Enhancement of photosensitivity of thermally evaporated crystalline PbS thin films by low energy oxygen ions implantation

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Abstract
This study presents the effect of low energy (120 KeV) O-ions implantation on the photosensitivity of PbS thin films by vacuum thermal evaporator (VTE). The crystallite size (D) of PbS films decreased from 32.8 nm to 17.4 nm and the bandgap (Eg) increased from 1.61 eV to 1.76 eV as the fluence increased from 0.5 × 10^16 ions cm⁻² to 1.5 × 10^16 ions cm⁻². The PL spectra of O-ions implanted PbS thin films showed a dominant peak at 381 nm regardless the fluence of implantation. The photocurrent sharply increased by the implantation of O-ions (0.5 × 10^16 ions cm⁻²) due to the creation of ‘shallow traps’ in the forbidden gap of PbS thin films under illumination of visible light (100 mW cm⁻²). The highest photosensitivity of O-ions implanted PbS thin films was observed due to the creation of proper traps for the photoconduction for the particular dose of 0.5 × 10^16 ions cm⁻².

1. Introduction

Lead sulphide (PbS) has been paid the attention for its technological relevance in the field of photosensitive devices [1, 2]. The photosensitive nature of PbS thin films can be used for the development of low-cost IR active burglar sensor alarms and highly sensitive detectors for missile technology. PbS has the large excitonic Bohr radius of 18 nm, which results in the strong quantum confinement of both electrons and holes of nano-sized materials [3]. The bandgap of nanocrystalline PbS can be tuned by varying the particle size according to the effective mass approximation [4]. The literature survey reveals that the bandgap of PbS thin films can be tuned by varying the particle size from 0.37 to 2.12 eV [5–8]. For deposition of PbS thin films, various methods have been used such as chemical bath deposition (CBD) [9], chemical vapor deposition (CVD) [10], vacuum thermal evaporation (VTE) [11], spray pyrolysis (SP) [12], RF sputtering [13], and atomic layer deposition (ALD) [13]. Among these deposition techniques, the VTE technique can be preferred due to ease of controlling the microstructure, stoichiometry and adhesion to the substrate by varying the deposition parameters such as the height of substrates from the crucible, substrate temperature and the ambient atmosphere during the deposition.

The doping of oxygen in stoichiometric PbS thin films leads to increase the hole concentration, which improves the photo-conduction. The oxygen concentration in PbS can be increased by sintering in the oxygen ambient or oxygen dopant during the growth and deposition or the implantation of high/low energy of oxygen ions [14]. There are some limitations of PbS thin films for annealing in oxygen ambient or the doping of oxygen during growth due to the complex morphology and the alteration of physical properties [15]. The alternate method has been considered for the oxygen ions implantation from the specific energy beam, where the oxygen can be implanted near the grain boundaries, which reduces the height of the potential barriers and improves the photosensitivity of PbS thin films [15–17].
Therefore, the low/high oxygen-ion implantation suggests a number of technological advantages for the trapping mode of photoconductors, that is, the foreign ions effectively incorporated in the host lattice by the implantation, which created collisions of incident ions and developed defects interstitials, and vacancies [16, 18, 19]. The penetration depth of ions depends not only on the energy but also upon the mass of ions and the atomic mass of the target [20, 21]. Oxygen can be used as the dopant from the implantation, which produces the sensitization of PbS thin films by forming photoconductive traps [22–24]. Oxygen was considered as the established dopant to enhance the photoconductivity of PbS thin films [15, 19, 25]. Popescu et al investigated the enhancement of photosensitivity (5.51–15.72 times) because of oxygen-ions electronegativity [26]. Ison et al demonstrated that oxygen increased the work function of PbS thin films by the implantation of high energy ions beam [27]. Despite the extensive study of PbS thin films for photo/IR detectors, the fewer understanding and analysis for the growth of films and low energy implantation dose of O-ions are available in the literature. Therefore, the incorporation of oxygen-ions into the lattice of PbS thin films by the low energy oxygen-ions beam implantation would help to establish the optimum beam specifications suitable for the best photoconductivity and photosensitivity.

