Microstructure and optical properties of Zn-doped BaTiO$_3$ thin films

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Abstract. The high-quality BaTiO$_3$ and Zn-doped BaTiO$_3$ thin films were prepared on Si substrates by choosing the suitable raw materials and optimizing the preparation of thin films and the post process of annealing. Through the characterization technique of x-ray diffraction (XRD) and atomic force microscope (AFM), the influences of the different doping levels was discussed on the sizes, shapes and uniformities of BaTiO$_3$ and Zn-doped BaTiO$_3$ thin films respectively. Raman spectra measurements were carried out to study the lattice vibration modes of thin films. Meanwhile, the type of dopant and the occupied site in the BaTiO$_3$ lattice were also discussed in detail. For investigating of the mechanism of the doping effects, the optical properties of thin films were studied by spectroscopic ellipsometry furthermore. And the optical constant refractive index and extinction coefficient have been obtained in the wavelength from 400nm to 700nm.

1. Introduction

Barium titanate is a kind of perovskite ferroelectric materials with the earlier investigation. It owns the excellent piezoelectric, ferroelectric, dielectric and pyroelectric qualities. BaTiO$_3$ (BTO) thin films can be used to develop microelectronic devices. With the combination of superconducting thin films, they can also be used to develop ferroelectric superconducting devices$^{[3,4]}$. In order to develop ultra large scale integrated devices, the new demands for the quality of the films have been put forward. The Sol-gel method is simple and easy to manipulate, which can be used to prepare BaTiO$_3$ based
ferroelectric thin films with low cost and high quality\cite{1,2}. With more in-depth research, metallic ion doping was also considered to be a good way to optimize the properties of BaTiO$_3$ thin films\cite{1,10,15}.

In spite of the facts that zinc compounds show excellent photoelectric and piezoelectric properties\cite{10}, few reports are available on the use of Zn as a doping in barium titanate. Therefore, this paper deals with the preparation and characterization of Zn-doped BaTiO$_3$ (Zn-BTO) thin films and its influence on the structural as well as the optical properties.

2. Experiment
The precursor solution of the BTO thin films were obtained by barium acetate [Ba(CH$_3$COO)$_2$] and titanium tetrabutoxide [Ti(OC$_4$H$_9$)$_4$]. Firstly, barium acetate and glacial acetic acid were mixed by constant stirring at 40 °C for 60 min. After cool to room temperature, the chelating agent acetyl acetone and absolute ethyl alcohol were added successively. Secondly, tianium tetrabutoxide in equimolar ratio was added. This solution which was at constant volume of 40 ml was dispersed on the substrates and then spin-coated at 4200 rev. /min for 45 s. Lastly, the as-spun films were annealed at 700 °C for 5 min. In order to prepare thicker BTO films, a multilayer deposition procedure was followed and the spin-coating/thermal treatments cycle was repeated up to 8 times.

The chemical solution of Zn-BTO was prepared by the same way with adding zinc acetate, at different molar ratio of Zn: Ti between 2% to 6% at a step of 2% on silicon substrates\cite{2,14}.

The microstructures of the films were characterized by X-ray diffraction (XRD; Rigaku D/max-2200) using CuK$_\alpha$ radiation and atomic force microscope (AFM; Dimension 3100). Raman spectras were investigated by Jobin-Yvon LabRAM HR 800UV micro-Raman spectrometer. The optical properties were studied by spectroscopic ellipsometry (SE) in the 400-1000 nm wavelength range using the angle of 65° incidence. All measurements were carried out at room temperature.

3. Result and discussion
3.1. Structure analysis-XRD
Figure 1 shows the X-ray diffraction patterns of BTO and Zn-BTO thin films with different doping levels grown on Si substrates by sol-gel method, respectively. From this graph, it can be seen that all the films were perovskite structures. The observation of the (110) peaks is in agreement with the formation of a BTO perovskite phase\cite{10,15}.

