ABSTRACT

Nanotechnology has been attracting massive attention from the researchers, industrialist and government on the belief that it has the power to transform the lives of common masses by the application of the exotic properties of nanomaterials. Large number of research works have been devoted to the semiconducting nanomaterials for their potential applications in optoelectronics by way of their size tunable optical and electrical properties. In this arena, PbS has been considered promising because of its low band gap of 0.41 eV at 300 K and high Bohr exciton radius of 18 nm. The relatively high value of the Bohr exciton radius means that the quantum size effect is very likely in this material and the low value of band gap implies that it can find new roles in optoelectronics by offering huge possibility of band gap tuning. Historically, PbS was used in IR detectors owing to its low band gap but now, quantum confinement enabled broadening of band gap makes it a promising candidate as solar cell absorber.

Chemical bath deposition (CBD) is very effective in fabricating nanostructured thin film. It has the additional advantages of cost effectiveness and simplicity with large area deposition. Moreover, the properties of the films can be changed simply by changing any deposition parameter, addition of complexing agent/inhibitors and impurities.

Considering all these aspects, experimental studies on synthesis and characterization of PbS nanocrystalline films by CBD methods have been undertaken. Based on the evaluated properties of the films deposited under various conditions, attempt have been made to suggest possible applications in optoelectronics.

The thesis has been organized into six chapters which are briefly described

below chapter wise.

CHAPTER 1: GENERAL INTRODUCTION AND MOTIVATION

In this chapter, a general introduction on nanotechnology, thin film, chemical bath deposition method and lead sulfide have been provided. A brief review on the PbS thin film deposited by CBD method is also presented. The aims and objectives of the thesis have been defined and the motivation of the work has been discussed. Lastly, the safety aspects of PbS have been discussed.

CHAPTER 2: PREPARATION OF THE FILMS AND MEASUREMENT OF PROPERTIES

In this chapter, the methods of preparation of the films and measurement of properties have been discussed. This chapter discusses the principles of basic characterization techniques – x ray diffraction, scanning electron microscopy, transmission electron microscopy, energy dispersive x ray spectroscopy, Raman spectroscopy, UV- visible- NIR spectrophotometry, photoluminescence spectrometry and measurement of conductivity. The measurement of thickness of the films by gravimetric method has also been discussed.

CHAPTER 3: STUDY OF THE STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF PbS NANOCRYSTALLINE FILMS PREPARED UNDER VARIOUS (i) DEPOSITION TEMPERATURES, (ii)CONCENTRATIONS OF LEAD ACETATE AND (iii) pH

This chapter discusses the variation of the structural, optical and electrical properties of the PbS nanocrystalline films with the variations of (i) deposition temperature, (ii) concentration of lead acetate and (iii) pH .

(i) The films were deposited by reaction between 0.4M $Pb(CH_3COO)_2.3H_2O$ complexed by 1M triethanolamine (TEA) and 1M $SC(NH_2)_2$ at pH=12. The deposition temperatures selected were 30º ,40º , 50º , 64º and 70º C. The XRD pattern revealed that the crystalline PbS formation occured only from 50ºC. The crystallite sizes were found to increase from 35.79 nm to 42.67nm and the microstrains were found to decrease with the increase of deposition temperature from 50ºC to 70ºC. The SEM image of the film deposited at 64ºC has shown that the the substrate is uniformly covered with faceted grains with varying sizes. This film was observed to be S rich.The optical absorbances in the wavelength range of 250-800 nm were found to increase with the increase of deposition temperatures. The direct band gaps were obtained as 1.74, 1.67 and 1.66 eV and the Urbach energies as 0.70, 0.75 and 0.76 eV for the films deposited at 50º , 64º and 70º C respectively. The conductivities were obtained as $3.56x10^{-7}$, 2.26 $x10^{-6}$ and $3.89x10^{-6}$ $(\Omega cm)^{-1}$ for the films deposited at 50º , 64º and 70º C respectively.

(ii) For studying the effect of concentrations of $Pb(CH_3COO)_2.3H_2O$ the solutions of $Pb(CH_3COO)_2.3H_2O$ of eight different concentrations - 0.5M, 0.6M, 0.7M, 0.8M, 0.9M, 1.0M , 1.1M and 1.2M were prepared in deionized water. These solutions were complexed by 1M TEA and made to react with 1M $SC(NH_2)_2$ at pH=11 and deposition temperature 60ºC, to yield PbS films on glass substrates. It was observed that the film deposited with 0.5 M $Pb(CH_3COO)_2.3H_2O$ yielded a stoichiometric film with largest crystallites (37.43 nm), least microstrain, dislocation density and Urbach energy. This film was highly absorbing with band gap of 1.4 eV and conductivity of 1.88x 10^{-3} $(\Omega cm)^{-1}$. In terms of stoichiometry, crystallinity, optical absorption and conductivity, the best film was obtained at 0.5 M concentration of $Pb(CH_3COO)_2.3H_2O$.

