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Influences of Zn and Mn ions co-dopants on the optical and ferroelectric properties of $BaTiO_3$ thin films

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Abstract: Zn-Mn co-doped $BaTiO_3$ films were fabricated on Si (100) and LNO/Si (100) substrates by a sol-gel procedure. In order to study the effects of different doping levels on the microstructure and ferroelectric phase of $BaTiO_3$ thin films, -BTO films doped with Zn and Mn, respectively, were also investigated. Both the characterization of X-ray diffraction (XRD) and atomic force microscope (AFM) indicate uniform and dense films with average grain size under 30 nm. By comparisons of the optical constant refractive index and extinction coefficient of $BaTiO_3$ films in the wavelength from 400 nm to 700 nm, it was obtained that there is a change in the optical band gap due to the different amount of Zn and Mn added. Furthermore, a better defined P-E loop with a remnant polarization of 11.26 $\mu C/cm^2$ shows that Zn and Mn dopanting play an essential role in ferroelectric improvement.

Key words: $BaTiO_3$ thin films, Zn-Mn co-doping; sol-gel method, optical properties, ferroelectricity
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Zn-Mn 共掺对 BTO 薄膜光学性质及铁电性能的影响

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摘要:利用溶胶凝胶法在 Si (100) 和 LNO/Si (100) 衬底上成功制备了 Zn-Mn 共掺钛酸钡薄膜. 为了更充分地研究掺杂量对薄膜的晶体微结构和铁电性的影响,利用同样的方法分别制备了不同掺杂量的掺 Zn 和掺 Mn 钛酸钡薄膜. X 射线衍射和原子力显微镜测量的结果表明薄膜均匀致密,且平均晶粒尺寸在30 nm 以内. 通过比较400 ~ 700 nm 范围内各钛酸钡薄膜的折射率和消光系数,可以得到,其禁带宽度随着掺 Zn 或掺 Mn 量的变化而变化. 对薄膜的铁电性能进行研究表明,Zn-Mn 钛酸钡具有良好的铁电性,其剩余极化值为11.26 $\mu C/cm^2$,说明微量的 Zn-Mn 共掺可以增强薄膜的铁电性.

关 键 词:钛酸钡薄膜;Zn-Mn 共掺;溶胶-凝胶法;光学性质;铁电性能
中图分类号:TB303 **文献标识码**:A

Introduction

Perovskite ferroelectric materials $BaTiO_3$ (BTO) (formula ABO_3), with different types of dopants such as Zn, Mn, Fe and Co at its B site has been focused on by extensive research activity[1-4]. It is of interest not only due to its large photorefractive effect when doped for optical processing applications[5-6], but also because of its excellent ferroelectric properties for developing ferroelectric dynamic random access memory devices[7-8].

In order to enhance its ferroelectric phase transition and ferroelectric properties, the new demands for films with high quality have been put forward. Based on the results of previous research works, metallicion

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doping was considered a good way to optimize the properties of $BaTiO_3$ thin films, especially two kinds of transition metals co-doping[4]. The sol-gel method, which is simple and easy to manipulate, can be used to prepare $BaTiO_3$- based ferroelectric thin films with low cost and high quality[9].

In spite of the facts that co-doped $BaTiO_3$ shows excellent photoelectric and piezoelectric properties, few reports are available on the use of Zn and Mn as dopants in barium titanate. Therefore, this paper deals with the preparation and characterization of Zn-Mn co-doped $BaTiO_3$ (ZnMn-BTO) thin films and the influences of doping on the optical properties as well as the ferroelectric enhancement of the films.

1 Experiments

The precursor solution of the BTO thin films were obtained by barium acetate [$Ba(CH_3COO)_2$] and titanium tetrabutoxide [$Ti(OC_4H_9)_4$]. Firstly, barium acetate and glacial acetic acid were mixed under constant stirring at 40℃ 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 at a constant volume of 30 mL was dispersed on the substrates and then spin-coated on Si (100) and LNO/Si (100) substrates at 4500 rev. /min for 20 s. Lastly, the as-spun films were annealed at 700℃ for 5 min. To prepare thicker BTO films, a multilayer deposition procedure was followed and the spin-coating/thermal treatment cycles were repeated up to 6 times. The chemical solution of Zn-BTO and Mn-BTO was prepared by the same way with adding zinc acetate, at different molar ratio of Zn:Ti and Mn:Ti between 2% to 10% with a step of 2% on silicon substrates. Similarly, the chemical solution of Zn-Mn co-doped BTO was prepared at molar ratio 1:1:98 of Zn:Mn:Ti. After repeating the spin-coating and thermal treatments on Si and La-NO_3/Si (100) substrates in the same condition, the final thickness of the films were about 500 nm.

