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Enhancing the Properties of Sol Gel Spin Coated PZT thin Films by Varying Annealing Temperature

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ABSTRACT

Investigations on the development of piezoelectric ceramics have recently claimed properties comparable to that of PZT-based materials. PZT thin films have been deposited on the substrate by the spin coating method.The optimized coating parameters used in the development of device quality PZT thin films are (1) Coating period of the sol - 6th day, (2) Spin rate – 2000 rpm, (3) Spin time – 10 Sec, (4) Number of coating – 10, (5) Heat treatment temperature - 350 °C and (6) Heat treatment duration – 8 Sec. X- ray diffraction spectra of the PZT thin films annealed at different temperature confirms the pervoskite phase with the dominant orientation along (110) plane, for all the PZT films, annealed at temperatures between 500^o C and 800^o C. The sheet resistance and resistivity are found to be maximum with the value 15.2 MΩ/square and 14.2 x 10^{-6} Ω-cm respectively, for the PZT thin films annealed at the temperature 800 ^{o}C. The thermal conductivity of the barest sample has been estimated as 281.97 watt / mK, whereas for the PZT coated samples, annealed at different temperatures, a steady fall in thermal conductivity has been observed. Microhardness have been evaluated in the Vickers scale. The hardness of the unannealed PZT thin film is determined as 130 VHN and the hardness is found to be the maximum value about 890 VHN and minimum value about 160 VHN, for the PZT thin film annealed at the temperatures 800 °C and 500 °C respectively The 2D and 3D AFM micrographs of the PZT thin film annealed at 800 °C illustrates uniform grain growth, smooth and uniform surface pattern. Further the surface studies indicate the presence of fine grains (average grain size 100 nm) with extremely least surface roughness about1.8 nm.

Keywords: PZT thin films, Solgel, Spin coating, Annealing temperature, Pyrochlore structure, Perovskite structure.

I. INTRODUCTION

Lead zirconate titanate (PZT) thin film is known to be a promising material for integrated memory, optical and microelectromechnical devices such as pressure sensors, piezoelectric micrometers, and pyroelectric infrared detectors, etc., [1-4] Among bulk materials it is known to be most common piezoelectric, with extremely high piezoelectric coefficients and electro-mechanical coupling factors. Reproducing these exceptional qualities in thin film form, however, requires precise tuning of composition and texture. Different techniques are being used to produce PZT films such as sputtering, PLD, MOCVD, solgel spin coating, dip coating, vacuum evaporation CVD and PVD [8]. Among these, solgel technique is the most used one due to its cost effectiveness, ease of fabrication and it maintains a stoichiometric ratio [5–7 & 10].

In this paper, solgel spin coated PZT thin films are prepared the influence of different annealing temperature on the structural, electrical, mechanical and surface morphological properties and also its related studies of solgel spin coated PZT thin films are discussed.

Piezoelectric has been studied in many areas related to precision position control, acoustic, pressure and gas sensors. Lead zirconate titanate (PZT) ceramics have been extensively used due to their superior piezoelectric properties for a wide range of sensors and actuators. One of the commonly studied chemical composition is

$PbZr_{0.48}Ti_{0.52}O_3$. The increased piezoelectric response and poling efficiency near to x = 0.48 is due to the increased number of allowable domain states at the MPB. At this boundary, the 6 possible domain states from the tetragonal phase <100> and the 8 possible domain states from the rhombohedral phase <111> are equally favourable energetically, thereby allowing a maximum 14 possible domain states. Like structurally similar lead scandium tantalate and barium strontium titanate, PZT can be used for manufacture of uncooled staring array infrared imaging sensors for thermographic cameras. Both thin film (usually obtained by chemical vapour deposition) and bulk structures are used. The formula of the material used usually approaches $Pb_{1.1}(Zr_{0.3}Ti_{0.7})O_3$ (called PZT 30/70). Its properties may be modified by doping it with lanthanum, resulting in lanthanum-doped lead zirconate titanate (PLZT, also called lead lanthanum zirconate titanate), with formula $Pb_{0.83}La_{0.17}(Zr_{0.3}Ti_{0.7})_{0.95}O_3$ (PLZT 17/30/70). In 1975 Sandia National Laboratories were working on anti-flash goggles protect aircrew from burns and blindness in the case of a nuclear explosion. The PLZT lenses could turn opaque in less than 150 millionths of a second.