2. Experimental

2.1. Deposition of PbS thin films

PbS thin films were deposited on sodalime/borosilicate glass substrates by the vacuum thermal evaporation (VTE) technique at room temperature. The highly pure PbS powder (99.9%) was purchased from Sigma Ardrich, India and used without further purification. Ultrasonically cleaned glass substrates were loaded on the substrate holder normal to the molybdenum (Mo) boat with the height of 17 cm. The PbS powder was put on the mouthed Mo boat for the evaporation in vacuum 1 × 10^{-6} torr. The heating of Mo boat was controlled by the voltage adjustment controller.

2.2. Low energy O-ions implantation on PbS thin films

The energy of O-ions beam for the implantation was manipulated with the consideration of PbS stoichiometry and the material properties. The amount of low energy ions beam (low energy ions beam facility: LEIBF) was determined with the help of Stopping Range of Ions in Matter (SRIM) calculation for PbS thin films of thickness of 350 nm measured by Rutherford backscattering spectrometry (RBS). The calculated value of the energy beam of oxygen ions was fixed to be 120 KeV. The oxygen ion beam was focused at 90° with the accelerating voltage of 105 kV under the vacuum of 1 × 10^{-6} torr. The value of fluence for O-ions implantation in PbS thin films was calculated by using the following formula:

\[ f (\text{ions/cm}^2) = \frac{25 \times 10^9 \times I(nA)/q}{A (\text{cm}^2)} \]  

where, \( f \) is the fluence ions per cm^2 to be implanted, \( A \) is the area, \( I \) is the current. The thickness of as-deposited PbS thin films was determined by RBS analysis. The experimental conditions for the RBS analysis are specified, that is, the source of beam: He^+; \( E_o = 1.7 \text{ MeV} \); Scattering angle \( \theta = 14^\circ \); Normal incidence of the beam, Geometry: General. Rutherford universal manipulation program (RUMP) code simulation was used to analyze the collected spectra [28]. The thickness \( t \) of as-deposited films related to the areal density (AD) measured by RBS through the film density ‘d’ is as follows:

\[ t = \frac{AD}{d} \]  

The thickness of as-deposited PbS thin films was found to be ∼350 nm determined by RBS.

2.3. Characterization of deposited and O-ions implanted PbS thin films

The crystalline behavior of as-deposited and O-ions implanted PbS thin films was determined from the XRD (Bruker AXS, D8 Advance) pattern. The crystallite size and strain of films were calculated from XRD peak profile analysis. Microscopic images were taken from the field emission-scanning electron microscopy (FE-SEM) at room temperature. The optical absorption spectra of as-deposited and O-ions implanted PbS thin films were measured at room temperature (Hitachi-U-3300 UV–vis Spectrophotometer). The bandgap of as-deposited and oxygen ions implanted PbS thin films was calculated from Tauc’s plot. The PL spectra of as-deposited and oxygen ions implanted PbS thin films was taken at room temperature (F-900, Edinburgh Instruments). For the electrical measurements, a pair of silver electrodes with a dimension of 5 mm^2 were prepared on as-deposited and oxygen ions implanted PbS thin films. The current–voltage (I–V) characteristics were measured in the dark and under the illumination of visible light (100 mW cm^{-2}) with a bias of −5 to +5 V.
3. Results and discussions

Figure 1 shows the XRD pattern of as-deposited and O-ions implanted PbS thin films with respect to the fluence of implantation of amounts $0.5 \times 10^{16}$ ions cm$^{-2}$, $1.0 \times 10^{16}$ ions cm$^{-2}$ and $1.5 \times 10^{16}$ ions cm$^{-2}$, respectively. The diffraction peaks of PbS thin films were observed at 26°, 30°, 43°, 51° and 62° corresponding to planes (111), (200), (220), (311), and (400), respectively. All diffraction peaks were detected in all samples regardless of O-ions implantation, which confirmed the cubic phase of PbS thin films (JCPDS card number: 05-05920) [29]. The dominant peak (200) of PbS films was observed at 30° ($2\theta$) in all samples. While the XRD peak intensity of O-ions implanted PbS thin films deteriorated due to the formation of point defects, defect clusters, formation of additional grain boundaries and partial amorphization [30–32].

