

Structural and optical properties of nano scale BaTiO₃ thin films prepared from BaTiO₃ nanoparticles synthesised by organic acid precursor method

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BaTiO₃ nanoparticles prepared by organic acid precursor method were thermally evaporated onto a well cleaned glass substrate under a vacuum of 2×10^{-5} Torr, using a Hindu High vacuum coating unit. Nano thin films of BaTiO₃ were prepared on well cleaned glass plates for the first time by vacuum evaporation method. The thickness of the coated films was measured by using quartz crystal thickness monitor. Energy dispersive Spectrum (EDS) were used to identify the composition of the nano powders and films. X- ray diffraction (XRD) spectrum indicated that the powder has tetragonal structure whereas the film was predominantly amorphous. Surface morphology of the powders and coated films were studied by scanning electron microscope (SEM). No pits and pin holes were found in the surface. As grown films showed smooth and compact structure. Optical properties were studied by using UV- Visible spectrophotometer. The band gap of the films were found to be 3.6eV to 3.75eV. It was found to be indirect allowed transition and decrease little with the increase of thickness. The extinction coefficient and absorption coefficient also reported. The observed smooth surface without any pinholes, pits and dendritic features and high band gap energy value indicated that the vacuum evaporated nano scale films could be used as dielectric layer in thin film transistor.

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1. Introduction

Ferroelectric thin films are very promising for a wide range of application such as high dielectric capacitors, insulating surface layer, non-volatile memories with low switching voltage, infrared sensors and electro optic devices. BaTiO₃ family ceramic thin films are receiving extensive investigation as the charge- storage dielectric for G-bit dynamic random access memory (DRAM), on-chip components such as de-coupling capacitors and positive temperature coefficient of resistance (PTCR) thermistors [1]. Traditionally BaTiO₃ has been produced via the hydrothermal synthesis of organic hybrid [2], polymeric precursor method [3], the solid state reaction of mixed oxide route [4] and solution methods include citrate [5,6] sol –gel [7,8]. The hydro thermal synthesis of organic hybrid method is attractive but this methods experimental setup is too expensive. The polymeric precursor method involves several solvents for synthesis process. The solid-state reaction of mixed route involves repeated calcinations and regrinding of BaCO₃ and TiO₂ powders above 1100°C, which tends to produce coarse agglomerated powders due to high sintering temperatures. Similarly the citrate and sol-gel methods have many steps and require a post – heat treatment to induce crystallization. Among the various synthesis methods, organic acid precursor method is a promising technique that offers low cost, uniform size, homogenous powder and high purity of the ceramics. In this method BaTiO₃

Nano particles were synthesised by using commercial available and cost effect Barium chloride, Titanium dioxide and oxalic acid as starting materials. Thin films of BaTiO₃ could be prepared by different technique like r.f sputtering [9], pulsed laser ablation [10] and metal-organic chemical vapour deposition [11] etc. Despite that several technique have been explored to deposit thin film of BaTiO₃, less attention has been devoted to thermal evaporation.

In the present study, we have reported about the applying of thermal evaporation technique for nano scale thin film preparation of BaTiO₃ nanopowder synthesised by using organic acid precursor method. Microstructure, surface morphology and optical properties of thin film prepared on well cleaned glass substrate have also been investigated.

2. Experimental

2.1 Synthesis of BaTiO₃ nanopowder

BaTiO₃ nanopowders were synthesized using organic acid precursor method. The starting materials used were barium chloride (BaCl₂.2H₂O), Titanium dioxide (TiO₂) powder and Oxalic acid. A solution of Ba: Ti: Oxalic acid having mole ratio: 1: 1: 1 was stirred and evaporated at 70°C till a clear, viscous resin was obtained and then dried

at 110° C for 20 hours. The precursor formed was heated at 900° C for 2 hours to form BaTiO₃ nanopowder.

2.2 BaTiO₃ thin film preparation

Thin films were thermally grown onto well cleaned glass substrate under a vacuum of 2×10^{-5} torr, using a Hind High vacuum coating unit. The growth rate and thickness were measured during growth using a quartz crystal oscillator thickness monitor. The growth rate was adjusted to be as low as 1 Å/sec to avoid the differential evaporation of elements of the alloy.