II. METHODS AND MATERIAL

PZT thin films have been prepared by the spin coating method. The sol solution has been prepared by dissolving 7.4 gm in a solvent solution (lead acetate trihydrate 4.2 gm and zirconium acetyl acetonate 3.2 gm) containing 10 ml titanium isopropoxide and 75 ml 2-methoxyethanol, and 25 ml acetic acid (Chelating agent) [9]. This solution has been well stirred, refluxed for one hour at 100 °C and allowed for ageing two days. The as prepared sol solution has been spin coated on the stainless steel substrate, using the optimized coating conditions. The Spin coated PZT films have been annealed in the temperature range 500 °C, 550°C, 600°C, 650°C, 700°C, 750°C and 800 °C. The optimized coating parameters used in the development of device quality PZT thin films are mentioned below.

(1) Coating period of the sol - 6^{th} day, (2) Spin rate – 2000 rpm, (3) Spin time – 10 Sec, (4) Number of coating – 10, (5) Heat treatment temperature - 350 °C and (6) Heat treatment duration – 8 Sec.

III. RESULTS AND DISCUSSION

A. Structural Characterization

X- ray diffraction spectra of the PZT thin films annealed at different temperature viz., 500 °C 550° C, 600° C, 650° C, 700 °C, 750 °C & 800 °C is shown in the Figure. 1. It confirms dominant pervoskite phase along with pyrochlore phase at 500 °C 550° C, 600° C, 650° C, 700 °C annealing temperatures and it indicates a oriented growth with preferred orientation along (2 0 0) plane, for all the PZT films, annealed at all temperatures between 500° C - 800° C. The other planes that are observed in the spectra are (1 0 0), (1 1 1), (1 1 0) and (2 1 1) and all these are characteristic peaks for PZT powder. When the heat treatment temperature increases pyrochlore phase decreases and pure pervoskite phase increases in the PZT samples annealed at 750˚C & 800˚C [9]. The experimentally observed values for I, 2θ, d are well in agreement with the standard values of JCPDS – PDF data for the PZT powder specimen. The figure depicts the excellent polycrystalline growth of the PZT films annealed at all the temperatures. The intensity of all the orientations gradually increases by increasing the heat treatment temperature increases and this may be attributed to the oriented overgrowth along all the planes caused by heterogeneous nucleation.

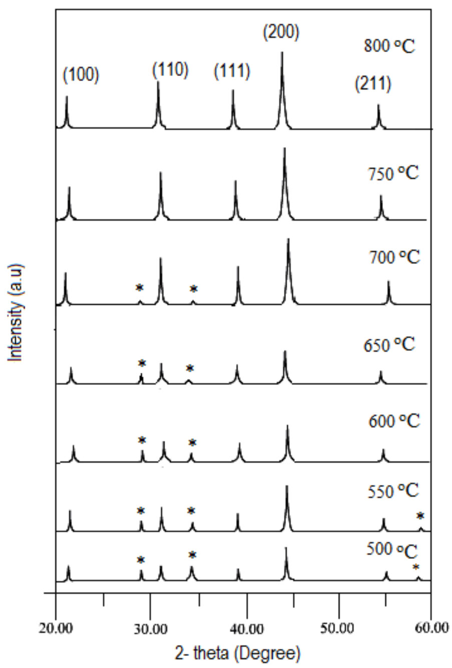

Figure 1: X- ray diffraction spectra of the PZT thin films annealed at different temperature 500 °C, 550 °C, 600 °C, 650 °C, 700 °C, 750 °C & 800 °C

B. Electrical Characterization

Hwa Min Kim, et. al [11] reported that TCO – PZT thin films shows sheet resistance about 2 × 10^{-4} Ωcm which is very low. But it is found to be the sheet resistance and resistivity, maximum with the value 15.2 MΩ/square and 14.2 x 10^{-6} Ω-cm respectively, for the PZT thin films annealed at the temperature 800°C. Variation of sheet resistance (R_{sh}) and resistivity (ρ) of the PZT thin films annealed at different temperatures is shown in the Figure. 2 which clearly illustrates that the rash and ρ value increases with the increase in annealing temperature.

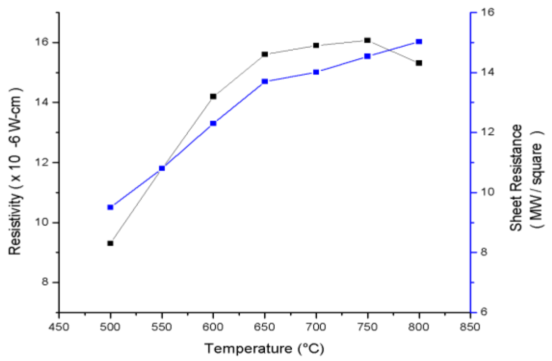

Figure 2 : Variation of Sheet Resistance and Resistivity with annealing temperature.

