Influence of Ni-dopant on structural and optical properties of Ba\textsubscript{0.6}Sr\textsubscript{0.4}TiO\textsubscript{3} thin film by sol–gel technique

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Abstract. The pure and Ni-doped Ba\textsubscript{0.6}Sr\textsubscript{0.4}TiO\textsubscript{3} thin films were prepared on Si and LaNiO\textsubscript{3}/Si substrates via sol-gel technique, respectively. The microstructure and surface morphology of the films were characterized using x-ray diffraction and atomic force microscope. The films on LaNiO\textsubscript{3}/Si substrate were well-crystallized of the perovskite structure, and the diffraction peaks corresponded to BST standard pattern quite well. The Raman spectra showed the Ni dopant could improve the crystal quality of the BST films on Si substrate. The optical properties of the pure and Ni-doped films were studied by spectroscopic ellipsometry at room temperature.

1. Introduction

Barium strontium titanate, Ba\textsubscript{0.6}Sr\textsubscript{0.4}TiO\textsubscript{3} (BST), has been investigated as a high-dielectric constant material for various applications in advanced electronic devices, such as storage capacitors in gigabit dynamic random-access memory, microwave tunable devices, and ferroelectric random-access memories. Recently, the ferroelectric thin-film optical devices are especially attractive because of their predominance for monolithic integration with electronic and optical electronic devices. As a typical ferroelectric material, the BST thin films have high optical transparency in the visible wavelength region, high refractive index, and low extinction coefficient, which have been used for integrated optic devices, such as optical memory, optical storage and low-voltage electro-optic switching.[1,2] As a result, it is worthwhile to investigate the optical properties of the BST thin films.

In this paper, the structural and optical properties of the pure and Ni-doped BST thin films were investigated, which were deposited on Si and LaNiO\textsubscript{3}-coated Si (LNO) substrates by sol-gel technique, respectively.

2. Experimental Details

The precursor solution of the BST thin films were obtained by barium acetate [Ba(CH\textsubscript{3}COO)\textsubscript{2}], strontium acetate [Sr(CH\textsubscript{3}COO)\textsubscript{2}·1.5 H\textsubscript{2}O], and tetra butyl titanate [Ti(OC\textsubscript{4}H\textsubscript{9})\textsubscript{4}]. Firstly, Barium acetate, strontium acetate and nickel acetate were mixed in a mole ratio of Ba: Sr = 6: 4, and then dissolved in heated glacial acetic acid with constant stirring. After cooling to room temperature, the

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mixture was added with tetra butyl titanate drop by drop (the mole ratio of Ni:Ti is 2:98). Then, an appropriate amount of acetylacetone was added to stabilize the solution. Lastly, glacial acetic acid was added to make sure the concentration of the final precursor solutions was 0.3 M in Ti.

The crystallization of the pure and Ni-doped BST (Ni-BST) thin films was achieved via a rapid thermal annealing (RTA) process. These thin films were grown on Si and LNO substrates by spin-coating of the above precursor solutions at 4000 rpm for 25 s. After the spin-coating of each layer, the films were dried at 200 °C, prefired at 400 °C to remove the residual organic groups, and then annealed at 750 °C for 300 s in air. Finally, the six-layered BST thin films were post-annealed at 750 °C for 10 min. [3] The average thickness of a single-annealed layer can be obtained by spectroscopic ellipsometry, found to be about 65 nm. The desired films with a thickness of about 400 nm were achieved by repeating the spin-coating and heat treatment cycles.

The structure of the BST and Ni-BST films was analyzed by x-ray diffraction (XRD; D/max2200VPC), using CuKa radiation. The surface morphology of the films was examined using atomic force microscopy (AFM; Dimension 3100). Raman spectra were investigated by Jobin-Yvon LabRAM HR 800UV micro-Raman spectrometer. The thickness and the optical constants were determined by spectroscopic ellipsometry (SE). All the measurements were carried out at room temperature.

3. Results and Discussions

![Figure 1. XRD patterns of BST and Ni-BST films deposited on Si and LNO substrates.](image)

Fig. 1 shows the XRD patterns of the BST and Ni-BST thin films annealed at 750 °C on Si and LNO substrates, respectively. It can be seen that the film directly on Si substrate was not well crystallized, because the lattice constants of BST and Si do not match well. As shown in Fig. 1, the films deposited on LNO substrate were well crystallized to be perovskite structure, and the dominant orientations of the film were (100) and (200). LaNO₃ used as buffer layers can lead to a relatively high quality of the BST thin films. Compared with the BST film, the intensity of the diffraction peaks for the Ni-BST film is relatively strong, and no other phase is observed. It means that a small amount of Ni dopant can improve the crystal quality of the BST film without changing perovskite structure.

