The Effect of Substrate Temperature on the Structural Properties of Spray Pyrolysed Lead Sulphide (PbS) Thin Films

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***Abstract*—Lead sulphide (PbS) films were prepared by the chemical spray pyrolysis technique using a solution of Lead nitrate and thiourea. PbS films were deposited (prepared) on glass substrate at varied temperature (250-350 ^{o}C). Effects of substrate temperature on the structural characteristics of the films were studied. The X-ray diffraction patterns' results reveal that the all of PbS films have a face centered cubic structure. The X-ray diffraction study showed that irrespective of substrate temperature all the films exhibits a preferred orientation along the (200) plane. The degree of preferred orientation increased with the substrate temperature. It was observed that the increase of the substrate temperature increase the diffraction peak intensity of (200) plane which resulted in increase in grain size and good crystallinity of the films.**

***Index Terms*—Chemical spray pyrolysis, lead sulphide, semiconductor, thin film.**

I. Introduction

PbS is a IV-VI compound semiconductor has a cubic lattice with unit cell face center cube (Lui and Zhang, 2000; Seghaier, et al., 2006), as shown in Fig.1.

Due to their direct narrow gap properties of PbS thin films regarded as a promising candidate for infrared detection for solar-control coatings (Thiagarajan, Beevi and Ramesh 2012; Choudhury and Sarma, 2009). Thin films of PbS have been prepared with various physical and chemical thin film deposition techniques, such as chemical bath deposition (Raniero, et al., 2012), physical vapor deposition (Mohammed, et al., 2012) and spray deposition (Anusuya, et al., 2012). Among these different techniques, spray technique is advantageous on account of the low cost and its suitability for forming large area thin films (Ashour, Afifi and Mahmoud 1995).

In this paper, PbS thin films deposited on glass substrate by chemical spray pyrolysis at different substrate temperatures (250, 300 and 350 ^{o}C).The influence of substrate temperature on the structural properties of the PbS thin films was observed and the results are reported.

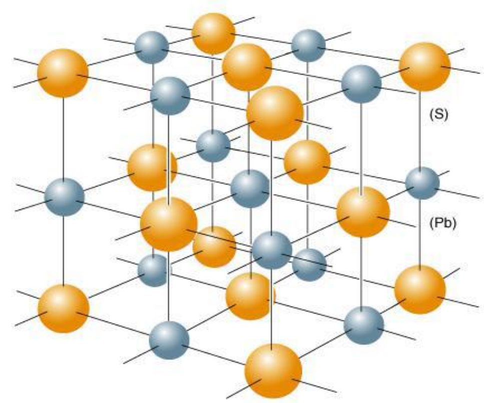

Fig.1. Crystal structure of PbS, adapted from Sze and Ng, (2007).

II. Experimental Details

The glass substrates were washed with alcohol and then ultrasonically cleaned in alcohol for 10 minutes. Later, deionized water was used to rinse the substrate. Lastly, dried with nitrogen gas.

Before starting the deposition, the solutions are mixed according to the film components (after found their weight by this equation (W=M×M.wt×V/1000, where M is the molarity, M.wt is the molecular weight and V is the volume) by solving the salts in the distilled water as follows:

a. Thiourea solution [$CS(NH_2)_2$]: This solution was prepared with molarities (0.1 M), from solving (0.761 gm) of thiourea in (100 ml) of distilled water.
b. Lead Nitrate solution [$Pb(NO_3)_2$]: This solution was prepared with molarities (0.1M), from solving (2.78 gm) of lead acetate in (100 ml) of distilled water.

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After getting the different amount of solutions according to the required ratio and volume, the prepared solution was put on magnetic stirrer about 10 minutes to be sure the solutions have been mixed properly. Then the solution of Lead Nitrate and Thiourea are mixed to obtain the PbS and ammonium nitrate according to the reaction equation:

$$Pb(NO_3)_2+CS(NH_2)_2+3H_2O \longrightarrow PbS+2NH_4NO_3+CO_2\uparrow + H_2O \quad (1)$$

The resulting solution was deposited on glass substrate at different temperature (250, 300 and 350 ^oC), and the ammonium nitrate dissolved by heating as seen in the reaction equation (Ibrahim, 2012).

$$PbS+2NH_4NO_3+H_2O \xrightarrow{\text{Heat (250-350 } ^oC)} PbS+NO_2\uparrow+NO\uparrow+2NH_3\uparrow+4/2H_2O\uparrow \quad (2)$$

