Materials Properties of Sol Gel Spin Coated Lead Zirconium Titanate Thinfilms

K. Kathiresan[1], N. Sanakara Subramanian[2]

[1]Department of Physics, PSNA College of Engineering and Technology, Dindigul – 624 622, India
[2]Thinfilm Research Laboratory, Department of Physics, Thiagarajar College of Engineering, Madurai – 625 015, India

Abstract: ***The sol solution is prepared by dissolving appropriate amount of Lead acetate and Zirconium acetylacetonate in a solution containing 2- methoxyethanol, Titanium isopropoxide and acetic acid (Chelating agent), mixed in a stochiometric ratio. This mixed solution has been well stirred, refluxed for one hour at 60 °C and allowed for ageing. The as prepared sol solution has been spin coated on to mineral glass substrate under optimized coating conditions. The prepared PZT films have been annealed at 500 °C for 2 hours. XRD profile of the PZT thinfilms confirms the formation of poly crystalline pervoskite structure. Optical transmittance of the spin coated pzt thinfilms have been recorded and investigated in the UV- Visible region. FTIR spectrum is absorbed and the results are discussed. Thermal properties of the PZT thinfilms are analyzed from the TGA and DTA measurements and the results have been reported. The surface morphology of the PZT thin films have been recorded and discussed using Atomic Force Microscopic (AFM) technique.***

Keywords: PZT, Sol-gel, Spin coating, DTA, TGA, and AFM

1. Introduction

Lead zirconate titanate (PZT) thinfilm is known to be a promising material for integrated memory, optical and microelectro mechanical devices such as pressure sensors, piezoelectric micromotors, and pyroelectric infrared detectors,[1-5] etc., PZT films can be fabricated by solgel, spin deposition which is a film fabrication method based on solidification by impact of submicron particles onto a substrate, has been attracting much attention for the fabrication of ferroelectric films[6-9] because this deposition method enables film fabrication at a high deposition rate and low process temperature.

2. Experiment

The sol solution is prepared by dissolving appropriate amount of Lead acetate and Zirconium acetylacetonate in a sol solution containing 2- methoxyethanol, Titanium isopropoxide and acetic acid (Chelating agent), mixed in a stochiometric ratio[10]. This mixed solution has been well stirred, refluxed for one hour at 60 °C and allowed for ageing. The as prepared sol solution has been spin coated on to mineral glass substrate under optimized coating conditions Viz., Spin rate – 2500 rpm, Spin time – 10 Sec, viscosity - 25 MPa.s, Heat treatment temperature - 450 °C and Coating period of the sol solution - 2nd and 4th day. The prepared PZT films have been annealed at 500°C for 2 hours, under the atmospheric condition.

3. Result and Discussion

3.1 Structural Analysis

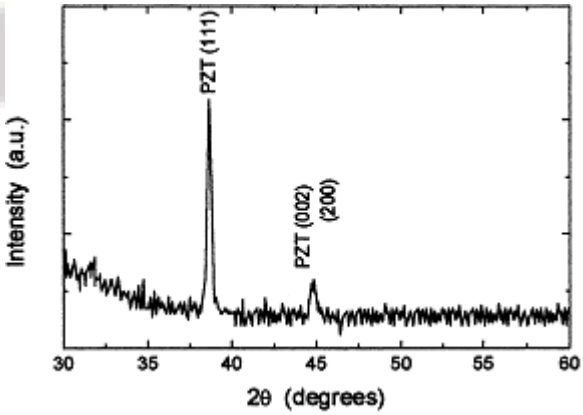

Figure 1: X-ray diffraction for PZT film

X-ray diffraction patterns of the 500°C annealed PZT films shown in figure.1 and it shows a main peak corresponding to the perovskite phase with (111) orientation and another peak corresponding to a crystalline phase with (002) orientation [11].

3.2 FTIR analysis

FTIR absorption spectra of the PZT thin films annealed at 500ºC are shown in Figure. 2 in which a broad absorption peaks of the BO6 stretching mode, at 389, 428 and 676 cm-1, that are due to resonance with the longitudinal optic (LO) phonon modes become sharper and narrower, and they shift very slightly toward higher wave numbers. This is considered to be network stiffening and a structural rearrangement, which

leads to the perovskite phase formation [12], [13] increasing the crystallinity of the PZT films.