2.3 Characteristics of BaTiO₃ nanopowder and BaTiO₃ thin films

Energy Dispersive X-ray micro analyser (EDS) were used for the identification of the chemical composition. The XRD patterns of the resulting products were obtained from X- ray powder diffraction with CuK α radiation. The micrograph of BaTiO₃ was examined by direct observation via scanning electron microscope (SEM). The optical transmission measurements were made in the UV and visible regions at near normal incidence for all the film samples deposited on glass substrates. In the investigation, JASCO-UV/VISIBLE spectrophotometer (model UVIVDEC 610, Japan) was used. It is also provided with CRT (Cathode Ray Tube) monitor having graphic display at high resolution.

3. Result and discussion

3.1 EDS Analysis

Fig.1 (a) and 1 (b) shows the EDS spectrum of as prepared BaTiO₃ nano powder and as deposited BaTiO₃ nano scale thin film on glass plate respectively. Elemental composition analysis indicated the presence of Ba, Ti and O in the synthesized BaTiO₃ nano powder as well as in the BaTiO₃ nano scale thin films.

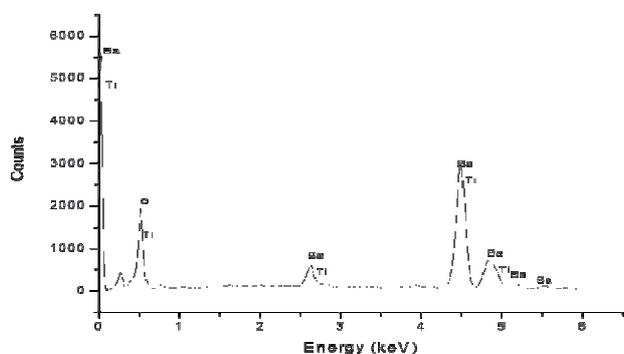


Fig. 1a EDS spectrum of BaTiO₃ nano powder.

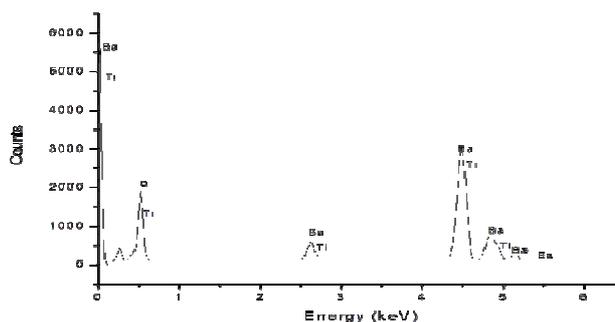


Fig. 1b EDS spectrum of BaTiO₃ nano scale thin film.

3.2 X – Ray Diffraction Analysis

Figure 2a shows XRD patterns of precursor sample produced from solution mixture of barium chloride, titanium dioxide and oxalic acid mole ratio 1:1:1 evaporated at 80° C and thermally treated at 900° C to a well crystalline barium titanate BaTiO₃ phase (JCPDS Card # 79-2263). The crystallite size of BaTiO₃ powder was determined from the X-ray diffraction data using the Debye-Scherrer formula

$$d = k\lambda/\beta \cos \theta$$

Where d is the crystallite size, k = 0.9 is a correction factor to account for particle shapes, β is the full width half maximum (FWHM) of the most intense diffraction peak, λ is the wave length of Cu target = 1.5406 Å, and θ is the Bragg angle. The average crystallite size of the prepared BaTiO₃ powder was 55 nm. The system of the nano powder has Tetragonal nature. In the XRD plot, the peak positions from $2\theta = 44^\circ$ to 46° play important role in determining the tetragonal nature of the system, the peak splitting was found clearly in the (002) plane which shows its high degree of tetragonality [12].

