Effect of lead ion concentration on the structural and optical properties of nano-crystalline PbS thin films

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Abstract. PbS thin films have received considerable attention because of their potential applications in opto-electronics applications. Spontaneous reaction of lead acetate and thiourea in aqueous hydrazine hydrate has been used for depositing PbS thin films on glass substrates. Structural and optical properties of PbS thin films are greatly influenced by the morality of the reactants and crystal defects in the lattice. Our work focuses on the variation in lead ion concentration and its effect on the structural and optical properties of PbS thin films. The deposited films were analyzed using XRD, SEM, spectrophotometer and dark resistance measurement. XRD patterns indicated the formation of major phase of nano crystalline PbS with minor presence of lead oxide phase. We also noticed that peak intensity ratio of I₁₁₁/I₂₀₀ varied by changing the Pb ion concentration. The film thickness and dark resistance increased whereas optical band gap decreased with the decreasing Pb ion concentration. SEM scans showed that the grain size is less than 100 nm and is not affected by varying Pb ion concentration.

1. Introduction
Thin films form the basis for today’s electronic components. Even complicated device structures are constructed from thin films, deposited one by one. Nanocrystalline thin films make up a group of materials attracting a great deal of interest both from fundamental and applied point of view. This is due to the fact that these materials display a large surface to bulk ratio, which distinguishes them from bulk materials. A nano-crystalline material contains a high concentration of grain boundaries or in case of porous films, a high internal surface compared to the bulk material. These properties are of considerable importance for electrical transport, optical and mechanical properties [1-4]. Thin films of metal nanoparticles connected in a percolating network display high optical absorption in infrared wavelength range due to the small size of individual metal particle [5-6].

Lead sulphide (PbS) has been a rapidly growing area of importance to study the quantum size effect in recent years [7-9]. Structural, optical and electrical properties of PbS nanoparticles have been studied extensively [10-13]. Nanocrystalline PbS is a material of interest due to its potential application for infra-red detection. However, reduction of grain size extends the employability of the material over wide spectral range. Grain boundaries in compound semiconductor films are different from those in elemental semiconductors. Boundaries for larger crystallite films differ from those for small-grained ones. In a polycrystalline semiconductor thin film, factors like film defects, surface scattering and grain boundaries complicate identification of electrical properties.

The physical, structural, electrical and optical characteristics of grain boundary regions are drastically altered by exposure to impurities, diffusion and field effects [14]. Considering the fact that
stoichiometric excess of lead (Pb) in PbS (bulk) imparts n-type character whereas deficient lead makes it p-type [15], a similar change in carrier type can be expected in PbS films by manipulating the lead content. In chemical bath deposition technique, which has been used for the growth of PbS films for the present study, the stoichiometry is determined by the relative availability of the ions reaching the substrate to undergo reactions at the surface. A change, intentional or otherwise, in relative concentrations of the ions reaching the substrate surface can lead to non-stoichiometry in the resulting films. It is thus possible to grow films with excess or deficit lead by modifying its supply to the substrate during growth of films. We have reported that an appropriate choice of lead ion concentration could modify the carrier or conductivity type of PbS thin films. The availability of lead ions to the substrate during growth effect average grain size, film thickness and optical band gap of PbS films. An attempt to correlate the lead ion concentration with thickness, structural and optical properties has been made.

2. Experimental

The thin films of PbS were deposited onto chemically cleaned glass substrates using AR grade chemicals by CBD process. Thiourea was used as a source of sulphide ions and lead acetate as Pb$^{+2}$ precursors in alkaline medium, using hydrazine hydrate as base instead of commonly used basis such as sodium hydroxide. Chemical bath was prepared by mixing aqueous solutions of thiourea and hydrazine hydrate in 1M: 7M respectively while lead acetate concentration was varied from 1.2M to 0.6M according to Table 1. The starting solution had pH 12. The substrates were mounted on the external walls of a beaker fitted with an immersive heater. The beaker was then filled with water and placed in the chemical bath solution. The temperature of substrates was kept close to boiling temperature of water throughout the experimentation. The deposition time was 30 minutes, as given in Table 1. After deposition, films were rinsed in de-ionized water and dried in oven at 60-80°C.

| Table 1. Concentration of Lead ions used for different baths |
|-----------------|-----------------|-----------------|
| Bath | Conc. Of Pb$^{+2}$ | Bath | Conc. Of Pb$^{+2}$ |
| A    | 1.2             | G    | 0.8             |
| B    | 1.1             | H    | 0.75            |
| C    | 1               | I    | 0.7             |
| D    | 0.95            | J    | 0.65            |
| E    | 0.90            | K    | 0.60            |
| F    | 0.85            | L    | 0.55            |

The annealing of films was done at 100°C for 7 hours. The structure and crystallite sizes were measured by X-ray diffractometer. The films were well adherent to the substrates, as tested qualitatively by tape test. Film thickness was determined by gravimetric method. The surface morphology of films was studied by scanning electron microscope. The dark resistance of film was measured with a two probe method. The optical properties were studied on UV/VIS/NIR spectrophotometer.