The microstructures of the films were characterized by X-ray diffraction (XRD; Rigaku D/max-2200) using CuKα radiation and atomic force microscope (AFM; Dimension 3100). The optical properties were studied by spectroscopic ellipsometry (SE) in the 400-1000 nm wavelength range at an angle of 65° incidence. Ferroelectric property was measured by Precision Materials Analyzer (Preciosion Premier II) at 1 kHz with different applied electric field. All measurements were carried out at room temperature.

2 Results and discussion

2.1 Microstructure and composition

Fig. 1 shows the X-ray diffraction patterns of BTO and doped-BTO thin films, respectively, with different doping levels grown on Si substrates by sol-gel method. As is shown that all the films exhibit a pure perovskite phase structure with six characteristic peaks. Additionally, the observation of the (110) peaks is in agreement with the formation of a BTO perovskite phase[8-9]. Comparing with that of BTO films, the intensity of the diffraction peaks for the doped-BTO thin films are relatively strong. Moreover, no other phases are observed. It can be concluded that doping with little amount of Zn and Mn by sol-gel method improves successfully the crystal quality of the BTO films.

From the appearance of the peak on the curve of ZnMn-BTO thin films at 31.62°, it can be deduced that the changes of lattice parameters caused by dopant exist but inconspicuous. It can also be seen that the lattice parameter of (110) is found to be 3.93Å taking account of the residual peak at 31.48°. By using Scherrer's equation[2], the calculated value of ZnMn-BTO grain size is approximately 29.2 nm.

The surface of BTO, Zn-BTO and Mn-BTO films grown on Si substrates were observed by AFM micrograph, respectively, as displayed in Fig. 2. The results show that the surfaces of all these films are uniform, dense and crack-free. The average size of the Zn-BTO grains estimated in Fig. 2 (b) is slightly smaller than the grain size of the BTO thin films shown in Fig. 2 (a). On the contrary, the average

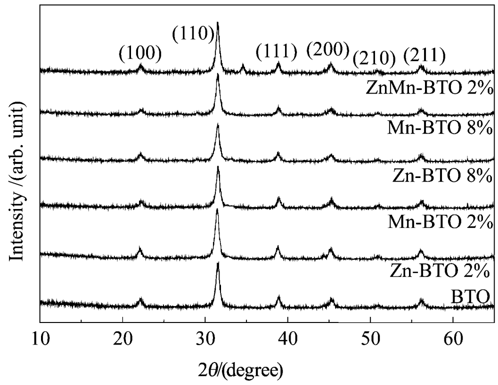

Fig. 1 XRD patterns of doped-BTO thin films grown on Si substrates
图 1 硅衬底上生长的掺杂 BTO 薄膜的 X 射线衍射图

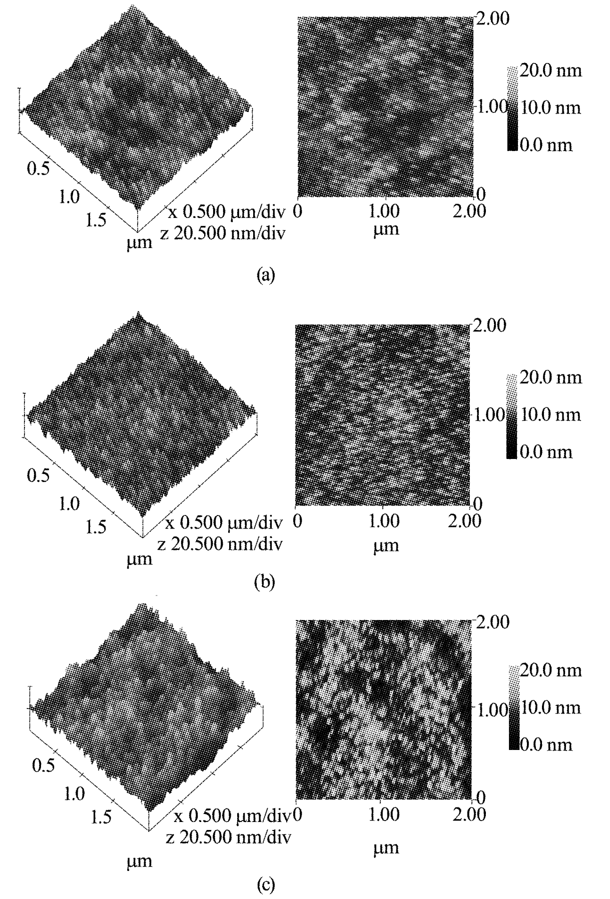

Fig. 2 AFM three dimensional surface micrographs of (a) BTO/Si, (b) Zn-BTO/Si 10%, (c) Mn-BTO/Si 10% thin films

图2 (a)未掺杂,(b)掺Zn10%,(c)掺Mn10%的BTO薄膜的AFM三维形貌图

size of the Mn-BTO grains observed in Fig. 2 (c) is slightly bigger than that. Moreover, the surface roughness determined for Zn-BTO films is much smaller than that of Mn-BTO films. It may indicate that Zn dopant can lead to atomic rearrangement and pore elimination at high annealing temperature[2]. Meanwhile Mn-BTO films present columnar growth properties due to the differences between the radius and electronic configuration of Zn and Mn ions[12-13].

