PHYSICAL PROPERTIES OF SPRAY PYROLYTICALLY Li DOPED PbS THIN FILMS

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Lithium (Li) doped Lead sulfide (PbS) thin films were prepared by a home built spray pyrolysis method. The starting precursor solution containing of Lead acetate, Thiourea and Lithium were sprayed on to the glass substrate at 493K. The concentration of Lithium in the precursor solution of Lead Sulphide was varied from 0.001M to 0.003M. The resultant films were characterized by XRD, SEM and UV– visible spectroscopy. The structural properties of as deposited films were characterized by X-ray diffraction. XRD patterns indicated the presence of multi-phase cubic PbS with preferential orientation along (111) plane. SEM analysis revealed that the film was polycrystalline nature and the crystallinity improves with the concentration of the dopant. Optical absorbance in visible region of the film increases with dopant concentration. The transmittance and reflectance were calculated. The optical band gaps of 0.001M of Li, 0.002M of Li and 0.003M of Li films were found to be 2.1, 1.9 and 1.4 eV respectively.

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1. Introduction

Polycrystalline PbS thin films is an important direct narrow gap semiconductor material very suitable for infrared detection for solar-control coatings [1-6] .These films can be obtained by several methods [7,8]. Among these different techniques, spray technique is advantageous on account of the low cost and its suitability for forming large area thin films. PbS thin films deposited by spray pyrolysis are normally found to narrow band gap (Eg=0.4eV). In addition, its relatively large Bohr exciton radius (~18nm) makes it an attractive material for fabrication of quantum confinement structures. The present work is to prepare the doped lead sulfide films by spray pyrolysis technique in different molarities.

2. Experimental

Lead sulfide thin film doped with Lithium were prepared from the precursor solution by dissolving the of lead acetate, thiourea and lithium acetate in triple distilled water. Then the aqueous solution was sprayed on the preheated substrate by spray pyrolysis method. Films were prepared at temperature 493K. Compressed dry air at a pressure of 12 kg/cm^2 from an air compressor and spray rate of the solution was maintained at 3ml/min. Different films were prepared by varying the molarity of the Lithium compound such as 0.001M, 0.002M and 0.003M and keeping the molarity of the lead acetate as constant such as 0.01M in the aqueous solution. Films were deposited on the glass substrate by maintaining the temperature at 220 ^{o}C. The

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deposited films were then annealed at 280 ^{o}C for an hour to form homogeneous film. X-ray diffraction patterns were identified at room temperature by using (RIGAKU- model RAD II A) with CuKα radiation (1.5406Å) where other radiations are suppressed using Ni filter. The data were recorded at a scan rate of 0.2^0 /min and in the range of $20^0<2\theta<80^0$. A computer controlled ELICO make (SL 159 UV - VIS) Spectrophotometer was used to obtain optical properties of Lithium doped Lead sulfide films over a wide wavelength range of 400 nm to 1000 nm. Surface morphology was studied using cold field emission of SEM (JEOL, JSM 6701F, Japan). Prior to the observation, using an auto sputter fine coater (JFC 1600, JEOL Japan) about 50 Å gold was sputtered on the thin film surface for better contrast and to avoid charge accumulation. The thickness of the films were determined gravimetric technique and it is found to be 825, 925 and 1043 nm of 0.001M, 0.002M and 0.003M of lithium respectively.

3. Results and Discussion

3.1. Structural studies

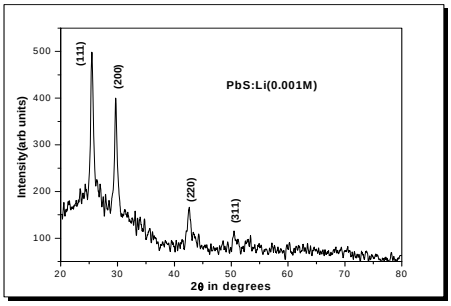

Fig.(1a). XRD patterns of PbS:Li (0.001) films

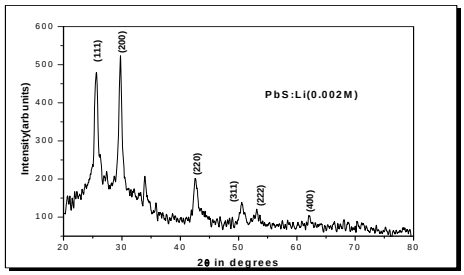

Fig.(1b). XRD patterns of PbS:Li (0.002) films

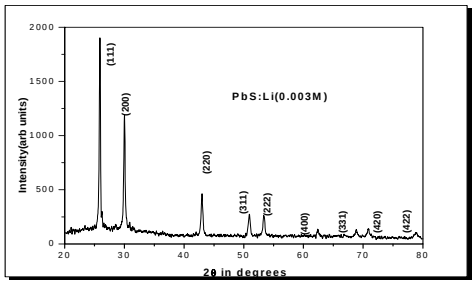

Fig.(1c). XRD patterns of PbS:Li (0.003) films

XRD spectra of lithium doped lead sulfide films are shown in Fig.(1a), (1b) and (1c). These results indicate that all of the films have a polycrystalline nature. All the peaks in the diffraction patterns correspond to the structure of lead sulfide, which are found to be good

