Chapter 2

Fabrication of Automated Chemical Spray Pyrolysis Unit

2.1. Introduction

Chemical spray pyrolysis (CSP) is used for depositing a wide variety of thin films, which are used in devices like solar cells, sensors, solid oxide fuel cells etc. It has evolved into an important thin film deposition technique and is classified under chemical methods of deposition. This method offers a number of advantages over other deposition processes, the main ones being scalability of the process, cost-effectiveness with regard to equipment costs and energy needs, easiness of doping, operation at moderate temperatures (100-500°C) which opens the possibility of wide variety of substrates, control of thickness, variation of film composition along the thickness and possibility of multilayer deposition.

Many studies were done on CSP process since the pioneering work by Chamberlein and Skarman in 1966 on CdS films for solar cells [1]. Several reviews on this technique have also been published. Mooney and Radding reviewed CSP technique in which properties of specific films (particularly CdS) in relation to deposition parameters and their device applications were discussed in detail [2]. Tomar and Garcia discussed the preparation, properties and applications of spray-coated thin films [3]. Albin and Risbud presented a review of equipment, processing parameters and opto-electronic materials deposited using this technique [4]. R.Krishnakumar et al. did an exclusive review of sprayed thin films for solar cells in which a variety of solar cell materials and their preparative parameters were detailed [5]. Different atomization techniques and properties of metal oxide, chalcogenide and superconducting films prepared using CSP were discussed by Patil [6]. Recently, Perednis and Gaukler gave an extensive review on the effect of spray parameters on films as well as models for thin film deposition by CSP [7].
Present chapter discusses various aspects of CSP technique. Different models of deposition processes proposed in literature and the effect of spray parameters are included here. Details of the indigenously fabricated automated spray unit and the modifications made so as to obtain good quality films are also described.

2.2. The deposition process and models of deposition

CSP technique involves spraying a solution, usually aqueous, containing soluble salts of the constituents of the desired compound onto a heated substrate. Typical CSP equipment consists of an atomizer, a substrate heater, temperature controller and a solution container. Additional features like solution flow rate control, improvement of atomization by electrostatic spray or ultrasonic nebulization can be incorporated into this basic system to improve the quality of the films. To achieve uniform large area deposition, moving arrangements are used where either nozzle or
substrate or both are moved. The schematic diagram of a typical spray unit is given below (Figure 2.1).

Only crude models about the mechanism of spray deposition and film formation have been developed. There are too many processes that occur sequentially or simultaneously during the film formation by CSP. These include atomization of precursor solution, droplet transport, evaporation, spreading on the substrate, drying and decomposition. Understanding these processes will help to improve film quality. Deposition process in CSP has three main steps: atomization of precursor solutions, transportation of the resultant aerosol and decomposition of the precursor on the substrate.

Atomization of liquids has been investigated for years. It is important to know which type of atomizer is best suited for each application and how the performance of the atomizer is affected by variations in liquid properties and operation conditions. Air blast, ultrasonic and electrostatic atomizers are normally used. Among them, air blast atomization is the simplest. However this technique has limitation in obtaining reproducible droplets of micrometer or submicron size and in controlling their distribution [8].

In ultrasonic nebulized atomization, precursor solutions were fogged using an ultrasonic nebulizer [9]. The vapour generated was transported by carrier gas to the heated substrate. Precursor solution was converted to small droplets by ultrasonic waves and such droplets were very small with narrow size distribution and had no inertia in their movement. Pyrolysis of an aerosol produced by ultrasonic spraying is known as pyrosol process. Advantage of this technique is that gas flow rate is independent of aerosol flow rate, unlike in the case of air blast spraying.

Electrostatic spray deposition technique has gained significance only in recent years. Electrostatic atomization of liquids was first reported by Zeleny [10]. Grace et al. published a review on this type of atomization [11]. A positive high voltage applied to the spray nozzle generated a positively charged spray. Stainless steel discs acted as cathode and the droplets under electrostatic force moved towards the hot substrate where pyrolysis took place. In electrostatic spray, depending on the
spray parameters, various spraying modes were obtained. They were classified as cone-jet mode and multi-jet mode. Cone-jet mode split into multi-jet mode with increase in electric field, where number of jets increased with applied voltage.

