Synthesis of $SrTiO_3$ thin films by spray pyrolysis technique

[1]R.B.Ahirrao, [2]M.S.Wagh

[1]Department of Physics, Uttamrao Patil College, Dahivel, Maharashtra, India.
[2]Department of physics, Pratap College, Amalner, Maharashtra, India.

Abstracts: The SrTiO3 (STO) thin films are synthesized by spray pyrolysis system. $SrCl_2 6H_2O$ and $TiCl_3$ were the starting precursors. The solution is sprayed on preheated glass substrate at 350℃ subsequently the films are fired at 500℃ for half hour. The spray parameters are optimized for well and good films. Pilling-Bedworth Ratio of films was calculated. The XRD was offered for the structural verification. The FE-SEM offered for morphological study.

Keywords: Spray pyrolysis technique, STO films, XRD, FE-SEM.

1. Introduction:

The interest to non vacuum methods for thin films deposition has increased in the last decades. The solution based processes have several advantages like simplicity of process, access to a wide range of metal oxide stoichiometries, precise composition control, and applicability to substrates of any size. These peculiarities are important for some of the practical application of the layers, for example in the superconducting devices [1-2]. The spray pyrolysis method meets practically all of these requirements to the method of film deposition.

When a source solution is atomized, small droplets splash and vaporize on the substrate and leave a dry precipitate in which thermal decomposition occurs [3]. Organometallic compounds and inorganic salts are used as source materials, which are dissolved in water, ethanol or other solvents to prepare source solutions. Because the source materials dissolve in a solvent as an ion, oligomer, cluster or sol, depending on their chemical properties, the surface morphology of deposited films is easily controlled by choosing species of the source materials [4-7].

Spray pyrolysis is a versatile method for the continuous synthesis of metals, metal oxides, and multicomponent particles. It has been applied to deposit a wide variety of thin films. These films were used in various devices such as solar cells, sensors, and solid oxide fuel cells. It is observed that the properties of deposited thin films depend on the preparation conditions. An extensive review of the effects of spray parameters on film quality is given to demonstrate the importance of the process of optimization. The substrate surface temperature is the most critical parameter as it influences film roughness, cracking, crystallinity, etc.

2. Experimental technique

2.1. Fabrication of spray pyrolysis system

Figure 1 shows the schematic diagram of a chemical spray pyrolysis system. This contains a spray nozzle, solution reservoir combine known as spray gun. The 2000Watt heater, Thermocouple, DPM, platform for heating the glass substrate, and a electromechanical assembly for x-axis (Horizontal movement), thermocouple included temperature controller and air compressor. Air flow meter to measure air presser has been used. The spraying system and heater are kept inside an airtight metallic chamber of size 1x1x1 m^3 and the outlet of the box is fitted with an exhaust fan to remove the toxic gases produced during the decomposition of the spray solution. The inner surface of the box is painted by epoxy liquid, to reduce the heat loss through the surface.

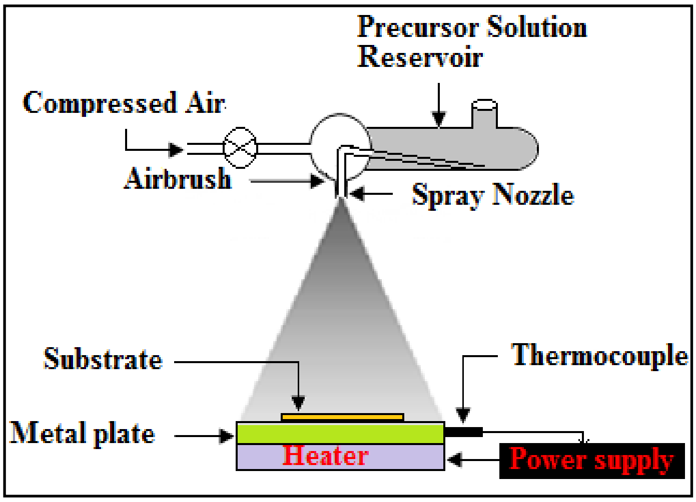

Fig.1.Schematic sketch of spray pyrolysis system set up.

2.2. Synthesis of pure STO thin films

The $SrCl_2 6H_2O$ and $TiCl_3$ are dissolved in the deionized water for 0.1 molar concentrations. The chlorine was used as the source for the preparation of pure STO films. The solution is stirred for 1h so as to mix the solution thoroughly. The solutions have been sprayed on preheated ultrasonically cleaned glass substrates kept at 350^{o}C. The aqueous solution gets thermally decomposes when fallowing over the surface of preheated substrates. This results in the formation of well adherent and uniform pure STO film. The spray deposition parameters optimized for preparation of good quality STO thin films are-

Table 1. Deposition parameters of the pure STO thin films.

