

STRUCTURAL STUDIES OF FERROELECTRIC BaTiO_3 NANO PARTICLES AND VACUUM EVAPORATED BaTiO_3 NANO SCALE THIN FILMS

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ABSTRACT

Barium titanate (BaTiO_3) nanoparticles were prepared by wet chemical method using commercially available materials barium chloride, titanium dioxide and oxalic acid. Nano scale thin films of different thickness were coated on pre - cleaned glass substrate by using vacuum evaporation technique under a vacuum of 2×10^{-5} Torr. The X - ray analysis showed that the particles have tetragonal structure. The deposited films of a lower thickness were found to be amorphous in nature, whereas the crystallinity increases with increase of thickness. The estimated value of grain size (D), strain and dislocation density (δ) were also reported in this paper.

Key words: BaTiO_3 , Thermal Evaporation, XRD

1. INTRODUCTION

The discovery of ferroelectric barium titanate (BaTiO_3) opens the present era of ceramic dielectric materials. BaTiO_3 having the perovskite structure with tetragonal symmetry at room temperature, possesses a relatively large dielectric constant (ϵ') and electro optic coefficient. Now-a-days BaTiO_3 has become the basic capacitor material in semiconductor technology. BaTiO_3 ceramics have a strong piezoelectric effect. These ceramics find wide applications in devices such as microphones, ultrasonic and underwater transducers, sensors and actuators, electro - optic device, multilayer capacitors and spark generators. BaTiO_3 is one of the ABO_3 type (A = mono or divalent, B = tri-hexavalent ions) ceramic materials which have been examined in search of ferroelectric applications. Due to the desirable properties and applications, over the last few decades, synthesis of BaTiO_3 nanopowder and thin film has attracted great attention. Various chemical methods could be employed for the production of these fine particles like sol-gel techniques (Tangwiwat and Milne, 1988), coprecipitation, alkoxide hydrolysis (Kirby *et al.*, 1988), metal-organic processing (Shaikh and Vest, 1986), hydrothermal treatment (Boulos *et al.*, 2005) and mechanochemical synthesis (Stojanovic *et al.*, 2005). Wet chemical method is a promising technique that offers relative low cost, uniform size, homogenous powder and high purity of the ceramics. In addition to that different techniques have also been applied to prepare thin film of barium titanate such as r.f.- sputtering (Bhattacharya *et al.*, 1993), pulsed laser ablation (Yoon *et al.*, 1995) and

metal-organic chemical vapour deposition (Tahan *et al.*, 1996).

Dent *et al.*, have successfully optimized high velocity oxy-fuel (HVOF) spraying for the deposition of barium titanate as dense thick dielectric layer (25-150 μm) and compared the dielectric constant (k) values of these deposits with those (k) values of BaTiO_3 layers produced by plasma spraying. The maximum dielectric constant values achieved by HVOF method of deposition are in the range 70-115. Plasma spraying of these materials has produced layers with k values close to 200. However, considerable success has been achieved for both process, some of the problems inherent in each type of deposition are still to be overcome. Despite several techniques have been explored to deposit thin film of BaTiO_3 , less attention has been devoted to thermal evaporation. In this paper, we have reported about the preparation of nanoscale BaTiO_3 thin films by thermal evaporation technique from BaTiO_3 nanoparticles synthesised by wet chemical method. Structure parameters of BaTiO_3 nanoparticles and vacuum evaporated nano scale thin films have also been reported.

2. MATERIALS AND METHODS

2.1. Synthesis of BaTiO_3 nanoparticles

BaTiO_3 nanoparticles were synthesized using wet chemical method. The starting materials used were barium chloride ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$), titanium dioxide (TiO_2) powder and oxalic acid. A solution of barium chloride, titanium dioxide and oxalic acid having mole ratio 1: 1: 1 was stirred and evaporated at 80°C

till a clear, viscous resin was obtained and then dried at 100° C for 20 hours. The precursor formed was heated at 1000° C for 2 hours to form BaTiO₃ nanoparticles.