During transportation of the aerosol, it is important that as many droplets as possible are to be transported to the substrate without forming powder. Sears et al. investigated the mechanism of SnO$_2$ film growth [12]. Gravitational, electric, thermophoretic and Stokes forces were taken into account in the proposed model. From the study, it was concluded that the film growth was from vapour of droplets which passed close to the hot substrate (in a manner similar to CVD), and that droplet on striking the substrate, formed a powdery deposit. However, spreading of the droplet on the substrate, which more significantly contribute to film growth, was not considered.

Yu and Liao proposed a model for evaporation of solution droplets [13]. The aerosol droplets experience evaporation during transport to substrate leading to size reduction and concentration gradient within the droplet. Precipitation may occur on the surface of droplet resulting in the formation of porous crust and hollow particles which is not desired because it increases surface roughness of the films. The probability of this is more if droplet size is large and number concentration low. Smaller droplets produce solid particles as diffusion distance for solute is shorter, leading to more uniform concentration distribution within the droplet. Increasing the number of droplet increases solvent vapour concentration resulting in delayed precipitation.

The reaction process taking place in CSP is interesting. Many models exist for the decomposition of precursor. Many simultaneous processes occur when a droplet hits the substrate surface: evaporation of residual solvent, spreading of droplet and salt decomposition.

Vigue and Spitz proposed that the following processes occur with increasing substrate temperature [14]. The below given figure illustrates the four possible processes that occur with increasing temperature (Figure.2.2).
In process A, droplet splashes on substrate, vaporizes and leaves a dry precipitate in which decomposition occurs.

In process B, solvent evaporates before the droplet reaches the surface and precipitate impinges on the surface where decomposition occurs.

In process C, solvent vaporizes as droplet approaches the substrate, then solid melts and sublimes and vapour diffuses to substrate to undergo heterogeneous reaction there.

In process D, at highest temperature, the metallic compound vaporizes before it reaches the substrate and chemical reaction takes place in vapour phase.

Most of the spray pyrolysis deposition is of type A or B and our discussion will naturally center on these two.
2.3. Deposition parameters

Properties of film deposited depends on various deposition parameters like substrate temperature, nature of spray and movement of spray head, spray rate, type of carrier gas, nature of reactants and solvents used. The effect of some important spray parameters are discussed here.

2.3.1. Substrate temperature

Substrate temperature plays a major role in determining the properties of the films formed. It is generally observed that higher substrate temperature results in the formation of better crystalline films [15, 16]. Grain size is primarily determined by initial nucleation density and recrystallization. Recrystallization into larger grains is enhanced at higher temperature [17]. By increasing the substrate temperature, the film morphology can be changed from cracked to dense and then to porous [18]. Variation of substrate temperature over different points results in non-uniform films. Composition and thickness are affected by changes in substrate temperature which consequently affect the properties of deposited films. For example, while preparing SnS films using CSP, single phase films are obtained only in a narrow range of temperatures. Secondary phases like Sn\textsubscript{2}S\textsubscript{3}, SnS\textsubscript{2}, SnO\textsubscript{2} etc. are present in films prepared at lower and higher temperatures [19].

High substrate temperature can also result in the re-evaporation of anionic species as in the case of metal sulfide films [20]. In metal sulfides, re-evaporation of sulfur from film occurs at high substrate temperature, leaving metal rich surface, which may react with oxygen to form oxides.

Though surface temperature is a critical factor, most investigators have not known the actual surface temperature of the substrate. Also, maintenance of substrate temperature at the preset value and its uniformity over large area are challenging. Liquid metal baths offer good contact at the interface and are widely used. But when solid surfaces are used, the actual area of contact is less than 1% of the surface area. Spraying in pulses or bursts also has been used to assure that surface temperature is reasonably constant [21].
2.3.2. Influence of precursors

Precursors used for spraying is very important and it affects the film properties seriously. Solvent, type of salt, concentration and additives influence the physical and chemical properties of the films. Usually, de-ionized water which is ideal for a low cost process is used as solvent. Use of alcohol as solvent has also been reported. It was observed that transparency of as deposited ZnO films increased when ethanol was used instead of water as solvent for zinc acetate [22]. Properties of films varied with type of precursors. For example, when In$_2$S$_3$ thin films were deposited from chloride based and nitrate based precursors, their properties differed significantly. Films from chloride based precursors were crystalline and highly photosensitive compared to those formed from nitrate based precursors which were amorphous [23, 24].

