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Nebulized Spray Pyrolysis Technique For The Preparation Of Mns, Cds, And Cdi$_x$mn$_x$s Thin Films

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ABSTRACT

Nebulized Spray Pyrolysis (NSP) technique is a simple, low-cost, non-vacuum system of deposition method for the manufacture of MnS thin fdms. Furthermore, the benefit of NSP over traditional pneumatic spraying is its minimal material consumption combined with greater control of the spray particles and low carrier gas pressure, resulting in a very thin layer of homogeneous, pinhole-free films with the appropriate qualities. However, no attempt has been made to deposit MnS thin films utilising the inhaler and nebulized spray pyrolysis. In this study, a nebulized spray pyrolysis approach is used to make MnS, CdS, and Cdi-xMnxS thin films. This method involves spraying a solution, usually aqueous, over a substrate that contains soluble salts of the constituent atoms of the target molecule. Another important spray parameter that affects the morphology and properties of the deposited films is the precursor solution concentration. Changing the content of the precursor solution can alter the structure and characteristics of a deposited film.

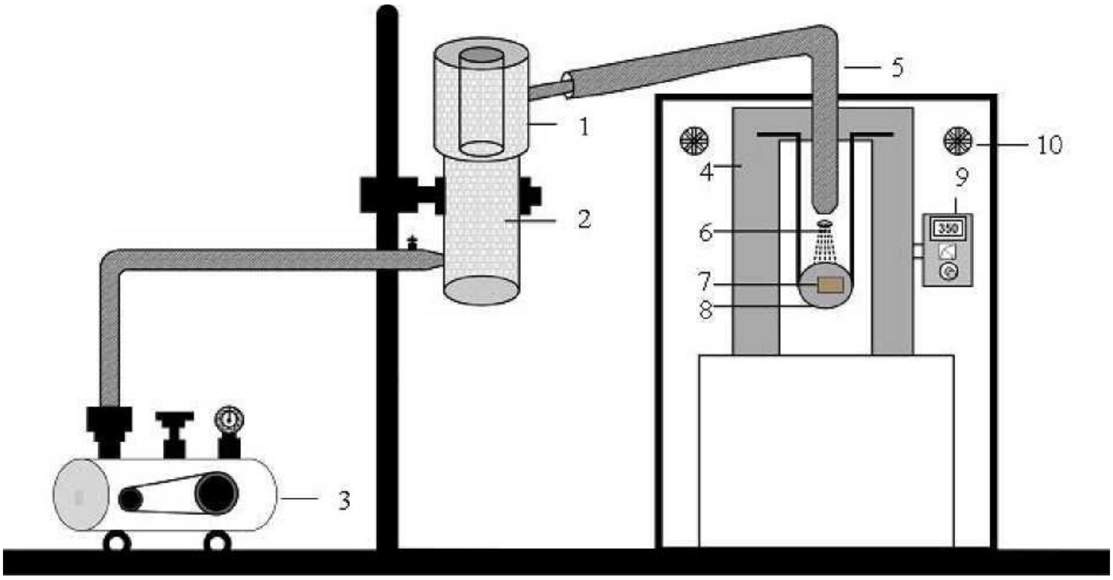
Keywords: Nebulized Spray Pyrolysis, Thin, Films, Substrate.

INTRODUCTION:

Radiofrequency sputtering [1], vacuum thermal evaporation [2,3], and molecular beam epitaxy (MBE) [4] have all been used to make MnS thin films thus far. These procedures, on the other hand, entail numerous complex processes that necessitate expensive equipment and strict experimental conditions. As a result, creating a straightforward way to deposit MnS films in a laboratory environment with desired properties is currently a hot topic of research for a variety of applications. With this in mind, we've implemented a new sort of spray pyrolysis called nebulized spray pyrolysis (NSP), for the preparation of MnS, CdS, and Cdi-xMnxS thin films which is completely different from the traditional method. NSP (nebulized spray pyrolysis) is a simple and flexible deposition process that requires no vacuum and is a quick and straightforward way to make films of varied compositions. It also makes it simple to dope any element in the desired proportions using the solution medium. This approach works well for making pinhole-free, uniform, smoother thin films of the desired thickness. An ionic solution containing the constituent elements of a compound in the form of soluble salts is sprayed on to a heated substrate in this chemical deposition technique. Droplets collide with the substrate surface, spread into a disk-shaped structure, and decompose thermally. The disk's form and size are determined by the droplet's momentum and volume, as well as substrate temperatures [5]. As a result, the film is commonly made up of overlapping discs of salt that are heated and transformed into film.