The crystallite size, $D$, of as-deposited and O-ions implanted PbS thin films were calculated from the Debye–Scherrer’s formula [33]:

$$D = \frac{0.9\lambda}{\beta \cos \theta}$$  \hspace{1cm} (3)

where, $\lambda$ is the wavelength of x-ray of CuK$_\alpha$ (0.154 056 nm) radiation and $\beta$ is the FWHM of the peak at an angle $\theta$. The developed strain in O-ions implanted PbS thin films was calculated from the following formula [3]:

$$\varepsilon = \frac{\beta}{4 \tan \theta}$$ \hspace{1cm} (4)

where, $\beta$ is the FWHM of the diffracted peak. Figure 2 shows the variation of FWHM, crystallite size ($D$), and the strain ($\varepsilon$) of as-deposited and O-ions implanted PbS thin films. The crystallite size of as-deposited PbS thin films was observed to be 32.8 nm. Whereas, the 'D' size of O-ions implanted PbS thin films decreased from 21.3 nm to 17.4 nm as the fluence increased from $0.5 \times 10^{16}$ ions cm$^{-2}$ to $1.5 \times 10^{16}$ ions cm$^{-2}$, respectively. The 'D' decreased with respect to the fluence of O-ions implantation due to increase in the FWHM of the dominant peak (200).

The strain of as-deposited PbS thin films was observed to be $4.3 \times 10^{-3}$. Whereas, the strain of O-ions implanted PbS thin films was observed to be $6.2 \times 10^{-3}$, $7.2 \times 10^{-3}$ and $7.6 \times 10^{-3}$ corresponding to the implantation dose of $0.5 \times 10^{16}$ ions cm$^{-2}$, $1.0 \times 10^{16}$ ions cm$^{-2}$, and $1.5 \times 10^{16}$ ions cm$^{-2}$, respectively. The strain of PbS thin films increased as the fluence of O-ions implantation dose increased. The decreasing crystallite

![Figure 1. XRD patterns of as-deposited and O-ions implanted PbS thin films with respect to the implantation dose of $0.5 \times 10^{16}$ ions cm$^{-2}$, $1.0 \times 10^{16}$ ions cm$^{-2}$ and $1.5 \times 10^{16}$ ions cm$^{-2}$.](image.png)
size and increasing the strain by implantation of O-ions dose might be transpired due to the formation of new grain boundaries and occupancy of oxygen. The dislocation density, \( \delta \), of O-ions implanted PbS thin films was determined by using the following formula [3]:

\[
\delta = \frac{1}{D^2}
\]  

(5)

where, \( D \) is the crystallite size. Figure 3 shows the variation of dislocation density versus O-ions implantation dose of as-deposited and O-ions implanted PbS thin films.

The \( \delta \) increased from 9.3 × 10^{-4} \text{ nm}^{-2} to 3.3 × 10^{-3} \text{ nm}^{-2} as the fluence increased from zero to 1.5 × 10^{16} \text{ ions cm}^{-2} indicated the falsification in lattice planes and augmented to change the strain in films. The increased dislocation density by increasing the fluence of O-ions in PbS thin films is attributed to the formation of additional grain boundaries and partial amorphization.

