Effects of site substitutions and concentration on the structural, optical and visible photoluminescence properties of Er doped BaTiO₃ thin films prepared by RF magnetron sputtering

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ABSTRACT

The structural, optical and visible photoluminescence of the Erbium (Er) doped BaTiO₃ (BT:Er) thin films were studied in terms of Er^{3+} substitutions for Ba and Ti sites with different Er^{3+} doping concentrations (0, 1, 3 and 5 wt%). X-ray diffraction pattern of BT:Er films with different Er^{3+} concentration showed tetragonal phase with preferred orientation along (1 0 1) plane. The lattice constant of BT:Er film of 1 wt% Er^{3+} shrank and then expanded for higher concentration. This indicates that Er^{3+} ions are completely incorporated into the host lattice by substituting for Ba^{2+} sites for 1 wt% Er^{3+} and then Ti^{4+} sites for higher Er^{3+} concentration in the BaTiO₃ host. The crystallite size decreased for 1 wt% and then increased for higher Er (3 and 5 wt%) concentrations. The Scanning electron microscopy images revealed well patterned arrangement of larger spherical grains with neck formation. X-ray photoelectron spectroscopy analysis confirmed the presence of barium, titanium, erbium and oxygen in BT:Er films. An average transmittance >80% in visible region were observed for all the films. Optical band gap energy of BT:Er films were found to vary with increase in Er^{3+} concentration. The high refractive index >2 of these films can be used in optical application and anti-reflection coatings. Photoluminescence spectra of the films exhibited an increase in the emission intensity up to 3 wt% of Er^{3+} and then a decrease, due to self quenching. The improved optical properties of BT:Er films makes suitable for optical applications.

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1. Introduction

Barium Titanate, BaTiO₃ (BT) is one of the most widely used ceramic material in electronic industry. BT has a perovskite structure made upon a framework of corner linked TiO₂ octahedral with centrally occupied Ba^{2+} ions. The influence of the dopant ion depends on the substitutional site (Ba^{2+} or Ti^{4+}) as well as on the defects. The ionic radius of the dopant ion is essential for the determination of the substitutional site of the host material. The luminescence spectrum of lanthanides in the trivalent state caused by the ionization of $6s^2$ and 5d electrons and intracenter transitions of 4f electrons shielded by outer 5s and 5p electrons. It consists of a set of fairly narrow spectral lines from UV to IR range. Study on the luminescent properties of rare-earth (RE) doped materials are strongly motivated because of their technological applications

in photonic devices, next generation flat-panel displays, planar waveguide and structural probe. It is well known that the characteristic luminescence features of these materials are determined by the electronic structure of the rare-earth dopant, while the bandwidth and relative intensity of the PL spectra frequently depend on the crystal symmetry of the host matrix.

Erbium (Er^{3+}) is a potential phosphor for the fabrication of luminescent devices, because of its intense intra-4f transitions at wavelengths in the green ($^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^2H_{11/2} \rightarrow {}^4I_{15/2}$) and red ($^4F_{9/2} \rightarrow {}^4I_{15/2}$) spectral regions with a long intrinsic life time [1–3]. Erbium has a fixed 3^+ oxidation state, and due to its ionic radius of 1.004 Å, compared with the radius of 1.61 Å for Ba^{2+} and 0.74 Å for Ti^{4+}, it will occupy A (Ba) or B (Ti) sites within the perovskite lattice [4]. It is observed that the cation vacancy strongly depends on both sintering conditions and the nature of the donor dopant [5]. In BT films, the ionic compensation can occur (i) exclusively by titanium vacancies, and (ii) by equal concentrations of barium and titanium vacancies. In each case, the variation depends on the sintering temperature and synthesis conditions. BT:Er can be a promising candidate for optoelectronic devices

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due to the incorporation of Er^{3+} into BT thin films to form a solid matrix. BT:Er thin films can also be used in optical amplifiers and electroluminescent devices where electron–hole energy is transferred to Er^{3+} ion.

BT:Er thin films were fabricated using various methods, including metal organic chemical vapor deposition (MOCVD), RF sputtering, thermal evaporation, Molecular beam epitaxy (MBE) and laser ablation [6–11]. Among these, sputtering is the most widely used method due to its simplicity and effectiveness for fabricating thin films. So far, there have been only a few reports on the optical properties of BT:Er thin films. The optimizations of the film are very important for tuning the optical properties, in order to get better optical devices. By modifying the site substitution, varying the concentration of Er, the refractive index and the optical band gap can be varied. These films can be used in optoelectronic devices and antireflection coatings. The BT:Er films show emissions in 550, 630 and 690 nm regions. Such films have applications in display devices requiring these emission wavelengths.

