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Large nonlinear refraction and two photon absorption in ferroelectric $Bi_2VO_{5.5}$ thin films

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ABSTRACT

Ferroelectric c-oriented $Bi_2VO_{5.5}$ (BVO) thin films (thickness ≈300 nm) were fabricated by pulsed laser deposition on corning glass substrates. Nonlinear refractive index (n_2) and two photon absorption coefficient (β) were measured by Z-scan technique at 532 nm wavelength delivering pulses with 10 ns duration. Relatively large values of $n_2 = 2.05 \pm 0.2 \times 10^{-10}$ cm^2/W and $\beta = 9.36 \pm 0.3$ cm/MW were obtained for BVO thin films. Origin of the large optical nonlinearities in BVO thin films was discussed based on bond–orbital theory of transition metal oxides.

1. Introduction

Development of the nonlinear optical materials associated with large nonlinearities accompanied by fast response time is of great interest for the optoelectronic device applications [1]. Semiconductors and chalcogenide based systems were found to have the superior nonlinear optical properties, but their resonant absorption limits the response time and wavelength range. Ferroelectric materials are found to be excellent candidates for optical devices due to their wide optical transmission, fast response times and stability. These have been widely used in non-volatile memory devices, electro-optic devices, pyroelectric sensors and waveguides in integrated photonics [2–4]. Among the ferroelectric materials Aurivillius family of oxides whose general formula is $[Bi_2O_2]^{2+}[A_{n-1}B_nO_{3n+1}]^{2-}$ have been of considerable interest owing to their layered structure [5–8]. Nonlinear optical properties of bismuth based ferroelectric thin films such as $Bi_4Ti_3O_{12}$ [9], $Bi_{1.5}ZnNb_{1.5}O_7$ [10], $SrBi_2Nb_2O_9$ [11], $BaBi_4Ti_4O_{15}$ [12] were investigated. Bismuth vanadate, $Bi_2VO_{5.5}$ (BVO) is a vanadium analogue of an $n = 1$ number of Aurivillius family of oxides. BVO could be represented as $[Bi_2O_2]^{2+}$ $[VO_{3.5}\square_{0.5}]^{2-}$, where □ represents oxygen ion vacancies. BVO has been extensively investigated for its ferroelectric, dielectric and oxygen ion conduction properties [13,14].

This article reports the details concerning the nonlinear optical properties of BVO thin films for the first time deposited by pulsed laser deposition (PLD) technique using the single beam Z-scan measurements. The relatively large values of positive nonlinear refractive index and two photon absorption (TPA) coefficient obtained for BVO films could be exploited in the design and fabrication of optical limiters, optical switches, and modulators in integrated photonic devices.

2. Experimental

2.1. Fabrication of thin films

Polycrystalline $Bi_2VO_{5.5}$ high-density targets were used for the deposition of films. BVO thin films were deposited on Corning glass (Corning 7059) substrates using a KrF (Lambda Physik Compex 201, wavelength 248 nm) excimer laser with 10 ns pulse duration. The output laser beam was focused onto a rotating target at an angle of 45° by a UV lens associated with a focal length of 30 cm. The energy stability of the incoming beam was monitored using an external energy meter. Laser energy of 160 mJ/pulse was maintained constant during the deposition and the laser beam was focused to obtain a fluence of approximately 2.5 J cm^{-2} for all the samples under study. The base vacuum was maintained at 1×10^{-6} Torr. The optimization of the oxygen partial pressure was carried out and the films were deposited at the oxygen ambient pressure of 100 mTorr.

The substrate temperature during deposition was maintained at 600–700 °C in order to achieve good crystallization. The X-ray powder diffraction studies were carried out on BVO films using Cu Kα (1.541 Å) radiation (Bruker D8 Diffractometer). The surface features of BVO films were examined by means of an ex situ contact mode Atomic Force Microscope (AFM) (Veeco CP-II). The

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AFM images were obtained in the repulsive force regime with a force constant of 1.5 nN between the AFM tip and the sample surface. The linear optical parameters were obtained by spectroscopic ellipsometry (SENTECH 850, SENTECH Instruments).

2.2. Z-scan measurements

Q-switched Nd: YAG laser, having 10 ns pulse width with the repetition rate of 10 Hz (Spectra Physics, Lab 150) of 1064 nm wavelength was frequency doubled using KDP crystal to obtain laser pulses at 532 nm. Z-scan measurements were carried out at 532 nm. The beam was focused using convex lens of 10 cm focal length. The sample was mounted along laser path on a computer controlled linear stage (Newport, MFA-CC) in front of a convex lens before focal spot. The schematic experimental set up used for Z-scan measurements is shown in Fig. 1. The optical transmission of the BVO films was monitored in the far field with and without aperture by moving the sample along laser path through the focal spot. The transmitted signal is detected using a monochromator (Jobin Yvon Triax) with integration time of 1 s. Each datum point in the measurements is an average of ten pulses per second. The laser beam was calibrated using CS_2 (filled in quartz cuvette of 1 mm path length).

