Automated Flame-Assisted Spray Pyrolysis Unit: A Home-Made Solution for Thin Film Deposition

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Abstract

Spray pyrolysis is a versatile technique for the continuous synthesis of different kinds of metals, metal oxides, and multicomponent nanostructured materials. It has been utilized to deposit a variety of thin films. Thin films of nanomaterials sprayed on different substrates are worthwhile for novel applications such as sensors, solar cells, solid oxide fuel cells etc. Thin films are produced in this technique by gas which atomizes the solution into tiny droplets that are then transferred to the heated substrate, mainly consists of a precursor chamber for loading the solution; spray nozzle unit, compressor and heating unit. This article reports design and fabrication of a low-cost automated flame assisted liquid spray pyrolysis system with control setups monitored by a microcontroller-based control system. A mobile application on android studio was developed to monitor and control the working of the home-made spray pyrolysis equipment to obtain the nanoparticles or deposition of thin film. The mobile application allows users to change the spray pyrolysis equipment's operational settings, including the plotter speed, solution speed, temperature etc. The flutter framework and the dart programming language were used to develop the application. Using automated homemade spray pyrolysis system, ZnO thin films were coated onto glass substrates for the use of this techniques simplicity and effectiveness of preparation. Using XRD and FE-SEM, the structural verification and morphological characteristics were examined, ZnO of Wurtzite structure was evidenced and observed particle size variation was between 40 to 60 nm.

Keywords: *Spray pyrolysis, Zinc oxide, thin films, microcontroller, android studio, dart, platform IO.*

1.0 Introduction

Thin films are essential in modern technology for a variety of purposes. The key forces of on-going technological advancements in the fields of

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optoelectronic, photonic, and magnetic devices involve thin film materials. Thin films have become very important two-dimensional materials used in microelectronics, antennas, energy generation, solar cells, light emitting diodes, light crystal displays, lithography, micro-electromechanical systems, coatings, as well as other emerging cutting technologies, connected to a number of real-world challenges [1-3]. Thin films made from materials may be easily integrated into a variety of devices. The material costs when compared to corresponding bulk version, are very small, yet perform the same way in case of 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, spray pyrolysis etc.

Spray pyrolysis is one of the most popular bottom-up techniques in which a thin film is deposited by atomizing chemical precursors into aerosol droplets and sprayed onto a heated surface, the ingredients evaporate during the travel of aerosols in a heated reactor, resulting in the formation of ultrafine particles or thin films. The chemical reactants are selected so that, at the temperature of deposition, the by-products other than the desired products are volatile. Using this technique, a number of nanoparticles of metal oxides, mixed metal oxides, including nanocomposites have been prepared. It is a simpler and more cost-effective procedure as compared to many other methods and precursors utilized in this process are quite inexpensive [4-5].

The properties of a film are generally sensitive to their structure, thickness, 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]. 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 the past ten years, many researchers have developed spray pyrolysis equipment to synthesize a variety of complicated materials for various applications. A microcontroller system, low cost and with almost nil mechanical arrangement along with a display and keyboard unit ensures reasonable control over the spray parameters [7]. It might be beneficial to use specially designed, inexpensive spray pyrolysis equipment to generate novel materials with distinct material morphologies. The article describes the design and development of flame-assisted liquid spray pyrolysis apparatus and synthesis of ZnO powders and thin films at high production rates. During the spraying procedure, the precursor solution's aerosols are produced by a pneumatic system.

To monitor and control the operation of home-made spray pyrolysis equipment, a smartphone application was developed using flutter framework. The plotter speed, solution speed, temperature, and other factors can be all changed by the user to produce thin films or nanoparticles. Features of the Flutter are Just-in-time compilation which executes the computer code that encompasses compiling during program execution at run time rather than preceding execution. Flutter has a feature called as hot reload which helps to design the applications, build UIs, add features, and fix bugs. Hot reload works by inserting updated source code files into the running Dart Virtual Machine (VM).

