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Study on dielectric and tunable properties of Cr-doped $Ba_{0.6}Sr_{0.4}TiO_3$ thin films by rf sputtering

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Abstract $Ba_{0.6}Sr_{0.4}TiO_3$ dielectric thin films doped by Cr(0, 1, 2.5, 5, 10 mol%) (BSTC) were prepared by radio frequency magnetron sputtering on $Pt/Ti/SiO_2/Si$ substrates. The structure and morphology of the BSTC thin films were studied by atomic force microscopy and X-ray diffraction. The effect of Cr doping on the dielectric properties of BST thin films were analyzed. The results show that the dielectric loss of Cr doping BST thin films is lower than that undoped, and the tunability increased with Cr doping. The thin film doped with 5 mol% Cr has the best dielectric properties. The tunability, loss and figure of merit (FOM) at 1 MHz were 38.9%, 0.0183, and 21.3, respectively.

Introduction

In recent years, ferroelectric thin films have been studied extensively due to their various interesting properties, such as high dielectric constant, nonzero remnant polarization, and electric field dependent dielectric constant. The high dielectric constant of ferroelectric thin films and its non-linear dielectric property make ferroelectric thin films very attractive for applications in tunable microwave devices such as electrically tunable mixers, delay lines, filters, decoupling capacitors, oscillators, resonators, and phase shifters [1–4].

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Ferroelectric $(Ba,Sr)TiO_3$ (BST) is one of the most widely investigated tunable materials, which possesses a particularly high tunability, but there are several problems such as that high tunability of BST thin films is accompanied by a high loss tangent [5–7]. In order to reduce the dielectric loss of BST thin films, methods such as doping has been used. It is well known that small concentrations of dopants can dramatically modify the properties of ferroelectric materials such as BST. In particular to reduce the dielectric loss, the dopants occupied B site in the ABO_3 perovskite structure (Fe^{2+}, Fe^{3+}, Co^{2+} [8], Co^{3+}, Mn^{2+} [9], Mn^{3+}, Ni^{2+}, Mg^{2+}, Al^{3+}, Ga^{3+}, In^{3+}, Cr^{3+} [10], and Se^{3+}) is used [7, 11, 12]. There was a report about Cr-doped BST thin films fabricated by sol-gel method. It showed that doped BST had better dielectric properties than undoped [10].

In this article, we investigate the influence of the acceptor substitution of Cr in the B(Ti4+) site of the ABO_3 perovskite structure, on the dielectric properties and structure of BST thin films by rf magnetron sputtering.

Experimental details

The stoichiometric $Ba_{0.6}Sr_{0.4}Ti_{1-x\%}Cr_{x\%}O_3$ (x = 0, 1, 2.5, 5, 10) targets with diameter of about 60 mm were prepared via the conventional ceramic processing for sputtering. The (001) silicon substrates were cleaned by RCA cleaning process, and we made Si substrates oxidation diffuse a layer of SiO_2.Ti (20 nm) and Pt (111) (100 nm) were deposited on this silicon substrates at 150 °C. Then the substrates were annealed at 400 °C. Thus we get the $Pt/Ti/SiO_2/Si$ substrates.

BST/BSTC films with about 450 nm thickness were sputtered from the $Ba_{0.6}Sr_{0.4}Ti_{1-x\%}Cr_{x\%}O_3$ (x = 0, 1, 2.5, 5, 10) targets onto Pt/Ti/SiO_2/Si substrates under the conditions listed in Table 1. A post-deposited anneal was performed in a quartz tube furnace for 30 min in O_2 at 750 °C to crystallize the films. Then Pt top electrodes with 0.3 mm diameter were deposited onto the films through a shadow mask by dc sputtering for electrical testing. The samples were annealed at 550 °C for 30 min in air in order to improve the interface between the top Pt electrode and BSTC films.

