# Flame Assisted Liquid Spray Pyrolysis for Thin Film Deposition

**Divakara SG[1*], Ravishankar Holla[2], Meghanatha KL[2], Ranjith Kumar HN[2]**

[1]*Department of Chemistry, RV College of Engineering®, Bengaluru*

[2]*Department of Electronics and Communication Engineering, RV College of Engineering®, Bengaluru -59*

## Abstract

Spray pyrolysis offers significant potential for the synthesis of different kinds of functional nano-structured materials. It is a highly scalable technology and is suitable for continuous film coating. Thin films of nanomaterials sprayed on different substrates are worthwhile for novel applications. Spray pyrolysis system mainly consists of a precursor chamber for loading the solution; spray nozzle unit, compressor and heating unit. Cost effective automatic flame assisted liquid spray pyrolysis system was fabricated in which control arrangements were managed by a microcontroller based control circuit. In the preliminary tests, ZnO thin films were synthesized and characterized by SEM and XRD. Presence of Wurtzite ZnO structure was evidenced and particle size distribution showed size variation between 35 and 60 nm.

**Keywords:** *Spray pyrolysis, Zinc oxide, thin films, microcontroller*

## 1.0 Introduction

Thin films have gained great importance in applications related to several real-world problems as a two dimensional system in microelectronics, antennas, array antennas, optical electronics, energy generation and energy conservation strategies [1-3]. Their material costs when compared to corresponding bulk material, are very small, yet perform the same function when it comes to surface processes. The various physical and chemical methods of fabricating film coating for required thickness are namely pulsed laser deposition, electron beam sputtering, thermal evaporation, vacuum deposition, chemical vapor deposition, co-precipitation, sol-gel, chemical bath deposition, spray pyrolysis etc. Spray pyrolysis doesn’t need high vacuum environment making it very much suitable for use when low complexity, low cost is needed. Precursors used for this spray pyrolysis isn't expensive comparatively [4-5].

The properties of a film are generally sensitive to their structure, thickness, surface states and morphology. In spray pyrolysis, controlling of spray time and substrate surface temperature during deposition results in variation of properties of the deposited film [6]. A microcontroller system, low cost and with almost nil mechanical arrangement along with a display and keyboard unit ensures

**Mail address: Divakara S G, Assistant Professor, Department of Chemistry, RV College of Engineering®, Bengaluru – 59,*

*Email: divakarsg@rvce.edu.in, Ph.: +91 8660159619*

reasonable control over the spray parameters [7]. In the last 10 years, Spray pyrolysis technology has developed substantially, attracting many researchers to synthesize a wide range of complex materials for various applications. Flexibility in producing nano structured powder and films of pure or mixed metal oxides have enabled advancements in spray pyrolysis equipment, reaction engineering and precursor chemistry. In order to prepare new materials and with unique material morphologies, custom designed low cost spray pyrolysis equipment is proposed. In this paper, fabrication of flame assisted liquid spray pyrolysis equipment and synthesis of ZnO powders or films through a pyrolysis process is presented. The aerosols of the precursor solution is generated by pneumatic system and used during the spraying process. The phase and surface morphology were studied using X-ray diffraction (XRD) and scanning electron microscope (SEM) measurements respectively.

## 2.0 Spray Pyrolysis System

The spray pyrolysis technique mainly involves the aerosol generation from various precursor solution of chemical compounds and very rapidly passing through a hot zone or spraying on to a hot substrate in a furnace. It consists of two basic steps, an atomizer, which creates the droplets, after that those droplets fall of on the heated substrate and evaporates the solvents with solid particles left behind. In flame assisted liquid spray pyrolysis technique, deposition of a film is performed by passing of precursor’s flux across a direct flame and directing on to the surface of the substrate. Spraying droplets of precursor solution at high temperature onto the substrate creates a coating on the substrate surface [8]. The high temperature of single / dual flame is also used for evaporation and decomposition of sprayed liquid precursors to achieve the gas-phase reaction to form particles in nanometers range [4, 8]. Fig. 1 demonstrates the schematic diagram of spray pyrolysis system having temperature controlling unit, electronic unit, flow and pressure controlling units. Equipment was fitted with accessories required for controlling the flame during the process. Spray nozzle unit is fitted onto a motorized linear movement stage.

