Optical and Gas sensing properties of Ba_xSr_{1-x}TiO_3 (with x=0.5 and x=0.7) thin films grown using Pulse Laser Deposition

Nipa M. Shastri1,*, Adhish V. Raval2,*, V.G. Joshi3

1,3 Department of physics, Veer Narmad South Gujarat University, Surat, Gujarat-395007, India.
2Department of Applied Physics, S. V. National Institute of Technology, Surat, Gujarat-395007, India

Email. shastrineepa2004@yahoo.com, adhraval0777@gmail.com

Abstract. Thin films of Barium Strontium Titanate (BST) have been fabricated using Pulse Laser Deposition (PLD) technique. Two stoichiometries of Ba_xSr_{1-x}TiO_3 with x=0.5 and x=0.7 are deposited on well cleaned quartz substrates in high vacuum chamber with oxygen pressure of 0.13mbar at 700˚C. XRD pattern shows perovskite structure of the films. Energy Dispersive X-ray (EDX) is used to determine the element concentration of both the films. Transmittance spectra of UV characterization shows decrement in transparency of the film as Barium (Ba) concentration increase and sharp cut-offs are observed at the band edge. Refractive Index (n), absorption coefficient (α), extinction coefficient (k), optical conductivity (σ) and optical band gap (Eg) are derived from UV-Vis spectroscopy. The calculated parameters for Ba_{0.5}Sr_{0.5}TiO_3 and Ba_{0.7}Sr_{0.3}TiO_3 are presented in this work. The present work also includes study of BST thin films as gas sensors.

1. Introduction
Barium Strontium Titanate (BST) is the material which shows very useful properties for opto-electronic and tuneable microwave devices, IR sensors and chemical sensors for sensing humidity and gases [1]. Because of high dielectric constant, high optical nonlinearity [2] and Curie temperature depending on composition [3], much attention has been paid to Ba_xSr_{1-x}TiO_3 ferroelectric materials. These BST materials are suitable for applications in phase conjugation, two beam coupling, dynamic holography and optical signal processing [4]. As BST has prominent properties like large electro-optic coefficient [5] and relatively low optical propagation loss [6], BST thin films show much more interest in opto-electronic device applications. These BST thin films can give great contribution in optical memory, Optical storage devices and low voltage optical switching.

The optical spectroscopy technique is used to investigate optical properties of Barium Strontium Titanate (BST) thin films. From these basic spectrometric measurements, related optical parameters like refractive index, absorption coefficient etc. are deduced by the method of Swanepoel [7] and reported using the measured transmittance response in the range of 200nm to 900nm.

Currently there is a great interest in the synthesis and investigation of material response to the variations in the gaseous environment. Sensors can detect the pollutants from environment [8, 9],
which are very useful to environment monitoring system. Semiconducting oxides based gas sensitive resistors are very strong and simple devices to fabricate. The perovskite oxides have a good steadiness in chemical and thermal atmospheres, so they have huge area of interest as gas sensors. Over a last decade the perovskite oxide materials like BaTiO$_3$ [10, 11], and (Ba, Sr) TiO$_3$ [12-16] have created interest in chemical sensors.

In present work we have calculated the optical parameters of Ba$_x$Sr$_{1-x}$TiO$_3$ (x=0.5, 0.7) thin films based on the UV spectroscopy data. The H$_2$S gas sensitivity of the samples has also been experimentally studied.

2. Experimental Details
Ba$_x$Sr$_{1-x}$TiO$_3$ (BST) solid solutions with two desire molar formula Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (BST0.5) and Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ (BST0.7) were prepared by Mixed Oxide Conventional route. Starting materials like BaCl$_2$.2H$_2$O, SrCl$_2$.6H$_2$O and TiO$_2$ of 99% purity were weighted according to molecular wt%, mixed and grinded well using mortal pestle to prepare BST0.5 and BST0.7 compounds. Acetone is selected as medium for mixing-milling process. Both the mixtures were annealed in an electrical furnace at 1020˚C for 12hrs, again milled well, mixed with Polyvinyl Alcohol (PVA) and pressed to yield pellet of about 5mm thickness and 15mm in diameter. These two pellets (BST0.5 and BST0.7), sintered at 1020˚C for 12hrs were used as PLD target.