Concentration of spray solution also affects the nature of the films formed. Usually it ranges from 0.001 M to 0.1 M and it is seen that smooth films of columnar grains are obtained with low concentration and low spray rates [2]. Chen et al. observed that surface morphology of the films changed from cracked to crack free reticular, after introduction of acetic acid into precursor solution [25]. The change in morphology was attributed to the chemical modification of precursor solution.

Caillaud et al. investigated the influence of pH on thin film deposition and found that the growth rate depended on pH [26]. Formation of basic salts, adsorption compounds or precipitates slowed down the growth at higher pH. At low pH, deposition rate decreased drastically.

2.3.3. Spray rate

Spray rate is yet another parameter influencing the properties of films formed. It has been reported that properties like crystallinity, surface morphology, resistivity and even thickness are affected by changes in spray rate [27]. It is generally observed that smaller spray rate favours formation of better crystalline films. Smaller spray rate requires higher deposition time for obtaining films of the same thickness prepared at higher spray rate. Also, the surface temperature of substrate may deviate to a lower value at high spray rate. These two factors may
contribute to the higher crystallinity at small spray rates. Decrease in crystallinity at higher spray rates is observed in sprayed CuInS$_2$ thin films [27]. Decrease in crystallinity usually results in increased resistivity of the films.

Surface morphology of the films varies with spray rate. Higher spray rate results in rough films. Also, it is reported that films deposited at smaller spray rates are thinner due to the higher re-evaporation rate.

2.3.4. Other parameters

Parameters like height and angle of spray head, angle or span of spray, type of scanning, pressure and nature of carrier gas etc., influence the properties of deposited films. Different types of spray heads which produce different spray patterns are commercially available. Relative motion of the substrate holder and spray head should ensure maximum uniformity and large area coverage.

2.4. Fabrication of CSP unit

As already mentioned, CSP involves spraying of solution containing soluble salts of the constituent atoms of the desired compound onto a preheated substrate. The sprayed droplet reaching the hot substrate surface undergoes pyrolytic decomposition and forms a single crystallite or a cluster of crystallites. Other volatile byproducts and the excess solvent escape in the vapour form. The substrate provides the energy for the thermal decomposition of the constituent species and their subsequent recombination. This followed by sintering and recrystallization gives rise to a continuous film.

Hence, while fabricating a spray system, special attention must be given to maintain the substrate temperature, spray rate, type and pressure of carrier gas, movement of spray head etc. From our experience in working with the manual spray unit, we could fix the range of operating conditions. Photographs of the automated system are shown in Figure.2.3 and Figure.2.4.
Figure 2.3. Photograph of the automated CSP unit.

Figure 2.4. Photograph of the spray unit.
2.4.1. Substrate heating

Spray head, heater and substrate were kept inside a chamber provided with an exhaust fan for removing gaseous byproducts and solvent vapour. Initially, a stainless steel base plate of 20 cm X 20 cm area and 3 cm thickness with embedded heater rods was used. The required surface temperature was attainable even if one of the rods was malfunctioning. But while spraying, substrate temperature varied spatially along the plate and created non-uniformity over the film surface. To overcome this serious limitation, a single heater coil (1450 W) was embedded in ceramic grooves attached to the machined stainless steel base plate (15 cm diameter). In this setup, the heater was thermally insulated from the chamber.

Temperature of the substrate can be varied from room temperature to 723 K. K-type thermocouple was placed in a groove, close to the surface of the base plate, to detect the substrate temperature. During spray, substrate temperature was kept constant (with an accuracy of ±5 K) using a temperature controller equipped with a feedback circuit to control the heater supply.