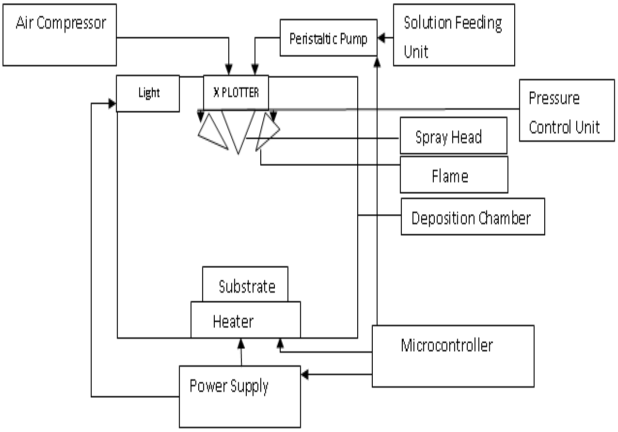


**Fig. 1.** Schematic representation of Spray pyrolysis system

Hot plate with temperature controlling arrangement and control units for gas and liquid flow were fixed in a stainless steel box.

The process of spraying a nano or sub-micron size particle involves 3 steps, out of which the first step is atomization. Their material costs when compared to corresponding bulk material, are very small, yet perform the same function when it comes to surface processes. Out of the various type of available atomizers, easiness of control and less cost involved resulted in selection of air blast atomizer (pneumatic) for the system. The limitation of this unit is in producing the droplets of uniform micrometer or nanometer size and control on the distributions of the droplets [8]. The solution spray using ultrasonic nebulizer instead of traditional atomizers enables production of good quality of films or monodispersive nanomaterials in the form of fine powders. But due to high cost involved, an air blast atomizer was used [9]. The second step of the process is on control over the spray. As the spray time increases, amount of droplets that would be deposited on the substrate from the spray head increases. For this, the atomizer itself has an air and solvent controlling option so that we can control the droplets. Temperature control is the final part of the process. The burner which produces flame using an oxy-LPG gas mixture was mounted near to the spray nozzle and normal heater which heats up to $400^{o}C$ was kept inside the chamber. Additional burner was also mounted near nozzle to provide required temperature and used depending on the application. As the droplets reach the heated substrate, the solvent is evaporated and the residual chemical compound sits on the surface of the substrate.

The air compressor and peristaltic pump used is shown in Fig. 2. The spray nozzle gets predetermined pressurized air and precursor solution using the control accessories. X direction movement of the spray gun was used to ensure uniform coating and is controlled by a unit consisting of a microcontroller [10]. A heater, heats the substrate and its temperature control is done using a thermocouple which senses the temperature of the surface of the substrate and flame is turned ON if required. The complete system is housed inside a stainless steel chamber. The exhaust fan was used to flush out the gasses in the chamber which are produced during the synthesis of material.

A. Flow and Pressure Control

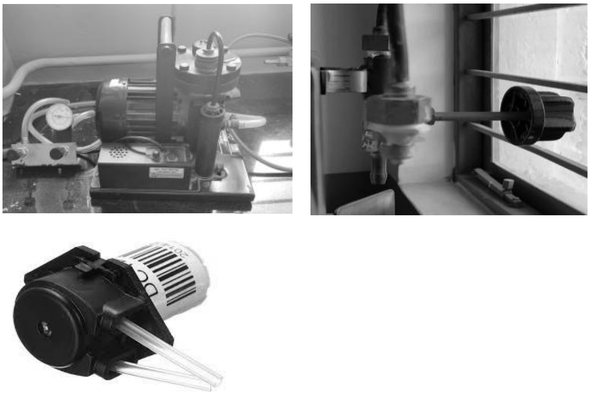

**Fig. 2.** Air compressor, gas control and peristaltic pump

Air compressor supplies pressurized air and peristaltic pump supplies precursor solution to the spray atomizer nozzle [11]. The high pressured air from compressor was regulated and was measured using the meter before it was supplied to the spray nozzle. The precursor solution was supplied to mixing chamber using a positive displacement pump which pumps from 0-50 ml/min depending on the voltage supplied to it. Finally the spray nozzle at predetermined constant pressure and flow rate of air and solution was sprayed on to substrate.