For the film deposition, multi step process was followed to clean the quartz substrates. The first step was to clean all substrate with deionised water properly. Second step was acetone soak for 10 mins followed by rinsing in deionised water. Third step was ultrasonically cleaning in the mixture of acetone and isopropyl alcohol for 15 mins at 70˚C followed by rinsing in deionised water. Then all substrates were dried in a process oven with air atmosphere at 80˚C.

The Pulse Laser Deposition process has been carried out using high power Nd: YAG (EKSPA, Lithuania) laser having wavelength of 355nm and the laser pulse energy density of 200mJ/cm$^2$. Inside PLD chamber the rotating target and quartz substrate were kept parallel to each other and both were spaced at few centimetres apart. The laser was focused on the rotating target resulting into ablation. This process results in deposition of quartz substrate. The frequent laser shots can damage the target material. In order to avoid it the target is rastered and rotated continuously in specified manner during the deposition process. Initially the PLD chamber was evacuated in the order of $10^{-6}$ mbar using a diffusion pump supported by rotary pump and pressurized with 0.13mbar oxygen (O$_2$) gas. The laser was pulsed at 10Hz for 35k pulses and for deposition of both the films 700˚C substrate temperature was maintained.

3. Result and Discussion

3.1. X-Ray Diffraction Analysis:
Figure 1 shows the X-Ray diffraction pattern of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (BST0.5) and Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ (BST 0.7) thin films grown on quartz substrate using PLD at 700˚C. The 2θ range is from 20° to 90° with step size $\Delta \theta = 0.02^\circ$. The X-ray diffractograms of films show polycrystalline structure which is in well agreement with standard peaks and found to be perovskite cubic structure (JCPDS card 39-1395) [17] with Pm3m space group for Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ and tetragonal structure (JCPDS card 44-0093) [18] with P4mm space group for Ba$_{0.7}$Sr$_{0.3}$TiO$_3$. Due to amorous nature of quartz substrate the broad spectrum was observed from 20° to 30°.
3.2. Energy Dispersive X-ray (EDX) Analysis:
Energy Dispersive X-ray analysis of both the thin films Ba$_x$Sr$_{1-x}$TiO$_3$ ($x=0.5$ and $x=0.7$) are shown in the figure 2. Figure 2(a) and 2(b) shows the element’s concentration for both the films Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ and Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ respectively.

3.3. Optical Properties:
The profile of optical transmittance spectra for the thin films BST0.5 and BST0.7 is shown in figure 3. BST0.5 has good transmittance behavior as compare to BST0.7 film. It is evident that transmittance suddenly decrease in the UV region of the spectrum band (320nm – 220nm).

Refractive index has been calculated from optical transmittance spectra using envelop method which is proposed by Swanepoel [7]. The Index of Refraction ($n$) for both the films BST0.5 and BST0.7 has been obtained from the equation as follows:

$$n = \left[ M + \left( M^2 - n_x^2 \right) \frac{1}{3} \right]^{1/2}$$

..........(1)
where, 
\[ M = \frac{2n_s T_m}{T_m} - \frac{(n_s^2 + 1)}{2} \] ; for all regions which are optically transparent. ........(2)

and
\[ M = \frac{2n_s (T_M - T_m)}{T_M T_m} + \frac{(n_s^2 + 1)}{2} \] ; for all regions which are medium and weak absorbents ........(3)

\( n_s \) is the refractive index of the quartz substrate (1.45). \( T_M \) and \( T_m \) are the values of maximum and minimum transmission respectively at the definite wavelength.

**Figure 3.** Percent Transmittance vs wavelength of \( \text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3(x=0.5, 0.7) \) thin films

The index of refraction can be determined by extrapolating envelopes corresponding to maximum transmission \( (T_M) \) and minimum transmission \( (T_m) \), using Swanepoel’s method [7]. The calculated average refractive index is 2.19 for \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3 \) thin film and 1.94 for \( \text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3 \) thin film for the wavelength 800-900nm.

The extinction coefficient \( (k) \) can be derived from the following equation [19],

\[ k = \frac{\alpha \lambda}{4\pi} \] ............(4)

Where \( \lambda \) = wavelength, \( \alpha \) = absorption coefficient and can be derived from the following equation [19],

\[ \alpha = \left( \frac{1}{d} \right) \log \left( \frac{1}{T} \right) \] ............(5)

Where \( d \) = film thickness and \( T \) = transmittance for definite wavelength.

