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# Effect of Substrate Temperature on Spray Deposited Zinc Sulphide Thin Films

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**Abstract:** Thin films of Zinc sulphide (ZnS) on glass substrate were prepared by chemical spray pyrolysis technique using precursor solutions of zinc chloride and n–n dimethyl thiourea at substrate temperatures of 598 K and 623 K. X ray diffraction analysis exposed the polycrystalline nature with growing crystallinity with respect to substrate temperature. The preferential orientation growth of ZnS compound increased with relatively higher substrate temperature having hexagonal structure along (019) plane. At 623 K, The size of the Zinc sulphide crystallite with nano dimension was determined using the Full Width Half Maximum value of the Bragg peak. The surface morphology had been analyzed using scanning electron microscope. The compositional analysis had been observed by Energy Dispersive Analysis by X-ray spectrum. FTIR study had been carried out for the bond evaluation.

**Keywords:** chalcogenides, crystallite, spray, energy dispersive, stretching mode.

## 1 Introduction

Zinc sulphide (ZnS) is chalcogenide II-VI semiconducting material with wide direct band gap chalcogenide semiconductor of 3.70 eV [1]. Recently zinc sulphide thin films evoked much attention due to their vast potential in various fields. It is used as key material for solar control coatings, antireflection coating for hetero junction solar cells, for light emitting diode and other optoelectronic devices such as blue light emitting diode, electro luminescence devices and photovoltaic cells which enable wide application in the field of displays, sensors and lasers [2-3]. These chalcogenide semiconductors have concerned the attention of researchers in the recent times due to their special properties and potential uses in photo voltaics and opto-electronic devices [4-12]. ZnS can be used as an antireflection coating n-window layers in hetero junction in solar cells as the wide band gap decreases the absorption losses and increases the short circuit current of the cell[1], a more environmental friendly option than CdS buffer layer[6], reflector in optics due to its high index of refraction 2.35 [1], in opto-electronics devices as electroluminescent display and light-emitting diodes in the blue to ultraviolet spectral region due to its wide band gap, dielectric filter due to its high transmittance in the visible region [5].

ZnS has been prepared by various techniques such as chemical spray pyrolysis [1], chemical bath method [5,6], co-precipitation method [7],chemical spray method [8,9], have been used to synthesize quality ZnS thin films [9],closed-space vacuum sublimation [10], resistive heating [11], wet chemical method[12] , vacuum evaporation technique [13]. Chemical spray pyrolysis technique is very interesting method of depositing thin films due to the fact that it simple, convenient, cost effective, capable of producing uniform and homogeneous films that can produced to industrial scale [13].In this present work, it is intended to prepare ZnS thin films using the precursor solutions of zinc chloride and n–n dimethyl thiourea with influence of substrate temperature on the structural and morphological properties of ZnS thin films for the applications of photo voltaics and optoelctronics devices.

## 2 Experimental Details

Spray Pyrolysis is basically chemical deposition technique in which fine droplets of the desired material solution was sprayed onto a heated glass substrate. A glass made double nozzle sprayer was designed and fabricated in our laboratory to prepare thin film samples by spray pyrolysis method. It is a coaxial assembly of two corning glass tubes, in which the diameters of inner and outer tubes

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are 6 and 14 mm, respectively. Both the tubes were tapered at one end with a tapering angle of 30toform the spray nozzle. The glass substrates are well cleaned and kept inside the furnace. The furnace was resistively heated with kanthal wire and the temperature was controlled by a dimmer stat. A chromel–alumel thermocouple based temperature controller is used to monitor and measure the temperature of the substrates. The inner tube of the spray nozzle was connected to the air compressor and the outer tube to the solution reservoir. The carrier gas pressure was monitored by valve flow meter. The solution flow rate was determined with the help of a graduated burette as the reservoir.

The precursor solutions of Zinc chloride and thiourea were dissolved separately in a solution containing de-ionised water and isopropyl alcohol in proper ratio. The molarities of tin and thiourea solutions were 0.05 and 0.1 M, respectively. A few drops of concentrated hydrochloric acid were added for complete dissolution. Equal volume of these two solutions was mixed together and sprayed on to the hot glass substrates with area of 75 x 25 $mm^2$. The precursor solutions were sprayed at substrate temperature 598 and 623 K and their films were prepared. The other deposition parameters like solution flow rate, carrier gas pressure and nozzle to substrate distance were kept as 5 ml/min, 1 $kg/cm^2$ and 30 cm respectively. After deposition of these films, it was allowed to cool to room temperature, cleaned with distilled water, dried and then stored in a dessicator. The colour of the deposited thin films is grey in colour and adheres to the substrate. The crystal structural study of these films were examined by the XPERT PRO diffractometer using CuKα radiation (k = 1.5406 A˚). The scanning angle 2θ was varied in the range of 10–80 in steps of 0.05. The thickness of the sample was determined using Mitutoyo- SJ301 surface roughness profilometer.