2.0 Spray Pyrolysis Unit

An equipment design was reported in detail in our prior publication. The main steps in the spray pyrolysis process involve the generation of aerosol from various chemical compound precursor solutions swiftly moving through a heated zone or spraying onto a hot substrate in a furnace. In the flame assisted liquid spray pyrolysis method, the precursor flux is passed via a direct flame and applied to the substrate's surface to deposit a layer. Spraying droplets of precursor solution at high temperature creates a coating on the substrate surface, while flame helps in evaporation and decomposition of sprayed liquid precursors to form particles in nanometers range [4, 8]. Fig. 1 demonstrates the schematic diagram of spray pyrolysis system having important units: temperature controlling unit, electronic unit, flow and pressure controlling units. Equipment is fitted with accessories required for controlling the flame during the process.

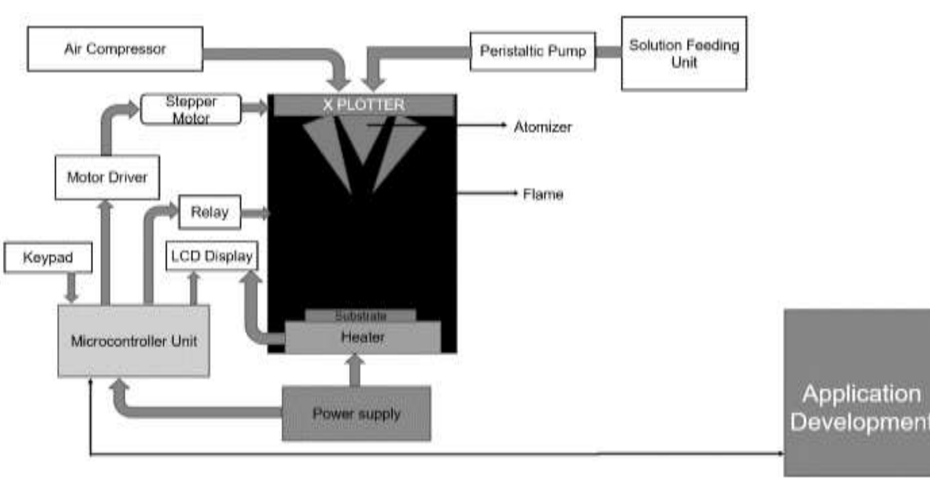

Fig. 1. Schematic representation of Spray pyrolysis system

A stainless-steel box included the spray nozzle unit, a hot plate with temperature control features, and control units for liquid and gas flow. The spray nozzle unit was mounted on a motorized linear movement stage. Atomization is the first step of spraying a nano or submicron size particle, which is determined by the properties of the liquid used and operating conditions. Air blast atomizer (pneumatic) was chosen due to its ease of control and cost, but its limitation is in producing uniform droplets of micrometer or nanometer size and control on distributions [8 - 9]. Controlling the spray is the second step in the procedure. The quantity of droplets that the spray head would deposit on the substrate would rise as the spray period lengthened. In order to manage the droplets, the atomizer itself gives an air and solvent regulating option. The process's last step is temperature regulation, with a conventional heater and burner positioned next to the spray nozzle. The solvent evaporates when the droplets come in contact with the heated substrate, leaving the chemical component behind to settle on top of the substrate.

It is set up with a device that automates the spray pyrolysis procedure by moving the spray head in the X plane in response to a stepper motor. A dispenser controlled by a stepper motor is used to get a precise flow rate. The device incorporates an axis stepper motor controller, a compressor with pressure control, a substrate heater with PC temperature control, and simple, user-friendly software. The air compressor and peristaltic pump are controlled by an electronic unit using a solenoid valve. The spray nozzle gets predetermined pressurized air and precursor solution, while a heater heats the substrate and its temperature control is monitored using a thermocouple. The complete system is housed in a stainless steel chamber.