2. Experimental details

BT:Er thin films were deposited onto quartz substrates by RF magnetron sputtering. The starting powders of $BaTiO_3$ and Er_2O_3 (99.9% purity, Sigma–Aldrich) were mixed in ethanol and ball-milled for 5 h. The resulting powder was then filtered and dried. The dried powder was mixed with binders, uniaxially pressed into a disk (5 cm diameter, 3 mm thickness). The disk was calcined at 1473 K for 3 h, to remove binders in an electric furnace, and then cooled to room temperature. The disc was employed for the sputtering target. The target to substrate distance was 5 cm. Before depositing the films, the quartz substrates were cleaned in alkaline solution, rinsed in deionized water, immersed in very dilute HNO_3 solution and then dipped in pure acetone. The sputtering chamber was initially pumped down to 5×10^{-5} mbar. The deposition of BT:Er layers was performed in an argon (purity: 99.99%) atmosphere and the deposition pressure was maintained at 0.01 mbar. The RF power was controlled at 100 W. Four different targets were prepared with different weight percentages of erbium: 0, 1, 3 and 5, respectively. All the as-deposited films were annealed at 1073 K for 1 h in air.

The X-ray diffraction (XRD) pattern of the films were measured by Philips X'pert Materials Research diffractometer operated at a voltage of 40 kV and a current of 30 mA, using Cu Kα (λ = 1.54 Å). The parameter setting for all XRD scans is 1.5 °/min and a step size of 0.0330° in a range of 20–60°. Surface morphology of the annealed films was examined by a Scanning electron microscope (SEM) (JEOL/EO JSM6390). XPS spectrum was recorded using a monochromatic Al Kα (1486.6 eV) source and a MAC-2 electron analyzer (RIBER system model-FCX 700). Optical transmittance measurements were carried out in the range 300–900 nm with a JASCO V-550 UV–visible spectrophotometer of 0.1 nm resolution. Swanepoel's envelope method [12] was used to calculate the optical constants such as film thickness and refractive index. Photoluminescence spectrum was recorded using the Horiba Scientific Fluoromax-4 Spectrofluorometer with a Xenon lamp as the excitation source having 0.3 nm resolution. The excitation wavelength used was 488 nm at room temperature.

3. Results and discussion

3.1. XRD studies

Fig. 1 shows the XRD pattern of BT:Er films deposited onto quartz substrates and annealed at 1073 K. The XRD pattern revealed the characteristic peaks of tetragonal BT phase at
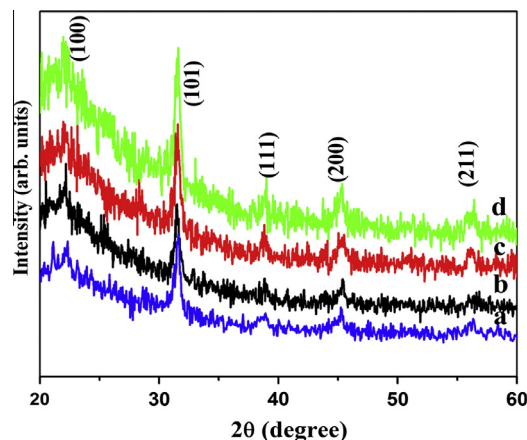

Fig. 1. XRD pattern of BT:Er thin films (a) 0, (b) 1, (c) 3 and (d) 5 wt%.

2θ = 22.15, 31.48, 38.81, 45.34 and 56.36° (PDF No.81-2203) corresponding to the (1 0 0), (1 0 1), (1 1 1), (2 0 0) and (2 1 1) reflection planes respectively. No other crystalline phase has been detected, indicating that all the as-synthesized samples are of single phase. These results illuminate that the doped Er^{3+} ions were completely dissolved in the BT host lattice without any significant change in the crystal structure. The intensity of diffraction peaks increased and FWHM of the films decreased with increase in Er^{3+} concentration, indicating improvement in crystallinity with reduction of micro strain.

The average crystallite size (D) of BT:Er films were calculated using Scherrer's formula [13]

$$D = \frac{k\lambda}{\beta \cos\theta} \qquad (1)$$

where k = 0.9 is a correction factor, β the full width at half maximum (FWHM) of the most intense diffraction plane, λ the wavelength of X-ray and θ the Bragg angle.

Since it is a tetragonal system, the lattice constants a and c were determined from the spectra using the equation

$$\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \qquad (2)$$

where d the inter planar distance, (hkl) the miller indices, a and c the lattice constants.

Table 1 summarizes Peak Position, reflection, crystallite size and lattice parameter of BT:Er thin films. It is well known that an acceptable percentage difference in ion radii between the doped and substituted ions must not exceed 30%. Herein, it is known that the ionic radius of Ba^{2+} is 1.61 Å, which is greater for Er^{3+} (1.23 Å) while the ionic radius of Ti is 0.74 Å, which is smaller for Er^{3+}. Thus Er^{3+} can be substituted in Ba^{2+} or Ti^{4+} ion sites. In the first case, the effective charge could be compensated by Ba^{2+} vacancies. When the rare-earth cations replace the Ti^{4+} sites, their negative charge must be compensated for oxygen vacancies. If Er^{3+} replaces both

Table 1
Peak position, reflection, crystallite size and lattice parameter of BT:Er thin films.

Erbium doping concentrations (wt%)	Peak position 2θ (°)	Reflection	Crystallite size[a] (nm)	Lattice parameter[a] c (Å)
0	31.62	T (1 0 1)	13.2	4.011
1	31.48	T (1 0 1)	11.1	4.004
3	31.55	T (1 0 1)	14.3	4.014
5	31.60	T (1 0 1)	16.0	4.026

[a] Estimated values, not quantitative.