Tunable 소자 응용을 위한 Sol-gel 법으로 제작된 BST 박막의 Cr 첨가에 따른 구조적, 유전적 특성

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Dielectric and Structural of BST Thin Films with Cr doped prepared by Sol-gel method for Tunable application

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Abstract

$Ba_{0.6}Sr_{0.4}TiO_3$ (BST) dielectric thin films doped by Cr were prepared using an alkoxide-based sol-gel method on the Pt/Ti/SiO2/Si substrate. Atomic force microscopy and x-ray diffraction analysis showed that increasing the Cr doping ratio causes increased grain size while the surface remains smooth and crack-free. It was also found that compared with undoped films the increase of Cr content in BST improves the dielectric constant and the leakage-current characteristics. The figure of merit reached the maximum value of 72.3 at the 5 mol % of Cr doping. This composition showed the dielectric constant of 426, the loss factor of 0.0065, tenability of 47.7%, and leakage-current density (at the electric field of 100 kV/cm) of 5.31×10^{-8} A/cm^2. The results show that the Cr-doped BST thin films are prospective candidates for applications in tunable devices.

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

1. 서 론

Dielectric thin films are attractive materials for applications in tunable microwave devices such as electrically tunable mixers, delay lines, filters, capacitors, oscillators, resonators, and phase shifters [1-2]. Furthermore, for all the 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.

A wide range of materials such as (Ba,Sr)TiO3 (BST), (Pb,Sr)O3, (Pb,Ca)TiO3 [3-5], and similar titanates were studied for applications in tunable microwave devices. Among them, BST thin films are characterized by a lower loss tangent and higher tunability. Therefore, these films may be considered as the preferable candidates. There are several previous works devoted to investigations of the capability of BST thin films for tunable microwave devices applications. Kawahara [3] and Cole et al. [6]mentioned the problem that high tunability of BST thin films (about 50% corresponding to a bias voltage of less than 10 V) is accompanied by a high loss tangent (more than 0.02). Therefore, the problem of improvingthe dielectric properties of BST thin films still remains important.

It is well known that some dopants are able to modify and improve the properties of dielectric materials, including BST. According to the previous investigations [7-8], the electrical properties (dielectric constant, dielectric loss, and leakage current) of BST thin films are affected by the deposition method, film composition and thickness, microstructure, and type of dopant. Particularly, to reduce the dielectric loss and leakage-current density, the dopants occupied the B site in the ABO3 perovskite structure (Fe2+, Fe3+, Co2+, Co3+,Mn2+, Mn3+, Ni2+, Mg2+, Al3+, Ga3+, In3+, Cr3+, and Sc3+) are used [9-10]. Nevertheless, although the positive effect of doping for the BST films is rather clear, the investigations made before involved only few types of dopants. Therefore, the previous work does not enough provide information to improve the characteristics of the BST thin films for the applications in tunable microwave devices.

In this paper, we investigate the influenceof the cationic substitution of Cr in the B site, such as the Ti site of the ABO3perovskite structure, on the dielectric properties and structure of BST thin films.

2. 실 험

The precursor solutions for both undoped and Cr-doped Ba0.6Sr0.4TiO3 were prepared by the sol-gel method using barium acetate, strontium acetate, chromium acetate,and Ti-isopropoxide as the starting materials. The solid-state barium acetate, strontium acetate, and chromium acetate (as a dopant precursor with concentrations ranging from 0.5 to 10 mol %) were initially dissolved in acetic acid and then mixed to obtain a Cr-doped (Ba, Sr) stock solution. Titanium iso-propoxide was dissolved in 2-methoxyethanol under a N2 atmosphere. Finally, both starting solutions were mixed to prepare the stoichometric, transparent, and stable Cr-doped BST precursor.

For the fabrication of Cr-doped BST thin films, the Cr-doped BST precursor solution was syringed through a 0.2 m syringe filter on the Pt(120 nm)/Ti(30 nm)/SiO2/Si substrate. The films were deposited by the spin-coating technique at 4000 rpm for 30 s. After the spin-coating procedure the 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 hrin oxygen atmosphere for crystallization. The final thickness of Cr-doped BST thin film was about 200 nm.

