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Influencing the structural, microstructural and optical properties of PbS nanocrystalline thin films by Mg^{2+} doping

Abdelaziz Gassoumi [a, b, *], Safia Alleg [c], Najoua Kamoun-Turki [a]

[a] Laboratoire de Physique de la Matière Condensée, Faculté des Sciences de Tunis, Tunis -El Manar University, 2092 Tunis, Tunisia
[b] Department of Physics, College of Science, King Khalid University, P.O. Box 9004, Abha 61413, Saudi Arabia
[c] Laboratoire de Magnétisme et Spectroscopie des Solides (LM2S), Département de Physique, Université Badji Mokhtar, Annaba B.P. 12, Annaba, Algeria

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ABSTRACT

The aim of the current work is study the effect of Mg^{2+} doping (0–4%) on lead sulfide (PbS) thin films prepared using a simplest and cost effective chemical bath deposition (CBD) technique on glass substrates at ambient temperature and pressure. The effect of Mg^{2+} content on structural, morphological and optical properties of PbS thin films was studied. Powder X-ray diffraction and Atomic Force Microscopic results showed that all the deposited thin films exhibits both nanostructured and polycrystalline nature with *cubic structure*. The remarkable effect on optical transmittance and band gap was observed due to Mg^{2+} doping for all the films. The optical energy band gap values were found to enhance with increasing the Mg^{2+} content in PbS thin films. Further, the refractive index was calculated and a relationship with energy band gap was investigated and also the high frequency dielectric constant (ε_∞) was determined using the energy band gap values as a function of the Mg^{2+} content.

1. Introduction

In recent past, thin films are found to play a key role in hi-tech industries and can be used in the development of microelectronics, communication, computers, drugs, dye-sensitized solar cell, optical electronics, catalysis, all kinds of coating, in energy generation and conservation strategies. Semiconductors from II–VI group have been widely used in the fabrications of solid-state devices such as photo detectors, light emitting diodes etc. Lead sulfide (PbS) is one of the most important semiconductor from this group and possesses direct narrow band gap (0.41 eV), outstanding optoelectronic characteristics and have widespread applications in radioactivity detectors, and optical communication and information storage devices [1–9]. PbS has large excitation Bohr radius (18 nm), which results in excellent quantum confinement of both holes and electrons in nano-sized structure. Therefore, the value of optical band gap can be effortlessly controlled by amending the particle size and shape according to the effective mass model [10,11].

On the basis of their extraordinary applications and properties, the fabrication of high quality PbS thin films with new and cost effective routes. Are of soaring interest in past few decades, various kinds of techniques (chemical and physical) have been applied for the fabrication of good quality thin films of desired shaped and structure. The chemical routes are inexpensive to fabricate the thin films of finest quality. However, the physical methods are also found to be appropriate but highly expensive and energy consuming for the fabrication of uniform and good quality thin films [12]. A variety of techniques have been used for the deposition and characterization of PbS thin films, like: molecular-beam epitaxy [13,14] spray pyrolysis [15], microwave heating [16], electro deposition [17], successive ionic layer adsorption and reaction (SILAR) [18], and chemical bath deposition (CBD) [7–9]. Among all these techniques, the chemical bath deposition (CBD) method is found to have several advantages and has been used extensively for the deposition of thin films, because of its low temperature operating conditions, little cost, no necessity of sophisticated instruments, freedom to deposit the materials on a variety of substrates, large scale deposition areas, ability of tuning the properties of thin films by adjusting and controlling the experimental parameters and non-polluting properties [19]. Therefore, the aim of the current work is to fabricate good quality PbS and magnesium (Mg^{2+}) doped PbS thin films using the chemical bath deposition (CBD) method by controlling the different relevant parameters. Recently, Mg has been used as a dopant, because of its exceptional

* Corresponding author. Laboratoire de Physique de la Matière Condensée, Faculté des Sciences de Tunis, Tunis-El Manar University, 2092 Tunis, Tunisia
E-mail address: abdelaziz.gassoumi@gmail.com (A. Gassoumi).

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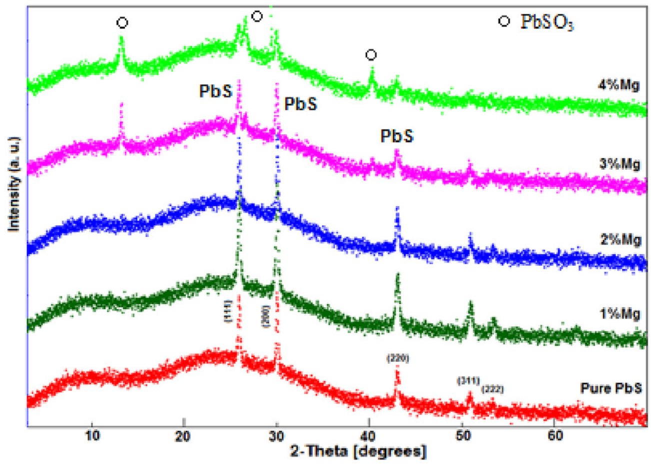

Fig. 1. XRD patterns of undoped and Mg^{2+} doped PbS thin films.

