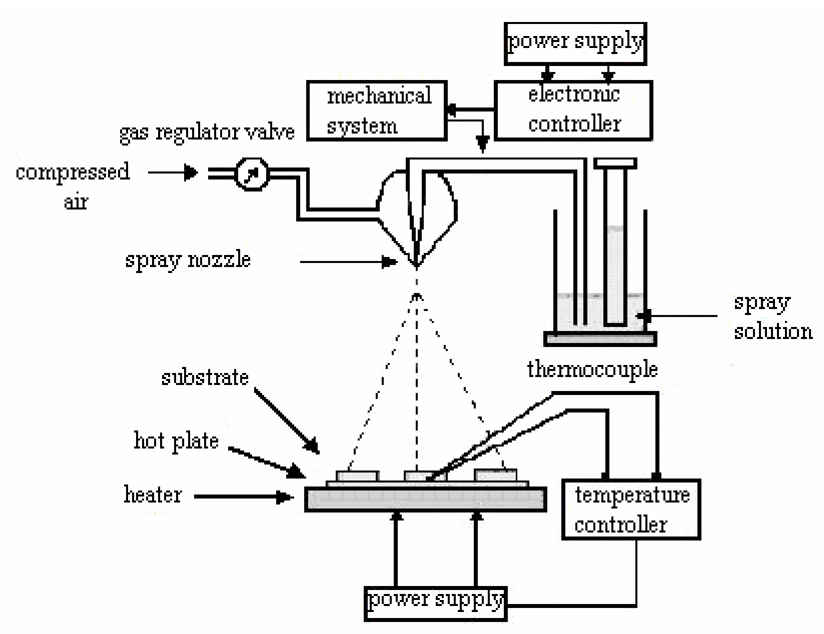
Chemical spray pyrolysis (CSP)

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].

2.2.The deposition process and models of deposition

CSP technique involves spraying a solution, usually aqueous, containing soluble salts of the onstituents 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



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].

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_2S_3, SnS_2, SnO_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 In2S3 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 andfound 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 CuInS2 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.