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STUDY STRUCTURAL PROPERTIES, ELEMENTAL ANALYSIS AND SURFACE MORPHOLOGICAL OF SILAR-GROWN HIGHLY ORIENTED LEAD SULPHIDE (PbS) THIN FILMS

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ABSTRACT

The Nanocrystalline lead sulphide (PbS) thin films were deposited on a clean glass substrate using successive ionic layer absorption and reaction (SILAR) method at the different number of cycles having pH value 11 treated at a room temperature 303K and annealed at 150^{O}C and then cool down at room temperature by using lead nitrate, thiourea, and sodium hydroxide as chemical precursors as Pb^{+2} and S^{-2} ions sources respectively. The structural studies, Elemental analysis and surface morphological were performed by X-ray diffraction (XRD), Energy dispersive spectroscopy (EDAX), and Scanning electron Microscope (SEM). The XRD showed films of cubic (galena), crystalline with the preferential (220) orientation. The PBS thin films were obtained under optimal deposition conditions were found to be polycrystalline with Rock salt (NaCl) face centered cubic structure. The lattice parameter, grain size, the strain was calculated. The values of the average crystalline sizes were found to be in the ranges of (33-39) nm. The EDAX investigation of the given example confirms the presence of Lead and Sulfur with no other component present, suggesting its virtue was additionally done, implying its purity was also carried out. The Grain size determined from scanning electron microscopy (SEM) increased from 450nm to 777nm.

KEYWORDS: ***Lead sulphide nanocrystalline; Thin film; SILAR; XRD; EDAX and SEM.***

1.INTRODUCTION:

In recent years, semiconductor materials have attracted great attention from chemists, physicists and materials scientists due to their unique and special chemical, physical and mechanical properties. Therefore, increasing attention is being paid to studies on less known chemical compounds able to act as semiconductors to meet the need of future technology. The thin films have received much awareness due to their wide range of applications of any metal chalcogenides in the manufacturing of large-area photothermal converters, solar absorbers, solar control coatings, photodiode arrays, electronic and optoelectronic devices, infrared photography, photoconductors and sensors. [1-4].

Chalcogenides Lead Sulphide is an important IV-VI group semiconductor, which has attracted much attention because of its special small direct-band gap value in the range of 0.26 eV and 0.41 eV which makes them interesting for infrared (IR) detectors and enormous excitonic Bohr span of 18 nm Chattarki, et al. (2012) [4,5]. Among them, it has been found to be an interesting narrow bandgap semiconductor of PBS material with an energy gap value of 0.45eV. By decreasing the sizes of the crystallites their bandgap can be enhanced [6]. This bandgap change can be obtained in PBS for comparatively larger crystallite sizes as its Bohr excitonic radius is comparatively larger than other chalcogenides. [7] Chalcogenide materials are good candidates for p-type semiconductors [8]. It has been demonstrated using various chemical methods including Chemical bath deposition (CBD) [9], Electrochemical [10], Successive ionic layer absorption and reaction (SILAR) [11], Spray pyrolysis deposition [11,12]. This paper aims for researcher to

Element	Weight %	Atomic %	Net Int.	Error %	K Ratio	Z	R	A	F
S	34.01	76.9	2,525.52	3.28	0.35	1.29	0.83	0.8	1
Pb	65.99	23.1	1,806.29	2.92	0.64	0.85	1.16	1.14	1

Table:1 Chemical composition (Wt.%) of grown (PbS) thin films by EDAX and eZAF smart Quant Results: -

investigate the effect of the number of cycles on the structure, morphology and optical properties of PbS thin film prepared by Successive ionic layer absorption and reaction (SILAR). Such parameters are pH value, deposition temperature, the concentration of lead and Sulphur ions are optimized to get good quality films.

Lead Sulfide thin films have been described utilizing x-beam diffraction (XRD) and EDAX investigation. These examples are incorporated and were investigated by different characterization, for example, Powder X-beam diffraction and EDAX analysis. Also, about surface morphology by using SEM and TEM.

In the present investigation, we have prepared nanocrystalline PbS thin films by SILAR and studied their Structural, Elemental analysis and surface morphology.