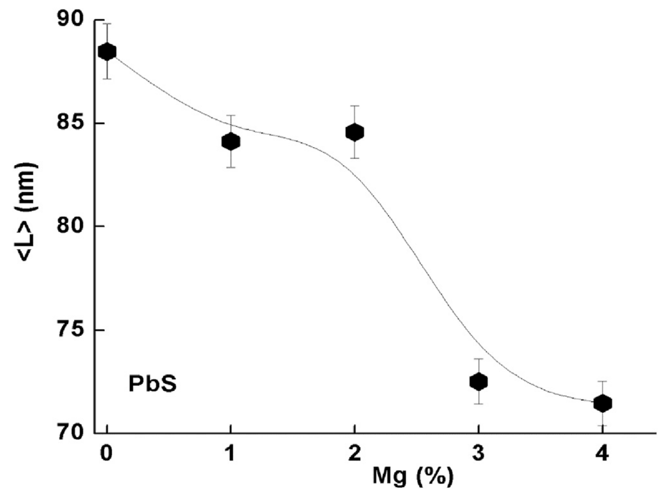

Fig. 2. Evolution of the crystallite size as a function of Mg^{2+} content.

characteristics, such as small ionic radius (0.066 nm) [20] and large activation energy [21]. The fabricated thin films were subjected to powder X-ray diffraction, atomic force microscopy (AFM), and optical and high frequency dielectric measurements. The various structural parameters, such as lattice constant, crystallinity, crystalline phase, grain size etc, were calculated and found to be strongly dependent on Mg^{2+} content. Further, the study of the effect of Mg^{2+} content on refractive index (n), and dielectric constant of the PbS thin films was also performed. A strong effect of Mg^{2+} content doping on the various properties of PbS thin film has been observed and rationalized.

2. Experimental details

All required materials have been purchased from Sigma Aldrich with high purity, ensuring fabrication of good quality thin films of undoped and Mg^{2+} doped PbS. Ordinary glass substrates were used for the preparation of thin films of both undoped and Mg^{2+} doped PbS. Before using these glass substrates we have cleaned them several times with different solvents in vacuum (to be sure that no impurities stick on substrate) and then used for the fabrication of the thin films by the chemical bath deposition (CBD) technique. The reactive medium was prepared by the sequential addition of an alkaline aqueous solution 0.17 molar (M) lead nitrate [$Pb(NO_3)_2$], 0.57 M sodium hydroxide [NaOH], 0.1 M thiourea [$SC(NH_2)_2$] in a 50 ml beaker. For magnesium (Mg^{2+}) doping, $MgCl_2$ was added slowly into the main solution. The pH value of the prepared solution was maintained at 12 by adding NaOH to the reaction bath. Finally, the cleaned glass substrates were vertically hanged in the beaker/bath containing the solution and immersed into water heating bath circulator placed on a highly stable heating magnetic agitator and then maintained at room temperature. The reaction mechanism for the fabrication of the pursued lead sulfide films is as follows [22]:

$$Pb(NO_3)_2 + 2NaOH \rightarrow Pb(OH)_2 + 2NaNO_3$$

$$Pb(OH)_2 + 4NaOH \rightarrow Na_4Pb(OH)_6$$

$$Na_4Pb(OH)_6 \rightarrow 4Na^+ + HPbO_2^- + 3OH^- + H_2O$$

$$SC(NH_2)_2 + OH^- \rightarrow CH_2N_2 + H_2O + SH^-$$

$$HPbO_2^- + SH^- \rightarrow PbS + 2OH^-$$

After deposition, the thin films were taken out from the chemical bath and rinsed many times with deionized water to remove the residuals and loosely adhered PbS particles from the film's surface. The grayish-black thin films were obtained in about 1 h time. The Mg^{2+} doped PbS thin films were deposited by changing the molar ratio of $Pb(NO_3)_2$ and $MgCl_2$ as Mg/Pb equal to 1%, 2%, 3% and 4%. The thicknesses of all the deposited undoped and Mg^{2+} doped PbS thin films were determined by a profile meter type Mitutoyo Surftest-301 and found to be around 400 nm.

Table 1
Variation of PbS peak orientation degree as a function of Mg^{2+} content.

	Pure PbS	1%	2%	3%	4%
$I(111)/I(200)$	0.9822	0.9709	0.9490	1.0164	1.0383
$I(220)/I(200)$	0.6214	0.6040	0.6099	0.6120	0.6907

3. Results and discussion

3.1. Structural properties

Fig. 1 shows the XRD patterns of the undoped as well as Mg^{2+}

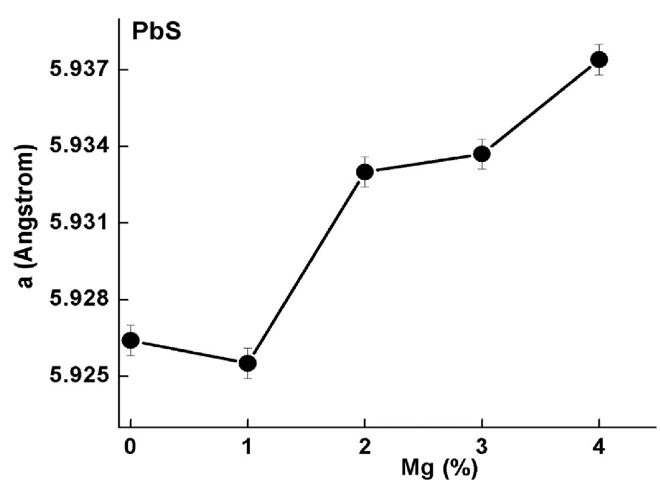

Fig. 3. Variation of PbS lattice parameter versus Mg^{2+} content.