(iii) For studying the effect of pH, the reactions between 0.5M $Pb(CH_3COO)_2.3H_2O$ complexed by 1M TEA and 1M $SC(NH_2)_2$ were carried out at four different values of pH = 8.22, 9.11, 10.70 and 12.46. The deposition was carried out at room temperature (30ºC). With the increase of pH, the crystallite size increased with the reduction of microstrain and Urbach energy, the direct band gap decreased, and conductivity improved with the maximum value being $5.08x10^{-3}$ $(\Omega cm)^{-1}$.

CHAPTER 4: STUDY OF THE STRUCTURAL AND OPTICAL PROPERTIES OF THE PbS NANOCRYSTALLINE FILMS PREPARED UNDER THE EFFECT OF Fe AND Zn IMPURITIES

In this chapter, effects of Zn and Fe impurities on the structural and optical properties of chemically prepared PbS nanocrystalline films are discussed. It was observed that doping deteriorated crystallinity and caused unusual lattice expansion. Adhesion became very poor in the Fe doped film. Due to reduced thickness, the doped films became transparent, particularly in the NIR region. The direct (indirect) band gaps were obtained as 1.55 (0.51), 1.3 (0.6) and 2.2 (0.51) eV respectively in the undoped, Zn doped and the Fe doped films. The Urbach energies were found to be 25% higher in the Fe doped film and 73% higher in the Zn doped film in comparison to the undoped film. The photoluminescence at 440 nm have reduced its intensity in the doped films and became insignificant in the Fe doped film.

CHAPTER 5: EFFECT OF TRIETHANOLAMINE (TEA) ON THE STRUCTURAL, OPTICAL AND ELECTRICAL PROPERTIES OF PbS NANOCRYSTALLINE FILMS

To discuss the effect of triethanolamine (TEA), this chapter has been divided into three parts-

(i) In the first part, we discuss the effect of TEA with respect to the deposition time. Films were deposited in two baths- one containing TEA of concentration 1M and the other without TEA. The sources of Pb^{2+} and S^{2-} respectively were $Pb(CH_3COO)_2.3H_2O$ and $SC(NH_2)_2$. The reactions were allowed to take place at pH=13 and deposition temperature 65°C. Substrates were removed from the baths after 0.25 h, 0.50 h, 1 h, 2 h and 3 h. It was observed that the presence of TEA slowed down the formation of crystalline PbS, increased the terminal thickness, impacted the orientation of crystallites, reduced the band gap and conductivity while increasing the Urbach energy.

(ii) In the second part, effect of TEA on the properties of the PbS films prepared from lead acetate bath at room temperature has been discussed. Here also, two baths have been prepared- one containing 1M TEA and the other without it. Other chemicals, their concentrations, sequences of addition and deposition parameters were same except that the deposition had been carried out at room temperature (29°C) for six hours. The films from both the baths developed into nearly the same thickness of 2 μm. It was observed that the film deposited without using TEA was superior in crystallinity and much better in conductivity which is (i.e. conductivity) about 4000 times larger than the TEA complexed film.

(iii) Films were deposited in four baths, three of which containing TEA of concentrations- 0.5M, 1M and 1.5M respectively and the fourth one containing no TEA. The sources of Pb^{2+} and S^{2-} respectively were $Pb(NO_3)_2$ and $SC(NH_2)_2$ .The deposition took place at pH=12 and at room temperature (30ºC) for 3 hours. The structural, optical and electrical properties of these films have been compared with. The film with the best crystallinity, optical absorption property and conductivity had been observed to be that film deposited in the bath containing no TEA.

CHAPTER 6: POSSIBLE APPLICATIONS OF PREPARED FILMS IN OPTOELECTRONICS: SOME SUGGESTIONS

In this chapter, possible applications of suitable films in optoelectronics (as absorber in solar cell) are suggested.

CHAPTER 7: GENERAL CONCLUSIONS AND SCOPE FOR FUTURE RESEARCH

This chapter presents general conclusions on the findings of the present study, the limitations of the thesis and scope for future works.