Table 1 Sputtering conditions for BSTC thin films depositions

Targets	$Ba_{0.6}Sr_{0.4}Cr_xTi_{1-x}O_3$($x$ = 0,0.01,0.025,0.05,0.1)
Targer diameter (mm)	60
Target-substrate distance (mm)	65
rf power (W)	90
Overall gas pressure (Pa)	2
Ar/O_2 flow rate ratio	10%
Substrate temperature (°C)	600

Phase composition and crystallization of the BST/BSTC thin films were characterized by X-ray diffraction (XRD), using a D8-advance diffractometer. The films thickness

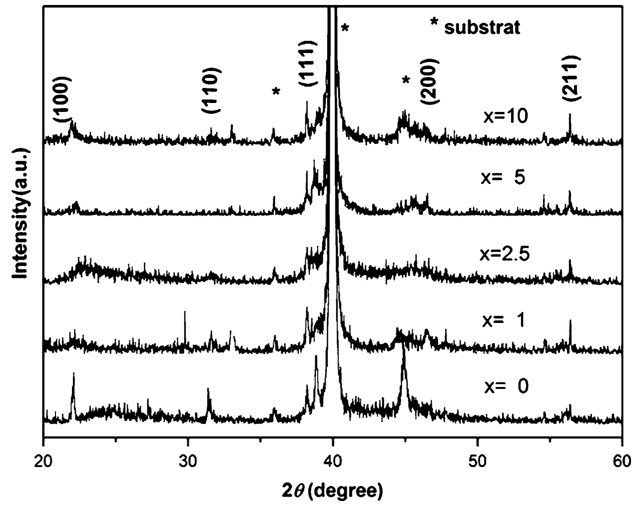
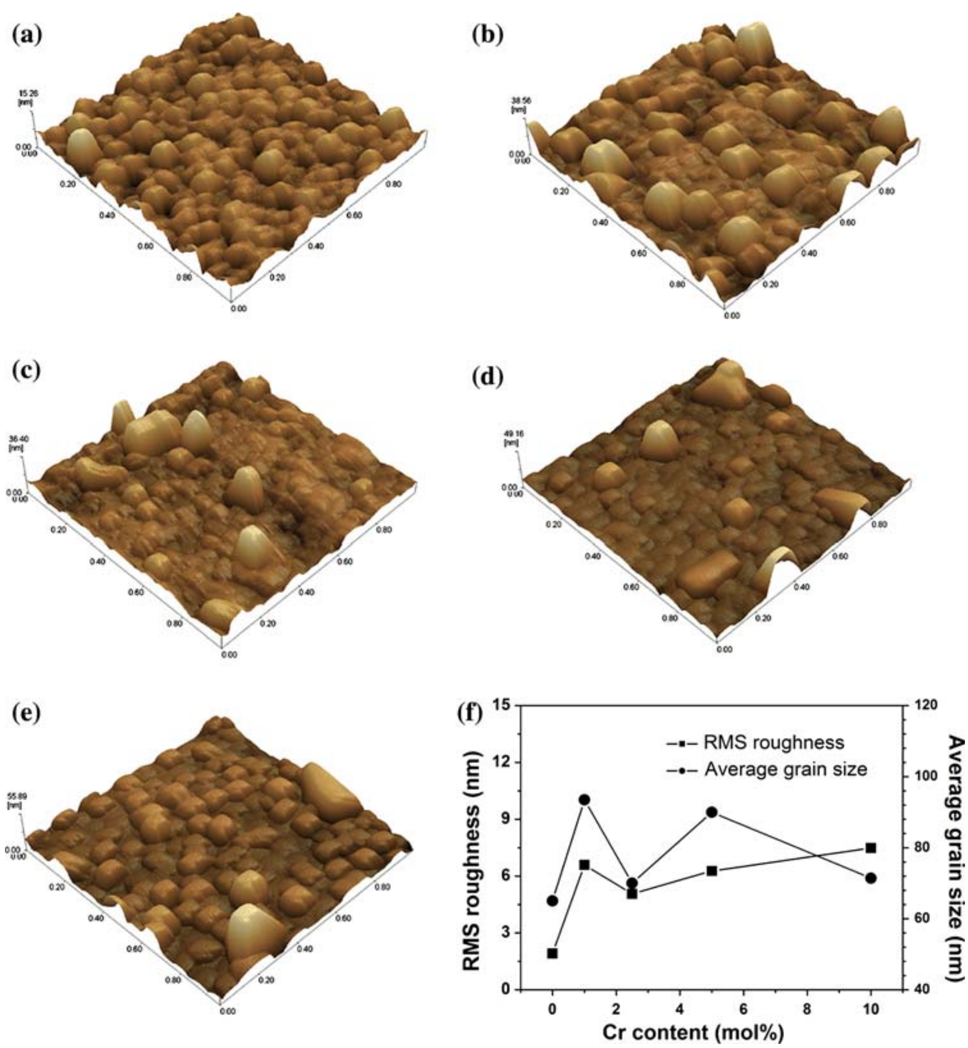


