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Optical properties of RF-sputtered $Ba_{0.65}Sr_{0.35}TiO_3$ thin films

T. J. Zhang · S. Z. Li · B. S. Zhang · R. K. Pan · J. Jiang · Z. J. Ma

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Abstract $Ba_{0.65}Sr_{0.35}TiO_3$ (BST) thin films have been prepared by radio frequency magnetron sputtering on fused quartz at different substrate temperatures. Optical constants (refractive index *n*, extinction coefficient *k*) were determined from the optical transmittance spectra using the envelope method. The dispersion relationship of the refractive index vs. substrate temperature was also investigated. The refractive index of BST thin films increased from 1.778 to 1.961 (at λ=650 nm) as deposited temperature increases from 560°C to 650°C. The extinction coefficient of as-deposited BST thin films increased with the increase of the oxygen-to-argon ratio, which was due to the change of the film stoichiometry, structure, and texture of BST thin films. The oxygen-to-argon ratio also affected the fluorescence spectra. The fluorescence peaks intensity was greatly increased, apparent frequency shift was detected, and the linewidth became narrow as the ratio of oxygen to argon increased from 1:4 to 1:1. The fluorescence spectra also indicated the band transition of BST thin films was an indirect gap transition.

Keywords BST thin films · Refractive index · Extinction coefficient · Fluorescence spectra

1 Introduction

Ferroelectric thin films with large electro-optic effects are potential materials for integrated optical devices, such as planar waveguides [1], gate dielectrics [2], optical switches [3]. The use of thin films in electro-optic device can lead to a reduction in device size and an increase in interaction efficiency. A large number of ferroelectric thin films have already been investigated as candidates for electro-optic applications, including PZT [4], PLZT [5], and SBN [6]. $Ba_{1-x}Sr_xTiO_3$ (BST) is an excellent material because of its unique combination of large dielectric constant, large electro-optic coefficient, and low optical losses.

There have been some investigations on the dependence of optical properties of $BaTiO_3$ [7], $SrTiO_3$ [8], and BST [9] on the film deposition condition during sputtering. But there are hardly any reports about the effect of oxygen-to-argon ratio on the extinction coefficient and the fluorescence spectra. It is well known that optical properties of the films are affected by the sputtering process. It is necessary to study the effect of deposition conditions on the optical properties of BST thin films.

In this study, BST thin films have been prepared by RF magnetron sputtering on fused quartz substrates. We reported the behavior of the refractive index affected by the substrate temperature. The effects of the oxygen-to-argon ratio on the extinction coefficient and the fluorescence spectra of BST thin films were also studied.

2 Experimental

RF magnetron sputter deposition technique from a single target has been used to deposit BST thin films. BST ceramic target was prepared from $BaCO_3$, $SrCO_3$, TiO_2 powers (purity 99.9%) using standard solid-state process. With a frequency of 13.56 MHz, all BST thin films were prepared in oxygen and argon atmosphere under a fixed power of 120 W and a constant pressure of 3.9 Pa. The base

T. J. Zhang (✉) · S. Z. Li · B. S. Zhang · R. K. Pan · J. Jiang · Z. J. Ma
School of Physics and Electronic Technology, Hubei University, Wuhan 430062, People's Republic of China
e-mail: tj65zhang@yahoo.com.cn

pressure should be 1×10^{-5} Pa before introducing argon and oxygen (99.99%). A mixture of oxygen and argon at various mixing ratios ranged from 1:4 to 1:1, with a total flow of 24 sccm. The sputtering parameters were list in Table 1. The substrate is fused quartz with high transmittance. During the sputtering, the substrate temperature was kept at 560, 600, and 650°C, respectively.

The envelope method was used to calculate the optical constants. The optical transmission spectra of BST thin films were measured in the wavelength range of 190~800 nm using a double beam spectrophotometer (Perkin-Elmer Lambda 17 UV/VIS). The fluorescence spectra of BST thin films were measured at room temperature in the wavelength range of 550~650 nm using a spectrophotometer (Shimadzu RF-540) with the excitation wavelength of 450 nm.

3 Results and discussion

The refractive index n was derived by using the envelope method [10] on the basis of the following expressions,

$$n = \sqrt{N' + \sqrt{N'^2 - n_s^2}} \tag{1}$$

$$N' = \frac{1}{2}\left(1 + n_s^2\right) + \frac{2n_s(T_{\max} - T_{\min})}{T_{\max}T_{\min}}, \tag{2}$$

in which $T_{\max}$ and $T_{\min}$ are the corresponding transmittance maximum and minimum at a certain wavelength λ in the optical transmittance spectrum as shown in Fig. 1, n_s is the refractive index of fused quartz.