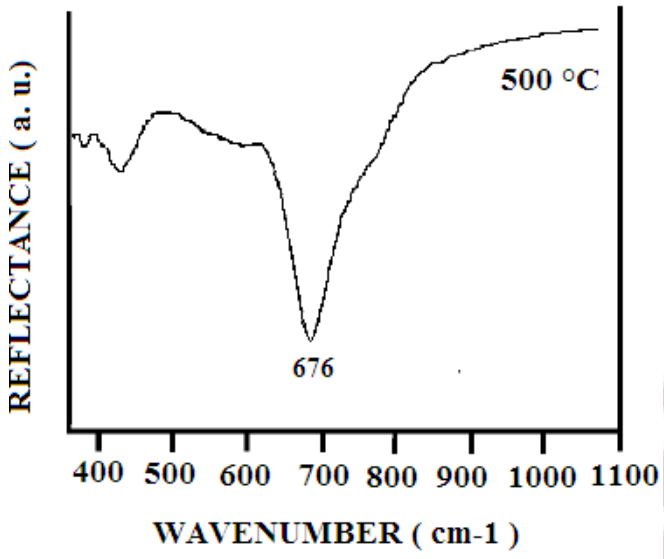

Figure 2: FTIR absorption spectra of the PZT thin films annealed at 500ºC

3.3 UV-NIR Spectroscopic Analysis Method

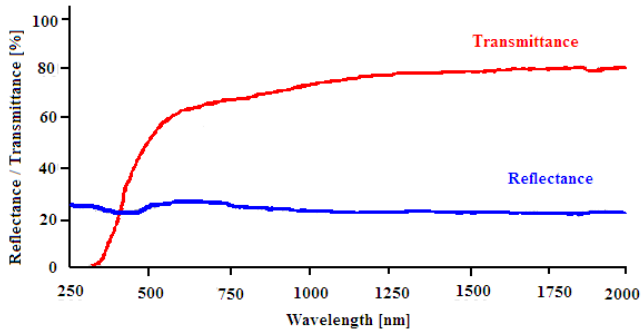

Figure 3: UV-NIR Spectroscopic Analysis

Reflectance and transmittance spectra of a PZT film annealed at 500◦C. The reflectance of PZT films remained constant at approximately 20%. The transmittance of the film sharply increased from the absorption edge at nearly 370 nm, and saturated in the near-infrared (NIR) region. The absorption edge of the annealed PZT film was a shorter wavelength is shown in figure 3. The band gap is measured as 3.4 eV and the optical constants (n & k) are evaluated as, 2.5 – 2.7 and < 0.01 of PZT film annealed at 500◦C respectively [15].

3.4 TG and DTA Thermal analysis

The thermal analysis result of TGA and DTA for the formulated PZT gel is shown in figure 4. The large weight loss between room temperature to 300º C is due to solvent evaporation and organic combustion. For the DTA curve, the endothermic peak at 78 ºC is due to organic solvent evaporation. The decomposition and combustion of the organic in the precursor contribute to the exothermal peaks before 300º C. According to the thermal analysis[16], the film drying temperatures in the process of fabricating PZT thinfilm were chosen at 150 and 280º C. the exothermal peak around 350 ºC is attributed to the decarbonization and glass transition of the PZT. The higher exothermal peak beyond is due to PZT crystallization.

