Nonlinear Optical Absorption in Multilayer BaTiO$_3$ Thin Films

Anwar Salah, V. V. Namboodiri, A. Deepthy, V. Kumar*, V. P. N. Nampoori and P. Radhakrishnan
International School of Photonics, CUSAT, Kochi, INDIA -682022;
*Centre for Materials for Electronics Technology, Trissur, INDIA-680771.

ABSTRACT

Barium titanate multilayer thin films were fabricated by sol-gel dip coating method. The films were characterized by x-ray diffraction and optical transmission spectra. Thickness and optical band gap of the film were calculated from the transmission spectrum. The nonlinear optical properties of the films were investigated using a single beam open aperture z-scan technique. The imaginary part of the third order nonlinear susceptibility $\chi^{(3)}$ for a ten layer film was found to be $-1.4057 \times 10^{-9}$ esu.

Keywords: BaTiO$_3$, sol-gel, nonlinear absorption, z-scan.

1. INTRODUCTION

BaTiO$_3$ is one of the most extensively studied ferroelectric materials due to its salient features such as high dielectric constant, ferroelectric activity and nonlinear optical property. These properties make BaTiO$_3$ attractive for versatile applications, which include nonlinear optical devices, wave-guides, surface acoustic wave devices, electro optic devices, etc. Reports on strong second harmonic generation from poled BaTiO$_3$ thin films and third order nonlinear optical studies on doped and undoped BaTiO$_3$ films are available in literature$^{1,2}$. A number of deposition techniques including pulsed laser deposition$^3$, r-f vacuum sputtering$^4$, metal –organic chemical vapor deposition,$^5$ hydrothermal growth,$^6$ and sol-gel deposition$^7$ have been used to fabricate the BaTiO$_3$ thin films. Compared with other fabrication methods, the sol-gel process offers low capital investment. On the other hand, it is compatible with continuous manufacturing techniques for production of thin film integrated circuit fabrication.

In this paper, we report the fabrication of multilayer BaTiO$_3$ thin film by sol-gel dip coating method and the first investigation of nonlinear absorption studies of the films by z-scan technique$^9$.

2. METHODOLOGY

2.1 Film preparation

The films used in this study are fabricated by sol-gel dip coating method. The starting materials used for sol preparation are barium acetate and titanium tetra isopropoxide, with isopropyl alcohol and 2-ethylhexanoic acid as solvents. Acetate precursor was selected for barium element as the di- and trivalent anhydrous metal acetates acts as active source of metal oxides and is able to form heteromettalic acetoalkoxides. In this method 1.59g of barium acetate was added to 5ml of 2-ethyl hexanoic acid and refluxed for one hour. The excess acetic acid formed was distilled out. An equimolar amount of titanium (IV) isopropoxide was taken in 20ml of isopropyl alcohol was then added and stirred to obtain a transparent sol. The sol thus prepared was filtered. The substrates were then dipped into the solution and taken out using a stepper motor arrangement. The dipping time was 30 seconds. The withdrawal speed of the substrate from the solution was 5 cm/minute. To get film on one side, the deposition on the other side was carefully wiped using the solvents used for the sol preparation. The thickness of the film was increased by coating multiple layers on the substrate. The dip coated substrates was dried at 80°C in a laboratory oven. Then it was fired by keeping it for half hour in a furnace set at 600°C. The drying and firing was repeated after each dip for 10 times to obtain a ten-layer film.

XRD of the thin films were recorded using Bruker X-ray diffractometer. The XRD patterns were recorded with 2 theta 20° to 60°. The optical transmittance was measured using UV–visible spectrophotometer (Jasco – V570) in the range 300 to 2000nm.
2.2 Z-Scan Experiment

The nonlinear optical properties of the films were characterized using single beam Z-Scan technique. An Nd:YAG Q-switched laser with a wavelength of 532 nm and a pulse width of 8ns (Spectra Physics – GCR 170) was employed as the light source. The samples were moved in the direction of the light incidence around the focal spot of a lens with focal length 20 cm. The radius of the beam waist was 26 $\mu$m which is calculated from the equation $\omega(z)^2 = \omega_0^2 \left( 1 + z^2 / z_R^2 \right)$, where $z_R = \pi \omega_0^2 / \lambda$ is the Rayleigh Length. $z_R$ is calculated to be much larger than the sample thickness. The transmitted beam energy, reference beam energy and their ratio were measured using an energy ratiometer (Rj – 7620, Laser Probe) simultaneously. The repetition rate of the laser was 10 Hz. The incident energy was fixed during the period of Z-Scan and open aperture Z-Scan measurements were made at several intensities.