Spray Parameter	Quantity	Unit
Spray solution volume	100	ml
Carrier-Air pressure	10	LPM
Nozzle to substrate distance	24	cm
Spray nozzle diameter (atomizer)	0.2	mm
Substrate temperature	350	^{o}C

The so prepared films are fired at $500^{0}C$ for half hours, so that, all the organic materials and impurities can evaporate from the films.

2.3. Kinetics involve in spray pyrolysis

Spray pyrolysis involves spraying of solution usually aqueous containing soluble salts of the constituent atoms of the desired compound onto a substrate maintained at elevated temperatures. The sprayed droplet reaching hot substrate the substrate surface undergoes pyrolytic (endothermic) decomposition and forms a single crystallite or cluster of crystallites of the product. The other volatile by-products and the excess solvent escape in the form of vapors. The substrate provides the thermal energy for thermal decomposition and subsequent recombination of the constituent species followed by sintering and recrystallization of the clusters of crystallites giving rise to coherent films.

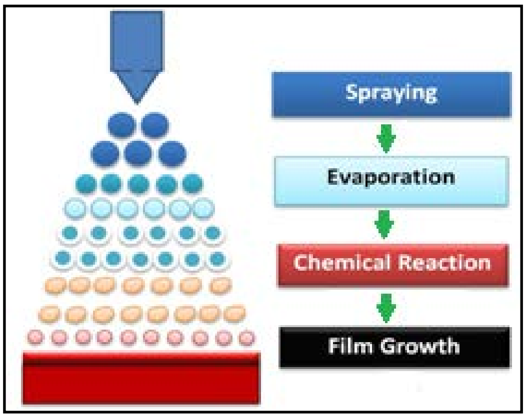

Fig.2.Schematic view of spray pyrolysis stages.

2.4. Characterization of thin films

The crystalline properties of prepared Pure STO thin films was identified by X-ray diffractometer (XRD, D8 ADVANCE BRUKER axs with Cu Kα, λ =0.15419 nm with scanning rate 4°/min) in the range of 30–80º. The surface morphology of as prepared $SrTiO_3$ particles was recorded by field emission scanning electron microscopy (FE-SEM) (JEOL JSM-6360A).

3. Results and discussion

3.1. Pilling-Bedworth Ratio of films

The P.B.R. of the STO film is 0.735 which is less than one; which means that formation of film would surface adherent and porous in nature.

3.2. Structural analysis of pure STO films

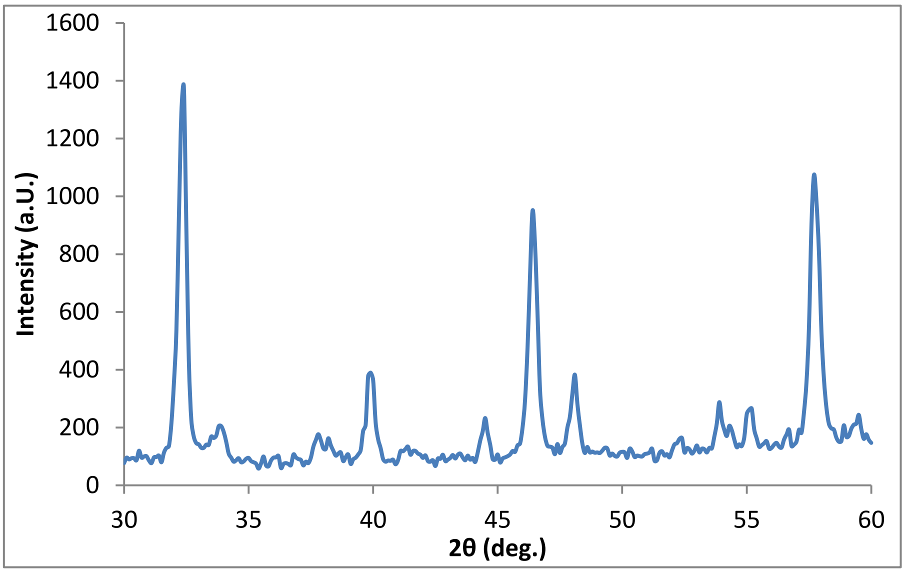

Fig.3. XRD pattern of pure STO of 0.1M concentration.