3. XRD Studies

Figure 1 shows the diffractograms of PbS thin films prepared at different Pb$^{+2}$ ions concentrations, from 0.6M to 1.2M for a constant deposition time of 30 mins. The diffraction peaks observed are at 2θ equal to 26, 30 and 43 degrees corresponding respectively to (111), (200), and (220) planes, confirmed cubic structure of PbS (JCPDS reference no. 78-1901) with slightly preferential (200) orientation of grains. In our study we reduced the concentration of lead ions while keeping the concentration of hydrazine hydrate constant. Hydrazine hydrate decreases the releasing rate of Pb$^{+2}$ ions by making complex with these ions. It was observed that the growth of crystallographic orientation and microstructure of the films depend on Pb$^{+2}$ ion concentration in the solution of the deposition process. The diffractogram ‘a’ shows that peak ratio of (111)/(200) is 80/100, when we lowered the concentration of lead acetate, the peak ratio of (111)/(200) also reduced almost linearly up to an optimum level and then became constant.
In the pattern ‘e’ this peak ratio of (111)/(200) is reduced to 25/100, that is an indicative that decreased Pb$^{2+}$ ion concentration favors growth along (200) plane. This can be explained by the fact that when Pb$^{2+}$ ion concentration decreases, the reaction rate slows down and chances of rapid precipitation of PbS salt decrease and hence nucleation growth increases.

One of the most important aspect revealed from these patterns is the growth of lead oxide phase Pb$_3$O$_4$ at 2θ equal to 26.15 and 32 degrees corresponding respectively to (211) and (310) planes according to JCPDS card # 76-1799 whereas at 2θ equal to 38 degree correspond to (020) plane of lead oxide phase PbO according to JCPDS card # 03-610, which appeared when Pb$^{2+}$ ion concentration was decreased up to 0.95M as shown in pattern ‘c’. The peak height of lead oxide phases increased with decreasing Pb content and become maximum at 0.8M Pb$^{2+}$ ion concentration. On further reducing the concentration of lead ions, the growth of lead oxide phases decreased as well.

The explanation of oxide growth comes from the changes occurring in chemical bath as a result of gradual decrease in Pb$^{2+}$ ion concentration. When we lowered lead acetate concentration, the influence of hydrazine hydrate became prominent. The reaction process slowed down and formation of lead oxide phases became more probable, and this process of oxide growth reached to maximum at an optimum level of Pb$^{2+}$ ion concentration and after that became constant.

![Figure 1. XRD comparison of PbS thin films deposited at different Pb$^{2+}$ ion concentrations.](image1)

![Figure 2. XRD comparison of as-prepared and annealed PbS thin films for Bath F](image2)
the deposited PbS thin films were thermally treated in air. The optimal temperature of treatment has been found to be 100°C in order to improve photoelectric properties. Figure 2 shows the comparison between diffraction patterns of as deposited and annealed PbS thin film for 0.85 M Pb\(^{2+}\) concentrations. Thermal treatment in air favors oxidation and hence we observed increase in intensity of lead oxide peaks. However this effect of thermal oxidation in air decreased with decreasing Pb\(^{2+}\) ion concentration. When Pb\(^{2+}\) ions decreased from an optimum level in bath, the chances of free lead to incorporate in the PbS structure/lattice also decreased and we obtained more closer towards pure galena phase. Due to decreased free Pb in the deposited PbS thin films the thermal oxidation becomes less pronounced after 0.8M Pb\(^{2+}\) ion concentration.

4. Morphological Studies
Surface morphology and grain size of the deposited films was studied by using scanning electron microscope. It is obvious from figure 3, that all deposited PbS films are nanocrystalline and compact with no voids or pinholes. The grains are homogenously distributed and less than 100nm in size. As we decreased the concentration of Pb ions there is no significant change in surface morphology, the overall grain size of the base is nearly same. There is some increase in number of facets at surface that can be attributed to increasing film thickness and resulting non homogeneity.