3. RESULTS

The XRD pattern of the ten layer BaTiO$_3$ thin film is represented in fig 1. The pattern shows the films are crystalline and cubic. The average particle size of the thin film was determined using Sherrer equation is found to be 20nm.

Fig 2 shows the optical transmittance as a function of wavelength for the 10-layer BaTiO$_3$ film fabricated. The films show good transmittance in the optical region. The thickness and optical constants (n, $\alpha$) of the film was computed using the method proposed by Manifacier etal$^{10}$. In this method the measurement of the transmission T of light through a parallel–faced dielectric film in the region of transparency is sufficient to determine the real and imaginary parts of the complex refractive index $\eta = n - ik$ and thickness t. The film thickness t can be calculated from two maxima or minima using equation $t = M \lambda_1 \lambda_2 / 2[n(\lambda_1) \lambda_2 - n(\lambda_2) \lambda_1 ]$, where M is the number of oscillations between the two extrema ( M = 1 between two consecutive maxima or minima); and $\lambda_1$, n($\lambda_1$) and $\lambda_2$, n($\lambda_2$) are the wavelengths and the corresponding indices of refraction.

The film thickness was found to be 670 nm. Also the optical band gap were determined to be 3.446 eV from the absorption coefficient versus energy (hv) graph. Fig 3. shows the plot of absorption coefficient versus wavelength for the 10 layer BaTiO$_3$ thin film.

![Fig 1. XRD pattern of 10 layer BaTiO$_3$ thin film](image-url)
Z-Scan data with open aperture is insensitive to nonlinear refraction and therefore the data is expected to be symmetric with respect to focus. For materials with multiphoton absorption, the transmittance is minimum at the focus \((z=0)\) and for saturable absorber samples, the transmittance is maximum at the focus.

The normalized transmittance for the open aperture is given by the relation\(^9\)

\[
T(z) = \frac{C}{q_0 \sqrt{\pi}} \int_{-\infty}^{\infty} \ln(1 + q_0 e^{-t^2}) dt
\]  

(1)
where \( q_0(z,t) = \beta I_0(t)L_{eff} z_0^2 / z^2 + z_0^2 \). \( L_{eff} = (1 - e^{-\alpha t})/\alpha \) is the effective thickness of the films, \( I_0 \) is the laser intensity at the focal point, \( l \) is the sample thickness and \( \alpha \) is the linear absorption coefficient. The imaginary part of nonlinear refractive index is given by the relation \( \chi^{(3)} = n_0^2 e_i c^3 \beta /\omega \).

A typical result of the open aperture z-scan measurement is shown in fig 4. The open aperture curve comprises a normalized transmittance peak, showing the presence of nonlinear saturation. The glass substrates used for coating the films were found to show no nonlinear response, which has been measured by the same method. Hence the nonlinear optical properties here result from the BaTiO\(_3\) films. The best fit for the experimental data was found using the theoretical expression (1). The solid line is the theoretical fit. The obtained \( \beta \) value for the film is \(-1.102 \times 10^{-6}\) m/W and the imaginary part of \( \chi^{(3)} \) is \(-1.4057 \times 10^{-9}\) esu.

4. CONCLUSIONS

BaTiO\(_3\) multilayer thin film was fabricated using sol-gel dip coating method. The nonlinear optical absorption studies are investigated using z-scan technique at a wavelength of 532nm. The nonlinear absorption coefficient for the 10 layer BaTiO\(_3\) thin film is calculated to be \(-1.102 \times 10^{-6}\) m/W and imaginary part of nonlinear refractive index is found to be \(-1.4057 \times 10^{-9}\) esu.

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REFERENCES