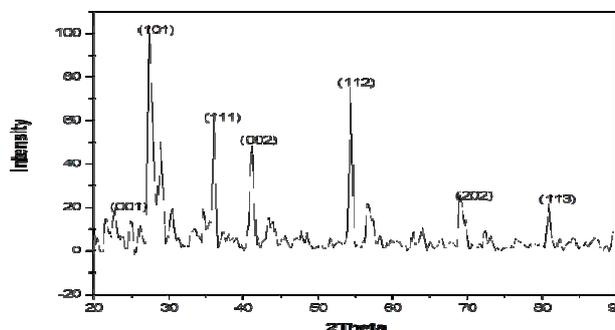


Fig. 2a XRD spectrum of BaTiO₃ nano powder

A typical X-ray diffraction (XRD) pattern of BaTiO₃ film thickness (200 nm) is as shown in the Fig.2b. The absence of sharp peaks in the spectrum indicated the predominantly amorphous nature of the film

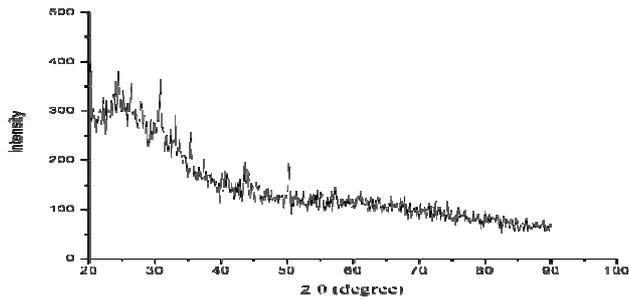


Fig. 2b XRD spectrum of BaTiO₃ nano scale thin film

3.3. SEM Analysis

Typical scanning electron micrographs of BaTiO₃ nano powder and BaTiO₃ film of (200) nanometer are as shown on Fig. 3 (a) and 3 (b). The particulate phase in the micrograph is the BaTiO₃ grains and the voids seen in the micrograph result from the micropores in the film. The micrograph indicates that the average grain size of BaTiO₃ nano powder varies from 90.68 nm to 133 nm. In the case of BaTiO₃ thin film the average grain size varies from 195 nm to 1270 nm. The grain size of vacuum evaporated BaTiO₃ thin films are relatively large compared to as prepared BaTiO₃ nano powder. Arlt.et.al [13] have reported that BaTiO₃ exists predominantly in the tetragonal structure for grain size of 1.5 μm and above and that, for an average grain size below 1.5 μm, tetragonal and orthorhombic phases coexist.

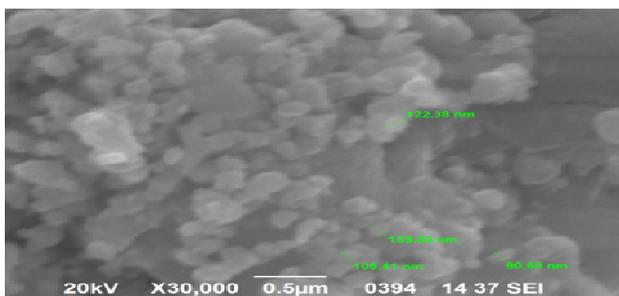


Fig. 3a SEM image of BaTiO₃ nano powder

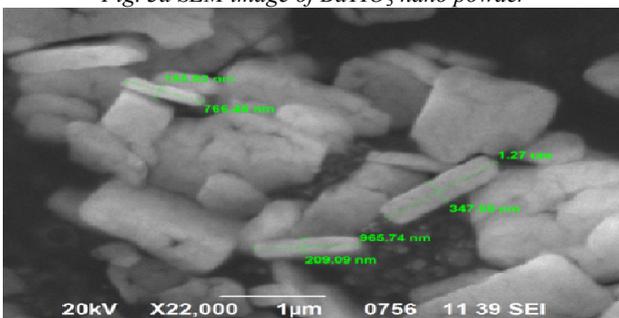


Fig. 3b SEM image of BaTiO₃ Thin film

Therefore, it seems that BaTiO₃ films prepared in this study also exists as a mixed system of tetragonal and

orthorhombic or pseudocubic structure. Our X-ray studies also support this conclusion, because the peaks corresponding to the (002) and (200) planes are not well resolved. The evaporated particles are of uniform shape with average grain size of few hundred nanometers and corresponding well to the evaporated powder. Beside, good distribution and complete surface coverage of glass by vacuum evaporated particles conformed that dense and void free deposit is produced by thermal evaporation of Barium titanate nano powder. No pits, pin holes and dendritic features are found on the surface in SEM micrographs.