2.EXPERIMENTAL METHOD AND MATERIAL PREPARATION

Lead sulphide thin films were grown by the method of SILAR (successive ionic layer absorption and reaction using glass substrate (microscopic slide size-75mm x 25mm and thickness-1.35mm), lead nitrate $[Pb(NO_3)_2]$ solution, thiourea solution$[SC(NH_2)_2]$ and sodium hydroxide solution $[NaOH]$ as the complexing agent. Lead nitrate is used as our lead ion source while thiourea is used as our sulphide ion source. The glass substrates were cleaned using nitric acid and acetone and after that they washed with distilled water several times. Lead sulphide were constituted from the solution for 15ml of 0.1 $M[Pb(NO_3)_2]$, 30ml of 0.8M thiourea $[SC(NH_2)_2]$, 15ml of 0.8M sodium hydroxide $[NaOH]$ and deep glass substrates in cationic precursor solution having distilled water for 30 secs, to be rinsed 5secs in high- purify deionized water, also immersed 30secs having distilled water in the given anionic precursor solution, the ions reacted with absorbed lead ions on the active center of the substrate and then again finally rinse it in deionized water for 5secs. It was also optimized by 40 cycles, 50 cycles, 60 cycles & 70 cycles, during the process of film formation the thickness of the film increases as the cycle increases. The PbS thin film resulting was homogenous, well adhered to the glass substrate with darker surface like mirror.

The suggested reactions are as follows (Tohidi et al., 2014; Osherov et al., 2007). [12]

Composition	(Wt.%) of elements from EDAX	
	Pb	S
PbS	65.99	34.01

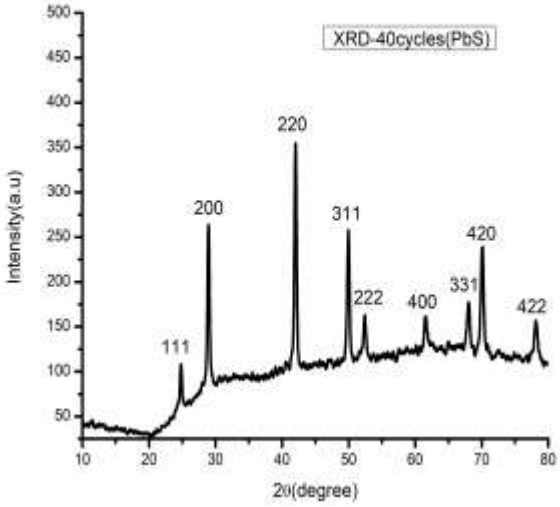
$$Pb(NO_3)_2 + 4NaOH \rightarrow [Pb(OH)_4]^{2-} + 4Na^{+} + 2NO^{3-}$$

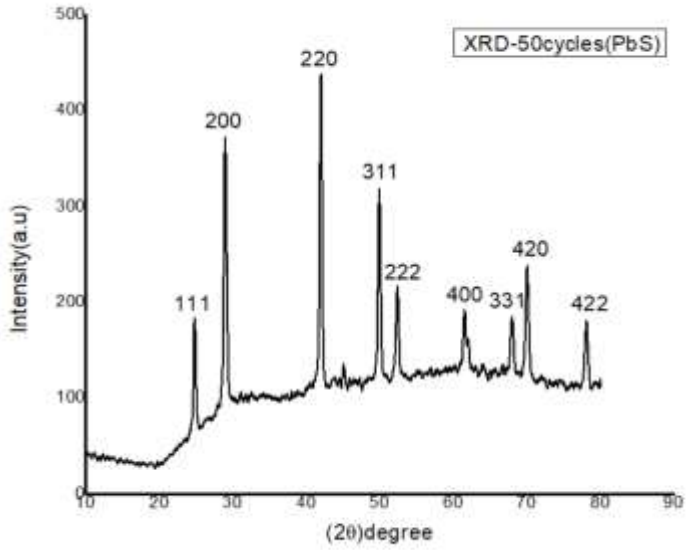
$$[Pb(OH)_4]^{2-} + SC(NH_2)_2 \rightarrow PbS + 2OH^{-} + CN_2H_2 + 2H_2O$$