C. Thermal Characterization

The electrical conductivity of the PZT thin films are evaluated using Techno Four conductivity meter. The electrical conductivity of the PZT thin films annealed at different temperatures is measured in terms of % IACS (International Annealed Copper Standards) and it can be related to electrical resistivity by the following relation

$$\% \text{ IACS} = \frac{172.41}{\text{Resistivity } (\mu\Omega - \text{cm})} \quad \text{---------- (1)}$$

The % IACS values are measured to all the PZT thin films, before and after coating and its value is found to be 65.75 % IACS for uncoated sample. On the other hand the % IACS values are found to decrease drastically for the PZT thin films annealed at higher temperatures. The thermal conductivity of PZT thin films has been evaluated using the Wiedemann – Franz law stated below. L=k/(σT) ------------ (2)

Where L is the Lorentz number (2.44 x 10^{-8} $\Omega W/K^2$), k is the thermal conductivity in watt / mK, σ is the electrical conductivity in mho / m and T is the absolute temperature in K. Using the above relation, thermal conductivity of the bare sample has been estimated as 281.97 watt / mK whereas for the PZT coated samples annealed at different temperatures a steady fall in thermal conductivity has been observed.

The thermal conductivity of the bare sample has been estimated as 281.97 watt / mK whereas for the PZT coated samples annealed at different temperatures a steady fall in thermal conductivity has been observed. The variation of thermal conductivity as a function of annealing temperature is shown in Figure 3. The plot shows a non – linear decrease in thermal conductivity with the increase in annealing temperature and this may be attributed to micro structural variation and gradual raise in thermal diffusivity with the increase in annealing temperatures.

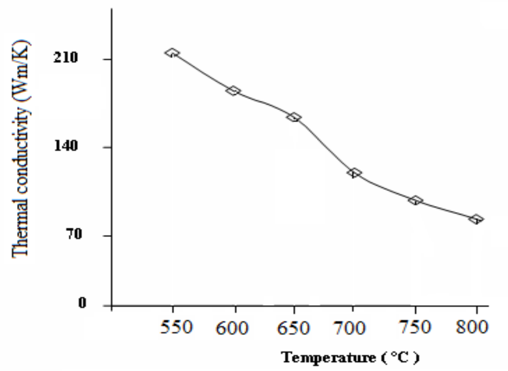

Figure 3 : Variation of Thermal Conductivity with annealing temperature.

D. Microhardness Studies

The micro hardness testing of the PZT thin film is conducted in Vickers hardness scale, using Zwick micro-hardness tester. The indentations have been made over the substrate surface with 70 gram load for 15 second along the axis of the coating thickness. The hardness of PZT thin films before and post annealed at different temperatures is recorded. The hardness of the unannealed PZT thin film is determined as 130 VHN and the hardness of the PZT thin films is found to increase drastically with the increase in annealing temperature.

The variation of VHN with an annealing temperature of the PZT thin films is shown in the Figure 4. The plot shows a non – linear increase in VHN with annealing temperature, indicating an improvement in the hardness of the films. This may be attributed to the higher densification of coating structures. The increase in hardness with the annealing temperature may be attributed to the increase in grain size and surface smoothness at higher temperatures as evidenced by the AFM images. This may also be attributed to the increase in the number of grain boundaries, which in turn increases the surface energy and reduces the dislocations and this fact is in agreement with other reported results. The hardness is found to be maximum with the value 890 VHN and minimum with the value 160 VHN, for the PZT thin film annealed at the temperatures 500 °C and 800 °C respectively.

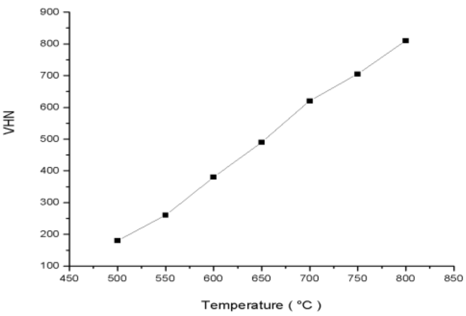

Figure 4 : Variation of VHN of the PZT thin films annealed at different temperatures

E. Surface Characterization

The 2D and 3D AFM micrographs of the PZT thin film annealed at 800°C is shown in the Figure. 5. The SEM images of the surface of the PZT thin films annealed at 600°C, 700°C, 800°C temperatures are offered in Figure 6, 7 and 8 respectively. Film compaction increases with increasing the annealing temperature and also figures show that the gap between grain boundaries becomes larger at higher annealed temperature, which may be attributed due to the evaporation of PbO [10].

The AFM and SEM images of the PZT thin films annealed at different temperature illustrate uniform grain growth, smooth and uniform surface pattern without any dark pits and pinholes. From the AFM micrograph analysis, the grain size is evaluated as 100 nm and it also confirmed by SEM images of the PZT thin film. D. A. Kiseley et.al [13] reported that the surface roughness of the film approximately 2nm. In this paper, the surface studies indicate the presence of fine grains with extremely least average surface roughness about 1.8 nm. It is comparatively slightly small in value of surface roughness.

