PAPER

Characterization of PbS films deposited by successive ionic layer adsorption and reaction (SILAR) for CdS/PbS solar cells application

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Abstract

The properties of PbS thin films deposited by Successive Ionic Layer Adsorption and Reaction (SILAR) method were analyzed and applied in PbS/CdS heterojunction solar cells. In this study for n-type layer, cadmium sulfide thin films were deposited on transparent conductive oxide (ITO) substrates by Chemical Bath Deposition (CBD) technique followed by deposition of PbS film using different deposition cycles, 15, 20, 30, 40 and 60 to obtain different thicknesses from 90 nm to 658 nm.

Morphological, structural and optical properties were investigated. The roughness of the PbS films were found to be in the range of 10–162 nm, depending on the number of cycles. The films of PbS present a band gap value of 0.6 eV. PbS/CdS heterojunctions were studied as solar cells, it was observed that 40 cycles PbS film has a greater photovoltaic conversion efficiency.

1. Introduction

Current research in alternative and renewable energies has opened the opportunities in the performance of solar cells that implies low cost of production. The chalcogenide semiconductor films are an appropriate alternative to be applied in solar cells. (Mane and Lokhande 2000) Lead Sulphide (PbS) has been widely studied because of its optical and photovoltaic properties, and has been used as p-type material in heterojunction solar cells (Najdoski et al 1995, Valenzuela-Jáuregui et al 2003, Patil et al 2006, Gaiduk et al 2008, Preetha and Remadevi 2013), the synthesis of PbS films has been made by chemical bath deposition (CBD), electrodeposition and Successive Ionic Layer Adsorption and Reaction (SILAR). (Nair and Nair 1990, Puíño et al 2002, Preetha et al 2012, Preetha and Remadevi 2013) which derives from chemical bath deposition. This last method has shown advantages of low temperature of synthesis, compatibility with other synthesis methods, well suited for large area coating, cost effectiveness and reproducibility; it does not require special equipment for the synthesis. (Gao et al 2004, Pathan and Lokhande 2004) It is possible to control the thickness of the film varying the number of cycles and immersion time in cationic and anionic precursors, thus increasing the absorption in p-type layer for solar cells. (Kanniainen et al 2000, Puíño et al 2002, Preetha et al 2012).

Since 1970’s the PbS/CdS heterojunction has been a research subject because of its significant photovoltaic effect. Mohamed calculated the theoretical efficiency of 4.13% for a PbS film thickness of 2 μm. (Watanabe and Mita 1972, Orozco-Terán and Sotelo-Lerma 1999, Hernández-Borja et al 2011, Mohamed 2014, Saikia and Phukan 2014).
In this work we investigated the effects of number of cycles immersion by SILAR technique of PbS films on the optical and morphological proprieties and their impact on the efficiency of PbS/CdS heterojunction solar cell.

2. Experimental details

For this work we used a Chemical Bath deposition technique (CBD) for the growth of the n-type semiconductor (CdS). Using a free ammonia formulation at 70 °C, based on previous works, (Hernández-Borja et al 2011, Pérez-Garcia et al 2015 a) Substrates were placed inside the beaker into a preheated water bath at 70 °C for 60 min, with the following formulation: cadmium chloride [0.05 M]; Sodium citrate [0.5 M]; Potassium hydroxide [0.5 M]; Buffer pH10 and the source of sulfide ions: thiourea [0.5 M]. The CdS films showed a polycrystalline hexagonal structure, with a 70% of transmittance and band gap of 2.35 eV.

For p-type semiconductor a SILAR technique was employed for PbS using 0.5 M lead acetate solution complexed with 0.1 M triethanolamine (TEA) and 0.2 M thioacetamide as cationic and anionic precursors respectively. The optimized absorption and reaction time for cationic and anionic precursors was found at 60 and 30 s correspondingly. One clean corning glass substrate was immersed in cationic precursor solution and unabsorbed ions were removed by rinsing substrate in distilled water, the substrate was submerged in anionic precursor solution, after this, the substrate had a dry time during 60 s; as final stage the substrate was submerged in distilled water to remove unabsorbed ions. The number of depositions was for 15, 20, 30, 40 and 60 cycles at room temperature, obtaining different thickness in the films. For structural characterization the PbS films were deposited on corning substrate, and for optical characterization were deposited on silicon wafers. For solar cell fabrication CdS layer was deposited on ITO-glass substrate followed by a PbS layer; finally, carbon paint contact was applied, using a Conductive carbon paint (SPI Supplies) with a colloidal content of Graphite in isopropanol-20% solids.