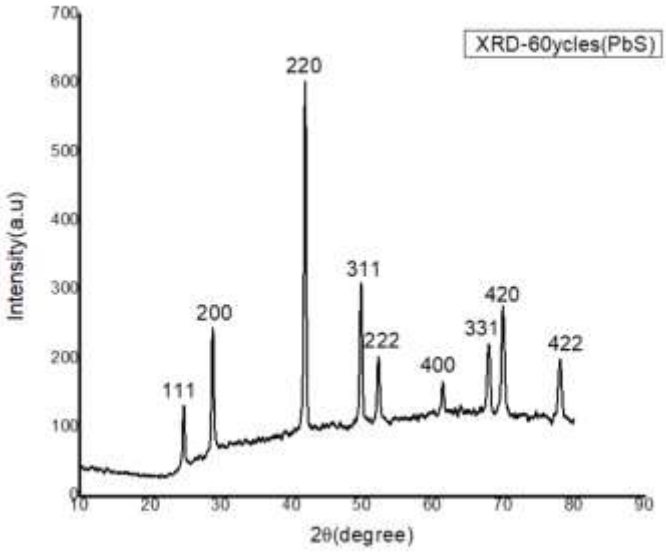
Table.2. Comparing the values of Experimental database from graphical representation for diffraction angles (2θ in degrees) and D spacing of lead Sulphide thin films.

Experimental Database							
Diffraction angle 40Cycles	**D spacing (Å)**	**Diffraction angle (2θ in degrees) 50Cycles**	**D spacing (Å)**	**Diffraction angle (2θ in degrees) 60Cycles**	**D spacing (Å)**	**Diffraction angle (2θ in degrees) 70Cycles**	**D spacing (Å)**
24.82	3.58	24.70	3.59	24.70	3.60	24.80	3.59
28.94	3.08	28.66	3.15	28.78	3.10	28.90	3.09
41.40	2.18	41.92	2.15	41.88	2.16	41.98	2.15
49.94	1.82	49.84	1.83	49.78	1.83	49.88	1.83
52.50	1.74	52.30	1.75	52.28	1.75	52.38	1.75
61.44	1.51	61.42	1.51	61.38	1.51	61.68	1.50
68.06	1.38	67.92	1.38	67.86	1.38	67.88	1.38
70.08	1.34	70.22	1.34	69.86	1.35	70.16	1.34
78.28	1.22	78.10	1.22	78.24	1.22	78.18	1.22

3. RESULT AND DISCUSSION







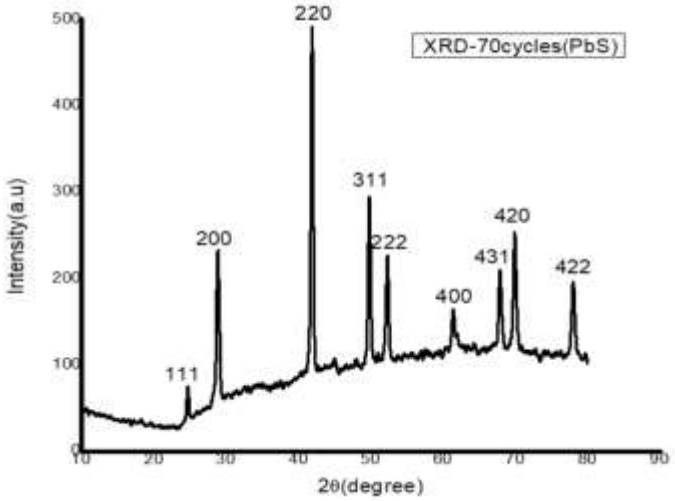


Figure 1: XRD pattern of lead Sulphide thin films for 40,50,60 &70cycles.