3. Results and discussion

3.1. Structural and linear optical studies

X-ray diffraction (XRD) pattern obtained for the as fabricated BVO thin films is shown in Fig. 2. The XRD studies confirm the films to be textured mostly associated with c-oriented grains. This XRD pattern is indexed to a polar orthorhombic phase which is in agreement with that reported in the literature (JCPDS 42-0135). The AFM micrograph (inset of Fig. 2) shows the surface topography of a BVO thin film containing a homogeneous distribution of grains. The grain size that is determined from the picture lies in the range of 0.3–0.35 μm. The BVO thin films were characterized for their optical properties by ellipsometry. Ellipsometry could effectively be used to determine the dielectric function and thickness of a thin-film by comparing the measured data with a best-fit model calculation. The thickness of the film was determined to be 300 nm. The optical transmission spectrum in the 300–1100 nm wavelength range for the BVO thin films is given in Fig. 3. The refractive index (n) vs. wavelength plot is also depicted in the same Fig. 3 as an inset. n values were found to be 2.22–2.58 from higher wavelength to the lower cut off wavelength ($\lambda_{cut\ off}$ = 360 nm). Optical band gap of the BVO thin films was determined using Tauc plot $(\alpha h\nu)^{1/2}$ vs. $h\nu$ (not shown) and found to be 2.91 eV.

3.2. Nonlinear optical studies

The closed aperture Z-scan measurement that was done for CS_2 was given in Fig. 4a. This is used for the calibration purpose as

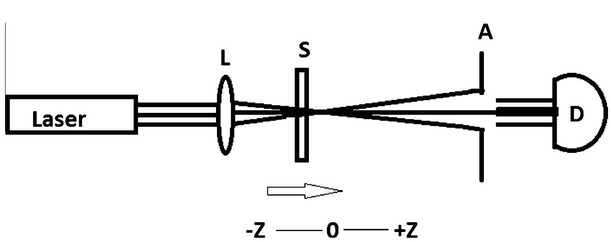

Fig. 1. Schematic Z-scan experimental setup where L-lens, S-sample, A-aperture and D-detector. Arrow indicates the direction of linear motion of the sample.

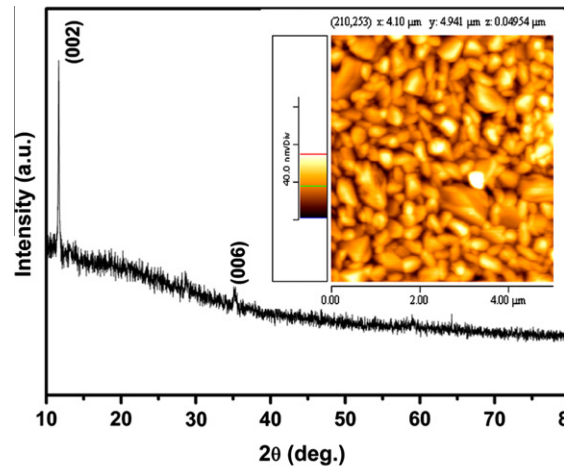

Fig. 2. X-ray diffraction pattern of BVO thin films and inset is an AFM image.

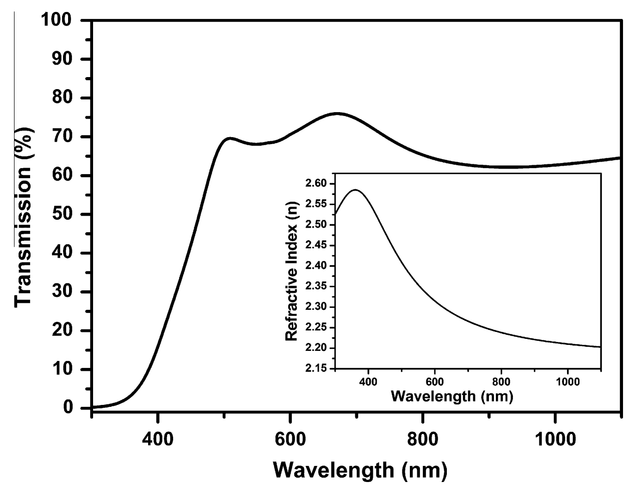

Fig. 3. Optical transmission spectra of BVO thin films and inset shows refractive index vs. wavelength.

standard material for n_2 measurements. The peak irradiance was found to be 1.5 GW/cm^2. All the measurements reported here were carried out at this intensity. The closed aperture (CA) Z-scan curve for BVO thin film is shown in Fig. 4b. The intense valley followed by a peak was observed while moving the sample through the focal point. This indicates the positive sign associated with the nonlinear refraction accompanied by nonlinear absorption. Because of slow repetition rate (10 Hz) and nano second pulses that were used in our experiments, the contributions from thermal and electrostriction to the nonlinear refraction and absorption were excluded. The nonlinear absorption of the films was determined through the open aperture (OA) Z-scan. OA Z-scan curve is depicted in Fig. 4c. The absorption associated refraction in CA Z-scan can be separated by the division of CA curve with OA curve in which refraction is absent as all the intensity transmitted is recorded. The curve that is shown in Fig. 4d gives the division of CA and OA. The solid lines shown are theoretical (fitted) curves to the experimental data as described by Sheik Bahae et al. [15,16]. The n_2 and β were evaluated from the data that are shown in Fig. 4. The following procedure was adopted for this purpose.

The CA normalized transmittance ($T(z)$) could be written approximately as given below and used to fit the CA curves:

$$T(z) = 1 + \frac{4\Delta\phi_0 x}{(x^2+9)(x^2+1)} \qquad (1)$$