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Effect of annealing temperature on optical and electrical properties of lead sulfide thin films

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ABSTRACT

Lead sulfide (PbS) thin films with 150 nm thickness were prepared onto ultra-clean quartz substrate by the RF-sputtering deposition method. Deposited thin films of PbS were annealed at different temperatures 100 °C, 150 °C, 200 °C, 250 °C and 300 °C. X-ray diffraction pattern of thin films revealed that thin films crystallized at 150 °C. Crystalline thin films had cubic phase and rock salt structure. The average crystallite size of crystalline thin films was 22 nm, 28 nm and 29 nm for 150 °C, 200 °C and 250 °C respectively. From 150 °C to 250 °C increase in annealing temperature leads to increase in crystallite arrangement. FESEM images of thin films revealed that crystallite arrangement improved by increasing annealing temperature up to 250 °C. Increase in DC electrical conductivity by increasing temperature confirmed the semiconductor nature of crystalline thin films. Increase in dark current by increasing annealing temperature showed the effect of crystallite arrangement on carrier transport. Photosensitivity decreased by increasing annealing temperature for crystalline thin films that it was explained at the base of thermal quenching of photoconductivity and adsorption of oxygen at the surface of thin films that leads to the formation of PbO at higher temperatures.

1. Introduction

Lead sulfide (PbS), as one of the most important IV–VI group semiconductors, have attracted considerable attention in recent years. PbS has a small direct band gap (0.41 eV) [1,2]. The large excitation Bohr radius of PbS (i.e. 18 nm) [3,4], results in strong quantum confinement of both electrons and holes in nano-sized structure, so that the value of the band gap can be controlled by modifying particle size according to the effective mass model [5]. PbS crystallizes in the rock salt (NaCl) type (B1) structure at normal condition [6]. PbS has a very large dielectric constant (17.2) and thus a strong electrostatic screening, leading to a long carrier lifetime (63 μs) in intrinsic PbS [7].

In recent years, interest in the physical properties of PbS thin films has considerably increased. Preetha et al. [8] examined the influence of annealing on optical and electrical properties of PbS thin films. Xu et al. [9] have studied physical properties of PbS thin films that prepared at different reaction temperatures. Physical properties of lead sulfide colloidal quantum dot photodetector have been investigated by He et al. [10]. New effects can appear in the film states that are not observed in the bulk samples. Crystalline PbS thin films have shown good photoconductive properties [11]. These properties have been correlated with the synthesis method, thickness, composition and structure. PbS thin films have been the subject of considerable research due to their technological importance in crystalline forms as gas sensors [12], infrared radiation detectors [13,14] and solar cells [15–18]. PbS thin films usually exhibit a p-type conduction, and their direct band gap can be varied in a wide range up to 2.3 eV from the bulk value of 0.41 eV [4].

The oldest and most studied PbS thin film deposition method is chemical bath deposition (CBD) method. But films that prepared by this method may not be pure due to byproducts that are produced in the solution during chemical reaction between precursors. Also impurities that added to the chemical deposition solution for PbS thin films have considerable effects on the photosensitivity characteristics of thin films. An important limit in CBD is that thickness of the films is limited in this method. The final thickness usually is 300–500 nm. Therefore in order to get a film with a sufficient thickness (e.g. approximately 1 μm in IR detectors) several successive depositions must be done [19]. Because of these problems we used physical method for deposition. Due to low ionic dissociation of lead sulfide, physical deposition is better than chemical methods. In sputtering the target contains a large amount of desired material with high purity, so there are very few impurities in films. Sputtering films typically have better adhesion to the substrate than films that prepared by other physical methods. An important advantage of sputtering deposition is

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that even materials with very high melting point are easily sputtered while evaporation of these materials with other physical methods such as thermal evaporation or electron beam gun (EBG) evaporation is problematic or impossible. In this research PbS thin films with 150 nm thickness were prepared by RF-sputtering deposition method and effect of annealing temperature on electrical and optical properties of thin films were investigated.

2. Experimental

Good quality lead sulfide (PbS) with high purity 99.999%, deposited onto ultra-clean 1 cm × 1 cm quartz substrates by RF-sputtering deposition method, keeping the substrates at room temperature. Before deposition, quartz substrates were washed frequently in several steps by organic and acidic cleaning methods. Briefly, ethanol, acetone and a weak solution of ammonium hydroxide (NH_4OH) with hydrogen peroxide (H_2O_2) have been used in separate steps to remove metallic and organic contamination from the surface of quartz substrates. For acidic solutions an aqueous solution of HCl (6 wt%) and after that a mixture of HF and HNO_3 have been used to dissolve metal ions oxides and inorganic etch byproducts from the surface of quartz substrates. After each cleaning step deionized water was used for washing substrates. Then clean quartz substrates were put on the sample holder and were inserted in the chamber for deposition. The target of RF-sputtering was a cylindrical tablet of PbS with high purity (99.999%) with 3 in. diameter and 0.125 in. thickness. Thickness of thin films was 150 nm. Thickness of the films has been measured using quartz crystal thickness monitor. Deposited films were annealed at different temperatures from 100 °C to 300 °C and cooled down slowly for avoiding thermal shocking. The X-ray diffraction patterns were taken using a diffractometer Bruker D8 with Cu Kα (1.5418 Å) radiation. FESEM images of thin films were taken using field emission scanning electron microscope Mira 3-XMU. Optical measurements were examined at room temperature using a UV/VIS/NIR Perkin Elmer Lambda 950 spectrophotometer at wavelengths ranging from 300 nm to 3000 nm. In order to measure the electrical properties, PbS photodetector has been used. For PbS photodetector, devices were fabricated by deposition on pre-fabricated interdigitated electrodes. A pair of interdigitated electrodes was deposited by a lift-off process, consisting 10 nm Cr and 100 nm Au on quartz substrate with area 1 cm × 1 cm. Active area for electrical measurement was 18×10^{-6} m^2. The DC electrical measurements of the fabricated device were performed using a Keithly 610C electrometer. To avoid photoelectric effects, all the dark measurements were carried out in a dark room.