Figure 1 shows the XRD pattern of Lead Sulfide compounds. The PbS material of structural identification was carried out with X-beam diffraction in the scope of the range of angle 2θ between 10◦ to 80◦.It shows the XRD pattern for PbS material, which was nanocrystalline in nature. All the defined diffraction peaks shown in the figure match well and are due to reflections from planes (111) (200) (220) (221) (311) (222) (331) (400) (420) and (422) saw in XRD pattern. [13,14,15,16]. The lattice cell constants (a=b= c=6.124 Å,6.153 Å,6.129 Å and 6.113 Å for 40,50,60, and 70 cycles respectively) with CuKα light (λ=1.5418) Calculated from the XRD pattern is consistent with the reported values and respond to the reflections of the cubic structure of PbS. [17,18] While the average grain size obtained for highest three peaks intensity from planes (200) (220) (311) for 40,50,60 and 70cycles thin films are 33.31nm,34.22nm,36.38nm and 39.15nm of PbS was calculated using the Debye Scherrer formula, their crystal sizes lie within the range of (33-39) nm.

$$D = \frac{k\lambda}{\beta\cos\theta} \quad \text{..... eqn (1)}$$

The grain size for was found to be the highest peak, this indicates that the plane (220) is preferentially oriented along (220) obtained for all 40,50,60 and 70 cycles from the above formula accordingly are 32.89nm,34.22nm,35.58nm and 37.07nm. of PbS their crystal sizes lie within the range of (32-38) nm. Also (200) plane reported by [19,20] Also, we conclude that Dislocation density and micro strain decreases the particle size and number of unit cell per unit volume increases.

Where D =Crystallize Grain Size, λ = the wavelength of CuKα target used, θ Bragg's diffraction angle at peak position in degree and β = Full width at half maximum of the peak in radian. [22].

Sr. no.	Cycles	Crystal size Range (D)	Micro-strain (ϵ)	Lattice constant (a)	Dislocation density (δ)	Number of Unit cell per unit volume(n)
1	40	33.31 nm	1.08x 10^-3	6.124	9.02x 10^14	1.18x 10^-22
2	50	34.22 nm	1.06x 10^-3	6.153	8.58x 10^14	1.30x 10^-22
3	60	36.38 nm	1.00x 10^-3	6.129	7.75x 10^14	1.59x 10^-22
4	70	39.15 nm	0.94x 10^-3	6.113	6.75x 10^14	1.99x 10^-22

Fig 3 shows Scanning electron microscope (SEM) which reveals that the surface morphologies of the PbS film deposited by SILAR method, it shows that the PbS thin films by SILAR technique were homogeneous in nature with a good sparely packed crystallites which appears to be randomly oriented with the irregular and spherical shapes of similar sizes distributed for the PbS thin films deposited by SILAR methods. This agrees with other reports. [21, 22].

EDAX ANALYSIS

It is also confirmed from EDAX images of PbS thin film that there are no contaminating elements present in it. The photographs of EDAX for these samples for 40,50,60, &70 cycles are shown in Plot belowrespectively.

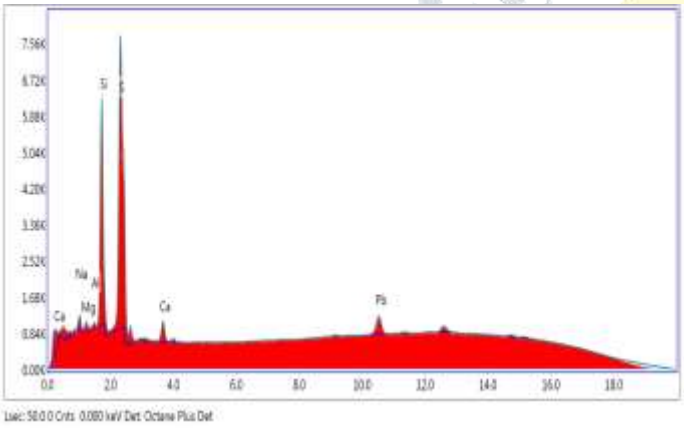


Figure 2(a): EDAX spectrum of PbS thin film for 40cycles.