agreement with the standard ASTM data. The XRD pattern of the prepared films shows crystalline in nature. For these films, main peaks are assigned to (111), (200) and (220) planes at 2θ = 25.6˚, 30.1˚ and 43.01˚ respectively with single phase of PbS. The presence of the other peaks such as (311), (222), (400), (331) and (420) was also identified with lower intensities. On Li doping at 220˚C, in the concentration of 0.001M only the two weak peaks (220) and (311) are detected. On this film the main peak (111) plane was growth in higher intensity. On increasing the Li doping concentration of 0.002M, other two weak peaks (222) and (400) are identified. But the main peak (111) plane are decrease in intensity than (200) plane. It is due to the replacement of PbS^{+4} ions with lithium ions in the lattice of lithium doped lead sulfide films. This process continues to increasing the Li doping concentration of 0.003M, other two weak peaks (331) and (420) are identified. The relative stronger intensity of the peak indicates preferential (111) orientation of the film. The average grain size for the films can be calculated by using the equation,

$$D = \frac{k\lambda}{\beta \cos \theta}$$

Where k =0.94 the shape factor constant, λ is the wavelength of X-rays (1.5406 Å for CuKα), θ is the Bragg's angle and β is the instrumental broadening corrected full width at half maximum of the prominent peaks in radian. The grain size found to be 23, 31 and 39nm of 0.001, 0.002 and 0.003M of Li concentration respectively.

3.2. Optical studies

Spectral absorbance of Lead Sulfide doped with different molarities of Lithium (0.001M, 0.002M, and 0.003M) prepared at 493K is displayed in Fig.2. It reveals that the absorbance of the film decreases gradually with increase in wavelength.

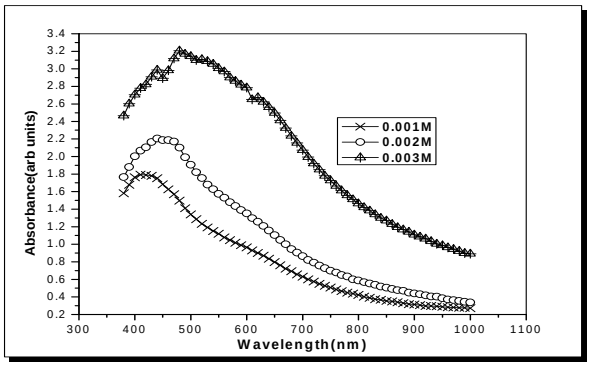

Fig.(2). Absorbance of PbS:Li thin films

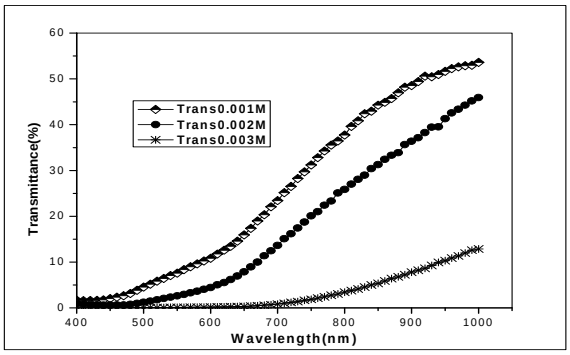

Fig.(3). Transmittance of PbS:Li thin films

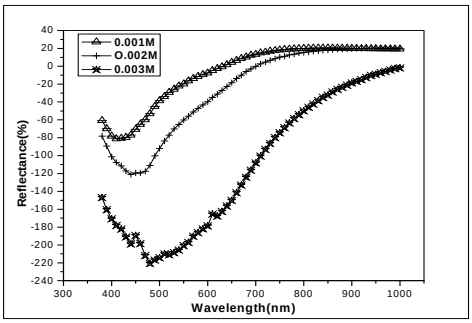

Fig.(4). Reflectance of PbS:Li thin films

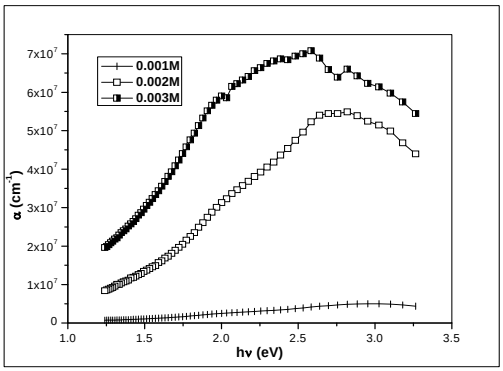

Fig.(5). Alpha Vs Photon energy of PbS:Li thin films

It is clear from the graph that, in the visible region there is no significant change in band edge by increasing the molarity of the dopant in the deposited film. This implies that the basic crystal structure is not changed [9]. The overall increase in absorbance with increase in molarity may be associated with the increase in film thickness.