The measurements of dielectric properties were carried out using a metal-insulator-metal capacitor cell. For these purposes, top Pt electrodes with the diameter of 200 mwere deposited on the Cr-doped BST films by the dc sputtering method. Capacitance-voltage characteristics, as well as dielectric constant and dielectric loss, were measured using a HP 4192 impedance analyzer. To investigate the crystallinity, phase formation parameters, and orientation of the Cr-doped BST thin films, X-ray diffraction (XRD) profiles were obtained using a CuK radiation source at 30 kV and 60 mA (Rigaku-D/MAX). Surface morphology of Cr-doped BST films was analyzed and quantified using an atomic force microscope (AFM, Digital Instrument NanoScope IIIa) under a contact-mode operation and the scanning speed of 1Hz and field emission scanning electron microscopy (FE-SEM, JEOL 6330F). The leakage-current densities of Cr-doped BSTthin films were measured using a semiconductor parameter analyzer (Agilent 4146C) at 0.1-V step voltage and delay time of 1 s.

3. 결과 및 고찰

Figure 1 shows the XRD patterns of BST thin films with various Cr doping ratios in the range of 0 - 10 mol %. Both undoped and doped BST thin films show crystallized cubic phase, perovskite polycrystalline structureswithout the preferred orientation and the absence of the pyrochlore phase. However, when the Cr doping ratio exceeds 10%, an undefined diffraction peak appears at 2 = 25.7. Considering the Joint Committee of Powder Diffraction Standard (JCPDS) data [11], this peak may be attributed to the formation of the CrO3 secondary phase. As a result, the formation of the secondary phase causes the decrease of the dielectric constant and the increase of leakage-current density, as compared with undoped BST films. Therefore, all the investigations of the dielectric and electric properties for Cr-doped BST films represented below were carried out at Cr-doping ratios 0 5 mol %. The XRD data also show that the increased Cr doping ratio from 0% up to 10% leads to the increase inintensity of diffraction peaks. However, the full widths at half maximum were found to be lower. This effect may be explained by the increase of the grain size with the increasing Cr content in BST films [12]. Additionally, as the Cr doping ratio increased, we obtained the systematic shift of all

reflection lines toward lower diffraction angles that indicate the decrease of cubic lattice parameters. The calculation of the lattice parameters on the basisof XRD data gives the value of 0.4018 nm for undoped BST films and value of 0.3923 nm for the films doped by 5 mol % Cr corresponding to the room temperature. The behavior of the lattice parameter may be explained as follows. The first expected reason is the gradual substitution of Ti ions by Cr ions in the BST structure. Actually, the ionic radius of Cr (0.64 Å) is noticeably lower than the ionic radius of Ti (0.98 Å). The second reason is that it is well known that the presence of oxygen vacancies increases the lattice parameter of oxide films. Therefore, the decrease of the lattice parameter with the increase of the Cr doping ratio may be related to the decreased concentration of oxygen vacancies that also improves the film crystallinity [13].

The data discussed above allows to predict the influence of Cr content on the ferroelectric properties of BST thin films. It is well known that the value of the dielectric constant of ferroelectric 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 to a higher value of dielectric constant. Accordingly, we expect that the doping by Cr will improve the dielectric constant of BST thin films.

Figure 2 represents the dielectric constant and dielectric loss of undoped and Cr-doped BST thin films as a function of Cr content and operating frequency. These results were obtained using an oscillation voltage of 0.1V and a frequency range of 100 Hz~1 MHz. The data show that the increased Cr doping ratio under the constant frequency conditions leads to the increase of the dielectric constant. Actually, as the Cr content increases, the dielectric constant increases from 386 (undoped films) up to the highest value of 426 for 5 mol % Cr-doped films. At the same time, the increased Cr doping ratio causes the decrease of the dielectric loss factor, which remains below 0.0065 (for 100 kHz) for all the samples of both doped and undoped BST films. As for the frequency effect, the result depends on the frequency range. The dielectric constant and dielectric loss show the rapid decrease in two frequencyranges below ~200 kHz. On the contrary, both parameters mentioned above demonstrate only a very slight decay in the higher-frequency range. The reason is that the dielectric constant and dielectric loss at the frequency scopes below 200 kHz are affected by the boundary layer between the grains and the electrode.