3.4 Optical properties

The transmittance spectra of the film in the visible region for the different thickness are shown in the Fig. 4. It was found that the transmittance of the film decreases as the increase of film thickness [14].

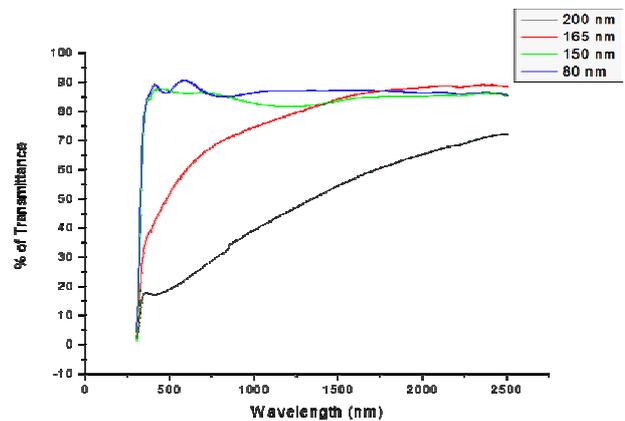


Fig. 4 Transmittance spectra of BaTiO₃ films.

The Absorption co-efficient (α) can be calculated from the relation,

$$\alpha = 4\pi k/\lambda$$

where d is the thickness of the films and λ wavelength of the light and the Extinction co-efficient (k) can be calculated from the relation,

$$k = 2.303\lambda \log(1/T_0)/4\pi d$$

Fig. 5 represents the variation of extinction coefficient (K) with wavelength for various thicknesses. It is seen that in all the films the extinction coefficient increases as the wavelength decreases [15]. In addition, the extinction coefficient is low at lower wavelength. The value of extinction coefficient decreases with increasing film thickness, which may be due to the improvement in the crystallinity with the increase in film thickness leading to the minimum imperfections.

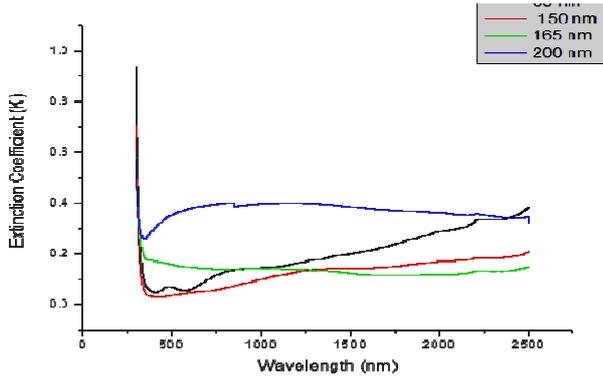


Fig. 5. Variation of extinction co-efficient (K) with wavelength for BaTiO₃ film at different thickness.

Fig. 6. shows the absorption spectrum of BaTiO₃ thin films of different thickness. The absorption coefficient increases as wavelength decreases [16]. In addition, the absorption coefficient decreases with increase in film thickness, which is an expected inverse nature of the transmittance spectra. The absorption coefficient is one of the very important factors for ferroelectric materials in the IR detectors and arrays, which make use of their pyroelectric properties [17, 18] by determining α from that transmittance curves.

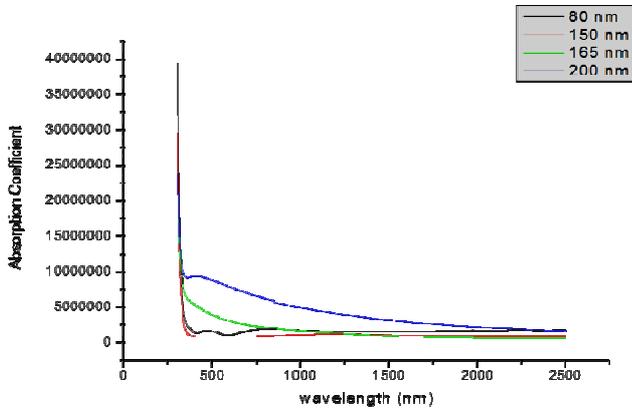


Fig. 6. Variation of absorption co-efficient (α) with wavelength for BaTiO₃ film at different thickness.