Fig. 1 X-ray diffraction patterns of the $Ba_{0.6}Sr_{0.4}Ti_{1-x\%}Cr_{x\%}O_3$ thin films

Fig. 2 AFM micrographs of the $Ba_{0.6}Sr_{0.4}Ti_{1-x\%}Cr_{x\%}O_3$ thin films (**a**) x = 0, (**b**) x = 1, (**c**) x = 2.5, (**d**) x = 5, (**e**) x = 10, and (**f**) the RMS roughness and average grain size of BSTC thin films as functions of Cr content



were measured by a Form Talysurf FTSS2-S4C Aspherics Measuring System (Taylor Hobson, UK). The surface morphologies and the grain size of the films were analyzed by atomic force microscope (AFM) (SPM-9500J3). The dielectric properties were measured with a 500 mV oscillating test field using an Agilent 4294A precision impedance analyzer.

Results and discussion

Figure 1 shows the X-ray diffraction patterns of the undoped and Cr-doped BST thin films. As shown by XRD patterns, it is clear that all BST/BSTC films are consisted of single-phase perovskite structures.

The surface morphologies of the undoped and Cr-doped BST thin films investigated by an atomic force microscope are shown in Fig. 2a–e. Figure 2f shows the grain size and surface root-mean-square (RMS) roughness of the films as a function of Cr content. It was found that all films were well crystallized. The grain size increased after Cr-doped, and when Cr content was 2.5 mol% the grain size was smallest. The surface RMS roughness was related to the grain size and orientation of the film.

Figure 3 shows the dielectric constant and dielectric loss of the BSTC films as functions of frequency, respectively. The results were obtained using an oscillation voltage of 500 mV from 100 Hz to 1 MHz at room temperature. We can see that dielectric constant of the Cr-doped films are lower than that of the undoped one, but the dielectric constants did not decrease too much with the Cr content increased. It is observed that the dielectric constant had bigger value when Cr content was 2.5 mol%, but the grain size was smaller than others. It was known that the value of the dielectric constant of ferroelectric thin films is strongly affected by microstructure, grain and size. A larger grain size results in a larger polarization; hence, higher value of dielectric constant is expected for larger grain size materials. The value of dielectric constant increases with increasing grain size since the value of dielectric polarization is proportional to the size of the grain [13]. In this work, we had reverse results. Further studies have to be carried out to explain this phenomenon. Dielectric loss of the Cr-doped BST films are lower than that of the undoped one too. Meanwhile, the increased frequency leads to the increase of the dielectric loss, because there is small dispersion at higher frequency ranges. The reason of the dispersion was that the presence of interfacial layers, such as surface pyrochlore phases and BSTC/Pt or Pt/BSTC interface in the films [6, 12, 14].