Figure 3 (a) shows the figure of merit (FOM) and tunability of undoped and Cr-doped BST thin films as a function of Cr content. 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 (%)], where dielectric loss is given on a percentage scale [14]. The FOM value reflectsthe 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. In Fig. 3 (a), we obtained the increase of both tunability and FOM with the increase of Cr content in BST thin films. The tunability and FOM of the 5 mol % Cr-doped film were 47.7% and 72.3, respectively. Additionally, Figure 3 (b) shows the tunability of the 5 mol % Cr-doped BST filmas a function of applied electric-field strength. As the electric field strength increases, the tunability increases monotonously, enriching the maximum value of 47.7% for 500 kV/cm. Note that this value is rather attractive for applications in tunable microwave electronics, such as, in phase shifter devices.

4. 결 론

In this study, we have shown that the alkoxide-based sol-gel method allows preparation of Cr-doped BST films with high tunabilities, low losses, and high FOMs. For Cr doping ranging between 0 and 5 mol %, the best dielectric properties were found to correspond to the 5 mol % of Cr doping. This composition showed the dielectric constant, loss factor, tunability, FOM, and leakage-current density (at the electric field of 100 kV/cm) such as 426.6, 0.0065, 47.7%, 72.3, and 5.31 10-8 A/cm2, respectively. These results suggest that improved dielectric properties such as dielectric loss,

constant, and leakage-current densities of Cr doped BST films are suitable for tunable devices.

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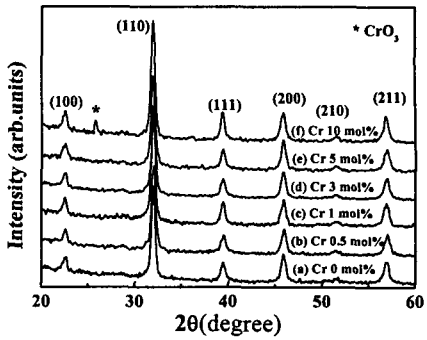

Fig. 1. X-ray diffraction patterns of undoped and Cr-doped BST thin films annealed at 700 C.

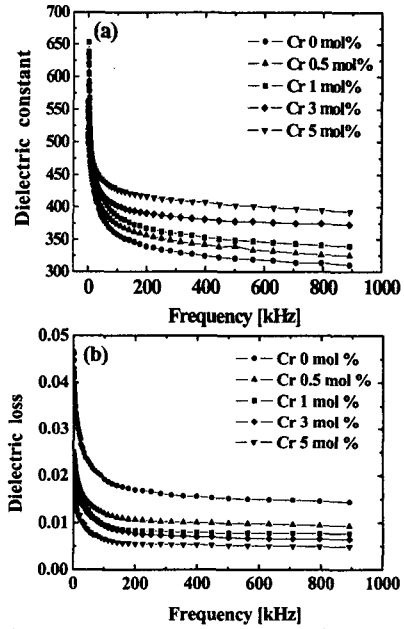

Fig. 2(a). Dielectric constant and (b) dielectric loss as a function of applied frequency for undoped and Cr-doped BST.

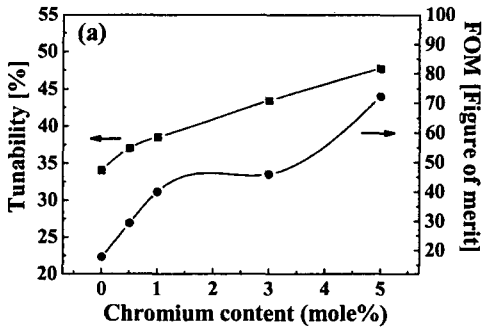

Fig. 3. Tunability and FOM of the undoped and Cr-doped BST thin films as a function of the Cr content