## 3 Results and Discussions

### *3.1 Structural Properties*

X-ray diffraction profiles of zinc sulphide thin films prepared at the substrate temperatures 598 K and 623K are shown in Figure. 1 a & b. At the substrate temperature 598 K, broad hump [figure1 (a)] is due to the amorphous glass substrate. The short intense peak at 2θ = 28.442º, corresponding to the (0 0 2) plane of ZnS with hexagonal crystal phase.

At the substrate temperature increased to 623 K, the increase of crystallanity with the preferential orientation growth of ZnS compound having hexagonal structure along (0 1 9) plane [Figure.1 (b)] diffracted with single prominent Bragg peak at the 2θ position 31.880º (JCPDS file no 892424).

The author Islam et.al had reported the same single prominent peak of ZnS thin film at 31.8º corresponding to the (0 02) hexagonal structure [14] using CBD technique.The crystallite size was determined by using the well-known Scherrer's formula 0.9λ / βcosθ, where λ = 1.5406 Å for CuKα, β is the full width at half maximum (FWHM) of the peak corrected for the instrumental broadening in radians and θ is the Bragg's angle [15].

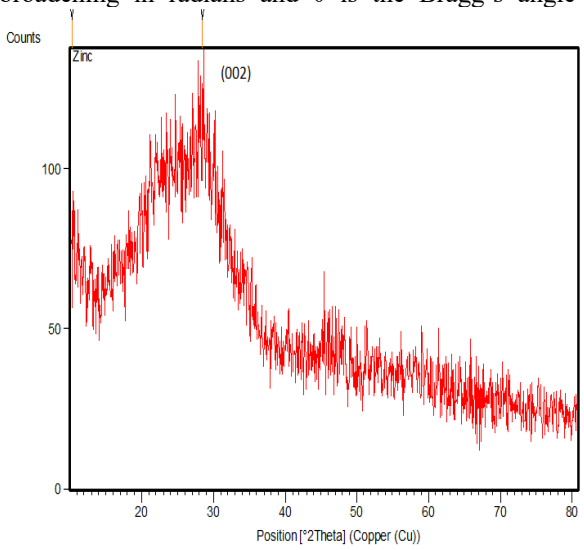


**Fig. 1(a):** XRD pattern of ZnS thin film at 598K.

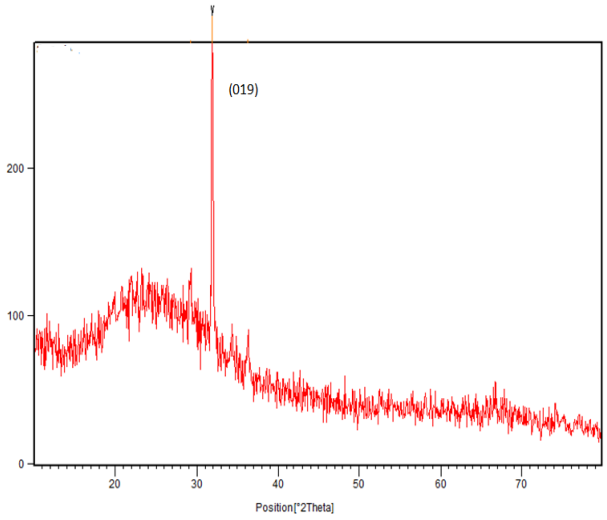


**Fig. 1(b):** XRD pattern of ZnS thin film at 623 K

Film deposited at 598 K has a broad hump, but in the substrate temperature increased to 623 K gives the prominent peak corresponding to the crystallite size of 46.20 nm. Similar size of crystallites 49 nm had been reported by [16] using simple precipitation method.

### *3.2 Morphology Characterization*

The surface morphology of the thin films deposited at different substrate temperatures were studied and analyzed by photographing the scanning electron microscope images of the above samples respectively as

shown in Figure.2 a & b. These SEM pictures were recorded with a magnification of 10 k for comparison. It is seen from Figure.2a, random shaped grains with an average size of 1micro meter was formed at the substrate temperature of 598 K. As the substrate temperature increases to 623 K the surface morphology of the films was found to become spherical structured nature with nanometer sized particles at the magnification of 40 k which is clearly observed from Figure. 2b.