From definition Extinction coefficient \( (k) \) is the imaginary part of complex index of refraction and it defines the several measures of absorption of light in a medium. The variation in extinction coefficient \( (k) \) with photon energy is shown in the figure 4(a). It is observed that for BST0.5 and BST0.7 thin films, extinction coefficient increase with photon energy up to 5eV and 4.62eV respectively and above these values it starts decreasing.
The absorption coefficient is dependent on material type and wavelength of the absorbed light. Figure 4(b) shows the behavior of absorption coefficient with respect to photon energy. The optical band gap can be derived from the variation of absorption coefficient ($\alpha$) with respect to photon energy. From graph, the energy band gap is 4.25 eV for BST0.5 and 3.7 eV for BST0.7 thin films. These values are close in agreement with the literature value 4.5 eV for BST0.5 [2] and 4.3 eV for BST0.7 [20] thin films.

The optical conductivity ($\sigma$) is determined by following relation [19],

$$\sigma = \frac{\alpha nc}{4\pi}$$

where $\alpha$=absorption coefficient, $n$=refractive index, $c$= velocity of light.

Figure 5 shows behaviour of optical conductivity ($\sigma$) with respect to photon energy. Optical conductivity ($\sigma$) is depends on absorption coefficient and refractive index. Figure 5 shows that optical conductivity increase sharply above photon energy 4.2eV and 4eV for BST0.5 and BST0.7 respectively.

Figure 4. For Ba$_x$Sr$_{1-x}$TiO$_3$($x=0.5,0.7$) films (a) Extinction co-efficient(k) vs. Photon energy (eV) (b) Absorption coefficient ($\alpha$) vs. photon energy (eV)

Figure 5. Optical conductivity ($\sigma$) vs. Photon energy (eV) for Ba$_x$Sr$_{1-x}$TiO$_3$($x=0.5,0.7$) thin films.
3.4. Gas Sensing Property:

In present work, sensitivity (Response) of the BST thin films, as gas sensor has been studied. Response of any sensor mainly depends on the interaction between gas and surface of sensing element. As resistance of sensor material changes, the change in Sensitivity or Response of the sensor can be determine. It is define as ratio of change in the resistance of sensor in the presence of gas to the resistance of sensor in ambient air [21], which is denoted as,

\[
\text{Response} = \left(\frac{R_g - R_a}{R_a}\right) \times 100\% 
\]

Where, \(R_g\) = Electrical resistance of sensor in presence of gas and \(R_a\) = Electrical resistance of sensor in ambient air (in the absence of test gas).

We have used Ba\(_{0.5}\)Sr\(_{0.5}\)TiO\(_3\) and Ba\(_{0.7}\)Sr\(_{0.3}\)TiO\(_3\) thin films as gas sensor and studied the H\(_2\)S gas (800 ppm) response against temperature. Figure 6 depicts behaviour of H\(_2\)S gas Response against temperature. Figure 6(a) and 6(b) shows that response increases with temperature and reach maxima at 330 °C, and then start decreasing.

![Figure 6](image)

Figure 6. H\(_2\)S (800 ppm) gas response against temperature for (a) Ba\(_{0.5}\)Sr\(_{0.5}\)TiO\(_3\) thin film and (b) Ba\(_{0.7}\)Sr\(_{0.3}\)TiO\(_3\) thin film.

Figure 6 shows, in operating temperature range, the Gas response decrease as Barium (Ba) concentration increase in BST thin film. Ba\(_{0.5}\)Sr\(_{0.5}\)TiO\(_3\) shows 57.57 % while Ba\(_{0.7}\)Sr\(_{0.3}\)TiO\(_3\) shows 41.61 % gas response to H\(_2\)S gas (800ppm) at 330 °C.

