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

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Abstract

$Ba_{0.65}Sr_{0.35}TiO_3$ thin films have been prepared by radio frequency (RF) 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 versus 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 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: 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], etc. 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 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 the optical properties of BST thin films as a function of deposition conditions.

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 pressure should be 1×10^{-5} Pa before introducing argon and oxygen (99.99%). A mixture of oxygen and argon at various mixing ratio 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

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Table 1
The sputtering parameters

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	120 W
Working pressure	3.9 Pa
Sputtering time	3 h

double beam spectrophotometer (Perkin-Elmer Lambda 17 UV–VIS). During the determination of the optical transmission spectra, the influence of the transmittance of the substrate has been eliminated. 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 optical constants were evaluated using the "envelope method" originally developed by J.C. Manifacier et al. [10]. For an insulating film on a transparent substrate, if we assume that (i) the film is weakly absorbing and (ii) the substrate is completely transparent, then using this method the refractive index (n), extinction coefficient (k) of the film can be evaluated from the transmission spectra.

The refractive index n was derived by employing the envelope method on the basis of the following expressions,

$$n = \sqrt{N' + \sqrt{N'2 - n_s^2}} \quad (1)$$

$$N' = \frac{1}{2}(1 + n_s^2) + \frac{2n_s(T_{max} - T_{min})}{T_{max}T_{min}} \quad (2)$$

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.

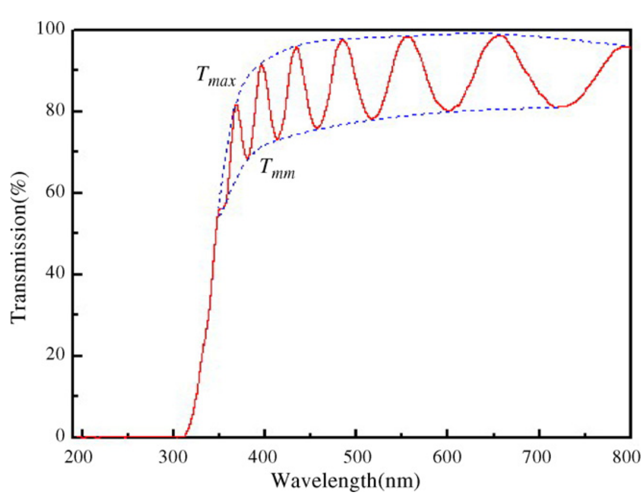


Fig. 1. Typical optical transmittance spectra of BST thin films with the T_{max} and T_{min} envelops.

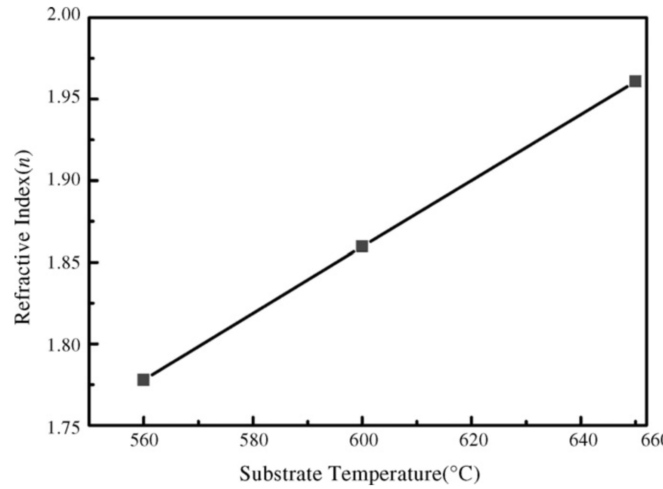


Fig. 2. The relationship between refractive index of as-deposited BST thin films and various substrate temperatures (at λ = 650 nm).

Keeping the ratio of oxygen to argon at 1:2, Fig. 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 substrate temperature increases from 560 to 650 °C. When the substrate temperature is lower than 560 °C, the refractive index remains almost constant. The dependence of the refractive index on substrate temperature is in agreement with those observed in many oxides [11–12]. At higher temperature 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.