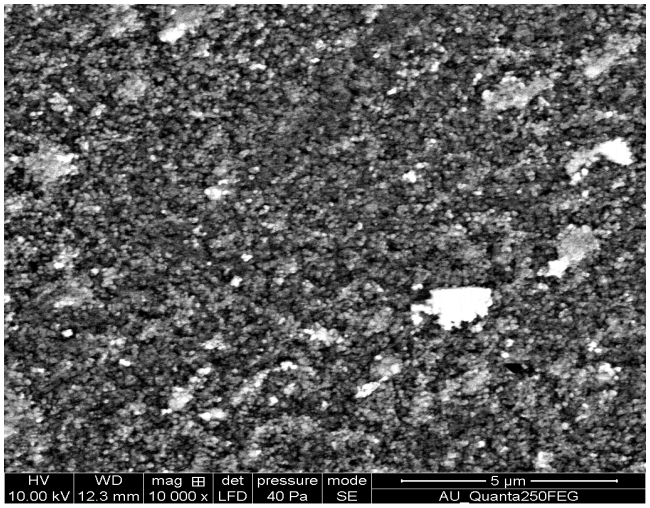


**Fig.2(a):** SEM photograph of ZnS thin film at 598K.

The observed grain size values from SEM images are much larger than the crystallite sizes measured from XRD peaks. This is due to the fact that in SEM images, the grain size is measured by the distance between the visible grain boundaries. Each grain constitutes aggregates of several crystallites [17]. In XRD, the diffraction of X-ray takes place inside the tiny crystallites and hence the measured size is always in the nm range, which is very much less than the grain size measured from SEM image studies.

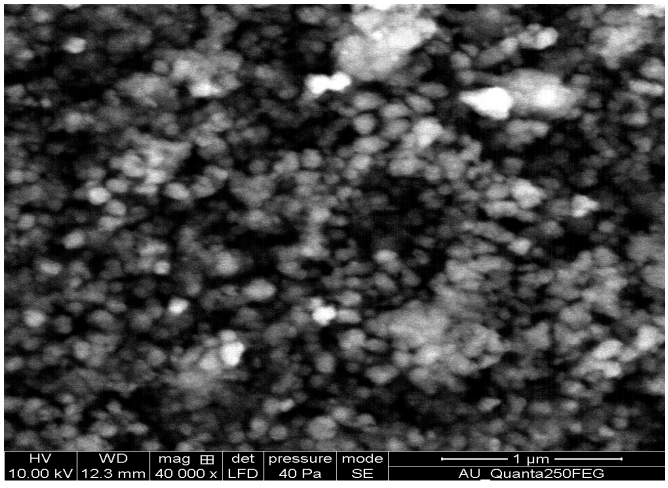


**Fig.2(b):** SEM photograph of ZnS thin film at 623K.

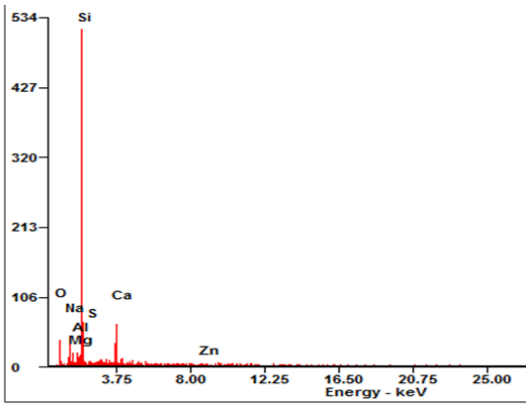


**Fig. 3(a):** EDAX spectrum of ZnS thin film at 598K.

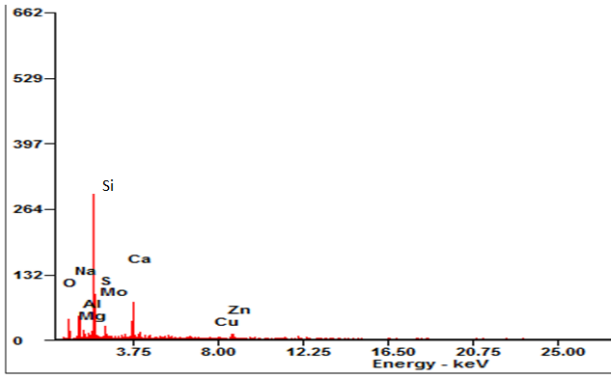


**Fig. 3(b):** EDAX spectrum of ZnS thin film at 623 K.

Figure 3(a) shows the EDAX spectra of ZnS thin film at 598 K. The film shows the composition of Zn and S elements present in a nearly stoichiometric atomic ratio of 0.97 and 0.90 and also the substrate temperature increased to 623 K (fig 3b), film shows Zn and S elements in the atomic ratio of 2.82 and 2.18respectively.