Figure 4 shows the dielectric constant and dielectric loss of the BSTC films as functions of applied dc electric fields, respectively. The curves were measured at 1 MHz and

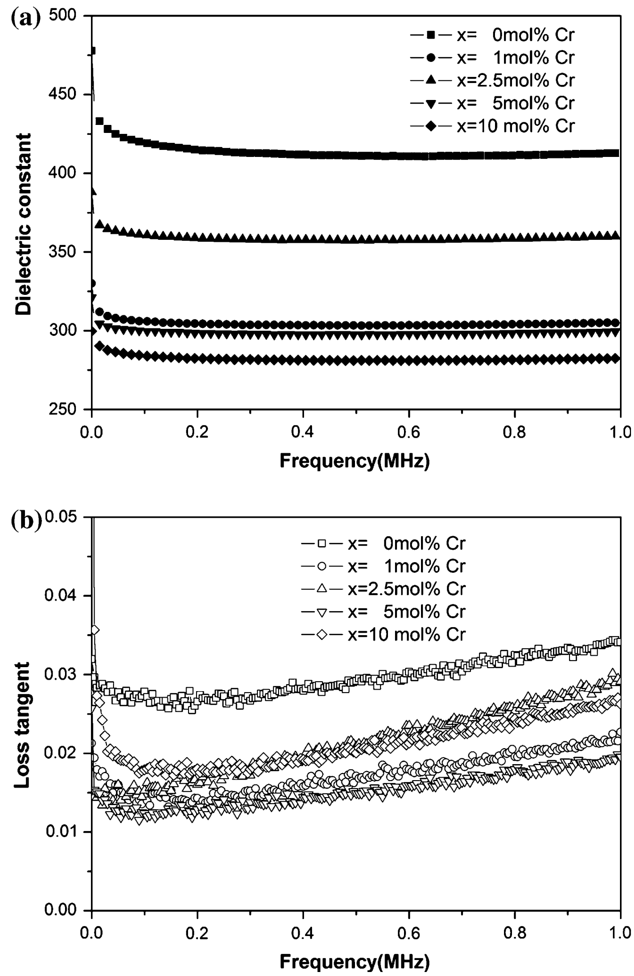
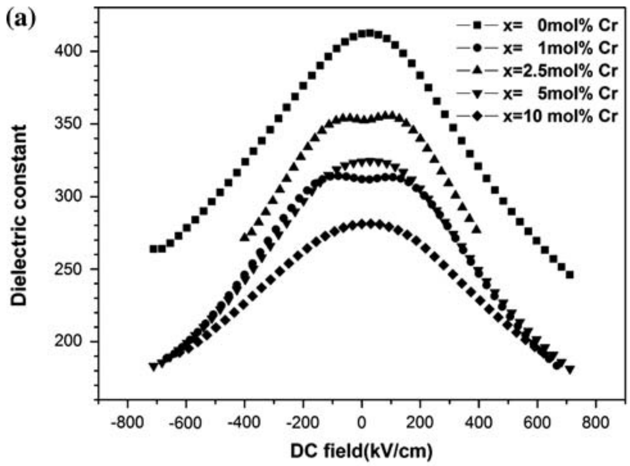


Fig. 3 (**a**) Dielectric constant and (**b**) dielectric loss as a function of frequency for the undoped and Cr-doped $(Ba_{0.6}Sr_{0.4})Ti_{1-x\%}Cr_{x\%}O_3$ thin films

room temperature. From the figures we can see that the dielectric constant and dielectric loss of the BSTC thin films nonlinearly vary with increasing applied dc field. But the curves are asymmetrical about $V = 0$ V. There are two factors that may reduce to the phenomenon. The one, this may be because the asymmetry of the top and bottom electrodes. In this work, we annealed three times totally, the bottom electrode had three times annealing but the top electrode had only one time. The other, this asymmetry may also be due to the acceptor dopants effect on the T_c. It was reported that lattice distortion could induce strains and strains can be impacted to thin films and have previously been used to alter the ferroelectric transition temperature (T_c) of ferroelectric materials. Therefore, misfit dislocations and interfacial space charge also could cause the asymmetry of the C–V curve [13, 15].