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

$$\alpha = \frac{4\pi k}{\lambda} \quad (3)$$

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

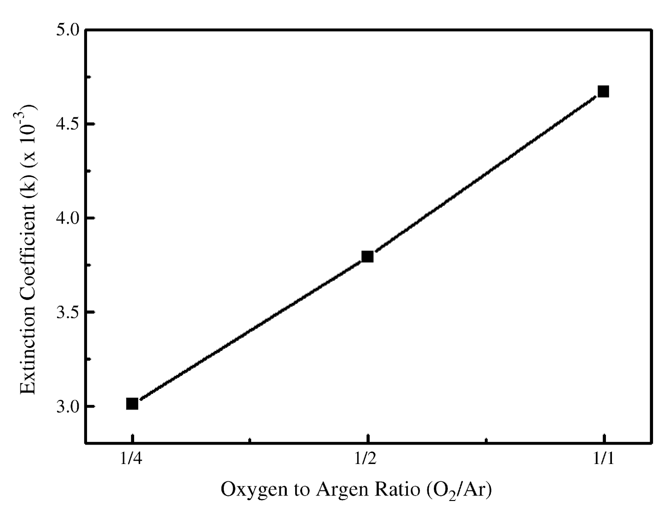


Fig. 3. The variation of extinction coefficient of as-deposited BST thin films with different oxygen to argon ratio (at λ = 550 nm).

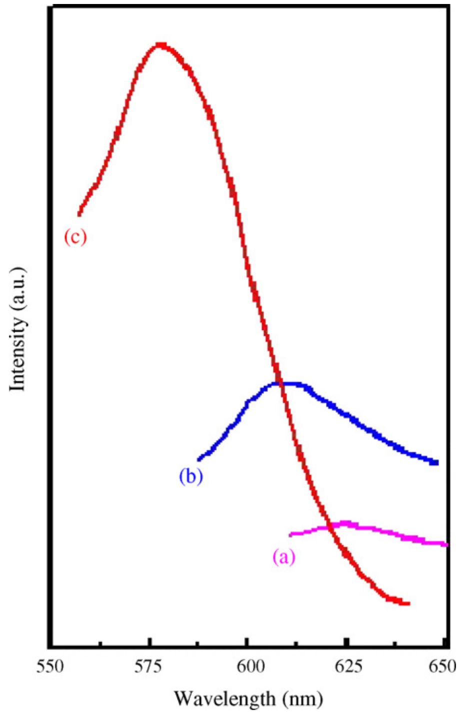


Fig. 4. The fluorescence spectra of BST thin films at different oxygen to argon ratio. (a) $Ar/O_2 = 1:4$, (b) $Ar/O_2 = 1:2$ and (c) $Ar/O_2 = 1:1$.

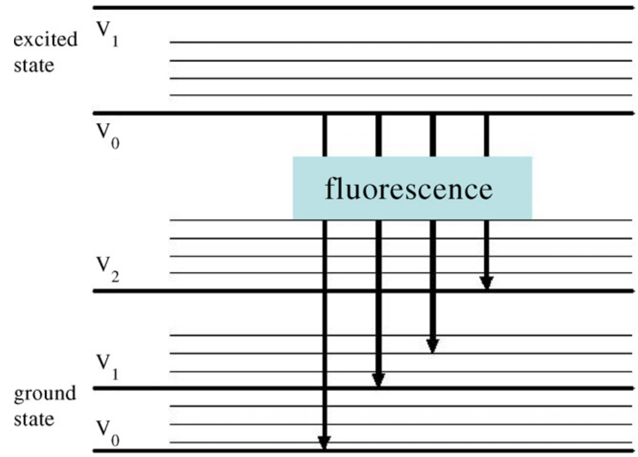
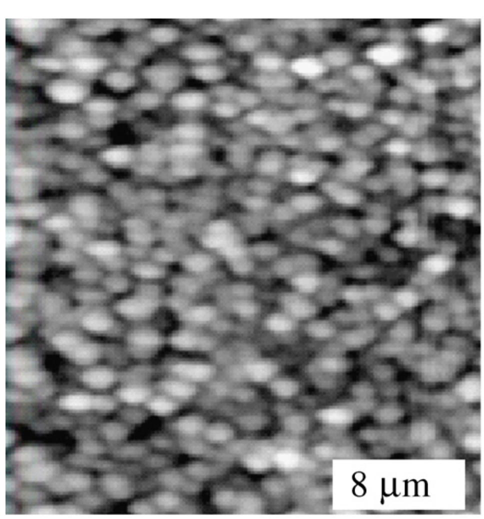