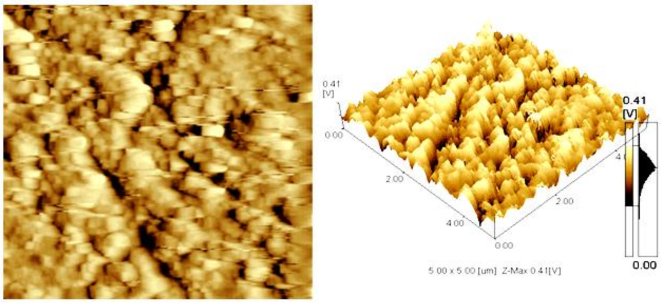

Figure 5 : 2D &3D AFM image of the PZT Thinfilm annealed at 800 ^{o} C

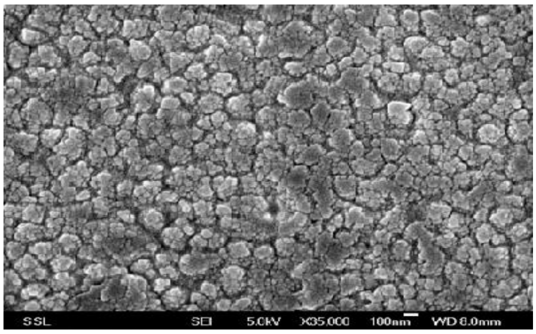

Figure 6 : SEM image of PZT thin film annealed at 600 °C

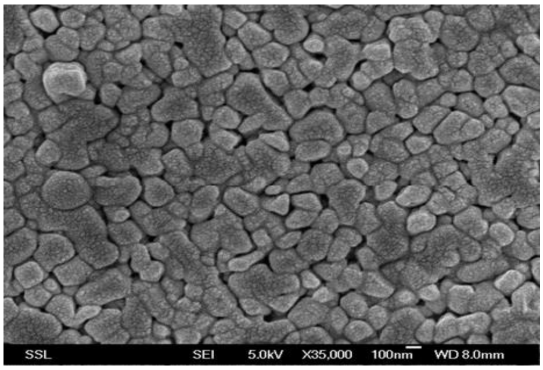

Figure 7 : SEM image of PZT thin film annealed at 700 °C

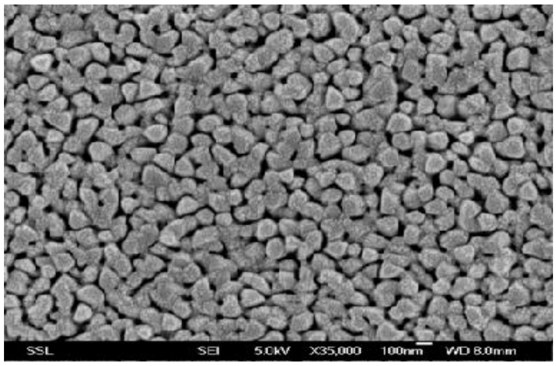

Figure 8 : SEM image of PZT thin film annealed at 800 °C

IV. CONCLUSION

PZT thin films have been prepared by the spin coating method with the optimized coating parameters used in the development of device quality PZT thin films. X-ray diffraction spectra of the PZT thin films annealed at different temperature confirms the pervoskite phase with the preferred orientation along (110) plane, for all the PZT films, annealed at temperatures between 550^{o} C and 750^{o} C. The other planes observed are (100), (111), (200) and (211) and all these are characteristic peaks for PZT powder.

It is found to be the sheet resistance and resistivity, maximum with the value 15.2 MΩ/square and 14.2×10^{-6} Ω-cm respectively, for the PZT thin films annealed at the temperature 800 ^{o}C. The thermal conductivity of the bare sample has been estimated as 281.97 watt / mK, whereas for the PZT coated samples, annealed at different temperatures, a steady fall in thermal conductivity has been observed. The studies on the variation of thermal conductivity as with annealing temperature shows a non – linear decrease in thermal conductivity with the increase in annealing temperature. The hardness of the unannealed PZT thin film is determined as 130 VHN and the hardness of the PZT thin films is found to increase drastically with the increase in annealing temperature. The hardness is found to be maximum with the value 890 VHN and minimum with the value 160 VHN, for the PZT thin film annealed at the temperatures 800°C and 500°C respectively. The 2D and 3D AFM micrographs of the PZT thin film annealed at 800 °C illustrates uniform grain growth, smooth and uniform surface pattern. SEM images also show that densification, compaction and crystallization with different annealing temperature. Further the surface studies indicate the presence of fine grains (average grain size 100 nm) and the average surface roughness is measured about 1.8 nm which is extremely least value.

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