PbS films were deposited on glass substrate by chemical spray pyrolysis technique. The description of the experimental set-up of chemical spray pyrolysis (CSP) system is presented in Fig. 2. PbS films were prepared by spraying an aqueous solution of Lead Nitrate and Thiourea on hot glass substrates at different temperature (250, 300 and 350 ^oC). The carrier gas used for spraying was compressed air. The thickness of the film was optimized to be 500 nm. The film thickness was measured by the weighting method via a digital balance type (Meter AE-160) with sensitivity of 10^{-4} gm, and the thickness was calculated according to the following equation (Faraj and Ismail, 2009):

$$t = \frac{\Delta m}{\rho . A} \quad (3)$$

where, t is the thickness of the film, Δm: is the mass of the film, ρ is the total density of the film and A is the area of the film.

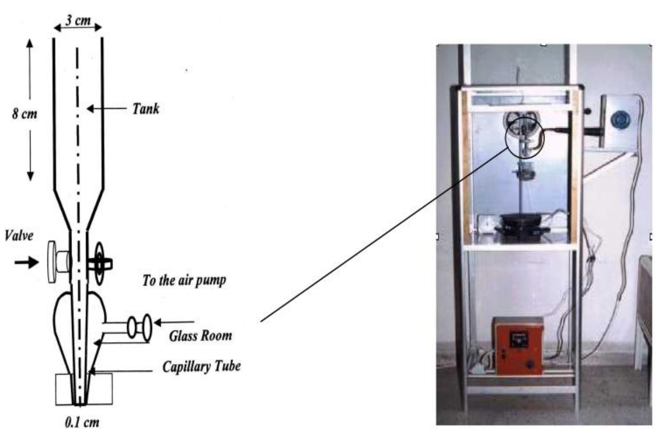
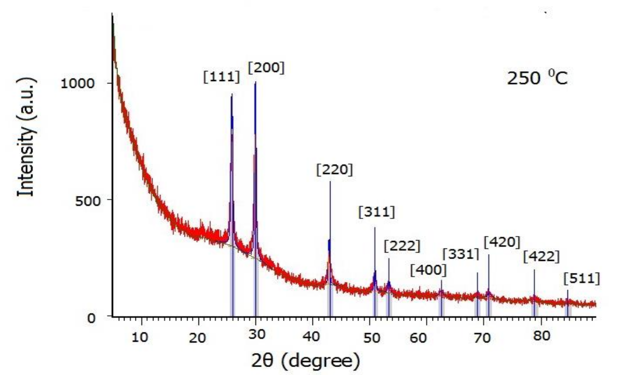


Fig. 2. Experimental set-up of spraying apparatus (right), and layout of enlarged spraying glass nozzle (left).

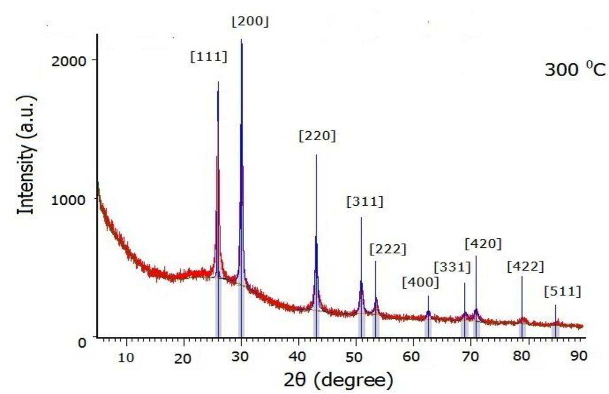
The crystallographic structure of the prepared PbS thin films was determined using a high resolution x-ray diffractometer system (model: panalytical empyrean) with cukα radiation (λ) of 0.154 nm at the department of Physics, Koya University.

III. Results and Discussion

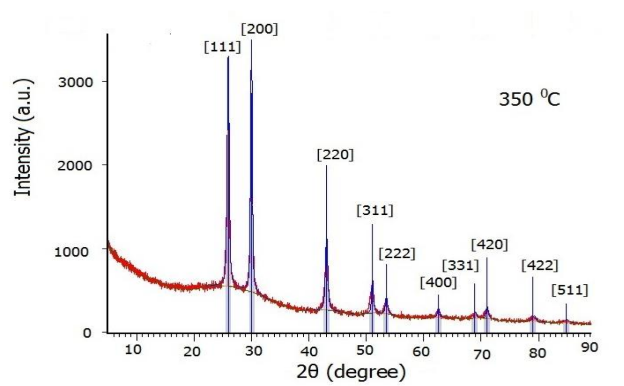
Fig. 3 shows the typical XRD pattern of the PbS samples for three different substrate temperatures. All PbS films have face centered cubic structure as confirmed by standard ASTM data (Masumoto, et al., 1992). XRD patterns of all the PbS thin films showed sharp [111] and [200] peaks along with minor peaks of [220], [311], [222], [420], [422] and [511] planes corresponding the face centered cubic structure of PbS thin films. These XRD results confirm the proper phase formation of the PbS films.