The average grain size the spray synthesized STO film is 229 nm. The observed peaks are matching with ASTM reported data of SrO, TiO_2, $SrTiO_3$. The XRD data shows three phases viz $SrTiO_3$, SrO and TiO_2. Single phase of $SrTiO_3$ was not obtained. The material was observed to be nanocrystalline in nature. The STO is ternary oxide with cubic crystal structure.

3.3. Surface Morphological Studies

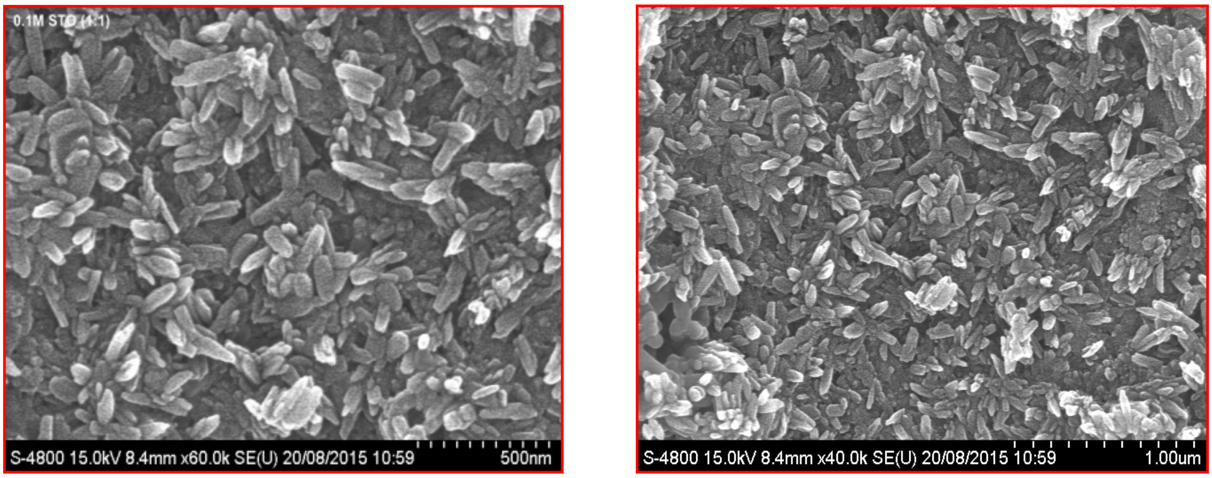

Fig. 4. The FE-SEM images of 0.1M pure STO.

Figure 4 shows FE-SEM images of pure STO thin films of 0.1M. Remarkably, it was observed that the average particle size is 299nm. As shown in figures, it is clear that the material is composed of particles with heterogeneous size. From the figures the morphology is clearly like a layer, with the particle are having rice like in shape.

4. Conclusion

The following conclusions are made in this study-

1. The versatility of the homemade spray pyrolysis unit has been demonstrated by way of preparing reasonably good quality thin films of STO.
2. The various parameters are optimized for good quality films at 350°C.
3. The XRD results suggest that, the film is nanocrystalline in nature. The peaks are matched with ASTM data.
4. The single phase STO is not ascertained by XRD.
5. Surface morphology gave insight of STO layers using FE-SEM.

Acknowledgment

The authors are thankful to the principal and head of the Department of Physics, Pratap College Amalner, allows to work inside the laboratory.

5. References:

1. M.O. Abou-Helal, W.T. Seeber, "Preparation of TiO_2 thin films by spray pyrolysis to be used as a photocatalyst", Applied Surface Science 195 (2002) pp.53-62.
2. B. G. Almeida, A. Pietka, J. A. Mendes,"Infrared characterization of strontium titanate

thin films", Applied Surface Science 238 (2004) pp. 395-399.
3. J.C. Viguie´, J. Spitz, J. Electrochem. Soc. 122 (1975) 583.
4. M. Okuya, N.A. Prokudina, K. Mushika, S. Kaneko, J. Eur. Ceram. Soc. 19 (1999) 903.
5. M. Okuya, S. Kaneko, N.A. Prokudina, T. Fujiwara, K. Murakami,Ceram. Trans. 109 (2000) 473.
6. M. Okuya, D. Osa, S. Kaneko, Key Eng. Mater. 228–229 (2002) 247.
7. M. Okuya, K. Nakade, D. Osa, T. Nakano, G.R.A Kumara, Shoji Kaneko, J. Photochem. Photobiol. A Chemistry 164 (2004) 167.
8. P. S. Patil, 'Versatility of spray pyrolysis technique', Material Chemistry and Physics, 59, 185-198 (1999).