Figure 2 displays the curve of refractive index of as-deposited BST thin films as a function of substrate temperature. The refractive index of the as-deposited film increases from 1.778 to 1.961 (at λ=650 nm) as deposition temperature increases from 560 to 650°C. The dependence of the refractive index on substrate temperature is agreeable with those normally observed in many oxides [11–13]. The refractive index of the films increases with the substrate temperature increasing, which may be attributed to an increase in packing density, crystallization, and also to the oxygen deficiency.

Table 1 Sputtering parameters.

Parameters	Description/Values
Target material	Ceramic BST
Base pressure	1.0×10^{-5} Pa
Substrate temperature	560°C, 600°C, 650°C
O_2/Ar	1:1, 1:2, 1:4
RF power on target	120 W
Working pressure	3.9 Pa
Sputtering time	3 h

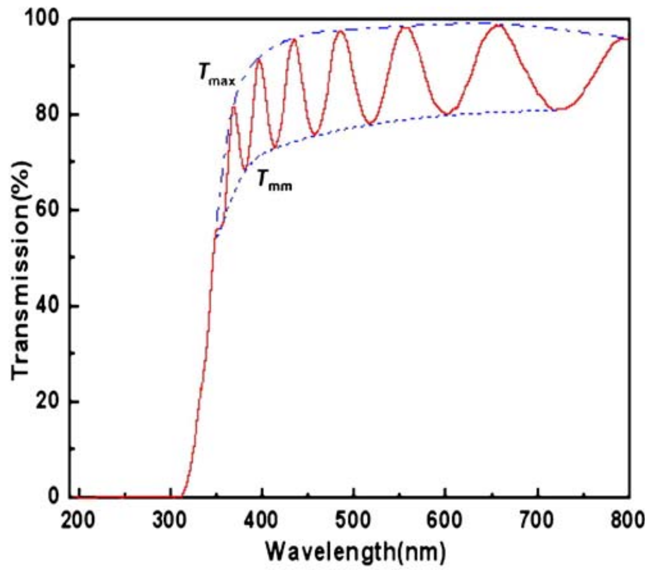

Fig. 1 Typical optical transmittance spectra of BST thin films with the $T_{\max}$ and $T_{\min}$ envelops

The extinction coefficient k can be calculated by using the following formulas,

$$\alpha = 4\pi k/\lambda \tag{3}$$

$$k = \frac{\lambda}{4\pi d}\ln\frac{(n-1)(n-n_s)\sqrt{\frac{T_{\max}}{T_{\min}}}+1}{(n+1)(n+n_s)\sqrt{\frac{T_{\max}}{T_{\min}}}-1}. \tag{4}$$

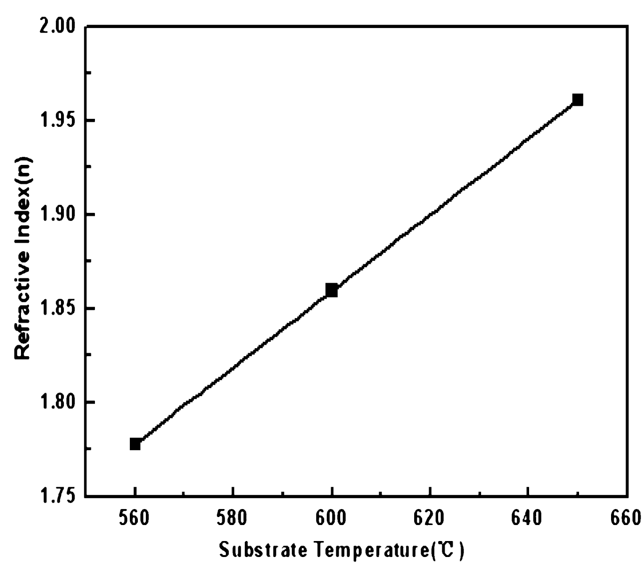

Fig. 2 The relationship between refractive index of as-deposited BST thin films and various substrate temperatures (at λ=650 nm)

Oxygen-to-argon ratio also plays an important effect on properties of BST thin films prepared by r.f. magnetron sputtering [14]. The extinction coefficient of as-deposited BST films is also affected by oxygen-to-argon ratio as shown in Fig. 3. The extinction coefficient has been found to increase from 3.01×10^{-3} to 4.67×10^{-3} with increasing the ratio of oxygen to argon. This behavior may result from the change of the film stoichiometry, structure, and texture, which are effected by oxygen-to-argon ratio. The atomic mass of Ba is heavier than Sr, therefore the Ba atomic sputtering rate is relatively reduced when the ratio of oxygen to argon increases, high temperature deposition of BST film under non-oxidizing atmosphere, such as Ar, generally produces oxygen vacancies in the film. As a result, the film stoichiometry, structure, and texture have been improved with increasing the ratio of oxygen to argon. So the extinction coefficient increases.

