



Tunability of band-gap in barium strontium titanate films on anodic aluminum oxide templates

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ABSTRACT

Evolution of the band-gap and surface topography in $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ films fabricated on the anodic aluminum oxide templates with different pore diameters has been investigated by forming the nanostructure. Scanning electron microscope images show that the films tend to grow along the edge of the pores of templates. The optical band-gap of films is broadened from 3.25 to 4.20 eV with the pore diameters decreasing from 400 to 30 nm. Meanwhile, the optical band-gap of films on templates with the 30 nm pore diameter is nearly independent on the deposition time. These results are attributed to the quantum size effect and the specific structure of films. Our experimental work provides a further understanding of the modulated optical properties of oxides by controlling the diameter of templates.

1. Introduction

Barium strontium titanate has been considered to be an important material for applications in tunable microwave devices, such as phase shifters, filters, oscillators, and antennas owing to their high dielectric constant [1–5], relatively low dielectric loss [6], resistive switching properties [7–11], optical properties [12,13] and ferroelectric [14,15]. In particular, the blue shift of optical band-gap has been an important issue considering the potential applications in stable detectors for the solar blind and deep ultraviolet. Previous works of the tuning optical band-gap have been discussed in barium strontium titanate films. For examples, Singh et al. have reported that the band-gap of films can be adjusted from 4.67 eV to 3.93 eV by controlling the crystallinity [16]. Gao et al. have revealed that the doping nitrogen would make the optical band-gap of films decreased [17]. Roy et al. have observed a large blue shift in the band-gap of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ films pre-sintered at 400 °C [18]. Furthermore, Turkey et al. have shown that the calcination temperature of $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ would modulate the optical band-gap [19]. Although these results provide a feasible way to tune the band-gap of films, nearly most of them focused on the prepared condition of crystalline or PH of precursor sol [20,21]. Thus, it is particularly important to seek another method to make the band-gap of barium strontium titanate films continuously tunable. When the excited electronic states of crystallites are sufficiently small, the electronic properties are completely different from their bulk state according to the Brus model [22–24]. Moreover, by fabricating the films with various nanostructures, such as the nanotubes at different diameters, it would present

a tunable optical band-gap [25–27]. Therefore, anodic aluminum oxide (AAO) templates are proposed and widely used in low dimensional nanostructures due to their unique structures, good insulation, and simple preparation method [28–33]. Many researchers have successfully fabricated the nanostructures by using AAO templates and investigated their properties. Yao et al. have synthesized highly ordered TiO_2 nanowire arrays using diverse AAO templates [34]. Wu et al. have found the size of the AAO nanopores would influence the orientation of syndiotactic polystyrene crystals [35]. Meanwhile, the pore diameters of AAO templates affect not only the crystallinity of materials, but also the optical properties. Yuan et al. have shown a blue shift with the decrease of wall thickness in the synthesized TiO_2 nanotubes and nanowires arrays [36]. Thus, in this paper, we fabricated $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ (BST)/AAO nanostructures by depositing BST films on the top of AAO templates with different pore diameters. The band-gap and surface topography of BST films are strongly dependent on the pore diameter, which provides us a crucial way to control the band-gap of the BST films by changing the diameter of AAO templates.

2. Experimental procedure

Commercially supplied AAO templates (with a diameter of 12 mm and the thickness of 50 μm , Shangmu Tech.) with pore diameters of 30, 60, 200 and 400 nm were used without any treatment. The BST films were successfully deposited on AAO templates by a pulsed laser deposition method using a KrF excimer laser ($\lambda = 248$ nm) with the energy of 150 mJ/pulse and the repetition rate of 2 Hz. The AAO