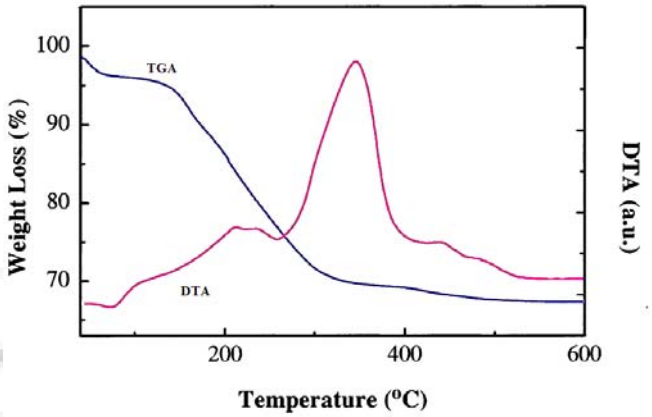

Figure 4: Thermal analysis result of TGA and DTA for the formulated PZT gel

3.5 Surface Characterization

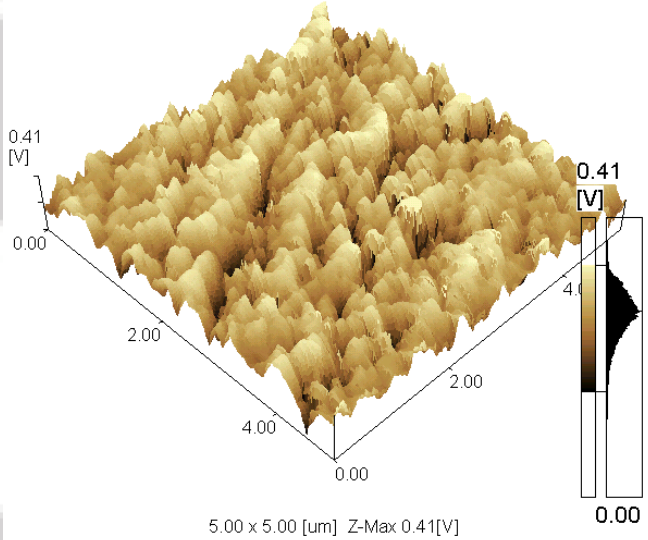

Figure 5: 3D AFM image

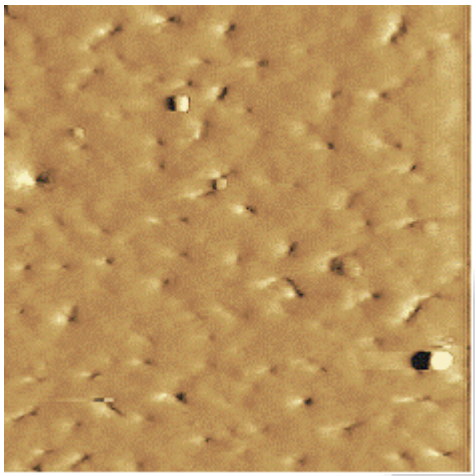

Figure 6: 2D AFM image

The 3D and 2D AFM micrographs of the PZT thin film annealed at 500 °C is shown in the Fig. 5&6 respectively. Both the images illustrate uniform grain growth, smooth and uniform surface pattern without any dark pits and pinholes. Further the surface studies indicate the presence of fine grains with extremely least surface roughness.

4. Conclusion

X-ray diffraction patterns of the PZT films revealed a main peak corresponding to the perovskite phase with (111) orientation and another peak. The FTIR absorption spectra of the PZT thin films annealed at 500ºC [17] shows that the perovskite phase formation, increasing the crystallinity of the PZT thin films. From the reflectance and transmittance spectra of a PZT film, the band gap is measured as 3.4 eV and the optical constants (n & k) are evaluated as, 2.5 – 2.7 and < 0.01 respectively. The thermal analysis result of TGA and DTA for the formulated PZT gel, the film drying temperatures in the process of fabricating PZT thinfilm were chosen at 150 and 280ºC. The exothermal peak around 350 ºC is attributed to the decarbonization and glass transition of the PZT. The 2D and 3D AFM micrographs of the PZT thin film both the images illustrate uniform grain growth, smooth and uniform surface pattern without any dark pits and pinholes.

References

[1] S. Muensit, P. Sukwitsu, P. Khaenamkeaw, S.B. Lang, Appl. Phys.A **92**, 659 (2008)
[2] T.Wei, Y.Wang, C. Zhu, X.W. Dong, Y.D. Xia, J.S, Zhu, J.M. Liu, Appl. Phys. A **90**, 185 (2008)
[3] U. Ellerkmann, T. Schneller, C. Nauenheim, U. Böttger, R.Waser, Thin Solid Films **516**, 4713 (2008)
[4] Polla DL, Ye C, Schiller P, Tamagawa T, Robbins WP, Glumac D,Hseuh C-C Proc Mater Res. Soc 243:55, (1992)
[5] Polla DL, Schiller PJ , Int Ferroelectrics 7:359, (1995)
[6] Tsurumi T, Ozawa S, Abe G, Ohashi N,Wada S, Yamane M Jpn J Appl Phys 39:5604, (2000)
[7] Barrow DA, Petroff TE, Tandon RP, Sayer M J Appl Phys 81:876, (1997)
[8] Wu A, Vilarinho PM, Miranda Salvado IM, Baptista JL Mater Res Bull 33(1):59, (1988)
[9] Wang Z, Zhu W, Zhao C, Tan OK, Mater Sci Eng B 99:56, (2003)
[10] S. K. Pandey, A. R. James, R. Raman, S. N. Chatterjee, A. Goyal, C. Prakash, and T. C. Goel, Phys. B: Condens. Matter, vol. 369, pp. 135–142, Dec. (2005)
[11] P. Verardi, M. Dinescu, F. Craciun, Applied Surface Science 154–155, 514–518 (2000)
[12] Cho, S. M. and Jeon, D. Y.,Thin Solid Films, 1999, 338, 149
[13] Yan, F., Bao, P., Chan, H. L. W., Choi, C. L. and Wang, Y., Thin Solid Films, 406, 282 (2002)
[14] F.M. Pontesa, E.R. Leitea, M.S.J. Nunesa, D.S.L. Pontesa, E. Longoa, R. Magnania, P.S. Pizanib, J.A. Varelac, Journal of the European Ceramic Society 24, 2969–2976 (2004)
[15] Hiroki Tsuda, Masafumi Nakada, Jun Akedo, and Keishi Ohashi., vol. 55, (2008)
[16] Anupama Sachdeva · Mahesh Kumar · Vandna Luthra ·R.P. Tandon, "Applied Physics A Materials Science", Vol 104:103–108 (2011)
[17] Izyumskaya, N., Alivov, Y. -I., Cho, S. -J., Morkoç, H., Lee, H. and Kang, Y. Critical Reviews in Solid State and Materials Sciences, 32: 3, 111 — 202