Figure 4 shows the fluorescence spectra of BST thin films at different oxygen-to-argon ratios. Increasing the ratio from 1:4 to 1:1 great increased the fluorescence peak intensity, detected an apparent frequency shift, and decreased the linewidth. It is well-known that the fluorescence peak intensity, frequency shift, and the linewidth strongly depend on the film's density. Increasing oxygen-to-argon ratio increase the grain size from 12.4 to 14.8 nm and decreases the ratio of the surface area to the volume; correspondingly, the defects of oxygen vacancy are down. As the films become more compact and contain fewer defects, the number of released photon increases, thus the intensity increases and the linewidth decreases. During the process of transition from the first electronic excited state lowest vibration energy level to the different vibration energy levels of the ground state, as shown in Fig. 5, there will be more electrons transferred to the lowest energy level of ground state if the film is more compact and has fewer defects. Thus more energy is released and the wavelength of the released photon will be decreased, as seen in Fig. 4. The fluorescence spectra also indicate the energy gap of

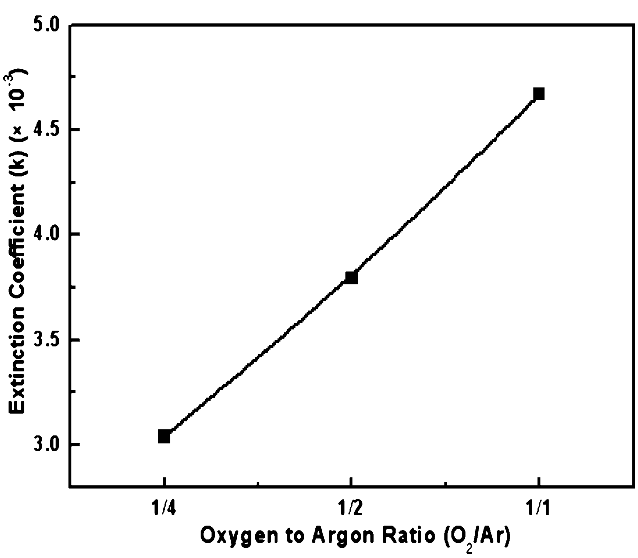

Fig. 3 The variation of extinction coefficient of as-deposited BST thin films with different oxygen to argon ratio (at λ=550 nm)

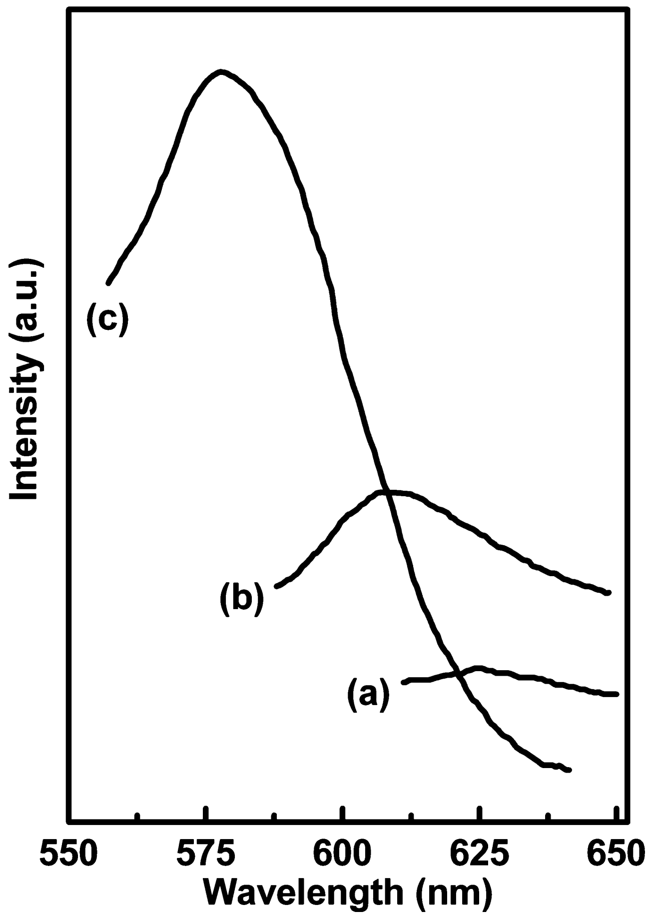

Fig. 4 The fluorescence spectra of BST thin films at different oxygen to argon ratio: (a) $Ar/O_2=1:4$, (b) $Ar/O_2=1:2$, (c) $Ar/O_2=1:1$