The superficial microstructures of as-deposited and O-ions implanted PbS thin films are shown in figures 4(a)–(d) with respect to the fluence of O-ions implantation dose of zero, 0.5 × 10^{16} \text{ ions cm}^{-2}, 1.0 × 10^{16} \text{ ions cm}^{-2}, 1.5 × 10^{16} \text{ ions cm}^{-2}, respectively. Microstructures of as-deposited and lowest fluence (0.5 × 10^{16} \text{ ions cm}^{-2}) of PbS thin films are almost similar grain boundaries and overall uniformly distributed (figures 4(a), (b)). While increasing the fluence from 1.0 × 10^{16} \text{ ions cm}^{-2} to 1.5 × 10^{16} \text{ ions cm}^{-2}, uneven microstructures were observed and increased the cavity at the grain boundaries due to the agglomeration of PbS molecules by the implantation. Even though, the additional grain boundaries were formed. For the highest O-ions implanted (1.5 × 10^{16} \text{ ions cm}^{-2}) PbS thin films, the rod-shaped grains with deeper voids were formed due to the formation of additional grain boundaries (figure 4(d)).
To understand the surface topography and the superficial roughness of as-deposited and O-ions implanted PbS thin films, the tapping mode of atomic force microscopy (AFM) measurements were conducted at room temperature. Figures 5(a)–(d) show the AFM images of as-deposited and O-ions implanted \((0.5 \times 10^{16} \text{ ions cm}^{-2}, 1.0 \times 10^{16} \text{ ions cm}^{-2} \text{ and } 1.5 \times 10^{16} \text{ ions cm}^{-2})\) PbS thin films, respectively. The corresponding histogram distribution of PbS thin films are given in figures 6(a)–(d), respectively. AFM images of all PbS thin films indicated the spherical shaped grains, which are distributed homogeneously over the entire surface. These clusters of spherically shaped grains with tightly packed structure possessing immense packing density have the progressive surface with exemplary columnar structure. These studies are revealed that there is a considerable change in the microstructure of as-deposited and O-ions implanted PbS thin films, which augmented the surface microscopic images (figure 4).

The surface roughness of PbS thin films was determined from the AFM measurements as shown in figure 7. The average surface roughness of PbS thin films decreased from 43.52 nm to 30.6 nm as O-ions implantation increased from zero to the fluence of \(0.5 \times 10^{16} \text{ ions cm}^{-2}\). While the average surface roughness of PbS thin films further increased from 30.6 nm to 40.4 nm as the amount of fluence increased from \(0.5 \times 10^{16} \text{ ions cm}^{-2}\) to \(1.5 \times 10^{16} \text{ ions cm}^{-2}\). The decreasing of \(D\) and increasing surface roughness of PbS thin films are expected due to increase the grain boundaries and formation of voids and agglomeration of grains.

Figure 8 shows the optical absorption spectra of as-deposited and O-ions implanted PbS thin films with respect to fluencies of zero, \(0.5 \times 10^{16} \text{ ions cm}^{-2}\), \(1.0 \times 10^{16} \text{ ions cm}^{-2}\), and \(1.5 \times 10^{16} \text{ ions cm}^{-2}\), respectively. The absorption spectra of as-deposited and O-ions implanted PbS thin films increased by increasing the fluence of O-ions. The blue shift in the absorption spectra of PbS thin films was observed due to the quantum confinement in nanocrystalline PbS thin films [34–36].

The absorption coefficients, \(\alpha\), of as-deposited and O-ions implanted PbS thin films were evaluated with the help of absorbance, \(A\), and the film thickness, \(t\), using the following formula [37]:

\[
\alpha = \frac{\ln(100)}{t} \frac{A}{C} \quad \text{cm}^{-1}
\]
The energy bandgap of as-deposited and O-ions implanted PbS thin films was determined from Tauc’s plot by the extrapolation of the linear portion of $(\alpha h\nu)^2$ versus the photon energy $(h\nu)$ \([38,39]\):

$$\alpha = 2.303 \times \frac{A}{\lambda}$$  \hspace{1cm} (6)

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$$(\alpha h\nu)^2 = A(h\nu - E_g)^n$$  \hspace{1cm} (7)

where, $\alpha$ is the absorption coefficient, $h\nu$ is the energy of incident photons, $E_g$ is the optical bandgap and $A$ is the proportionality constant and $n = 1/2$ for direct bandgap materials \([40]\).

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Figure 9 shows the Tauc’s plot for the bandgap of PbS thin films. The bandgap of as-deposited PbS thin films was observed to be 1.61 eV. Whereas, the bandgap of O-ions implanted PbS thin films increased from 1.65 eV to 1.76 eV as the fluence increased from $0.5 \times 10^{16}$ ions cm$^{-2}$ to $1.5 \times 10^{16}$ ions cm$^{-2}$. The blue shift in the bandgap of as-deposited and O-ions implanted PbS thin films was observed due to the quantum confinement effect, which can be explained by considering the condition like a particle-in-box, as the separation between the energy levels \([41]\). Thus, the increasing bandgap with respect to decreasing the crystallite size of PbS thin films is attributed towards lower the Bohr excitonic radius $(\alpha B)$, which is one of the most convincing characteristic in this material.