4. Conclusion

Ba\(_{0.5}\)Sr\(_{0.5}\)TiO\(_3\) (BST0.5) and Ba\(_{0.7}\)Sr\(_{0.3}\)TiO\(_3\) (BST0.7) thin films are fabricated by Pulse Laser Deposition method on quartz substrate. XRD shows perovskite structure of both the films. From UV-Vis spectroscopy, optical parameters have been calculated for both the samples. Calculated average refractive index is 2.19 for Ba\(_{0.5}\)Sr\(_{0.5}\)TiO\(_3\) thin film and 1.94 for Ba\(_{0.7}\)Sr\(_{0.3}\)TiO\(_3\) thin film for 800-900nm wavelength.

Absorption coefficient (\(\alpha\)) and so the Extinction coefficient (k) is large of BST0.7 than BST0.5. Optical band gap found for BST0.5 is 4.25ev while for BST0.7 is 3.7ev. Gas sensing test revealed that sensor based on BST0.5 sample exhibit high sensitivity for H\(_2\)S gas (800 ppm) than BST0.7 sample.
References

[1] S. J. Patil, A. V. Patil, C. G. Dighavkar, K. S. Thakar, R. Y. Borase, S. J. Nande, N. G. Deshpande and R. Ahire 2015 Front. Mater. Sci. 9 14-37.
[2] S. Behera, A. Khare 2019 AIP Conf. Proc. 2082 040006.
[3] M. Kocanda, I. Abdel-Motaleb 2009 J. Appl. Phys. 106 123916.
[4] F. Tcheliebou, H. S. Ryu, C. K. Hong, W. S. Park, S. Baik 1997 Thin Solid Films 305 30.
[5] M. Gaidi, M. Chaker, P. F. Ndione, R. Morandotti, B. Bessais 2007 J. Appl. Phys. 101 063107.
[6] Yu-Fu Kuo, Tseung-Yuen Tseng 1999 Materials Chemistry and Physics 61 244-250.
[7] R. Swanepoel 1983 J. Phys. E: Sci, Instrum. 16.
[8] S. Korgaokar, M. Moradiya, Om prajapati, P. Thakar, J. Pala, C. Savaliya, S. Parikh, J. H. Markna 2017 AIP Conf. Proc. 1837 040050.
[9] G. H. Jain, V. B. Gaikwad, D. D. Kajale, D. Kajale, R. Chaudhari, R. Patil, N. Pawar, M. Deore, S. Shinde and L. Patil 2008 Sensors and Transducers journal 90 160-173.
[10] D. N. Suryawanshi, I. G, Pathan, A. R. Bari, L. A. Patil 2017 AIP Conf. Proc. 1953 030041.
[11] G. H. Jain, S. B. Nahire, D. D. Kajale, G. E. Patil, S. D. Shinde, D. N. Chavan and V. B. Gaikwad 2011 New developments and Appl. In Sen. Tech. LNEE 83 157-167.
[12] G. H. Jain, L. A. Patil, P. Patil, U. Mulik and K. Patil 2007 Bull. Mater. Sci. 30 9-17.
[13] G. H. Jain, L. A. Patil 2006 Bull.Mater. Sci. 29 403-411.
[14] C. Huck, A. Poghossian, M.Backer, S. Reisert, J. Schubert, W. Zander, V. Begoyan, V. Buniatyan, M. Schoning 2014 Procedia Engineering 87 28-31.
[15] S. Sharma, A. Sharma, M. Toamar, N. Puri and V. Gupta 2014 Procedia Engineering 87 1067.
[16] ADe Kurniawan, Dani Yosman, Ardian Arif, Jajang Juansah, Irzaman 2015 Procedia Environmental Sciences 24 335-339.
[17] Anuradha Kumari, Barnali Dasgupta Ghosh 2018 Advances In Applied Ceramics DOI : 10.1080/17436753.2018.1491166.
[18] M. Enhessari, A. Parviz, K. Ozace, H. Habibi Abyaneh 2011 Int. J. Nano Dim. 2 85-103.
[19] Martin Kocanda, Syed Farhan Mohiudin, Ibrahim Abdel-Motaleb 2012 Crystal Structure Theory and Applications I 17-20.
[20] Zhimou Xu, Yuichiro Tanushi, Masato Suzuki, Keita Wakushima, Shin Yokoyama 2006 Thin Solid Films 515 2326-2331.
[21] Jeffrey W. Fergus 2007 Sensors and Actuators B 123 1169-1179.