B. Temperature Controlling Unit

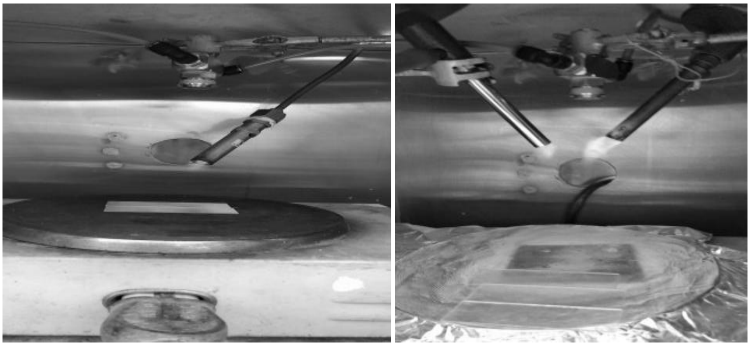

**Fig. 3**. Single and double flame unit fitted next to spray nozzle inside the chamber

One of the most important parameters to be controlled during the processes is the temperature inside the furnace because droplets drying, decomposition, crystallization, and grain growth strongly depend on this parameter [12]. Fig. 3, shows the temperature controlling unit with a normal heater which heats up to 400$^{o}$C and mounted flame burner units for the synthesis. The temperature of the hot plate surface was sensed using thermocouple and was controlled to desired level using a dedicated controller unit. The required intensity level of the flame was manually controlled using the control accessories fitted with the equipment. Depending on the application and precursor solution, we used only heater or flames for conversion of the salt into the metal oxide which occurs through pyrolysis reaction.

C. Electronics unit

Electronics unit had two parts namely microcontroller and x plotter. X plotter moves the spray head in x direction to achieve uniform coating on the substrate. The x plotter had a thread rod, spray head holder, stepper motor. To control the stepper motor, the microcontroller unit was designed and fabricated. The stepper motor was made to rotate in clockwise or counter clockwise direction to control the linear motion of a spray nozzle. The required power was supplied to peristaltic pump, microcontroller, heater, light, air compressor and stepper motor by power supply unit.

D. Complete Setup

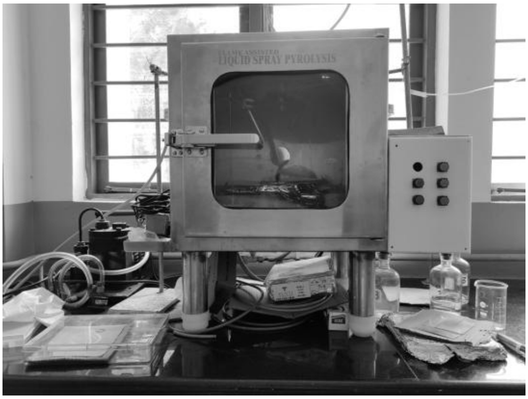

**Fig. 4.** Flame assisted liquid Spray pyrolysis chamber

All the units were fixed in a stainless box whose dimension is 15.5 X 15.5 inch. Fig.4 shows the front view of the complete set up.