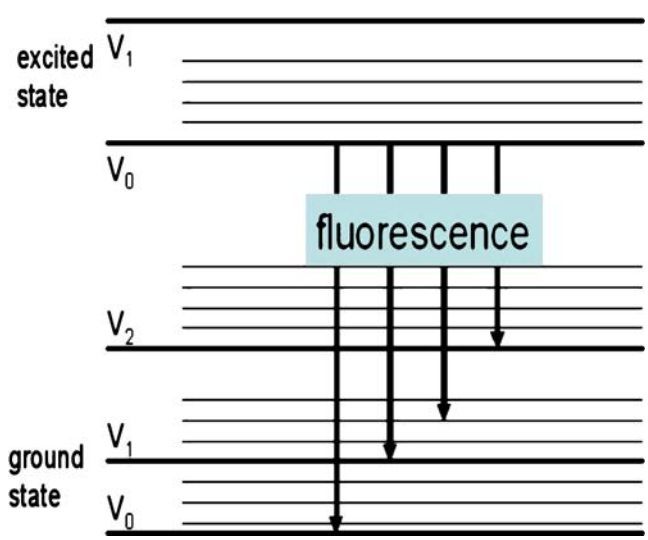

Fig. 5 The energy levels and transition of fluorescence

BST thin films is an indirect gap transition. It is known that the energy gap of BST obtained from the optical absorption edges is in a range from 3.0 to 4.2 eV [15–17]. The photon energy is 2.76 eV at the wavelength of 450 nm, which is apparently too low to give rise to a direct transition from valence band to conduction band. So there are some intermediate transition processes from valence band to intermediate defect energy levels, which dominate the transition. The indirect gap transition of BST thin films also has been reported in our research work [18].

4 Conclusion

BST thin films have been deposited on fused quartz substrates at different substrate temperatures by RF magnetron sputtering. The refractive index of as-deposited BST thin films increased from 1.778 to 1.961, with an increased substrate temperature from 560 to 650°C. The extinction coefficient increased with increasing the ratio of oxygen to argon. This behavior might result from the change of the film stoichiometry, structure, and texture, which were affected by oxygen-to-argon ratio. The oxygen to argon ratio also affected the fluorescence spectra. Increasing the ratio from 1:4 to 1:1 greatly increased the fluorescence peaks intensity, shifted the frequency, and decreased the linewidth. The intensity increase and the linewidth decrease resulted from the increase in the grain size, the decrease in the ratio of the surface area to the volume, and the decrease in defect density. The fluorescence peaks shift also resulted from the reduction of the number of defects and increase in film density. The fluorescence spectra also showed the energy gap of BST thin films was an indirect gap transition. All the above results show the optical properties of $Ba_{0.65}Sr_{0.35}TiO_3$ thin films are easily controlled, which indicates BST thin films are a promising candidate for electro-optic applications.

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References

1. C.S. Hwang, B.T. Lee, C.S. Kang, J.W. Kim, J. Appl. Phys. **83**, 3703 (1998)
2. D.Y. Noh, H.H. Lee, T.S. Kang, J.H. Je, Appl. Phys. Lett. **72**(22), 2823 (1998)
3. C. Hanson, H. Beratan, J. Belcher, SPIE **4288**, 298 (2001)
4. W.G. Liu, S.K. Jong, W.G. Zhu, Thin Solid Films **371**, 254 (2000)
5. W.F. Zhang, Y.B. Huang, M.S. Zhang, Appl. Surface Sci. **158**, 185 (2000)
6. C.H. Luk, M.T. Ho, C.L. Mak, K.H. Wong, K.H. Pang, J. Eur. Ceram. Soc. **19**, 1443 (1999)
7. M. Wohlecke, V. Marrello, A. Onton, J. Appl. Phys. **48**, 1746 (1976)
8. Y. Du, M.S. Zhang, J. Wu, L. Kang, S. Yang, Appl. Phys. A **76**, 1105 (2003)
9. C.B. Samantaray, A. Dhar, D. Bhattacharya, S.K. Ray, J. Mater. Sci., Mater. Electron. **12**, 365 (2001)
10. J.C. Manifacier, J. Gasiot, J.P. Fillard, J. Phy E: Sci. Instrum. **9**, 1002 (1976)
11. H. Kuster, J. Ebert, Thin Solid Films **70**, 43 (1980)
12. M.G. Krishna, K.N. Rao, M.A. Murty, J. Mater. Sci. Eng. **B5**, 427 (1990)
13. M.H. Suhail, G.M. Rao, S. Mohan, J. Appl. Phys. **71**, 1421 (1992)
14. M.S. Tsai, S.C. Sun, T.Y. Tseng, J. Appl. Phys. **82**, 3482 (1997)
15. M. Cardona, Phys. Rev. **140A**, 651 (1965)
16. C.N. Berglund, H.J. Braun, Phys. Rev. **164**, 1790 (1967)
17. Y.F. Kou, T.Y. Tseng, Mater. Chem. Phys. **61**, 244 (1999)
18. T.J. Zhang, H.S. Gu, Microelectron. Eng. **66**, 860 (2003)