2.2 Optical properties

In order to investigate the influence of Zn and Mn dopants on the optical properties of BTO thin films deposited on Si, spectroscopic ellipsometry was applied. Fig. 3 shows the refractive index n and extinction coefficient k of the Zn-BTO and Mn-BTO films in the ultraviolet-visible range respectively. In this range, both n and k decrease rapidly with the increase of wavelength. Besides, with the molar ratio of Zn rises from 2% to 8%, the refractive index of the films rises from 1.97 to 2.02 and the extinction coefficient of them declines from 0.0056 to zero at 600nm. Furthermore, with the molar ratio of Mn rises from 2% to 8%, the refractive index of the films rises from 1.97 to 2.04 and the extinction coefficient of them rises from 0.0026 to 0.01 at 600nm.

In the transparent region, refractive indexes of the Zn-BTO films and Mn-BTO films which decrease rapidly present the same tendency. The higher refractive index values may suggest a higher optical band gap of the Zn-BTO films, similar to that reported for pulsed laser deposited Zn-doping $BaTO_3$ thin films[2]. On account of the transition of Mn ion valence state that compensate for the oxygen vacancy formed, the band gap, which is related to the absorption cliff, increases with the rising of the Mn dopant level[10,11,13]. This high refractive index makes doped-BTO films suitable for antireflective coating[2]. Therefore, Zn and Mn dopants lead to the changes in the properties of polarization, deterioration and optical band gap of BTO films.

2.3 Ferroelectric properties

The polarization-electric field (P-E) hysteresis loops of Mn-BTO and ZnMn-BTO thin films measured at different applied electric field are displayed in Fig. 4, respectively. From the inset of Fig. 4, it can be seen that the P-E hysteresis loops of Mn-BTO films are unsaturated, although Mn dopant may optimize the ferroelectric properties of the BTO films. Moreover, the ZnMn-BTO films show a better-defined P-E loop with 11.26 $\mu C/cm^2$ of the remnant polarization (Pr) and 273.67 kV/cm of the coercive field (Ec) both of which are surprisingly large. In this work,

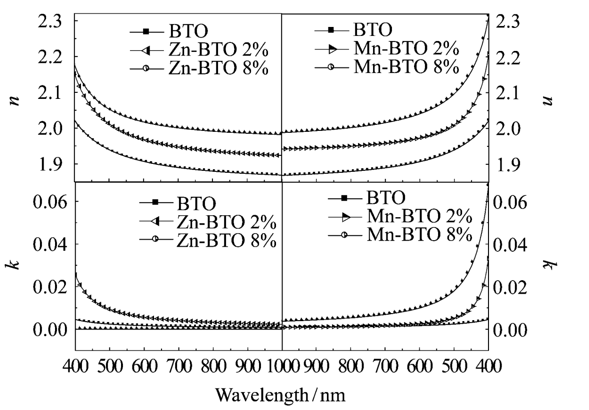

Fig. 3 Refractive index and extinction coefficient curves of the BTO and doped-BTO thin films on Si substructures at different doping levels

图3 硅衬底上未掺杂和掺杂BTO薄膜的折射率和消光系数

owing to leakage current, the P-E loops of undoped-BTO films are difficult to obtain and the remnant polarization of Zn-BTO films is also relatively weak which is estimated under 2.62 $\mu C/cm^2$.

In the past studies, the remnant polarization of the BTO films obtained by sol-gel method was always lower than that of bulk BTO[1,9]. In the meantime, the P-E hysteresis loops were often absent due to the leakage current and the oxygen vacancies which were produced during deposition and annealing[1,14]. From Fig. 4, it can be seen that the obtained Pr of MnZn-BTO thin films shows very high value. This value is not normal because there is some leakage current contibuted to the Pr as it is obvious in the P-E loop. In this work, Mn ions substituted for Ti^{4+} could be considered as negative centers. As the Mn^{3+} ions are reduced to Mn^{2+} ions, the electrons compensate the positive charges of the oxygen vacancies, thus reducing the leakage current. On the other hand, the acceptor states formed by Zn^{2+} may trap the unlocalized electrons thereby creating double charged acceptor centers that compensates for the oxygen vacancies[1,4]. These are reasons why Zn-Mn co-doped BTO films present a higher remnant polarization.