For indirect allowed transition the absorption coefficient and photon energy are related by expression.

$$\alpha h\nu = A (h\nu - E_g)^n$$

where A is a constant and E_g the optical band gap energy. The variation of $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$) at different film thickness is shown in Fig. 7a-d respectively. From the plot, it is concluded that the optical transmission in these films is in indirect and allowed. It is observed that the band gap decrease with increase in thickness as shown in Table I. It is in good agreement with the earlier

investigations on BaTiO₃ films [14]. The decreases in the band gap may be due to many reasons. It may be due to the increase of grain size, a decrease in strain, dislocation density and an increase of lattice constant.

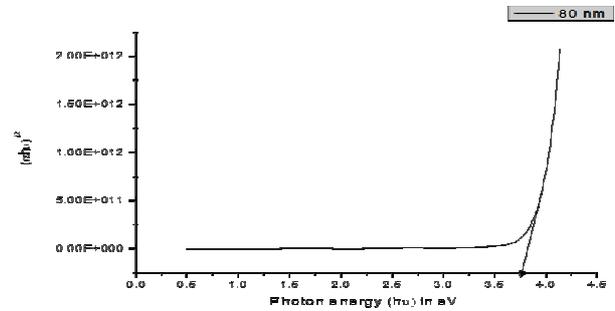


Fig. 7a. $(\alpha h\nu)^{1/2}$ with $h\nu$ of thickness 80 nm

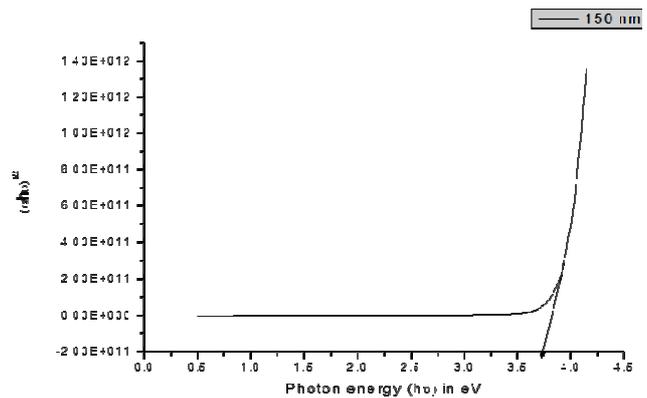


Fig. 7b. $(\alpha h\nu)^{1/2}$ with $h\nu$ of thickness 150 nm.

