined as (max-min)/max, where max and min are the maximum and minimum values of permittivity, respectively, measured at the zero electric field and 500 kV/cm electric field. The FOM is a frequently used parameter to characterize correlations between tunability and dielectric loss. This parameter is defined as FOM

= [(%) tunability / tan δ (%)], where dielectric loss is given on a percentage scale [10]. The FOM value reflects the fact that a tunable microwave circuit cannot take full advantage of high tunability if the loss factor is too high. Ideally, the FOM value should be as high as possible. The tunability decreased with increasing Ce content of the BST thin films. The highest FOM value found for BST thin films with Ce concentration of 1 mol% was 48.9. The value of the leakage current densities, measured at 300 kV/cm shows a dependence of Ce contents. As a Ce content increases from 0 to 1 mol%, the value of leakage current densities for the BST thin films decreased. For 1 mol% Ce doped BST film, we obtained the lower leakage current densities. As shown in Table 1, further addition of Ce causes the increase in the leakage current density. The improved leakage current density (compared with undoped BST films) may be explained as follows. Aliovalent, A site dopants such as La³⁺, Ce³⁺, and Bi³⁺ are known to produce n-type semiconductivity in BaTiO₃ [11] and Ce³⁺ with charge 3+ behaves similarly to La³⁺ [12]. The charge balance compensation mechanism when Ba²⁺ is replaced by Ce³⁺ may be represented as follows:



Therefore Ce acts as a donor in the BST structure suppressing the inherent oxygen vacancy concentration formed at the top electrode/BST interface. This prohibits a formation of charge carriers. The decreased leakage current was also found to be dependent on grain size of the film. The undoped BST films with large grain size have short conduction paths along the highly resistive grain boundary resulted in higher leakage current compared with Ce doped BST film with smaller grain size.

4. 결론

We have shown that Ce-doped BST films having variable Ce contents to form high tunabilities, low losses, and high FOMs, can be prepared on a Pt (120 nm)/ Ti (30 nm)/ SiO₂/ Si substrate using the sol-gel method. The dielectric constant and dielectric loss of the BST films decreased with increasing Ce content, while leakage current decreased with increasing Ce content of the BST thin films, reaching a

minimum leakage current at 1 mol%, and then increased with further addition. The improvement of the electrical properties of Ce-doped BST films may be related to the decreased concentration of oxygen vacancies due to improved oxygenation of BST films in the presence of Ce. The dielectric constant, loss factor, and tunability of the 1 mol% Ce doped BST thin films were 320, 0.011, and 53.7%, respectively.

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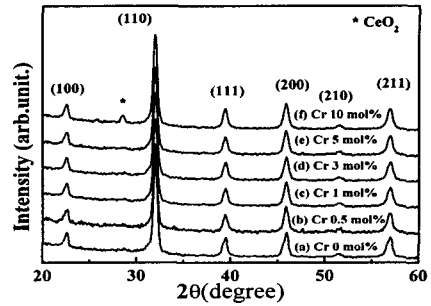


Figure 1. XRD patterns of the undoped and Ce-doped BST thin films annealed at 700 °C.

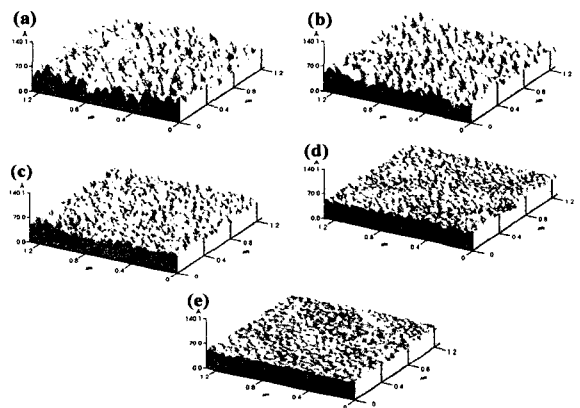


Figure 2. AFM micrographs of the 700 °C annealed (a) undoped, (b) 0.5 mol%, (c) 1 mol%, (d) 3 mol%, and (e) 5 mol% Ce doped BST thin films.

Table 1. Summary of dielectric and electric properties for undoped and Ce-doped BST thin films at a frequency of 100 kHz.

Ce mol%	ϵ	$\tan \delta$	Tunability (%)	FOM
0	358	0.025	34.2	13.7
0.5	339	0.021	42.5	20.2
1	320	0.011	53.7	48.9
3	298	0.018	46.3	25.7
5	263	0.019	38.1	20.1