EXPERIMENTAL DETAILS:

Nebulized Spray Pyrolysis set up used in the present work. The simple requirements for this technique are: furnace (homemade), temperature controller, compressor, inhaler (nebulizer), and 'L' shaped glass tube. It can be seen that the nebulizer was connected by tube with a compressor, which causes compressed air or oxygen to flow at high velocity through a chemical to turn it into an aerosol, which is then sprayed on the pre-heated substrate surface through the optimized 'L' shaped glass tube which has small tapering at the substrate side to transmit the fine droplets. The most commonly used nebulizers are jet nebulizers, which are also called "atomizers".



1. Nebulizer, 2. Precursor solution, 3. Ar compressor, 4. Furnace, 5. Spray nozzle, 6. Spray droplets, 7. Substrate, 8. Substrate holder, 9. Temperature controller, 10. Exhaust fan

This method involves spraying a solution, usually aqueous, over a substrate that contains soluble salts of the constituent atoms of the target molecule. For thin film deposition, the substrate must be carefully selected. The substrate serves as a foundation for the fabrication of thin film circuits and the deposition of various thin film multilayers. The substrate must meet certain mechanical requirements, and the film must adhere to the substrate adequately not just at room temperature but also during large temperature changes. The substrate's surface should be smooth and flat. The substrate chosen is determined by the qualities and uses of the deposited films. The films were deposited on a microscopic glass substrate covered with fluorine doped tin oxide (SnOuF or FTO) (Rsh 15Q/sq.) in this study.Many processes take place in NSP, either simultaneously or sequentially. Aerosol production and transport, solvent evaporation, droplet impact with subsequent spreading, and precursor degradation are the most critical. Except for aerosol production, all of the processes stated include the deposition temperature. As a result, one of the primary determinants of film shape and characteristics is substrate temperature. At the ideal substrate temperature, the solvent evaporates near the substrate, and the precursor is volatilized and adsorbed on the surface, followed by breakdown to produce a dense coating with high adhesion. Another important spray parameter that affects the morphology and properties of the deposited films is the precursor solution concentration. Changing the content of the precursor solution can alter the structure and characteristics of a deposited film [6].For thin film deposition, the substrate must be carefully selected. The substrate serves as a foundation for the fabrication of thin film circuits and the deposition of various thin film multilayers. The substrate must meet certain mechanical requirements, and the film must adhere to the substrate adequately not just at room temperature but also during large temperature changes. The substrate's surface should be smooth and flat. The substrate chosen is determined by the qualities and uses of the deposited films. The films were deposited on a microscopic glass substrate covered with fluorine doped tin oxide (SnOuF or FTO) (Rsh 15Q/sq.) in this study.

RESULTS AND DISCUSSION:

MnS thin films were deposited on well-cleaned glass and FTO coated glass substrates using nebulized spray pyrolysis technique. The precursor solution was prepared (Mn:S = 1:1) by dissolving the aqueous solutions of 10 ml of 0.25 M manganese chloride (MnCb) (manganese source) and 10 ml of 0.25 M thiourea (CS(NH**2**)**2**) (sulphur source) and continuously stirred for 10 mins. The nebulizer was connected to an air compressor and the prepared precursor solution was sprayed onto the pre-heated substrates. The solution flow was controlled by the pressurized air with a constant pressure of 1.2 kg/cm^2. The distance between nozzle and substrate was 4 cm and the film was deposited at different substrate temperatures like 300°C, 350°C, and 400°C for about 30 min. When the substrate temperature is too low (below 300°C), there is a possibility for the formation of oxide phase during film growth due to the slow dissociation of complexes. On the other hand, at higher substrate temperature (above 400°C) the re-evaporation of sulphur can take place due to its elevated vapour pressure [7]. Therefore, the substrate temperature was optimized between 300°C and 400°C. The deposited films were observed as brown in colour, well adherent to the substrate, pin hole free, and uniform in nature. The films were also deposited by varying the sulphur source concentration (Mn:S = 1:2 and 1:3 ratios). It may be mentioned that the ratio of Mn to S precursor is expected to play a vital role in the preparation of MnS film. Hence, the author has varied the concentration of thiourea (i.e. 0.25, 0.50 and 0.75 M) to study its effect on the resultant film properties. The reaction mechanism for the formation of MnS can be explained as follows [8]:

$CS(NH_2)2$ + OH- -► SH- + H2O + H2CN2 (1)

SH" + OH" —► S^{2}" + H2O (2)

MnCk —> Mn^{2+} + 2CF (3)

Mn^{2+} + S^{2}" —> MnS (4)

It is worth to mention that the ethylene diamine tetra acetic acid (EDTA) is a strong chelating agent to enhance the stable complexes between metal ions and to dissociate at low rate. Generally, EDTA captures metal ions and once it gets saturated in capturing, it releases the metal ions periodically for reaction to get the desired compound. The complex formation with cations leads to control over the reaction chemistry, so that one can easily change the growth mechanism and particularly the stoichiometry of compound semiconductors in a controlled manner [9]. The MnS film was also prepared by adding EDTA (0.1M) as a chelating agent along with above mentioned precursor solutions. All other experimental conditions like substrate temperatures (300°C, 350°C, 400°C) and the ratios of manganese to sulfur precursor (1:1, 1:2, and 1:3) are same. The reaction mechanisms involved in this process are [8]:

$CS(NH_2)_2$ + OH' -► SH- + H2O + H2CN2 (5)

SH- + OH' -> S^{2}- + H2O (6)

MnCh + EDTA -► Mn^{2+}EDTA-(compiex) + 2C1' (7)

Mn^{2+}EDTA-(compiex) + S^{2}- -> MnS + EDTA (8)

CdS thin films were deposited on glass and FTO coated glass substrates by nebulized spray pyrolysis technique. The precursor solution was prepared by dissolving equal amounts of aqueous solutions of 10 ml of 0.04 M cadmium chloride (CdCh) and 0.04 M thiourea ($CS(NH_2)_2$) and continuously stirred for 15 mins to get homogenous solution. The solution thus obtained was sprayed intermittently on well cleaned pre-heated substrates by means of nebulized spray pyrolysis at three different substrate temperatures like 300°C, 350°C, 400°C. The intermittent spray interval (30 sec) promotes the substrates to attain the expected temperature before the start of next spray. The solution flow was controlled by the pressurized air with a constant pressure of 1.2 kg/cm^2. In this technique, comparatively lesser air pressure is employed, even without any compromise in the quality of thin films. The low flow rate control the droplet size hence minimizing drift. The distance between nozzle and substrate was 4 cm. The films were deposited for about 30 min. The films were also prepared by varying the concentrations of CdCh and CS $(NH_2)_2$ as 0.08, 0.12, 0.16, 0.2 M. The deposited films were observed as yellow in colour, well adherent to the substrate, pin hole free, and uniform in nature. The reaction mechanisms for the formation of CdS are [8]:

CS(NH2)2 OH' -► SH' + H2O + H2CN2 (9)

SH" + OH"• S^2 + H 2 0 (10)

CdCk—► Cd^{2+} + 2C1" (11)

Cd^{2+} + S^2"—CdS (12)

Cdi-xMnxS thin films with different level of doping (x = 0.04, 0.06, 0.08, 0.10 and 0.20) were prepared on glass and FTO coated glass substrates by nebulized spray pyrolysis technique. Aqueous solutions of 10 ml of 0.3 M CdCk, 10 ml of 0.3 M CS(NH2)2 and 0.3 M MnCk were taken as the precursor for the preparation of Cdi-xMnxS thin films. By varying the volumetric proportion of Cd and Mn precursors as per the required ratio, the desired Mn content in the sample was achieved. The solution flow was controlled by the pressurized air with a constant pressure of 1.2 kg/cm^2 and the substrate temperature was maintained at 300°C, 350°C, and 400°C. The substrate to nozzle distance was maintained at 4 cm. The prepared thin films were yellow in color and well adherent on the substrate surface.

CONCLUSION:

MnS, CdS, and Cdi-xMnxS (x = 0.04, 0.06, 0.08, 0.10, and 0.20) thin films were produced using a nebulized spray pyrolysis approach in this study. To tune various properties of deposited films, the growth conditions were adjusted. The resulting films are homogeneous and adhere to the substrate well. In this study, it has been observed that the prepared thin films were yellow in color and well adherent on the substrate surface.

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