AFM investigation and optical band gap study of chemically deposited PbS thin films

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Abstract. The interest into deposition of nanocrystalline PbS thin films, the potential of designing and tailoring both the topographical features and the band gap energy ($E_g$) by controlling growth parameters, has significant technological importance. Nanocrystalline thin films of lead sulfide were grown onto glass substrates by chemical bath deposition (CBD) method. The experiments were carried out by varying deposition temperature. We report on the modification of structural and optical properties as a function of deposition temperature. The morphological changes of the films were analyzed by using SEM and AFM. AFM was also used to calculate average roughness of the films. XRD spectra indicated preferred growth of cubic phase of PbS films in (200) direction with increasing deposition time. Optical properties have been studied by UV-Spectrophotometer. From the diffused reflectance spectra we have calculated the optical $E_g$ shift from 0.649-0.636 eV with increasing deposition time.

1. Introduction
Semiconductor nano-materials are important due to their unique optical and electronic properties originating from quantum confinement and they exhibit size dependent band gap energies [1-3]. A nano-crystalline material contains high concentration of grain boundaries as in case of porous films, i.e. a high internal surface compared to the bulk material. These properties are of considerable importance for electrical transport, optical and mechanical properties [4-9]. Most of the work on nano-semiconductor particles reported so far has been restricted to optical absorption. The absorption edge shifted to blue as the particles size reduces. Most studied crystalline semiconductors, in recent years, belong to the II-VI and IV-VI groups, since they are relatively easy to synthesize and are generally prepared as nano particles or in the form of thin [10].

PbS thin film is an important binary IV–VI semiconductor with a narrow band gap (0.41 eV) and relatively large excitation Bohr radius (180 nm) [11], which results in strong quantum confinement of electrons and holes presents into the crystal lattice of PbS. Band gap of the PbS thin films can be controlled simply by modifying particle size and shape [12-14]. Structural, optical and electrical properties of PbS nanoparticles have been studied extensively [15-18]. Nano-crystalline PbS is important due to its potential application for infra-red region, however, reduction of grain size extends its application 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. Among the
different PbS thin film fabrication methods, chemical bath deposition CBD technique requires relatively mild conditions, is cost effective, scalable and technically straight-forward [19]. By CBD the dimensions of the crystallites can be varied by controlling deposition parameters. This paper focuses on the effect of temperature and dipping time on the growth of grains during deposition in a chemical bath and its influence on the morphology and size of grains and optical band gap of grown films.

2. Experimental
The thin films of PbS were deposited onto chemically cleaned glass substrates using AR grade chemicals by CBD process. Thiourea (Fluke) was used as a source of sulphide ions and lead acetate (Alfa Acer) as Pb^{2+} precursor in alkaline medium, using hydrazine hydrate (Aldrich) as base instead of commonly used basis such as sodium hydroxide. Chemical bath was prepared by mixing aqueous solutions of thiourea, lead acetate and hydrazine hydrate in 0.7M:0.7M:5M respectively. The substrates were mounted on a special holder that was immersed inside the chemical bath. The starting solution had 12 pH. The temperature of bath was raised to the boiling point of water and during this process substrates were removed from bath at different temperatures according to Table 1. After deposition, films were rinsed in de-ionized water and dried in oven at 60-80°C. Figure 1 shows the experimental setup for chemical bath deposition. The formation of PbS is governed by the equation (1),

\[ [Pb\,(HH\,)^{2+}] + NH_2CSNH_2 + H_2O \rightarrow PbS\downarrow + NHCNH + [HH\,2H\,]^{2+} + H_2O \] (1)

| Table 1. Details of samples collected during CBD process |
|---------------------------------------------------------|
| S. No. | Sample name | Deposition temperature | Deposition time |
|--------|-------------|------------------------|-----------------|
| 1      | A           | 30°C                   | 10 min          |
| 2      | B           | 50°C                   | 15 min          |
| 3      | C           | 70°C                   | 20 min          |
| 4      | D           | 90°C                   | 25 min          |
| 5      | E           | 100°C                  | 30 min          |

![Figure 1. Experimental Set Up for CBD](image)
The obtained samples were characterized to see their morphology and optical properties. The structure and phase studies were done by Jeol X-ray diffractometer. Topography and surface roughness was determined with help of easyscan2 Nanosurf atomic force microscope. 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 and the optical properties were studied on Shimadzu UV/VIS/NIR spectrophotometer.