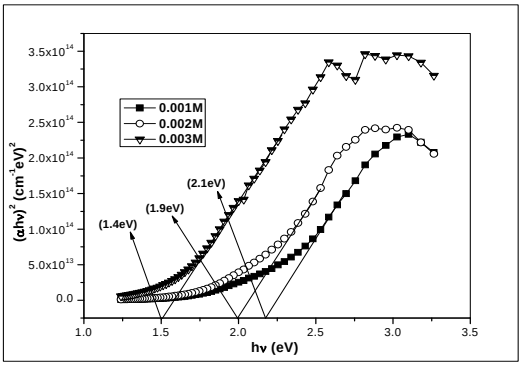

Fig.(6). Band gap energy of PbS:Li thin films

This is because of the reason that in case of thicker films more atoms are present in the film so more states will be available for the photons to be absorbed [10]. For all doping molarities of Lithium optical absorbance is found to be least in the visible region. Therefore, the films are measured to be a non absorbing film on non absorbing substrate. Transmittance spectra of the deposited film are as shown in Fig.3. The plot shows a sharp rise in transmittance near the band edge attributed to the good crystallinity of the film [11]. Transmittance spectra of as deposited films show a narrow range of variation with the increase in dopant molarity. It is felt that the doping of Lithium in Lead Sulfide may lead to increase in the degenerate (metallic) nature of the

films, which results in light absorption. The transmittance of the film is also influenced by a number of minor effects which include surface roughness and optical inhomogeneous in the direction normal to the film surface.

The variation in the reflectance with wavelength of the film shows an average of 10% reflectance in all region of the visible spectrum is shown in Fig.4. The reflectance spectra showed similar trends as absorbance curves, films prepared from higher solution molarity shows higher reflectance. This is consistence with the visual appearance of the films surfaces particularly for larger thickness. The absorption co-efficient (α) is calculated using Lambert's law [12]. The absorption co-efficient (α) is found to be in the order of $10^7 cm^{-1}$ is shown in Fig.5. The high α value ($>10^4$) shows that the transition corresponds to a direct electronic transition and the properties of this state are important since they are responsible for electrical conduction [13]. The optical band gap Eg was calculated using Tauc's plot $(\alpha h\nu)^2$ Vs hν. The photon energy at the point where $(\alpha h\nu)^2$ is zero represents Eg, which is determined by extrapolation of the linear portion of the curve. It was observed that increase in molarity of the dopant in the precursor solution yields slight shrinkage in optical band gap (2.1, 1.9 and 1.4 eV) shown in Fig.6. Here, it is observed that band gap decreases with increasing film thickness and in turn the molarity of the dopant. In case of much thicker films these allowed states could well merged with the conduction band resulting in the reduction of the energy band gap [10]. Generally, optical band gap widening and shrinkage was attributed to Moss-Burstein shift [14, 15] the optical band gap widening is due to optical band filling effect. The optical shrinkage is due to the electron - electron interaction at higher carrier concentration.

3.3 SEM Analysis

Fig.6a, 6b, and 6c show that the surface of films was quiet uniform although some pinholes are observed. The grain size is found to be of the order of 15-50 nm, which are in good agreement with the values obtained from the xrd studies.

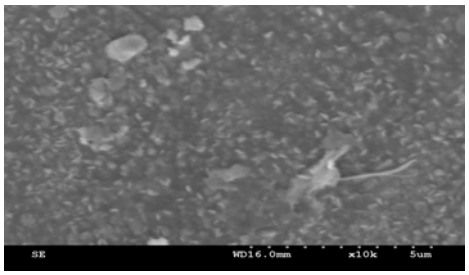

Fig.(6a). SE image of PbS:Li (0.001) film

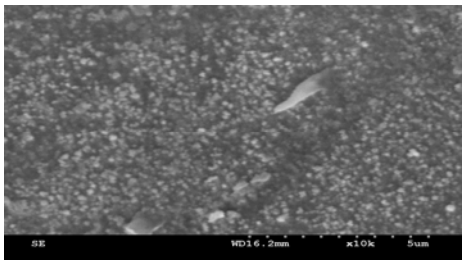

Fig.(6b). SE image of PbS:Li (0.002) film

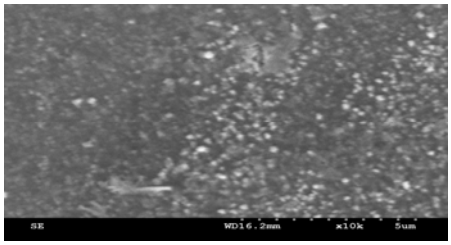

Fig.(6c). SE image of PbS:Li (0.003) film.

4.Conclusions

Lithium (Li) doped Lead sulfide (PbS) thin films were prepared by a home built spray pyrolysis methodby three different molarities. XRD patterns indicated the presence of multi-phase cubic PbS with preferential orientation along (111) plane. SEM analysis revealed that the film was polycrystalline nature and the crystallinity improves with the concentration of the dopant. Optical absorbance in visible region of the film increases with dopant concentration. The transmittance and reflectance were calculated. The optical band gaps of 0.001M of Li, 0.002M of Li and 0.003M of Li films were found to be 2.1, 1.9 and 1.4 eV respectively.

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