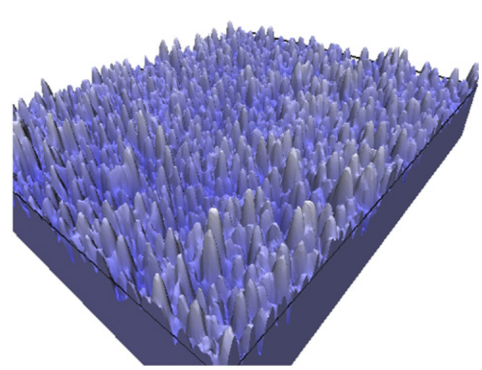
Fig. 5. The energy levels and transition of fluorescence.

Oxygen to argon ratio also plays an important effect on properties of BST thin films prepared by RF magnetron sputtering [13]. The extinction coefficient of as-deposited BST films which deposited at 600 °C is also affected by oxygen to argon ratio as shown in Fig. 3. The extinction coefficient has been found to increase 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. The extinction coefficient is also affected by the substrate temperature, which will be reported in another article.

Fig. 4 shows the fluorescence spectra of BST thin films at different oxygen to argon ratio. With increasing the ratio from 1:4 to 1:1, the fluorescence peaks intensity is greatly increased, apparent frequency shift is detected and the linewidth becomes narrow. It is well-known that the fluorescence peaks intensity, frequency shift and the linewidth are strongly depend on the films density. With increasing oxygen to argon ratio, the grain size becomes larger and the ratio of the surface area to the volume decreases, correspondingly the defects of oxygen vacancy get down. Then the films become more compact and 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



(a)



(b)

Fig. 6. AFM surface morphology and 3D-figure of BST thin films deposited at 600 °C and annealed at 700 °C: (a) surface morphology and (b) 3D-figure.

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. So the fluorescence peaks shift to high frequency. The fluorescence spectra also indicate the energy gap of 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 [14–16]. 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 have been reported in our research work [17].

On the other hand, AFM analysis also indicates BST thin film is more competitive for various electro-optic applications. AFM analysis of BST thin films deposited at 600 °C and subsequently annealed at 700 °C is shown in Fig. 6(a and b). The AFM morphology also indicates the film is dense and fine-grained. The surface average roughness of BST thin films is about 3 nm. This fine-grained thin film with higher packing density and smaller roughness is more important for electro-optic applications.

4. Conclusions

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. With increasing the ratio from 1:4 to 1:1, the fluorescence peaks intensity increased greatly, frequency shifted apparently and the linewidth became narrow. The intensity increase and the linewidth decrease resulted from the grain size became larger, the ratio of the surface area to the volume decreased and the defect density got down. The fluorescence peaks shift also resulted from the defects got down and the film became more compact. The fluorescence spectra also showed the energy gap of BST thin films was an indirect gap transition. AFM analysis of BST thin films which deposited at 600 °C and subsequently annealed at 700 °C indicated BST films had higher packing density and smaller roughness. All the above results show the optical properties of $Ba_{0.65}Sr_{0.35}TiO_3$ thin films are easily controlled, which indicate BST thin films are a promising candidate for electro-optic applications.

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