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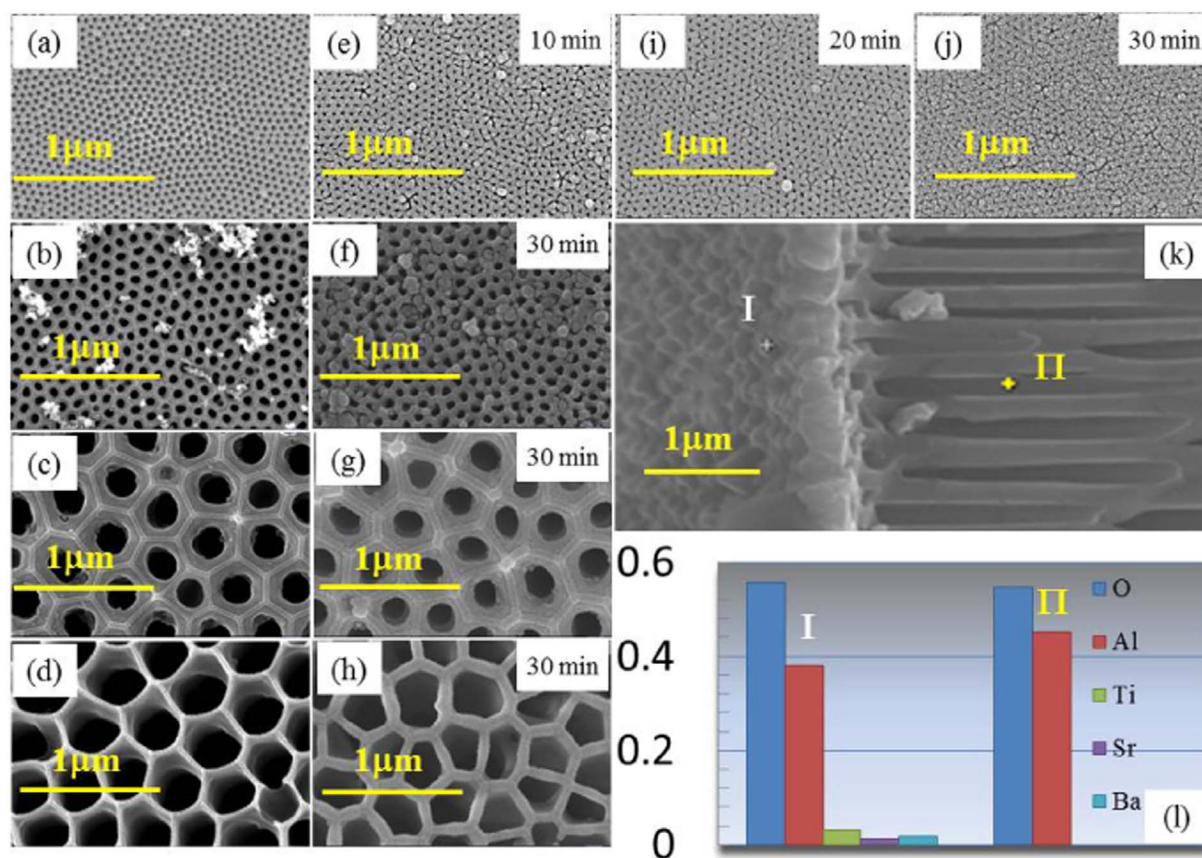


Fig. 1. (a), (b), (c) and (d) are SEM images of bare AAO templates with pore diameters of 30, 60, 200 and 400 nm, respectively; (j), (f), (g) and (h) are SEM images of corresponding BST/AAO with the deposition time of 30 min, respectively; (e), (i) and (j) are SEM images of BST/AAO (30 nm) with the deposition time of 10 min, 20 min and 30 min, respectively; (k) Cross-section SEM view of AAO/BST with AAO pore diameter of 200 nm. (l) EDS spectrum of BST/AAO (200 nm), the deposition time of 20 min, with the atomic percentage of the O, Al, Sr, Ba, Ti element on the surface and hole.