3. Results and discussion

3.1 XRD studies

X-ray diffraction patterns of PbS thin films were obtained using Copper Kα source. Figure 2 shows XRD graph of samples prepared at different temperatures, while going from room temperature to 100°C. In the start of deposition, up to 50°C, the PbS films are amorphous in nature, and on further increase in temperature some crystalline peaks starts to grow. At 90°C well defined crystalline structure is formed. A further 10 degree rise in temperature leads to increase in intensity due to increased number density of grains and preferential growth in one direction. The 2θ diffraction peaks observed are at 26, 30 and 43 degrees correspond respectively to (111), (200), and (220) planes. The XRD pattern confirms cubic structure of PbS (JCPDS reference no. 78-1901) with slightly preferential (200) orientation of grains.

![Figure 2. XRD comparison of PbS samples A, B, C, D and E showing evolution of crystalline structure with increasing deposition temperature and Td](image)

It was verified that the relative intensity of XRD peaks changes with respect to the temperature and dipping time.

3.2. AFM Studies

The surface topography and surface roughness of the deposited films was determined by atomic force microscopy. AFM measurements were performed in tapping mode in air. These studies revealed that there is a considerable change in morphology and surface roughness as the temperature and deposition time increases. Figure 3 shows that when deposition temperature is increased from 30 to 100°C, PbS films become more rough due to increasing grain size. The grains are spherical up to 70°C and start merging with neighboring grains on further increase in temperature. Some elongated grains are also seen at 100°C.
Surface roughness was calculated by using AFM measurement software. Increase in deposition temperature and time leads to growth of crystallites and film thickness that increases the surface roughness and average surface roughness ($S_a$) increase from 59.55 nm to 103.54 nm as shown in Table 2.
### Table 2. Change in Surface roughness of deposited films with increasing deposition temperature

| S. No | Sample | Average roughness Sa (nm) |
|-------|--------|--------------------------|
| 1     | A      | 59.55                    |
| 2     | B      | 72.43                    |
| 3     | C      | 83.78                    |
| 4     | D      | 94.17                    |
| 5     | E      | 103.54                   |

#### 3.3. SEM analysis

The surface morphology of deposited thin films was determined by scanning electron microscopy (SEM). Fig. 4 shows the SEM images of films obtained at different temperatures and time. SEM images, from A to E, show film growth sequence during whole deposition process. At 30°C, nucleation and coalescence of grains is visible. However, the grains are isolated and porosity in film is apparent. At 50°C and 70°C, the process of coalesces dominates and film starts becoming more compact. In the range of about 90°C the grains start to diffuse and grain growth dominates. Here the porosity of film diminishes. At 100°C the grain growth forms into pyramidal shape crystals. The porosity in film reaches to its minimum value.

![SEM images of PbS films A, B, C, D and E showing morphology evolution and grow that as mentioned deposition temperatures](image)

#### 3.4. Optical studies

Optical properties of the deposited films were determined with the help of their diffused reflectance graphs in the range of 1500nm to 3000nm, taken by using UV-3600 spectrophotometer. The diffused reflectance data was used to calculate absorptivity, and band gap by using Kubalka Munk function i.e.

\[
F[R] = \frac{(1-R)^2}{2R}
\]

Where \(F[R]\) denotes absorptivity i.e. \(\alpha^2\), for direct band gap materials \(n=2\). Plot of \(\alpha^2\) versus energy gives the band gap of materials as shown in Figure 5.
These graphs show that optical band gap is sensitive to deposition temperature. The band gap of PbS films decreases from 0.649eV to 0.636eV while going from 30°C to 100°C. The band gap varies with increasing grain size, although the variation is not as high as observed by Wang et al. [20]. This can be attributed to larger grain size, as the grains grow bigger; decrease in band gap becomes less effective. The value of F[R]^2 i.e. absorptivity^2 also increased with increasing deposition temperature and time as shown in Figure 6.
4. Conclusion

Structural and optical properties were determined and correlated with the different deposition temperatures. Some conclusions are made on the basis of the experimental data.

I. Growth of PbS films is greatly affected by deposition temperature. Films are amorphous at the start of growth but as the temperature increases and films become thick the crystallinity also increases and we get well defined peaks of nanocrystalline PbS films in XRD patterns.

II. AFM and SEM results revealed that temperature plays significant role in film growth and grain modification. The grains are spherical in start with a size of about 100nm. As the time passes and temperature rises, grains diffuse into larger pyramidal shape that are up to 400-500nm size. The surface roughness also increases with temperature, many facets are observed in AFM and SEM scans.

III. Optical studies revealed that on increasing deposition temperature there is a decrease in the optical band gap of PbS thin films as a result of increasing grain size. Absorptivity of films is also enhanced as a result of increased deposition temperature.

5. References

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