(a)



(b)



(c)

Fig. 3. XRD patterns of PbS films at substrate temperatures of; (a) 250 ^oC, (b) 300 ^oC and (c) 350 ^oC.

XRD patterns shows a clear dependent of the peaks intensity on the substrate temperature of the deposited films and suggests that the deposited PbS films are crystalline which is similar to reported in the literature (Rajashree, et al., 2014; Abbas and Jafir, 2012). The crystalline grain size (t) of the PbS films was determined with the Scherrer formula (Birks, 1946).

$$t=\frac{0.9\lambda}{\beta \cos\theta} \tag{4}$$

where, β is the full width at half maximum (FWHM) of the peak, λ is the wavelength of the X-ray, 1.5406 Å, and θ is the peak position. Based on the line width of the (200) diffraction peak, the crystalline grain size for the PbS films with differing substrate temperature shown in Fig. 4, and the grain size increase with increasing substrate temperature especially at 350 ^{o}C (Ibrahim, et al., 2012).

For studied films the preferential orientation value of (200) plane has the highest value compared to other planes. The obtained result indicates a strong orientation growth along the (200) plane which is agreed with that reported by (Seghaier, et al., 2006). The variation in preferential orientation factor f (h k l) for (200) as a function of substrate temperature shown in Fig. 5. The maximum peak value at 350 ^{o}C indicate the better crystallinity of the deposited PbS (Ibrahim, et al., 2012; Abbas and Jafir, 2012; Rajashree, et al., 2014).

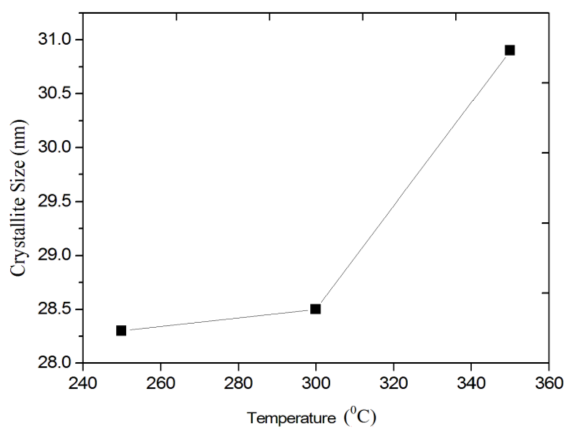


Fig. 4. Crystalline grain sizes as a function of substrate temperatures.

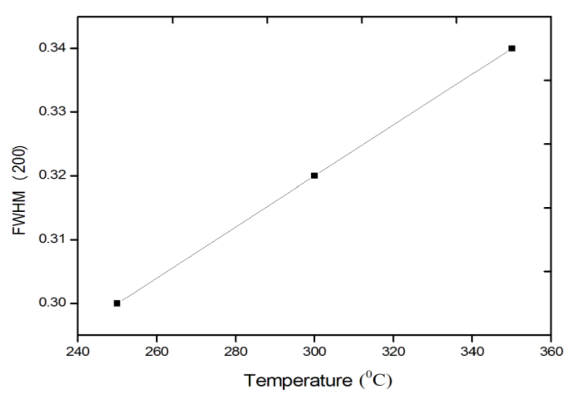


Fig. 5. Variation of FWHM of preferential orientation (200) of PbS films with substrate temperature.

IV. Conclusion

Lead sulphide (PbS) thin films were deposited on glass substrates with chemical spray pyrolysis. Effects of substrate temperature (250, 300 and 350 ^{o}C) on the structural characteristics of the films deposited were studied. X-ray diffraction patterns confirm the proper phase formation of the PbS. For studied films the preferential orientation value of (200) plane has the highest value compared to the planes. The grain size of the PbS films increased with increasing temperature. The values of crystallite size are temperature dependent were found to be in the range of 28.3 – 31 nm .The films were fabricated at the lowest temperature have the least crystalline quality as was observed in XRD patterns. The higher the substrate temperature the better crytallinity was observed.

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