templates were placed 6.2 cm away from the target on a heated holder. All the BST films were grown at the same condition. The deposition chamber was evacuated to a base pressure of 1×10^{-4} Pa. During the process of deposition, the temperature of AAO templates was maintained at 800 °C and the oxygen partial pressure was kept at 10 Pa. In this situation, the deposition rate was about 1.6 nm/min. After deposition, the BST films were annealed in situ at 800 °C with a dynamic oxygen pressure of 300 Pa for 1 h and then cooled down to room temperature at 5 °C/min [37]. The surface and cross-section morphology of the BST/AAO nanostructures were characterized by the scanning electron microscopy (SEM, JSM-6700F, JEOL). The elemental composition of nanostructures was analyzed by energy dispersive spectroscopy (EDS). The elemental composition of BST/AAO films was monitored by X-ray photoelectron spectroscopy (XPS, Axis Ultra DLD, Kratos) using Al K α radiation ($h\nu = 1486.6$ eV). The UV–vis absorption spectrum was measured using an UV–vis spectrophotometer (U-3010, Hitachi).

3. Results and discussions

Fig. 1 clearly demonstrates SEM images, cross-section SEM view of bare AAO templates and corresponding samples with the deposition time of 30 min. It can be seen that the bare AAO templates present quite well-distributed nanopores with different diameters. And the edges become slender with the increasing pore diameters. When the pore diameter is 30 nm, the hole can be hardly observed after depositing the BST film. As the pore diameters increasing, all the holes can be seen clearly and the surface shows relatively vague compared with bare AAO templates, indicating the presence of BST films on the surface. It is interesting that the BST films prefer to grow on the edge of the pores of AAO templates during the deposition process [30]. The SEM images of

BST/AAO (30 nm) with different deposition time are shown in Fig. 1(e), (i) and (j). With increasing the deposition time, the walls of AAO holes become thicker and the BST films nearly cover the AAO templates. In order to verify the distribution of the BST film, we measure the composition of BST/AAO (200 nm) on the surface and hole, as shown in Fig. 1(k) and (l). It is observed that the BST films only are deposited on the surface of the AAO templates. XPS analysis was used to explore the detailed surface chemical composition of films. The XPS survey spectra obtained from BST/AAO (30 nm) of three different deposition times are shown in Fig. 2. In Fig. 2(a), the peaks of Ba, Sr, Ti elements are enhanced as the deposition time increases, indicating that the BST films appear on the AAO surfaces. Fig. 2(b) shows the Ba3d spectra consists of two peaks of Ba 3d_{3/2} and Ba3d_{5/2} with the binding energy of 794.95 eV and 779.65 eV, respectively [38,39]. Fig. 2(c), (d), (e) and (f) illustrate the fitted narrow scan of spectra of Ba3d_{5/2}, Sr3d, Ti2p, O1s of the BST film with the deposition time of 20 min, respectively. As shown in Fig. 2(c), the Ba3d_{5/2} can be fitted to superposition 779.6 eV and 780.6 eV, corresponding to the Ba photoelectron line in (Ba, Sr)TiO₃ and BaCO₃. Fig. 2(d) presents the fitted Sr3d narrow scan spectra. The Sr3d peaks can be fitted by Sr3d_{3/2} (135.64 eV) and Sr3d_{5/2} (133.75 eV) [40]. Fig. 2(e) shows the fitted peaks of Ti2p. It can be separated with Ti2p_{3/2} (457.85 eV) and Ti2p_{1/2} (463.66 eV) [37]. The fitted O1s narrow scan spectra is shown in Fig. 2(f). An O1s (531.24 eV) peak consists of three sub-peaks located at 531.8, 531.6 and 529.15 eV. The three sub-peaks are mainly affected by Al₂O₃ template, oxygen vacancies [41,42] and BST film [43]. According to the XPS analysis, it can be concluded that the BST films are formed on the AAO templates.

Fig. 3(a), (b) and (c) show optical absorption spectra of BST films on AAO templates with different pore diameter, deposition times and bare AAO templates, respectively. Fig. 3(d) illustrates the relationship

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