2.4.2. Solution flow control and spray nozzle

In the present setup, solution was dispensed using a container with syringe-type arrangement (Figure 2.5). By varying the speed of the stepper motor attached to the container, dispensing rate of the solution could be controlled. The motor shaft was connected to a lead screw through a gear. During the rotation of the motor, a piston connected to the lead screw pushed out the liquid through the nozzle. Spray rate can be varied from 1 ml/min to 15 ml/min. The container was made of Teflon, a corrosion free material. Plastic tubes were used for carrying the solutions from container to nozzle.

A surgical needle made of stainless steel was used as the spray nozzle which was replaced after every spray. It was ensured that solutions do not come into contact with any metal parts except the spray needle. Air nozzle was placed at right angles to the needle which was mounted horizontally (Figure 2.6). The spray was in the form of a solid cone with a circular impact area (~3.0 cm²). Figure 2.7 shows full cone model spray and the resulting impact area pattern.
Figure 2.5. Schematic diagram of the syringe-type solution dispensing unit.

Figure 2.6. Photograph of the air blast type spray nozzle.
2.4.3. Movement of spray head

Uniform coverage of large area was achieved by moving the spray head over the substrate surface by employing a mechanism having two stepper motors. The spray head could scan an area of 150 mm x 150 mm. The X-movement was at a speed of 100 mm/sec and the movement in Y-direction at a speed of 50 mm/sec. At higher spray rates, the speed of movement of spray head was found to be a critical factor. For slow movement (100 mm/s in X direction and 50 mm/s in Y direction in steps of 5mm), it was seen that films could not be deposited beyond the spray rate 4 ml/min without increasing the speed of X-movement (at ~573 K). When the spray head movement was slow and the spray rate was high, larger number of droplets reached unit area of the substrate surface. This resulted in substrate wetting and the deposited film detached from the substrate surface. Hence, the speed of spray head movement in X direction was increased to 200 mm/s. In the present setup, the distance between spray head and substrate as well as the angle of spray head can be varied.

2.4.4. Carrier gas control

Air blast type of atomization was used in the present setup. Filtered air used as carrier gas was compressed using a ½ HP compressor. The pressure of the gas fed to the nozzle was measured by a mechanical guage. The pressure can be varied
between zero and 10 kg/cm$^2$. Typical value of pressure used for deposition was $\sim 0.6$ kg/cm$^2$. Carrier gases other than air may also be used for spraying and we have deposited films using air as well as nitrogen. An air nozzle with orifice diameter of 0.1 mm was used in the unit.

2.4.5. Control and data storage

The set up fabricated as described above was controlled by a microprocessor which communicated with the computer through a serial port. The spray parameters could be stored in the PC. Parameters of each spray were fed into the unit via. a user friendly window (Figure 2.8). Interfacing between the system and PC was done using Visual C++ programming and the microprocessor was programmed separately.

Figure 2.8. User friendly window for inputting spray parameters.
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2.5. Conclusions

Using the spray system fabricated, thin films of CuInS$_2$ and In$_2$S$_3$ were successfully deposited. It was observed that uniform films could be deposited over an area of 10 cm X 10 cm [28]. The figure given below shows the thickness profile of CuInS$_2$ film deposited over an area, 2.5 cm x 10 cm. The thicknesses were measured from thirty points using stylus profiler and surface mapping was done. The result of the mapping is presented in Figure 2.9. It is seen that the thickness variations are prominent at the edges and a major portion of the film has thickness within the range 315 nm - 370 nm. In other words, the spatial variation of thickness is less significant in the central region of the film.

The spray system has been designed as per our know-how and requirement by M/s Holmarc Opto-Mechatronics Pvt. Ltd., Kalamassery, Kochi. We have so far made three systems and all are working consistently for the past four years without

![Figure 2.9](image-url)
any major repairs or breakdowns. Several modifications have been made on X-Y movement. We have been able to deposit binary, ternary and quaternary compounds using it. The effect of different spray parameters on the properties of CuInS$_2$ and In$_2$S$_3$ films deposited using this system has been detailed in the next chapters.
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References