## 3.0 Experimental Details

### 3.1 Material preparation

Synthesis and characterization of ZnO thin films were carried out to study the reaction parameters influence in a spray chamber with flame. A detailed design and experimental setup were discussed previously. Experimental apparatus consists of a spray nozzle containing a capillary tube (0.3 mm diameter), a furnace and an atomizer. An amount of 8 g of Zinc acetate dihydrate (ZnAc) dissolved in 75mL of methanol and 25 mL of water at room temperature and stirred for 20 min till solution becomes transparent. Few drops of acetic acid were added. The precursor solution fed using a voltage controlled peristaltic pump through the capillary, thus allowing the system to spray ultrafine droplets. The spray was ignited with flame with (propane ($C_3H_8$, 99.5%)) fuel and $O_2$ oxidizer. Propane was fed at 1 lpm and the amount of oxygen for its combustion in 6 lpm. Deposition time, substrate temperature, and air flow rate were kept constant during the whole deposition process at 10 minutes (3 ml/min flow), 300°C, and 25 ml $min^{-1}$ respectively. The compressed air with controlled pressure was used to deliver aerosols to the substrate. Microscope glass slides were used as substrates, which were cleaned in acid and alcohol and then dried under air stream. The distance between the spray nozzle and the substrate was 17 cm. Finally, the material was annealed at 200 ºC for 1hour.

3.2 Characterization

XRD characterization (Shimadzu MAXima XRD -7000) gave the crystallinity of synthesized samples with Cu Kα radiation($\lambda$ = 0.1541 nm) at Bragg's angle ranging from $20^{o}$ to $80^{o}$ with $1^{o}$ per minutes for better resolution. The morphology of such samples was observed on a scanning electron microscopy (TESCAN-VEGA3 LMU).

## 4.0 Results and Discussion

Aerosols of the prepared ZnO precursor solution were sprayed as a fine mist into a flame from the nozzle and deposited onto the heated substrate. Initially, ZnO powders were prepared with Zinc acetate dihydrate precursor in order to understand how the chamber conditions, gas flow, and precursor solution flow affect morphology, particle size distribution, and crystalline phases of the deposited film or powder. Morphology and phase structure of ZnO was studied in single and double flame keeping all other conditions constant.

Using the spray head, an aqueous Zinc acetate dehydrate metal salt solution was sprayed as a fine mist pointing to the flame. As the solvent burns inside the flame, small droplets were formed. The conversion of the salt into the metal oxide occurs upon the pyrolysis reaction and Zinc metal oxide atoms aggregate into nanoparticles, which were then collected on a heated glass substrate. Very short residence times, typically a few seconds was enough for the formation of spherical nanoparticles. Fig. 5, shows scanning electron microscopy (SEM) image of the sample synthesized with a single flame. It demonstrates that the typical products consist of a large quantity of dispersed spherical shaped nanoparticles. The size of the nano structure was with a diameter of about 40-50nm. The phase structure of the as-synthesized samples was further characterized using powder XRD. Fig. 6, shows the XRD patterns of the ZnO synthesized under single flame. The XRD results represented that the zinc oxide nanoparticles exhibits high crystallinity of hexagonal Wurtzite crystal structure. The diffraction peaks located at 31.84°, 34.52°, 36.33°, 56.71°, 62.96°, 68.13°, and 69.18° have been keenly indexed as hexagonal Wurtzite phase of ZnO(JPCDS card number: 36-1451) [13].