## *3.3 FTIR Analysis*

Figure 4 (a & b) represents the FTIR spectra of ZnS thin film for different substrate temperatures. At the temperature 598 K, it is observed that the O-H stretching mode is represented [Figure 4(a)] by the absorption band at 3703.22 $cm^{-1}$ and 1675.88 $cm^{-1}$ absorption bands belong to O-H bending mode and the stretching is represented by absorption bands at 453.68 $cm^{-1}$. A good agreement of results of spectra is produced by 3342.4$cm^{-1}$,for O-H stretching mode and 1633.6$cm^{-1}$absorption bands and stretching is represented by absorption bands at 655.8$cm^{-1}$ [18].

When the substrate temperature increased to 623 K,FTIR spectra of zinc sulphide [Figure4 (b)] indicate a broad band at 3334.61$cm^{-1}$ which corresponds to the vibration mode of

OH group indicating the presence of small amount of water absorbed on the surface, And the CN stretching mode at agreement with the earlier value reported by [19]for the characteristic stretching vibration of ZnS bond at 675 $cm^{-1}$.

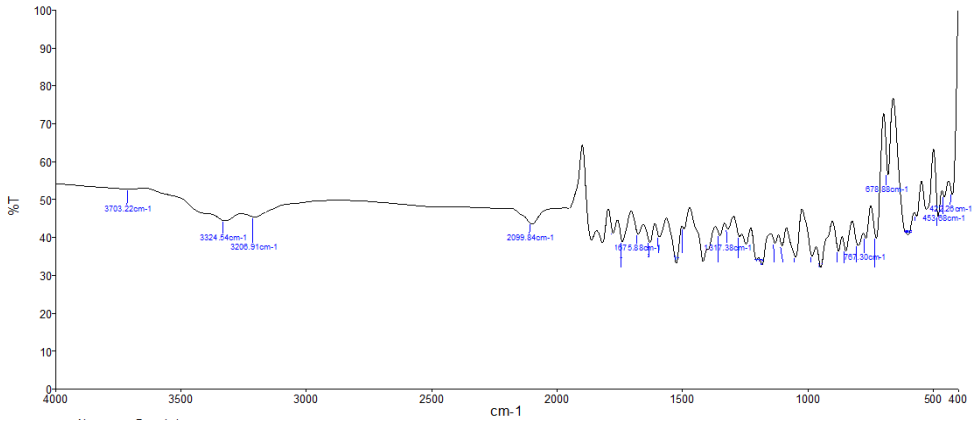


**Fig. 4(a):** FTIR spectrum of ZnS thin film at 598 K.

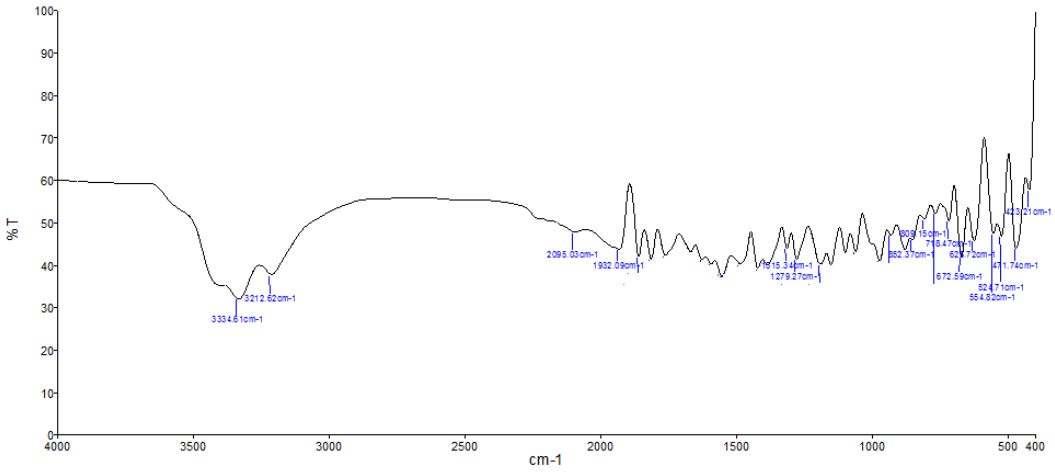


**Fig.4(b):** FTIR spectrum of ZnS thin film at 623 K.

## 4 Conclusions

Chemical spray pyrolysis method was used successfully to synthesize ZnS thin films using the precursor solutions at substrate temperatures of 598 K and 623 K. Studies on morphological, structural were performed on the samples using scanning election microscope, X-ray diffraction, Energy Dispersive X-ray analysis, Fourier Transform Infrared Spectroscopy. It has been noted that film structure and composition properties are very sensitive to the deposition temperature. At relatively higher substrate temperature, the film became polycrystalline with 2095.03 $cm^{-1}$. This study of zinc sulphide sample shows that the main band corresponding to the formation of zinc sulphide compound appeared around 672.59 $cm^{-1}$ is in good preferential orientation along stoichiometric composition, which suggest that this thin film could be a potential candidate for the applications of photovoltaics and opto electronic devices.

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