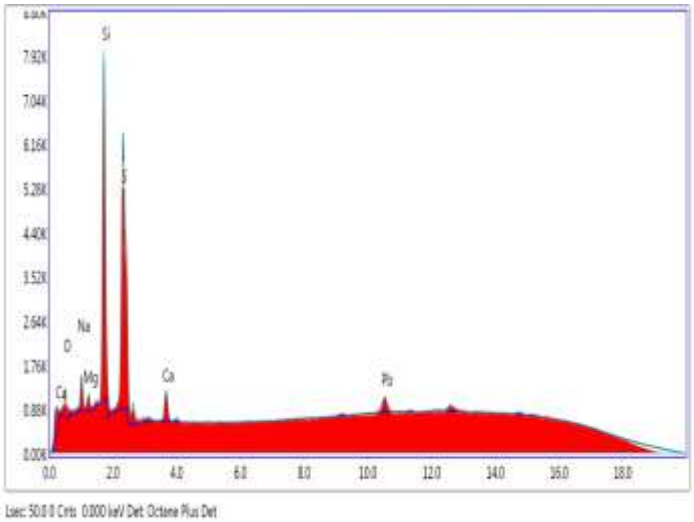


Figure 2 (b): EDAX spectrum of PbS thin film for 50cycles.

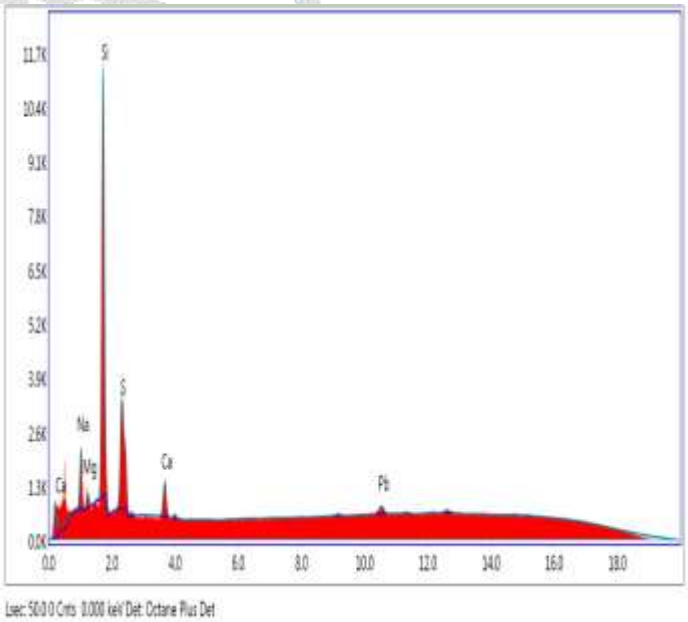


Figure 2(c): EDAX spectrum of PbS thin film for 60cycles.

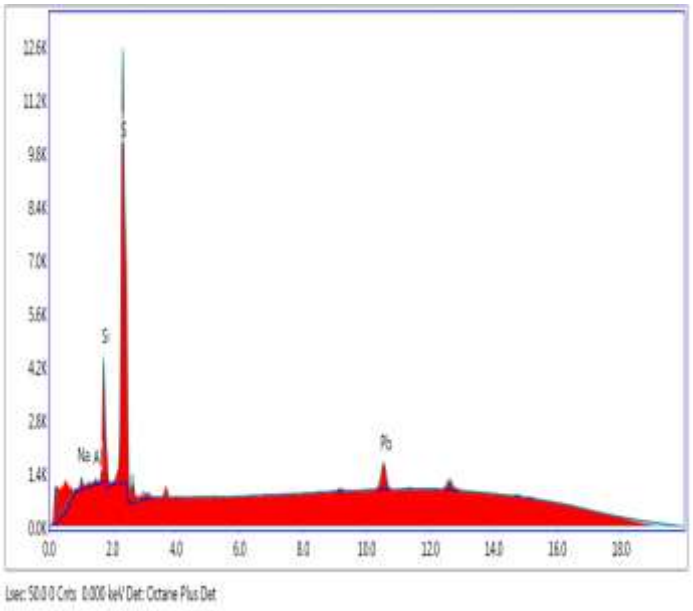


Figure 2 (d): EDAX spectrum of PbS thin film for 70cycles.

Figure 2(a, b, c, d) represents the spectrum of the PbS thin film respectively. The EDAX analysis of the above sample confirms the presence of Lead and Sulfur without any impurities present in it. EDAX is utilized to decide the stoichiometric extent of the constituent component. Here the image captured by the edax instrument shows the morphology of our sample and from image, we can clearly say that stoichiometric structure is available in the sample of PbS. Additionally, from the peak we can analyzed that the sample confirms the presence of two constituents Pb-lead and S-Sulfur with no other component or impurities present in it, implying its purity.