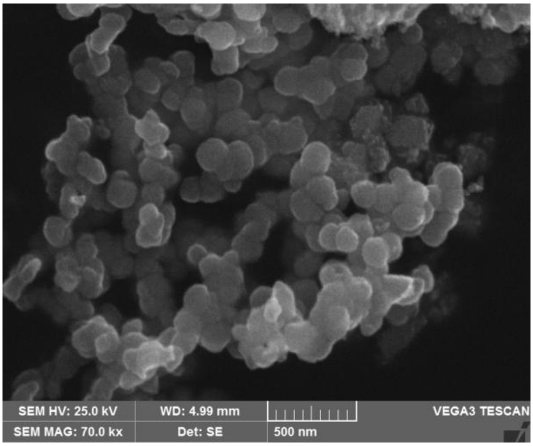


**Fig. 5.** SEM images of the ZnO films prepared using 0.35M Zinc acetate solution

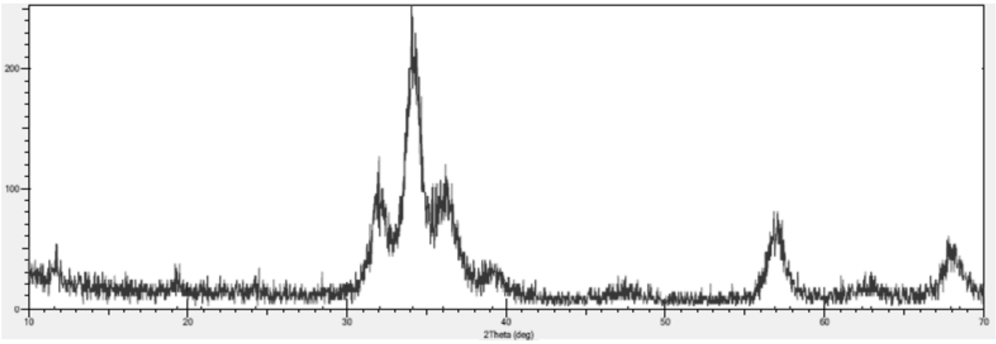


**Fig. 6.** XRD spectra of ZnO films with a thickness of around 500 nm.

An in house built spray pyrolysis deposition system consists of stainless steel chamber, a door with see through glass, substrate holder with heater, motor for linear motion, temperature controller, spray gun, peristaltic pump, air and solution flow control meters. It is observed that often the properties of deposited thin films depend on the preparation conditions. The system allowed variation of process parameters namely (i) spray gun nozzle to substrate distance, (ii) carrier gas flow rate, (iii) deposition time, (iv) solution flow rate, (v) substrate temperature, (vi) spray gun nozzle diameter and (vii) spray solution concentration. The quality of the thin/thick films and powder can be tuned by the optimizations of above process parameters. The reaction parameters such as temperature of substrate, flame temperature and the precursor solution composition also play crucial roles in controlling the size and morphology of the ZnO products. The influence of many operating conditions of the synthesis apparatus were optimized or kept constant and only the role of flame units upon the morphology of the nanostructured material has been preliminarily studied. To investigate the influence of flame in the formation of ZnO nanostructures, samples were also synthesized with participation of two flames under the same conditions. Fig. 7, shows the SEM images ZnO nanoparticles in the diameter range of 40 to 60 nm. The sample was found to be agglomerated compared to film prepared under single flame.

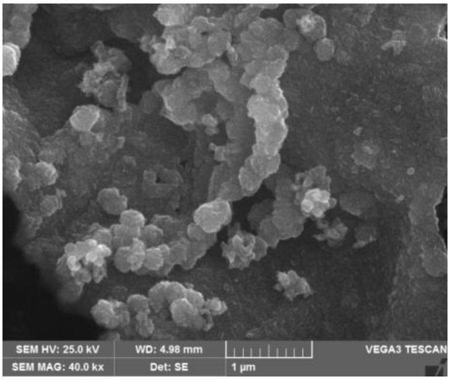


**Fig. 7.** SEM images ZnO nanoparticles prepared under use of dual flame.

## 4.0 Conclusions

Spray Pyrolysis equipment was designed and implemented, used for coating of ZnO thin films. This is a low cost though an efficient method that can be used for the deposition of films or synthesis of various nanopowders. The employment of an ultrasonic nebulizer instead of a conventional nozzle in the experimental set-up will shows good stability and reproducibility of the films or the powder produced. Further, interfacing with the computer will also increase its accuracy and control. In the preliminary tests of the equipment, deposited ZnO thin film showed size variation between 35 and 60 nm. Through XRD and SEM, the presence of wurtzite ZnO structure was evidenced which is suitable for photo catalysis applications, solar cell fabrication etc. The obtained results are promising and encourage the use of the designed experimental apparatus for future work in the field of controlled nanomaterial's synthesis and allow the investigation of a wide variety of nanostructured metal oxides.

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