3. Result and discussion

3.1. Structure characterization

Fig. 1 shows X-ray diffraction (XDR) patterns of thin films after annealing at 100 °C, 150 °C, 200 °C, 250 °C and 300 °C for 2 h. XRD patterns reveal that for 100 °C thin film has amorphous structure and crystalline structure has been obtained at 150 °C. As it can be seen all the sharp diffraction peaks, (111), (200), (220), (311) and (420) confirmed cubic phase of PbS and referred to the cubic rock salt structure of crystalline PbS thin films. Also patterns showed that crystallite arrangement increases by increasing annealing temperature up to 250 °C and after that thermal vibrations of particles overcomes the crystallite arrangement at 300 °C and amorphous structure has been obtained. Values of calculated ratios $I_{(111)}/I_{(200)}$ and $I_{(220)}/I_{(200)}$ were smaller than unity that confirmed the preferred orientation of crystalline thin films is (200).

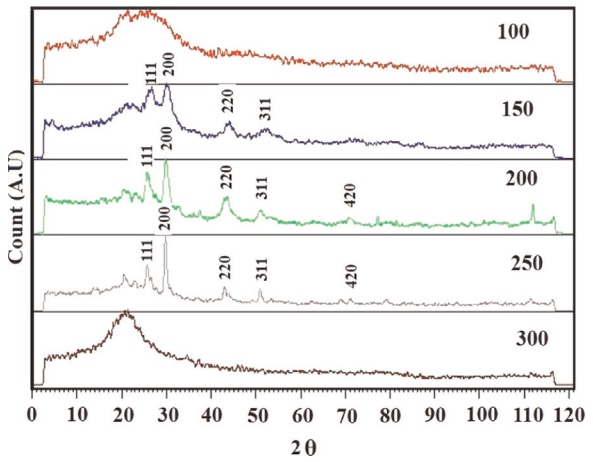

Fig. 1. X-ray diffraction patterns of PbS thin films annealed at 100 °C, 150 °C, 200 °C, 250 °C and 300 °C.

From 150 °C to 250 °C diffractions peak become sharper and preferred orientation of PbS thin films, (200), has been increased. Kumar et al. have observed (200) preferred orientation for vacuum evaporated PbS thin films [20].

The average crystallite size for crystalline thin films was determined from half width of major diffraction peak using Scherrer's formula.

$$D = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

That D is the crystallite diameter, k is a constant (shape factors, about 0.9 [21]) λ is the X-ray wavelength (1.5418 Å), β is the full width at the half maximum (FWHM) of the diffraction major line and θ is the diffraction angle. The average crystallite size for crystalline thin films was 22 nm, 28 nm and 29 nm for 150 °C, 200 °C and 250 °C respectively. These findings show that after 200 °C the given thermal energy leads to increase in crystallite arrangement rather than increase in crystallite size. Bruce et al. showed that increase in the annealing temperature beyond 200 °C does not have a considerable effect on average crystallite size [22]. Lattice constant of thin films were found using the following formula:

$$a = d_{hkl}\sqrt{h^2 + k^2 + l^2} \tag{2}$$

where a is lattice constant and d_{hkl} is interplanar crystal spacing at maximum peak (200) respectively and hkl are miller indices. Calculation of lattice constant revealed that lattice constant has been increased from 5.9712 Å to 5.9936 Å by increasing annealing temperature from 150 °C to 250 °C. Temperature dependence of the lattice constant describes by the following relation [23]:

$$a_T = 0.5868 + 2.164 \times 10^{-5}T + 2.305 \times 10^{-9}T^2 \tag{3}$$

So we can see that increase in lattice constant by increasing annealing temperature is in agreement with this relation. A similar result was observed by Sadovnikov et al. for lead sulfide nanofilms [23]. Deviation of lattice constant for crystalline thin films from PbS bulk value, a=5.9362 Å showed that particles in thin films are under strain due to deposition and heat treatment. Micro-strain of thin films calculated using Williamson–Hall formula.

$$\beta \cos\theta = \frac{D}{\lambda} + 4\varepsilon \sin\theta \tag{4}$$

that ε determines micro-strain in thin films. Fig. 2 shows variations of $\beta \cos\theta$ versus $\sin\theta$ for crystalline thin films. So