3 Conclusions

In this work, the high-quality ferroelectric BTO and Zn-Mn co-doped BTO thin films were successfully fabricated on Si substrates by the sol-gel method. According to the X-ray diffraction patterns and the AFM images, a little amount addition of both Zn and Mn did not modify the perovskite structure of BTO which remained tetragonal, and the surfaces of Zn-doped films were more compact than un-doped ones.

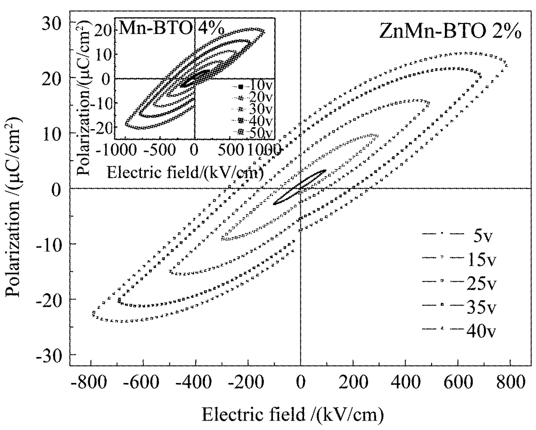

Fig. 4 Polarization-electric field hysteresis loops of Mn-BTO and ZnMn-BTO thin films
图4 掺 Mn 以及 Mn 和 Zn 共掺的 BTO 薄膜的 P-E 回线

By comparisons of the optical constant refractive index and extinction coefficient of films, it was obtained that there was a change of optical band gap due to the different amount of Zn and Mn added. Zn-Mn co-doped BTO films presented a better-defined P-E loop with a remnant polarization of 11.26 $\mu C/cm^2$.

REFERENCES

[1] LIU Zhi-Peng, DENG Hong-Mei, YANG Ping-Xiong, *et al.* Enhanced ferroelectric properties of Fe-doped $BaTiO_3$ thin film deposited on $LaNiO_3$/Si substrate by sol-gel technique[J]. *Materials Letters*, 2009, **63**: 2622-2624.

[2] Fasasi A Y, Maaza M, Rohwer E G, *et al.* Effect of Zn-doping on the structural and optical properties of $BaTO_3$ thin films grown by pulsed laser deposition[J]. *The solid films*, 2008, **516**: 6222-6232.

[3] HU Zhi-Gao, LI Ya-Wei, CHU Jun-Hao, *et al.* Composition dependence of dielectric function in ferroelectric $BaCo_xTi_{1-x}O_3$ films grown on quartz substrates by transmittance spectra [J]. *Applied Physics Letters*, 2008, **92** (081904).

[4] ZHOU Qi-Gang, ZHAI Ji-Wei, YAO Xi. Influence of Mn-Mg co-doping on the dielectric properties of barium strontiun titanate thin film[J]. *Journal of Inorganic Materials*, 2007, **22**(3): 519-523.

[5] Clark N A, Lagerwall S T. Submicrosecond bistable electro-optic switching in liquid crystals[J]. *Applied Physics Letters*, 1980, **36**(11): 899-901.

[6] Scott J F. Applications of modern ferroelectrics[J]. 2007, *Science*, **315**: 954-959.

[7] Fong D D, Stephenson G B, Streiffer S K, *et al.* Ferroelectricity in ultrathin perovskite films[J]. *Science*, 2004, **304**: 1650-1653.

[8] Choi K J, Biegalski M, Li Y L, *et al.* Enhancement of ferroelectricity in strained $BaTiO_3$ thin films[J]. *Science*, 2004, **306**: 1005-1009.

[9] Manso-Silvan M, Fuentes-Cobas L, Martm-Palma R J, *et al.* $BaTiO_3$ thin films obtained by sol-gel spin coating[J]. *Surface and Coatings Technology*, 2002, 151-152.

[10] YANG Ping-Xiong, GUO Min, *et al.* Spectroscopic ellipsometry of $SiBi_2Ta_{2-x}Nb_xO_9$ ferroelectric thin films [J]. *Journal of Applied Physics*, 2005, **97**.

[11] YANG Ping-Xiong, QIN Su-Mei, *et al.* Optical and electric properties of strontium bismuth tantalate thin films [J]. *Materials Letters*. 2007, **61**: 2687-2691.

[12] Jung H Park, Hyun M Jang, Hyung S Kim, *et al.* Strain-mediated magnetoelectric coupling in $BaTiO_3$-Co nanocomposite thin films[J]. *Applied Physics Letters*, 2008, 92.

[13] Qian L, Bi X F. Evaluation of magnetoelectric coupling in a $BaTiO_3$-Ni composite ferroic film by impedance spectroscopy[J]. *Applied Physics Letters*, 2008, **92**.

[14] Xu J B, Shen B. Zhai J W. Structure, dielectric and ferroelectric properties of highly (100)-oriented $BaTiO_3$ grown under low-temperature conditions [J]. *Applied Surface Science*, 2009, **255**: 5922-5925.