Flow, Pressure Temperature Controlling Units

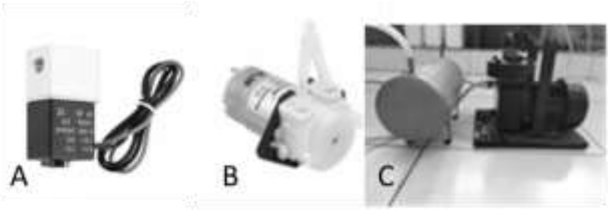

Fig. 2. a) solenoid valve, and b) Peristaltic pump air compressor

The air compressor supplies pressurized air with a solenoid valve and peristaltic pump to the spray atomizer nozzle (Fig.2). The air is regulated and measured with a meter before it is supplied to the spray nozzle. The precursor solution is supplied to the mixing chamber using a positive displacement pump, which pumps from 70-250 ml/min depending on the voltage supplied to it. Finally, the spray nozzle is sprayed onto the substrate at a predetermined constant pressure and flow rate.

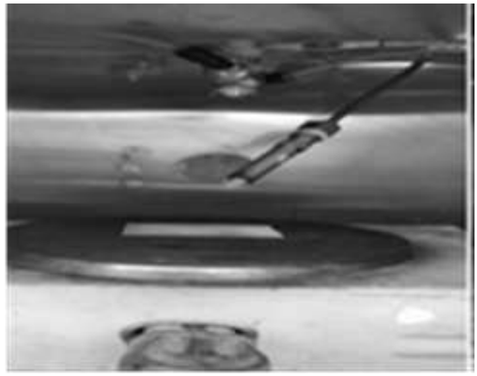

Fig. 3. Flame unit and heater

Temperature is an important parameter to control during processes, as it affects droplets drying, decomposition, crystallization, and grain growth [10-11]. Fig. 3 shows a temperature controlling unit with a heater that heats up to 400^{o}C and flame burner units for the synthesis. The temperature of the hot plate surface was sensed using thermocouple and controlled with a SSR controller unit. The control accessories included with the device were used to adjust the flame's intensity to the desired level. We employed a heater or flames, depending on the application and precursor solution, to convert the salt into the metal oxide that results from a pyrolysis method.

Electronics Unit

The electronics unit consisted of an x plotter and a microcontroller. The x plotter included a stepper motor, spray head holder, and thread rod. The microcontroller was used to control the stepper motor, which was designed to rotate either clockwise or counterclockwise. Limit switches were installed on each end of the rod to shift the stepper motor's motion direction.

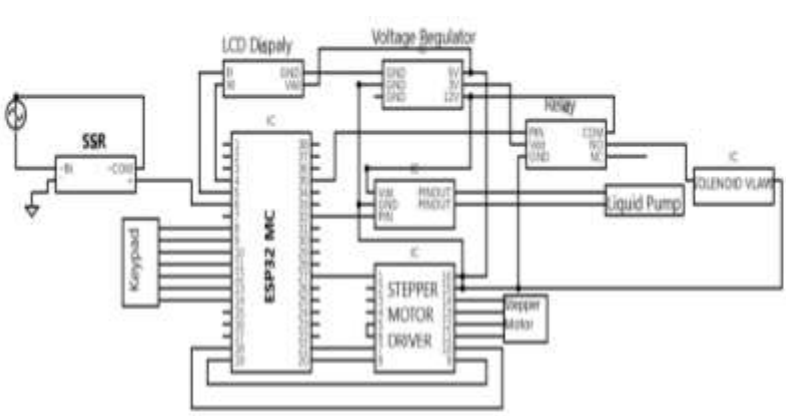

Fig. 4. Circuit diagram of electronic unit

The power supply unit provided power for the peristaltic pump, microcontroller, heater, light, air compressor, and stepper motor. The complete electronic unit required to control the spray pyrolysis equipment. The connection of the individual electronic component with microcontroller unit is shown in Fig. 4

Complete Setup

Fig. 5. Complete setup of the equipment

All the units were fixed in a stainless box whose dimension is 15.5 X 31 inch. Fig.5 shows the front view of the complete set up of hardware and connected to mobile application.