SEM ANALYSIS

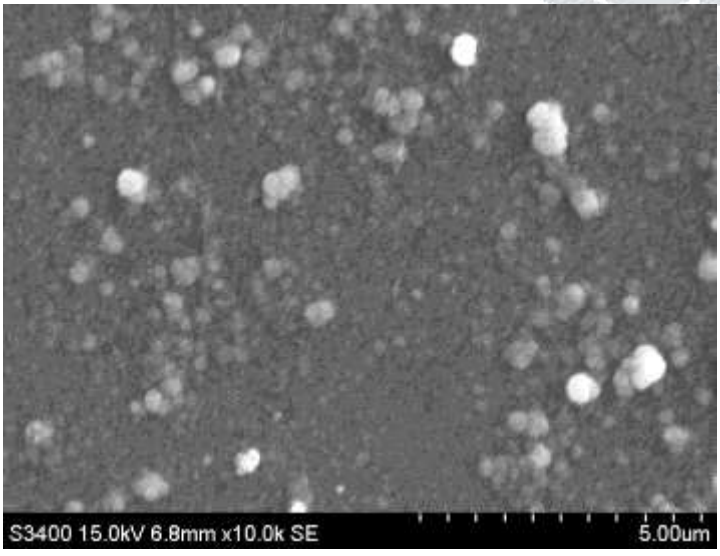


Figure: - 3(a) SEM Micrograph for 40 cycles

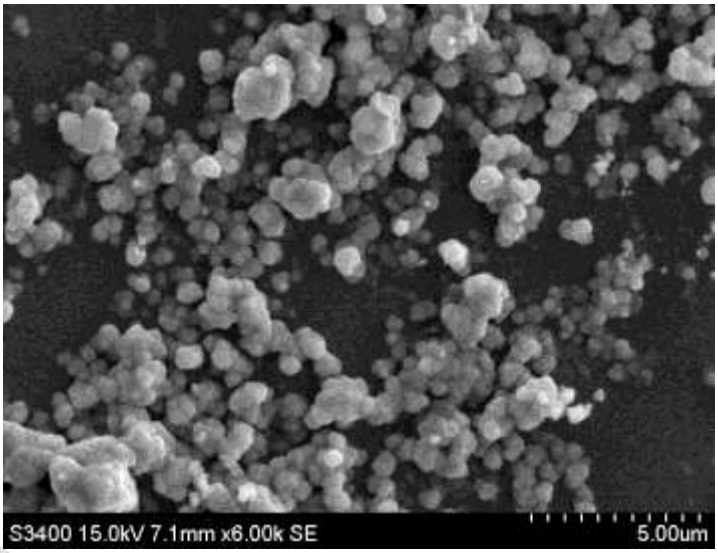


Figure: - 3(b) SEM Micrograph for 50 cycles

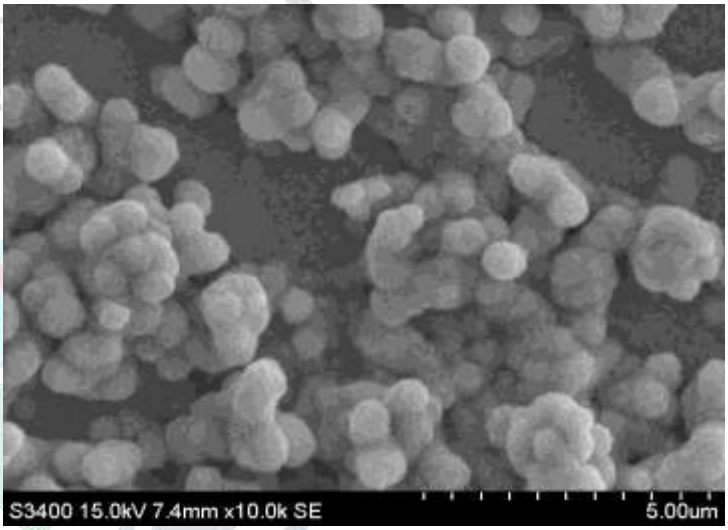


Figure: - 3(c) SEM Micrograph for 60 cycles

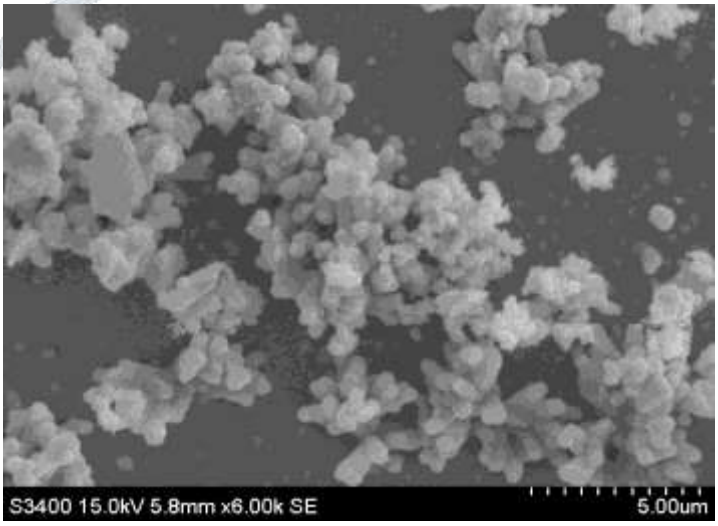


Figure: - 3(d) SEM Micrograph for 70 cycles

As from above figures 3(a, b, c, d) the SEM image at a higher resolution reveals the morphology of the sample as a cluster of cubic particles with spherical in shape with the sizes ranging from 283 to 632 nm,395 to 996nm,399 to 942nm and 500 to 1061nm for 5um for 40,50,60 and 70 cycles respectively. While mean diameter of the crystallize size for 40,50,60 and 70 cycles SEM image are 450nm, 657nm, 666nm and 777nm respectively.

The Scanning electron microscope (SEM) micrographs show the surface morphology is composed largely of compact sharp edged cubic shaped grains, of different sizes and uniformly distributed over a smooth homogenous background without visible defects such as, cracks, peeling or pinholes for 40,50 and 60 cycles. While the micrograph of the film deposited at 70 cycles shows a plate-like morphology. From the Scanning electron microscope (SEM) micrographs it is easily observed that the deposition time plays a vital role on the morphological properties of the nanocrystalline PbS thin films. This agrees with other reports. [23, 24].

4. CONCLUSION