Figure 10 shows the PL spectra of as-deposited and O-ions implanted PbS thin films with respect to the fluence of O-ions implantation. The PL spectra showed the broad band emission in the range of 335 nm–600 nm. The highest PL peak point of as-deposited PbS thin film was observed at 372.6 nm, which is a higher emission wavelength than that of the excitation laser (325 nm). The peak position was shifted to 367.2 nm for all samples of O-ions implanted PbS thin films regardless the fluence of ions indicated the changes in the crystal structure. The additional Gaussian fitting peaks were observed at 394.9 nm and 437.8 nm for the fluence of $0.5 \times 10^{16}$ ions cm$^{-2}$. The Gaussian fitting peaks were observed at 397.3 nm and 434.7 nm for the higher fluence irradiation of $1.0 \times 10^{16}$ ions cm$^{-2}$ to $1.5 \times 10^{16}$ ions cm$^{-2}$. As the fluence of O-ions implantation increased, the PL intensity increased, that might be occurred due to the generation of defects by the O-ions implantation.
Figure 11 shows the time-resolved photoluminescence (TRPL) spectra of as-deposited and O-ions implanted PbS thin films with respect to fluencies of ions/cm². It was observed shorter for pure highly oriented crystal and longer for polycrystalline phase. The efficiency of the radiative recombination is strongly associated with the decay time of the particular transition. The defect density of the material was inversely proportional to the carrier lifetime. The effective carrier lifetime of O-ions implanted PbS thin film ($1.5 \times 10^{16}$ ions cm⁻²) was observed to be the longest. For the fluence of $0.5 \times 10^{16}$ ions cm⁻², the carrier lifetime was observed the shortest, which suggested the highest non-radiative recombination.

Figure 6. The histogram of PbS thin films (a) as-deposited, (b) $0.5 \times 10^{16}$ ions cm⁻², (c) $1.0 \times 10^{16}$ ions cm⁻², (d) $1.5 \times 10^{16}$ ions cm⁻² of O-ions implantation.

Figure 7. The variation of average surface roughness versus implantation dose of as-deposited and O-ions implanted PbS thin films.
Figures 12, 13 show the current-voltage (I-V) characteristics of as-deposited and O-ions implanted PbS thin film for the dark and under the illumination of the visible light (100 mW cm⁻²), respectively. The I–V characteristics of all PbS thin films were measured in the voltage range of −5 V to +5 V. To test the ohmic contacts, the co-planar silver electrodes were prepared at two ends of films. The dark current increased from $5.19 \times 10^{-5}$ to $7.13 \times 10^{-5}$ mA as the implantation dose increased from zero to $0.5 \times 10^{16}$ ions cm⁻² and then decreased from $6.43 \times 10^{-5}$ to $5.38 \times 10^{-5}$ mA as the implantation dose increased from $1.0 \times 10^{16}$ ions cm⁻² to $1.5 \times 10^{16}$ ions cm⁻². The photocurrent increased from $7.98 \times 10^{-5}$ to $1.41 \times 10^{-4}$ mA as the implantation dose increased from zero to $0.5 \times 10^{16}$ ions cm⁻² and then decreased to $1.01 \times 10^{-4}$ as the implantation dose increased to $1.5 \times 10^{16}$ ions cm⁻².

The variation of typical dark and photocurrent at 4 V of all PbS samples is shown in figure 14. The highest dark and photo current was observed at the particular sample with the fluence of $0.5 \times 10^{16}$ ions cm⁻² implantation, and further decreased the dark and photo current by increasing the O-ions implantation dose. The increasing dark and photocurrent with respect to O-ions implantation with a fluence of $0.5 \times 10^{16}$ ions cm⁻² was valued due to the alignment of crystallite size and reduced surface roughness.

Figure 15 shows the variation of resistance of all PbS thin films measured in the dark and under illumination of visible light. The least resistance in both cases of dark and under illumination was observed for O-ions implantation with a fluence of $0.5 \times 10^{16}$ ions cm⁻² sample and optimized the best performance. The doping of oxygen ions by the implantation created ‘shallow traps’, which located in the forbidden gap of PbS thin films.