2.2. BaTiO₃ nanoscale thin film preparation

Nano scale thin films of BaTiO₃ were prepared by thermal evaporation of BaTiO₃ nanoparticles evaporated onto pre-cleaned glass substrate under a vacuum of 2x 10⁻⁵ torr, using a Hind High vacuum coating unit. The growth rate and thickness were measured during growth process by using a quartz crystal oscillator thickness monitor attached inside the vacuum evaporation chamber. 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. Structural studies of BaTiO₃ nanoparticles and BaTiO₃ nanoscale thin films

The XRD patterns of the BaTiO₃ nanoparticles and their nanoscale thin films were obtained from X-ray powder diffraction with CuKα radiation (λ = 1.5418 Å).

3. RESULTS AND DISCUSSION

3.1. X – Ray Diffraction Analysis

Fig.1 shows the X – ray diffraction pattern of the BaTiO₃ nanoparticles. The spectrum obtained exhibits a tetragonal polycrystalline structure with the preferred orientation along (101), (111), (002), (112), (003) and (113) and the value of interplanar spacing d were evaluated and compared with the standard JCPDS values of BaTiO₃ (Pattern: 00 – 003 – 0725) and are found to be in good agreement with the standard data [Hu et al.,].

The grain size is calculated from the full with half – maximum (FWHM) of the XRD peaks by using Scherrer formula

$$D = 0.94\lambda/\beta\cos\theta \quad (1)$$

Where k is the wavelength of the X-rays used, 2θ is the angle between the incident and scattered X-rays, and β is the full width at half maximum. The strain (ε) was calculated from the formula

$$\epsilon = \beta\cos\theta/4 \quad (2)$$

The dislocation density (δ) is defined as the length of dislocation lines per unit volume of the crystal and is given by

$$\delta = 1/D^2 \quad (3)$$

Table.1 shows the calculated interplanar spacing (d), grain size (D), strain (ε) and dislocation density (δ) and the standard 'd' values of

corresponding predominant peaks. The calculated 'd' values are found to be in agreement with the standard values. The average grain size (D), strain (ε) and dislocation density (δ) were found to be 26 nm, 1.40x10⁻³ lin⁻²m⁻⁴ and 1.58x10¹⁵lin/m².

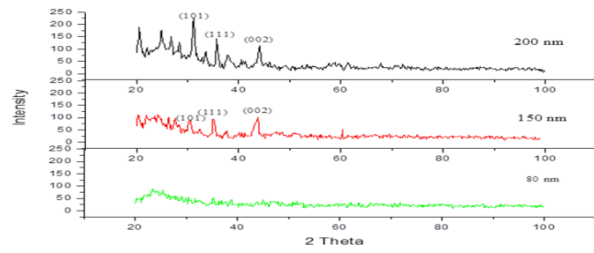


Fig. 1. XRD Spectrum of BaTiO₃ nanoparticles

The X – ray diffraction pattern of the BaTiO₃ nano scale thin films of different thickness are shown in figure 2. It reveals that the films of lower thickness (80 nm) appear to be amorphous in nature without well-defined peaks, whereas the films of higher thickness are polycrystalline in nature. It is observed from diffractogram that the crystallites are preferentially oriented along (002) plane of the tetragonal structure. The intensity of the predominant peaks increases with increase in film thickness, indicating the high degree of preferential orientation towards these directions (12). This means that, at the initial state of film formation, i.e.; during the atomistic condensation of the film formation, the deposited atoms are at random orientations. As the film thickness increases, the polycrystalline grains begin to orient along their direction which is evident from the diffractograms of thickness 150 nm and 200 nm. The lattice parameter values determined for the peaks in the diffractograms coincide fairly well with the standard JCPDS data (pattern: 00 – 003 – 0725).