Compared with the BTO film, the intensity of the diffraction peaks for the Zn-BTO thin film are relatively strong. Moreover, no other phases are observed. It can be concluded that a minute amount of Zn dopants can improve the crystal quality of the BTO film without changing perovskite structure. According the parallel slight movements of the curves of Zn-BTO thin films, it can be deduced that the changes of lattice constantly caused by dopant are existed but inconspicuous. The a(110) cell parameter is found to be 39.3nm taking account of the residual peak at 31.48°.
3.2. Surface analysis-AFM

The surface conditions of BTO and Zn-BTO films grown on Si substrates are observed by AFM micrograph, as shown in Figure 2. The results can be seen that the surfaces of all these films are uniform, dense and free of voids. However, the average size of the BTO grains estimated is much bigger than critical size of 49 nm for BTO thin films. It can be inferred that the growth properties of these BTO films present columnar with its particular orientation figure at high annealing temperature [9,10].

From images of Figure 2 it can also be included that Zn dopant can improve the crystal quality of BTO thin films on Si.

Figure 2. AFM images (10µm×10µm) (a) BTO/Si, (b) Zn-BTO/Si 2%, (c) Zn-BTO/Si 6% of thin films by sol-gel method.

3.3. Optical properties analysis
Since Raman selection rules are strictly associated with the orientation of the polar axis, the presence of only one kind of domains with polarization normal to the substrate (c-domains) or parallel to the substrate (a-domains) can be easily determined from polarized Raman studies.

In the tetragonal ferroelectric BTO one expects $3A_1 + 4E + B_1$ Raman active optical phonons. Here, $A_1$ is a nondegenerate mode, $E$ is the double degenerate mode, and $B_1$ is the silent mode. Due to the action of the long-range electrostatic potential field, the polar $A_1$ and $E$ modes split into transverse (TO) and longitudinal (LO) components \[11-13\].

Figure 3 shows the peaks at $\sim 305 \text{ cm}^{-1}$ ($E(\text{TO}_2+\text{LO}_2)$) and $\sim 719 \text{ cm}^{-1}$ ($A_1(\text{LO}_3)$) are specific to the tetragonal phase of BTO and the peak at $\sim 504 \text{ cm}^{-1}$ ($A_1(\text{TO}_2)$) which occurs both in the tetragonal and cubic phase of BTO. It, increasing the amount of doping, leads to the enhancement of the specific peaks of BTO. These observations indicate that Zn dopant improves the density and the crystal quality of BTO films.

In order to investigate the optical properties of the Zn-BTO thin films deposited on Si substrate, spectroscopic ellipsometry is used. Figure 4 shows the refractive index, $n$ and extinction coefficient, $k$ of the Zn-BTO thin films. Comparing with the films of different doping levels, it can be clearly seen that both $n$ and $k$ decrease obviously with the doping addition increases. Moreover, $k$ decreases rapidly with the increasing wavelength \[7\].

With the molar ratio of Zn rises from 2% to 6%, the refractive index of the films declines from 2.15 to 1.98 at 400 nm. Meanwhile the extinction coefficient of them decreases rapidly from 0.025 to 0.0135 at 400 nm and to zero at 700 nm. The implausible conclusion is that higher Zn dopant level leads to an increase in the band gap, due to Zn irons can compensate for the oxygen vacancy formed. Take the changes of deterioration “” for account, it presents the same tendency as the refractive index,
which means the crystal structure and atomic arrangement is experiencing the transitions from disorder to order with adding the amount of dopant.

![Graph](image)

**Figure 4.** Refractive index and extinction coefficient curves of the Zn-BTO thin films on Si substructures at different doping levels

4. Conclusion

In this work, the high-quality ferroelectric BTO and Zn-BTO thin films were successfully fabricated on Si substrates by sol-gel method. The principle of the chemical solution for preparing Zn-BTO thin films was analyzed, and the theory showed that the best way to produce Zn-BTO thin films on Si substrates was by using zinc acetate, titanium tetrabutoxide and barium acetate as raw materials, acetic acid as the solution mixed with the chelating agents, with multi-times repeats of spin-coating and thermal treatments.

According the X-ray diffraction patterns, the addition of Zn did not modify the perovskite structure of BTO, which remained tetragonal, but led to lattice expansion a little which was caused by microstructure changes. It could be seen from the AFM images that the surfaces of Zn-doped films are more uniform and denser than un-doped ones. There was an increase of the optical band gap with the amount of Zn addition increased, which is due to the improvement of crystal quality and the changes of deterioration by dopants.

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