3.0 Application Development

The hardware equipment can be controlled by developing an application that communicates with the microcontroller using wi-fi connection. The application was developed using flutter framework and dart programming.

Flutter SDK, Dart

Flutter SDK is an open-source UI software development kit created by Google to develop cross platform applications for Android, iOS, Linux, macOS, Windows, Google Fuchsia, and the web from a single codebase. It is one of the best solutions to develop apps for Android and iOS without having to write in a different codebase for each platform [11 - 14].

Dart is an open-source general-purpose programming language developed by Google and later approved as a standard by ECMA. It is object-oriented, optionally typed, and a class-based language with excellent support for functional and reactive programming. It is designed for client development, such as for web and mobile apps, and is not bloated at all. Fig 4 shows the complete circuit diagram of the electronic unit.

Communication between Mobile and Spray pyrolysis system

The mobile and the microcontroller of the spray pyrolysis system are connected through wi-fi and communicate using REST API requests established using HTTP protocol. The control of the spray pyrolysis system is controlled through the HTTP requests.

The mobile application is used to control the different stages of process during the deposition of nano particles. After power supply is given to the system, the microcontroller of the system is connected to the mobile through wi-fi. The process of deposition can be start in the mobile application using start button which available in the mobile application as shown in Fig. 6a. The mobile application displays the different parameters of the system such as x-plotter speed, speed of solution that is to be deposited and the temperature of the system during the processing state of the spray pyrolysis system as shown in Fig. 6b. The process of the system can be ended using the stop button in the mobile application. Once the process is ended the mobile application displays the total time taken to complete the process in the system as shown in Fig. 6c, Similarly the parameters of the system can be varied in the mobile application as shown in the Fig. 6d. The complete design flow of mobile application and control of the equipment with the application is shown in Fig. 7.

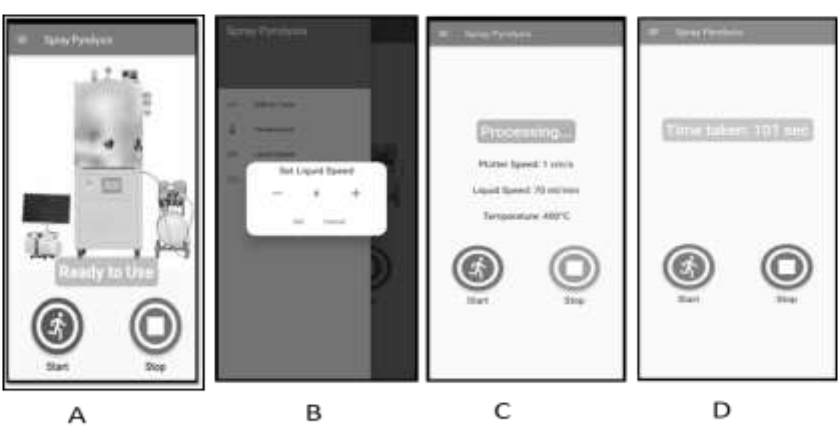

Fig. 6. a) Before the process, b) Set parameters, c) During process stage, and d) After the process

4.0 Experimental Details

Material preparation and working

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. The experimental apparatus consists of a spray nozzle, furnace, and atomizer. 8 g of Zinc acetate dihydrate (ZnAc) along with few drops of acetic acid were dissolved in 75mL of methanol and 25mL of water at room temperature and stirred for 20 min. The precursor solution was fed through a voltage controlled peristaltic pump and ignited with propane and oxygen. Deposition time, substrate temperature, and air flow rate were kept constant during the deposition process. Microscope glass slides were used as substrates and the distance between the spray nozzle and the substrate was 20 cm. The material was annealed at 200^{o}C for 1 hour.