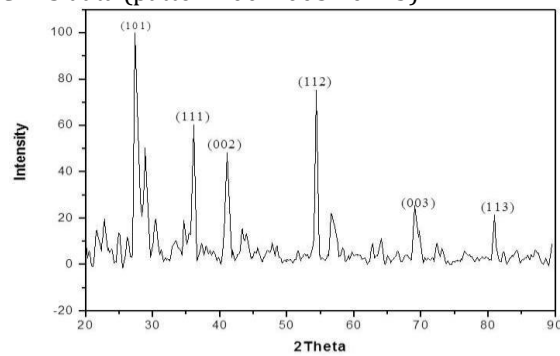


Fig. 2. XRD spectrum of BaTiO₃ nano thin film at different thickness

Table. 2 show a comparative look of the grain size, strain and dislocation density of the BaTiO₃ films of different thickness. It is observed that the grain size increases with film thickness and attained a value of 23 nm for 200 nm thickness film. Due to the increase in grain size with film thickness, the

defect in the lattice are decreased, which is turn reduce the internal microstrain and dislocation density or the columnar grain growth is increased. The strain and dislocation density decreases with increase of thickness, which may be due to increase in crystallinity.

Table 1. Structural parameters of BaTiO₃ nano particle.

2θ	Standard JCPDS d- values (A°)	hkl	Calculated d- values(A°)	D(nm)	ϵ x10 ⁻³ lin ⁻² m ⁻⁴	δ x10 ¹⁵ lin/m ²
28.80	2.83	101	2.94	29	1.18	1.18
36.08	2.31	111	2.39	24	1.46	1.73
41.19	1.8	102	1.88	23	1.62	1.89
54.28	1.64	112	1.73	25	1.38	1.10
68.91	1.34	003	1.36	25	1.52	1.73
80.88	1.21	113	1.18	27	1.25	1.37

Table 2. Structural parameter of BaTiO₃ nano scale thin films

Thickness (nm)	2θ	hkl	D(nm)	ϵ	
				x10 ⁻³ lin ⁻² m ⁻⁴	δ x10 ¹⁵ lin/m ²
150	30.50	101	21.69	1.59	2.12
	35.19	111	21.06	1.64	2.25
	43.79	002	12.06	2.75	6.29
200	31.13	101	24.54	1.41	1.66
	35.65	111	22.73	1.52	1.93
	44.24	002	20.43	1.69	2.39

4. CONCLUSION

Nanoparticle of BaTiO₃ were successfully synthesised by low cost wet chemical method using commercially available chemicals such as oxalic acid, TiO₂ and BaCl₂. Thin films of few hundred nanometer thickness were prepared on well cleaned glass plate for the first time using thermal evaporation method. X-ray analysis showed that the nanoparticles have tetragonal nature and the deposited films at lower thickness have amorphous structure, whereas film of higher thicknesses showed increase in crystallinity.

The crystallinity increases with increase of film thickness where as strain and dislocation density decreases with increase of film thickness. The improved crystallinity with temperature and thickness indicated the feasibility of utilising them for sensor applications.

REFERENCES

- Bhattacharya, P., T. Komeda, D. Park and Y. Nishioka, Japan. (1993). *J. Appl. Phys.* **32**: 4103.
- Boulos, M., S. Fritsch, F. Mathieu, B. Durand, T. Lebey and V. Bley. (2005). *Solid State Ionics* **170**: 1301.
- Dent, A.H., A. Patel, J. Gutleber, E. Tormey, S. Sampath, H. Herman. (2001). *Mater. Sci. Eng. B* **87**: 23.
- Hu, Z.G., G.S. Wang, Z.M. Huang and J.H. Chu. (2003). *Journal of Physics and Chemistry of solids* **64**: 2445-2450.
- Kaur, J., R.K. Kotnala, K.C.Verma. (2012). *Journal of optoelectronics and advanced materials* **14**: 219-223.
- Kirby, K.W., Mater. (1988). *Res. Bull* **12**: 881.
- Shaikh, A.S. and G.M. Vest. (1986). *J. Am. Ceram. Soci.* **69**: 682.
- Stojanovic, B.D., A.Z. Simoes, P.C.O. Santos, C. Jovalekic, V.V. Mitic and J. A. Varela. (2005). *J. Euro Ceram. Soci.* **25**: 1985.
- Tahan, D., A. Safari, L.C. Klin. (1996). *J. Am. Ceram. Soci.* **79**: 1593.
- Tangwivat, S. and S.J. Milne. (1988). *J. Non-Crystalline Solids* **351**:
- Yoon, S.G., L. Lee and A. Safari. (1995). *Integrated Ferroelectrics* **7**: 329.