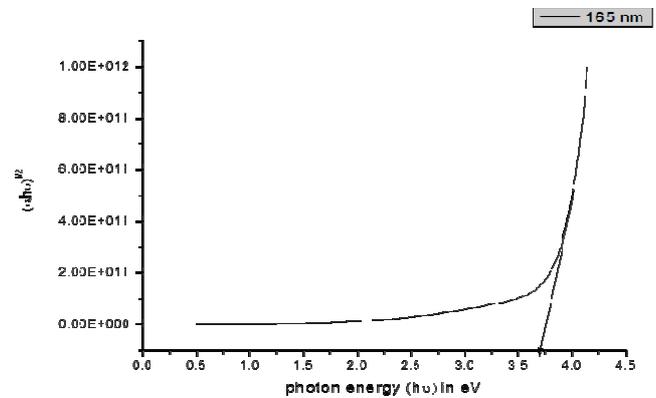


Fig. 7c. $(\alpha h\nu)^{1/2}$ with $h\nu$ of thickness 165 nm

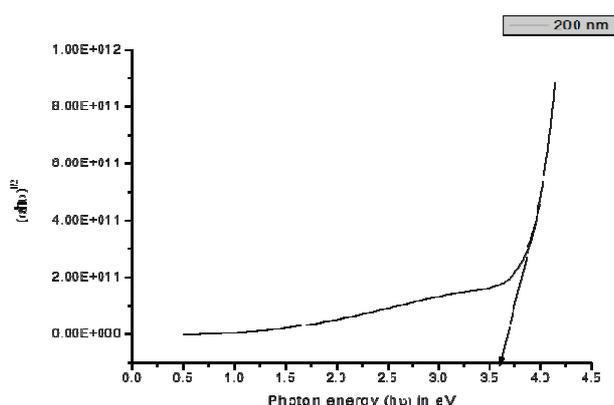


Fig. 7d. $(\alpha hv)^{1/2}$ with $h\nu$ of thickness 200 nm

Table.1. Thickness dependence on optical band gap

Thickness (nm)	Band gap (eV)
80	3.75
150	3.72
165	3.70
200	3.60

4. Conclusion

We have successfully synthesized nanopowder of BaTiO₃ by low cost organic acid precursor method using commercially available chemicals such as oxalic acid, TiO₂ and BaCl₂. Thin films of few hundred nanometer thickness was prepared on well cleaned glass plate for the first time using thermal evaporation method. The composition of BaTiO₃ nanopowder and the BaTiO₃ film were confirmed by EDX analysis. XRD indicated the powder has tetragonal structure and the film predominantly amorphous in nature. The presence of small peaks indicated the presence of crystallites of very low dimension in the amorphous region. No pits, pin holes and dendritic features are found on the surface in SEM images. The absorption co-efficient and extinction coefficient of the films were determined from optical transmission study. From the transmission spectra, the transmission is found to decrease with increase of film thickness. The optical transition in BaTiO₃ films was found to be indirect allowed. A decreasing trend in the optical band gap energy was observed with increase in thickness. The observed smooth surface without any pinholes, pits and dendritic

features and high band gap energy value indicated that the vacuum evaporated nano scale films could be used as dielectric layer in thin film transistor.

References

- [1] J.F.Scott, Annu. Rev. Mater. Sci., **28**, 79 (1998).
- [2] Hiromichi Hayashi, Takio Nogusi, Nazrul U. Islam, Yukiya Hakuta, Yusuke Imai, Nobuhiko Veno, Journal of crystal growth **312**, 3613 (2010).
- [3] V. Vinothini, Paramanand Sigh, M. Balasubramanian, Ceramics International **32**, 99 (2006).
- [4] A Beuser, J.C. Niepce, J. Mater. Sci., **19**, 195 (1984).
- [5] L.A. Perez – Maqueda, M.J. Dianez, F.J. Gotor, M.J. Sayagues, C. Real, J. M. Criado, J. Mater. Chem. **2234** (2003).
- [6] P.R. Arya, P. Jha, A. K. Ganguli. J. Mater. Chem, **13**, 415 (2003).
- [7] Y Kohayashi., A. Nishikawa, T Tanase., M, Konno. J. Sol- Gel Sci. Technol. **29**, 49 (2004).
- [8] B. A Hernandez., K.S Chang, E.R Fisher, P.K Dorhount, Chem. Meter **14**, 480 (2002).
- [9] P. Bhattachariya, T. Komeda, D. Park, Y. Nishioka, Japan J. Appl. Phys. **32**, 4103 (1993).
- [10] Yoon. S.G, Lee. J. and Safari. A, Integrated Ferroelectrics, **7**, 329 (1995).
- [11] Tahan. D, Safari. A and Klin. L.C, J. Am. Ceram. Soci, **79**, 1593 (1996).
- [12] Sundararajan Tirumalai, Balasivanandha prabu Shanmugavel, journal of Microwave Power and Electromagnetic Energy. **45**(3) 121 (2011).
- [13] G. Arlt, D. Hennings, G. Dewith, J. Appl. Phys., **58**(4), 1619 (1985)
- [14] Haizhong Guo, Lifeng Liu, Zhenghao Chen, Shuo Ding, Hubin Lu, Kui- Juan Jin, Yueliang Zhou Bolin Cheng, Europhys. Lett; **73**(1), 110 (2006).
- [15] Z. G. Hu, G.S. Wang, Z.M. Huang, J. H. Chu, Journal of Physics and Chemistry of solids **64**, 2445 (2003).
- [16] Jinbao Xu . Jiwei Zhai . Xi Yao . Jianqiang Xue. Zhiming Huang, j Sol-Gel Sci Techn **42**, 209 (2007).
- [17] Z. M. Huang, Z. H. Zhang, C. P. Jiang, J. Yu, J. L. Sun, Chu JH, Appl. Phys. Lett **77**, 3651 (2000).
- [18] A. Y. Liu, X. J. Meng, J. Q. Xue, J. L. Sun, J. Chen, J. H. Chu, Appl. Phys. Lett **87**, 072903 (2005).

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