![Figure 3. SEM micrographs of PbS thin films deposited at various Pb\(^{2+}\) concentrations.](image)

5. Thickness measurement
The thickness of deposited PbS thin films was measured by gravimetric method. Figure 4 shows the effect of lead ion concentration on the thickness of PbS thin films. It was observed that lead ion concentration has marked effect on film thickness. Initially at 1.2M Pb\(^{2+}\) ion concentration the observed film thickness was 268nm and it increased up to 935nm when Pb\(^{2+}\) ion concentration was decreased to 0.6M. The observed results can be explained on the basis of ion-ion condensation. The formation of PbS is governed by the equation (1),

\[
[Pb (HH)^{2+}] + NH_2CSNH_2 + H_2O \rightarrow PbS_n + NHCNH + [HH.2H]^2+ + H_2O
\]  

(1)
at a particular temperature PbS will be deposited if the ionic product of Pb$^{2+}$ and S$^{-2}$ exceeds the solubility product. The Pb$^{2+}$ released by the hydrazine hydrate (HH) complex and S$^{-2}$ released by thiourea combine at the nucleation centers on the substrate to produce PbS. The quantity of ions utilized for film formation depends on the rate of formation of PbS on the substrate surface, which in turn, depends not only on the ratio of the nucleation centers available at the surface of the substrate to those in the volume of the solution, but also on the rate of release of Pb$^{2+}$ and S$^{-2}$ ions. As we reduce the concentration of Pb$^{2+}$ ions in chemical bath, the release of Pb$^{2+}$ from its HH complex becomes slow and the whole deposition process slows down, as a result chances of rapid precipitation of PbS decrease and that of nucleation growth at the substrates increase. Due to increased nucleation growth, the growth along (200) plane dominated and as a result thickness of PbS film also increased.

![Figure 4](image1.png) **Figure 4.** The effect of Pb$^{2+}$ concentration on the thickness of PbS thin films.

![Figure 5](image2.png) **Figure 5.** The effect of Pb$^{2+}$ concentrations on the dark resistance of PbS thin films.

6. **Dark Resistance**

The dark resistance of the deposited films was measured at room temperature by using a multimeter. Figure 5 shows the effect of decrease in Pb ion concentration on the dark resistance of deposited films. There is a gradual increase in dark resistance up to 0.70M Pb ion concentration and then resistance increases rapidly up to 0.55M, after that it remained almost constant. This effect can be described by keeping in view that with the decreasing lead in chemical bath there is a stoichiometric decrease of Pb content in the deposited PbS thin films. The carrier type is shifted from n to p-type, as a result hole concentration decreases and the net dark resistance of PbS films increases.

7. **Optical Studies**

The optical reflection spectra of chemically deposited PbS thin films were recorded on a Shimadzu UV/VIS/NIR 3600 spectrophotometer in the range of 190-3100nm. Reflectance is less than 20% for almost all samples but increases slightly with annealing. With the help of this reflectance data, absorptivity was calculated by using Kubelka-Munk function, i.e.

\[ F(R) = (1-R)^2 (2R)^{-1} = \alpha S^{1/4} \]

where $\alpha$ is absorptivity and S is scattering factor. The energy band gap was found by plotting Kubelka-Munk function “F(R)$^{2/3}$” against energy, the intercept of the plot gives the value of band gap. Figure 6 shows the effect of decreasing lead ion concentration on lowering the energy band gap of deposited films. This effect can be contributed to increase in film thickness. As we decreased the lead ion concentration the film thickness increased.
Many references from literature show that annealing improves the photosensitivity of PbS films. The photosensitivity increases about four to ten times by optimized thermal treatment [16]. The effect of prolonged annealing could be explained by desorption of water and by the appearance of oxidation products [17].

![Figure 6. The effect of lead ion concentration on energy band gap of as-prepared and annealed PbS thin films.](image)

Annealing process is expected to relieve stresses effectively and modify grain boundaries to some extent [16]. This results in photoconductivity enhancement. The deposited films were annealed at 100°C for 30 minutes. Annealing decreased the optical band gap of samples. This effect is marked at the start but less pronounced after 0.6M Pb ion concentration.

8. Conclusion

Structural and optical properties were determined and correlated with the different molarities of Pb ion concentrations. Several conclusions can be drawn on the basis of the experimental data.

- Thickness of the film increased as a result of decreasing Pb ion concentration, it is due to the fact the nucleation phenomena of PbS growth became more dominant and more time was available for the reaction to complete as a result thickness of PbS films enhanced.
- Dark resistance increased as a result of decreasing Pb ion concentration, it is due to fact that with the decreasing Pb content in the deposited PbS thin films, the carrier type is shifted from n to p-type, as a result the net dark resistance of PbS films increases.
- SEM scans indicated the formation of nanocrystalline PbS thin films having grain size less than 100 nm, it is also evident the grain size is not affected by the Pb ion concentration but the number of facets increases which is also responsible for the enhancement of thickness with decreasing Pb ion concentration.
- Optical studies revealed that by lowering the Pb ion concentration decreases the optical band gap of PbS thin films. The optical band gap decreases for annealed thin films which is responsible for the enhanced photosensitivity of annealed films.

9. References

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