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. The designed mobile application connects to the equipment's microcontroller unit through wifi, a capability of the ESP32 microcontroller unit.

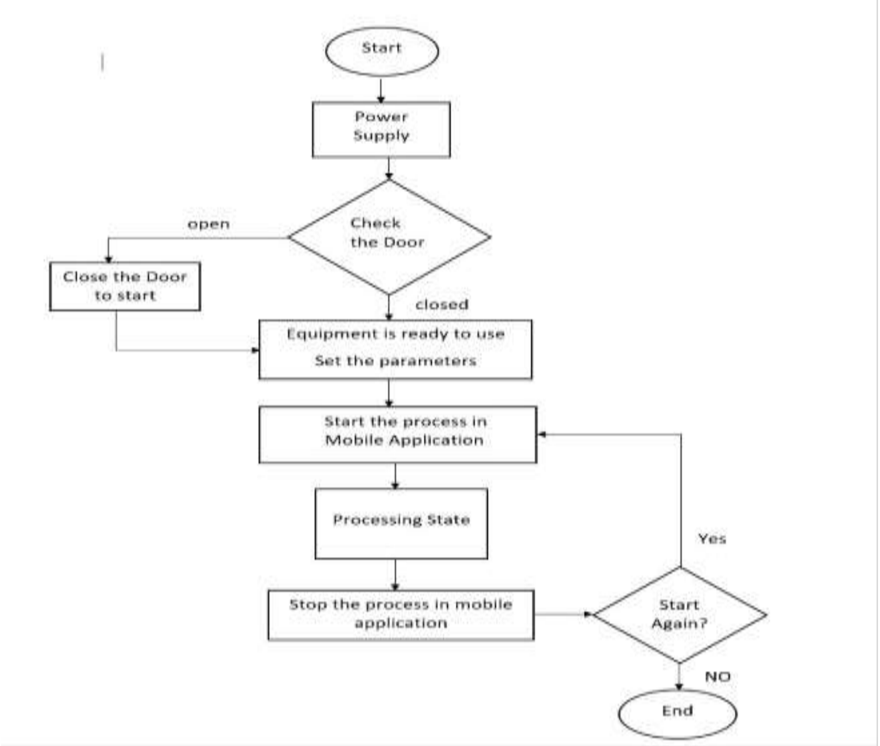

Fig. 7. Workflow of the Equipment

5.0 Results and Discussion

A microcontroller unit controls the apparatus. The atomizer and flame torch's stepper motor were moved by the microcontroller unit under control. Equipment parameters including temperature, liquid flow, and x-plotter speed may be changed on the LCD display using the keyboard. The whole amount of time needed to finish a procedure was presented on LCD or in mobile application together with the temperature at which operation is operating. In equipment where the process can be carried out if the door is closed, a limit switch used to monitor the door. To change the direction of the stepper motor, two more limit switches are used.

Mobile application developed is connected to microcontroller unit of the equipment through wi-fi which is an available feature in ESP32 microcontroller unit. The equipment is controlled using the different options available in application. Each operation of the equipment is done by calling the REST API requests using http protocol. Different operations such as setting the parameters of equipment beginning the process and termination of the process and monitoring process are done using the htttp methods.

Aerosols of ZnO precursor solution were sprayed into a flame and deposited onto a heated substrate. Morphology and phase structure of ZnO was studied in single flame, keeping all other conditions constant. The spray head was used to spray an aqueous Zinc acetate dehydrate metal salt solution into a flame. As the solvent burns, small droplets are formed. The conversion of the salt into the metal oxide occurs upon the pyrolysis reaction and Zinc metal oxide atoms aggregate into nanoparticles. Fig. 7 shows a scanning electron microscopy (SEM) image of the sample synthesized with a single flame, showing that the typical products consist of a large quantity of dispersed spherical shaped nanoparticles with a diameter of about 40- 50nm.