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The created traps in PbS matrix was responsible to increase the photocurrent under the illumination of visible light. The 'trapping' of one or both of charge carriers (electron-hole pairs) created under the illumination, which facilitated for the movement of photoexcited charge carriers from valance band to the conduction band.

**Figure 10.** The PL spectra of as-deposited and O-ions implanted PbS thin films for different fluencies of implantation i.e. $0.5 \times 10^{16}$ ions cm$^{-2}$, $1.0 \times 10^{16}$ ions cm$^{-2}$ and $1.5 \times 10^{16}$ ions cm$^{-2}$.

**Figure 11.** TRPL spectra of as-deposited and O-ions implanted PbS thin films for different fluencies of implantation dose i.e. $0.5 \times 10^{16}$ ions cm$^{-2}$, $1.0 \times 10^{16}$ ions cm$^{-2}$ and $1.5 \times 10^{16}$ ions cm$^{-2}$. 

The created traps in PbS matrix was responsible to increase the photocurrent under the illumination of visible light. The 'trapping' of one or both of charge carriers (electron-hole pairs) created under the illumination, which facilitated for the movement of photoexcited charge carriers from valance band to the conduction band.
Therefore, the probability of the rate of recombination was reduced and the photoconduction process improved.

The photosensitivity of as-deposited and O-ions implanted PbS thin films was calculated by using the following formula [42, 43].

\[
S = \frac{I_{\text{light}} - I_{\text{dark}}}{I_{\text{dark}}}
\]  

(9)

Where \(I_{\text{dark}}\) is the current measured in the dark, and \(I_{\text{light}}\) is the current measured under the illumination of visible light of 100 mW cm\(^{-2}\).
Defects were produced in the grain boundaries and created some short-range stress or strain in the lattice, that affected the atomic displacements in the crystallites [44]. When O-ions were implanted into PbS lattices, they replaced some sulfur ions/atoms. Therefore, the interplaner spacing and lattice constants might not be uniform throughout the lattice and introduced the strain in the lattice. The induced lattice strains affected the electrical properties by affecting the flow of charge carriers. The induced strains might be expected to increase or decrease the electrical current due to mobile charge carriers in the lattice [45]. The increasing strains in PbS thin films by O-ions implantations is attributed to decrease the photocurrent due to the reduced electron mobility.

Figure 16 shows the sensitivity of PbS thin films measured at the particular voltage of 4 V with respect to O-ions implantation dose. The amount of sensitivity was calculated to be 53% for as-deposited PbS thin films. For O-ions implantation dose with the fluence of $0.5 \times 10^{16}$ ions cm$^{-2}$, the sensitivity increased to 96%. Further increasing O-ions implantation dose to $1.5 \times 10^{16}$ ions cm$^{-2}$, the sensitivity decreased to 25%. The highest photosensitivity of PbS thin films were observed for O-ions implantation dose of $0.5 \times 10^{16}$ ions cm$^{-2}$, which is attributed to the formation of proper traps for the photoconduction and reduction rates of recombination.
4. Conclusions

PbS thin films were deposited on glass substrates from the VTE and implanted O-ions using low energy (120 KeV) oxygen-ion beam. Microstructures and the corresponding histogram distribution of PbS thin films indicated the spherical grains distributed homogeneously over the entire surface. The decreasing crystallite size and increasing surface roughness of PbS thin films were observed due to the development of grain boundaries/voids and agglomeration of grains from O-ions implantation. The optical bandgap increased from 1.61 eV to 1.76 eV as O-ions implantation dose increased from zero to \(1.5 \times 10^{16}\) ions cm\(^{-2}\) owing to the quantum confinement effect. The highest dark and photocurrent of O-ions implanted (fluence of \(0.5 \times 10^{16}\) ions cm\(^{-2}\)) PbS thin films were achieved due to the alignment of crystallite size and reduced the surface roughness, that optimized the best performance. The maximum sensitivity of PbS thin films was appraised at 4 V for O-ions implantation dose of \(0.5 \times 10^{16}\) ions cm\(^{-2}\) due the development of proper traps for the photoconduction.

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