Figure 5 shows tunability, dielectric loss tangent (tanδ), and the figure of merit (FOM) of BSTC thin films as a function of Cr content at 1 MHz, 600 kV/cm electric field



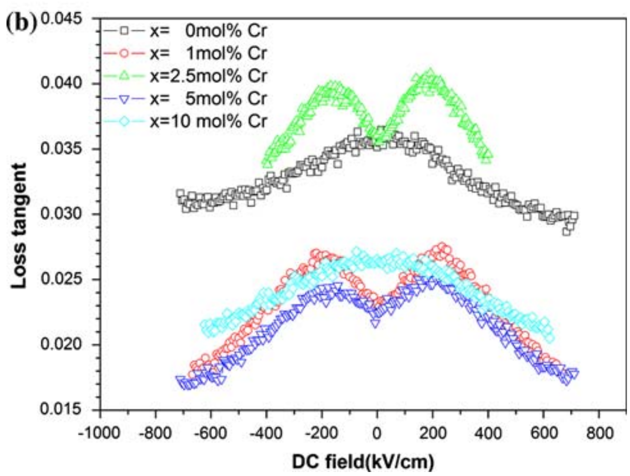


Fig. 4 Variation of the (**a**) dielectric constant and (**b**) dielectric loss of BSTC thin films as a function of applied dc electric fields at 1 MHz

and room temperature. The tunability is calculated from the equation $\Delta\varepsilon/\varepsilon_0$, where ε_0 is the capacitance at the zero-bias dc electric field, $\Delta\varepsilon$ is the change in dielectric constant relative to ε_0 at the maximum applied dc electric field. Here FOM is defined as FOM = tunability/tanδ. We can see that all of the Cr doped thin films exhibited lower loss tangent. It was reported that the acceptors-type dopants ions with a charge less than 4+ could substitute for Ti^{4+}, to prevent the reduction of Ti^{4+} to Ti^{3+} by neutralizing the donor action of the oxygen vacancies. As the electrons produced by oxygen vacancy can hop between different titanium ions and provide a mechanism for dielectric loss, the compensation for the oxygen vacancy with the correct amount of acceptor dopants helps to lower the loss tangent [6]. The tunability and dielectric loss for the BSTC thin films are 38.9% and 0.0183 when Cr content was 5 mol%, respectively, and the FOM value reaches a maximum value of 21.3. Such good properties are attractive for applications in tunable microwave electronics.

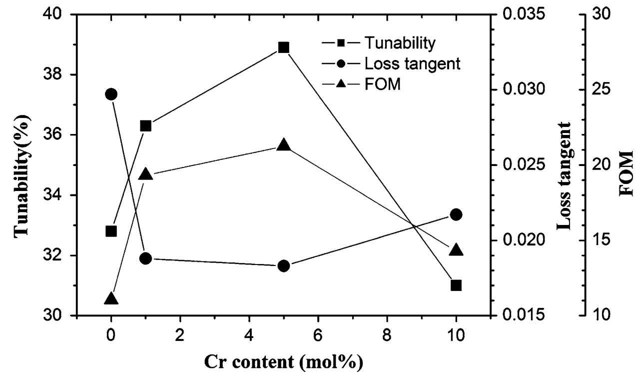


Fig. 5 Tunability, dielectric loss, and the figure of merit (FOM) of BSTC thin films as a function of Cr content at 1 MHz

Conclusion

In this study, we have prepared $Ba_{0.6}Sr_{0.4}Ti_{1-x\%}Cr_{x\%}O_3$ (x = 0, 1, 2.5, 5, 10) thin films by radio frequency magnetron sputtering on $Pt/Ti/SiO_2/Si$ substrates. It found that the Cr doped BST thin films have a better dielectric properties than undoped thin film. The Cr concentration in BST thin films has a strong influence on the properties of BSTC films. When Cr content was 5 mol%, the BSTC thin films obtained best dielectric properties, which can applied for tunable devices applications.

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