Fig. 2 presents the 2D and 3D AFM images of the BST and Ni-BST thin films grown on LNO substrates by sol-gel technique. The surfaces of the films are, in general, very smooth. The grains are densely and regularly packed without cracks or voids. The surface roughness is below 4 nm for both of them via AFM measurement. The average grain sizes on the surface of the BST and Ni-BST thin films
Figure 2. AFM images (2µm×2µm) of (a) 2D BST, (b) 3D BST, (c) 2D Ni-BST and (d) 3D Ni-BST thin films grown on LNO.

are nearly the same, about 60–100 nm, indicating that Ni dopant has little influence on grain size of the BST thin film. According to Chen’s article,[4] the crystal structures of the BST thin films are very close to cubic phase when grain sizes are smaller than 20 nm at the room temperature, while, they are tetragonal phase when grain sizes are > 20 nm. Namely, in this paper the crystal structures of the BST and Ni-BST thin films are tetragonal phase.

Figure 3. Raman spectra of the BST and Ni-BST thin films grown on Si.

Fig. 3 shows the Raman spectra of the BST and Ni-BST films grown on Si substrate by sol-gel method, annealed at 750 °C. From the figure, we found that a broadband centre at 264 cm⁻¹ corresponds to the A₁(TO₂) phonon mode, the peak at ~520 cm⁻¹ corresponds to A₁(TO₃) modes, and the peak at ~740 cm⁻¹ is attributed to A₁(TO₃).[3,5] Anyway, the characteristic Raman peaks persist for
all BST films in the tetragonal phase. The Raman spectra confirm that these films prepared in the present work have an excellent crystallinity with a tetragonal crystal structure. Compared to the BST film, no other Raman peaks appear in the Ni-BST film. However, Ni dopant enhances the specific peaks of the BST film. It means that Ni dopant improves the crystal quality of the BST film. This result is consistent with what was analyzed above.

**Figure 4.** Refractive index of the BST and Ni-BST films deposited on Si.

Spectroscopic ellipsometry (SE) is a powerful technique to investigate the optical constants of the materials. [3] The refractive index and the extinction coefficient of the BST films can be obtained by fitting the model function to the experimental spectroscopic ellipsometric data in expression.

The refraction index of the BST and Ni-BST thin films as a function of wavelength which range from 300 to 800 nm are shown in Fig. 4. As can be seen, the curve of the refractive index of the BST film is fairly flat above 500 nm, rises in short wavelength range, and increases quickly when the wavelength arrives at ultraviolet range (380 nm). The refractive index of the Ni-BST film increases slightly from 1.70 to 1.92 as wavelength decreases from 800 nm to 430 nm. It is obvious that the refractive index of the Ni-BST film is lower than that of the BST film in the metrical wavelength range. The difference is due to the Ni dopant in the BST thin films. The refractive index of the BST film decreases abruptly in comparison with that of the Ni-BST film. This means that the Ni dopant can change the optical properties of the BST films.

4. **Conclusions**
In this paper, the BST and Ni-BST thin films were successfully prepared on Si and LNO substrates by sol-gel method, annealed at 750 °C. The x-ray diffraction showed that all the films were perovskite structure. However, the films deposited on LNO substrate were crystallized much better, suggesting that the use of buffer layers strongly affected the crystallization and structural orientation. According to the AFM images, the surfaces of these thin films are smooth, and the grains are dense. All the grain sizes are over 20 nm, indicating that the crystal structures of the present thin films are tetragonal phase. The Raman spectra can also confirm the conclusion. From the XRD patterns and Raman spectra, it can be found that the crystal quality of the films with Ni dopant was improved, without changing perovskite structure. The effects of Ni dopant on the refractive index of the BST films have been studied by spectroscopic ellipsometry in the visible region. The result shows that the refractive index of the Ni-BST film is lower than that of the BST film in the metrical wavelength range, and increases more slowly as wavelength decreases in short wavelength range. This means that the Ni dopant changes the optical properties of the BST films.
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