In conclusion, the structural, Elemental analysis and Surface morphology of Lead Sulphide thin films has been successfully characterized, measured, and analyzed by using an X-Ray powder Diffractometer, Energy- dispersive Spectroscopy and Scanning Electron microscope were carried out. The result obtained from the structural XRD pattern investigations of the PbS thin films sample indicates the formation of the cubic structure of PbS sample. PbS thin films have been grown on glass substrates by SILAR method at different dipping cycles. XRD studies confirmed the cubic phase formation of PbS. Intensity of the peak has increased with the increase of dipping cycles and the oriented of the peak also have changed with this process. This effect can be related to the increase of grain size. SEM studies shown that increasing grain size and the grain size shape turn into sphere when dipping cycle is increased. The results of EDAX confirmed the presence of Pb and S in the films. While the average grain size obtained for highest three peaks intensity from planes (200) (220) (311) for 40,50,60 and 70cycles thin films are 33.31nm,34.22nm,36.38nm and 39.15nm, their crystal sizes lie within the range of (33-39) nm. The EDAX analysis of the above sample confirms the presence of Lead and Sulfur without any impurities present in it. EDAX is utilized to decide the stoichiometric extent of constituent components and from graph, we can clearly say that stoichiometric structure is present in the sample of PbS. The SEM micrographs show the surface morphology is composed largely of compact sharp edged cubic shaped grains, of different sizes and uniformly distributed over a smooth homogenous background without visible defects such as, cracks, peeling or pinholes for 40,50 and 60 cycles. While the micrograph of the film deposited at 70 cycles shows a plate-like morphology.

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