The crystallinity of synthesised materials was determined by XRD using Cu K radiation (0.1541 nm) at Bragg's angles ranging from 20o to 80o with 1o per minute for greater resolution. Fig. 8, shows the XRD patterns of the ZnO synthesized under single flame. The XRD findings showed that the hexagonal Wurtzite crystal structure of the zinc oxide nanoparticles displays remarkable crystallinity. The hexagonal Wurtzite phase of ZnO has been sharply indexed as the diffraction peaks at 31.84°, 34.52°, 36.33°, 56.71°, 62.96°, 68.13°, and 69.18° (JPCDS card number: 36-1451) [11].

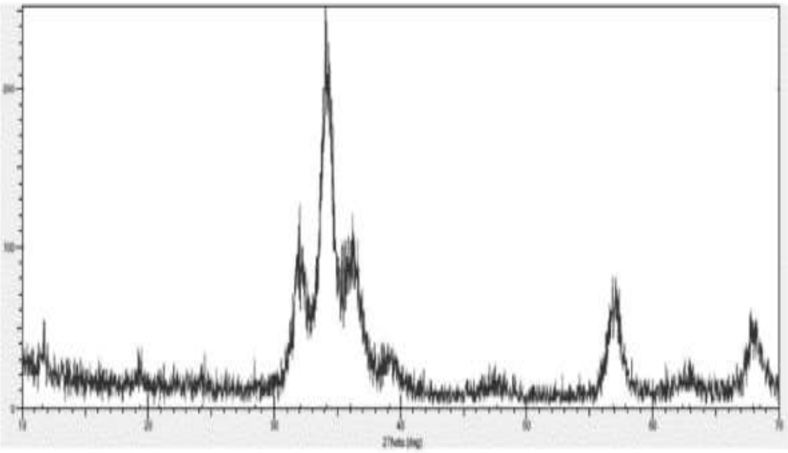

Fig. 8. XRD spectra of ZnO films

The morphology of these materials was examined using a SEM (TESCAN-VEGA3 LMU). Fig. 9. shows SEM images of ZnO nanoparticles with sizes between 40 and 60 nm. When compared to film made under a single flame, the sample was found to be aggregated.

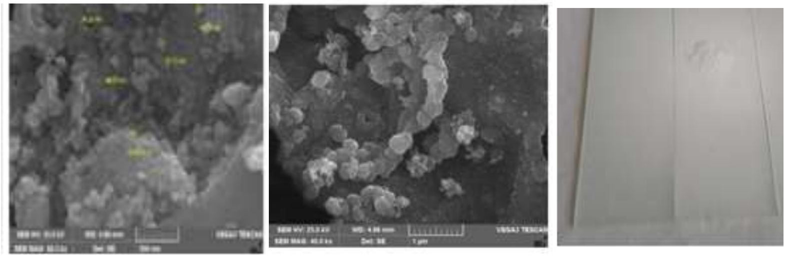

Fig. 9. SEM images of the ZnO films prepared and image of coating on glass.

It has been noted that preparation circumstances frequently affect the characteristics of thin films that have been deposited. The system allowed for changes to be made to the following process variables: (i) distance from spray gun nozzle to substrate, (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 optimisation of the aforementioned process parameters may be used to adjust the quality of thin/thick films and powder. The size and shape of the ZnO products are greatly influenced by the reaction parameters, including substrate temperature, flame temperature, and precursor solution composition. Only the concentration and amount of precursor upon the morphology of the nanostructured material has been first explored since several operational settings of the synthesis equipment were optimised or kept constant.

6.0 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 nano powders. The microcontroller unit is used to control the process. The microcontroller controls the direction of rotation of stepper motor using limit switches. Parameters of the equipment such as plotter speed, temperature, liquid speed and SSR on time are adjusted and displayed in LCD using keypad. A mobile application is developed to control the flow of the equipment. Setup of equipment parameters can also be adjusted in the mobile application. The employment of conventional nozzle in the experimental set-up showed 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 40 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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