The surface morphology on the films was studied using a scanning electron microscope (Philips-FEG-XL30), a layer of gold was evaporated on the films to be able to get the image. X-Ray diffraction (XRD) patterns for the films were recorded in a Rigaku D/MAX–2000 diffractometer, using a Cu-Kα radiation. The average crystallite size of the films was evaluated using the software (JADE) supplied. Optical transmittance and reflectance of the films were obtained using a spectrophotometer Film-Tek (TM-3000) in the UV–vis spectral range of 230 to 800 nm. The index of refraction (n) and extinction coefficient (k) were obtained using the Film-Tek software. The energy band gap (Eg) of the PbS films was calculated from the transmittance spectra obtained using a FTIR spectrometer Perkin Elmer GX, in the range of 400 to 7800 cm⁻¹ corresponding to NIR and Medium IR region. As it will be discussed in detail later.

To obtain the resistivity of the films, a pair of colloidal silver paint electrodes were applied on the films. Current (I) versus voltage (V) measurements on the solar cells obtained were made with a Semiconductor Parameter Analyzer Aglient 4155C, for obtaining IV curve.

3. Results and discussions

3.1. Morphology of PbS films

Figure 1 shows images of the thin films corresponding to the growth of (a) 15, (b) 30 and (c) 60 loops of deposition. In these images it is possible to identify a regular and homogeneous surface with spherical particle shape and size (110.4 nm in average), also aggregates can be observed, and the formation of these clusters is even higher, increasing with the number of cycles. The formation of these clusters of grains on the PbS films surface has been observed on CBD technique, generally caused of a consequence of two growth mechanisms, ion-by-ion and cluster-by-cluster (Hernández-Borja et al 2011).

3.2. Structural analysis

Figure 2 shows the x-ray diffraction (XRD) data of PbS thin films deposited as function of number of cycles by SILAR. The XRD data show intense peaks at 2θ ~ 26.1° and 30.1° corresponding to (111) and (200) reflection and lower intensity peaks between 40°–55°. All these peaks are compatible with mineral Galen (PbS, PDF 05–0592). As can be observed, for films grown from 15 to 60 cycles, similar XRD results were obtained, with a comparable crystallite size of 22 nm indicating a nanocrystalline film, the crystallite size was obtained using the planes (111), (200) and (220). In the case of the film with the lowest numbers of cycles, the peaks are the widest. It is noteworthy to point out that diffraction peaks due to number of cycles of deposition carry to the films at high quality on the crystal as XRD data shows. As well as XRD presents, the SILAR deposition does not promotes other kind of composites associated to the chemical process, the limited sensitivity of XRD does not rule out the
presence of other compounds in the form of amorphous or nano-aggregates phases on similar materials like [(Arreola-Jardón et al. 2014)].

3.3. Optical characterization

In figure 3 it can be noticed that the reflectance %R spectra of the films that goes from 15 to 60 cycles of deposition shows a low %R caused probably by the effect of high absorption in the Infrared and UV-Visible range. The maximum value is noticed in the spectra of the film with 15 SILAR cycles. The difference in the %R may be due to some effects present on this set of samples, one of them is the thicknesses of roughness which goes from 10 nm for 15 cycles film until more than 108 nm corresponding to film with 30 cycles as shown in table 1, films with more than 30 cycles of deposition were not possible to obtain the roughness. Another effect is the high dispersion of incidence light caused by high roughness which could reduce the %R, this corresponds with AFM images inserted on figure 3.

Figure 3 also shows the normal incidence transmittance spectra (T) of the PbS films as function of cycles deposition, the transmittance presents a band gap with approximate values of Eg corresponding to photonic
energies around 0.48–0.67 eV, higher but close to the PbS band gap $E_g$ (0.4 eV) (Gaiduk et al 2008). Similar features are observed in samples grown from 15 to 60 cycles of deposition showing that $E_g$ value is almost not affected by the cycle’s number of depositions by SILAR. A further increase in the number of deposits of these PbS films largely decreases the T and R values in the near infrared range. A detailed study of the optical properties of these materials is in progress and the results will be reported elsewhere. Finally, the abrupt gain of roughness of PbS thin films decreases the $\%R$, this is caused mainly for non-specular reflections over irregular surface.

The value of the $E_g$ for the films was determined from the transmittance spectra obtained with IR. The plot of the $(OD^2 E)$ versus E spectra in the IR absorption edge region were fitted to the model for direct allowed transitions between parabolic energy bands (Abbas et al 2011), figure 4 where, OD is the optical density and E is the photon energy shows the gap values for PbS deposited by SILAR technique, the $E_g$ value goes from 0.63 to 0.67 eV, it only increases in $E_g$ (0.67 eV) for the 50 cycles sample due to the loss of material.

As mentioned above in table 1, we carry out a set of measurements of thickness for different PbS thin films as function of cycles deposition; the thickness was from 90 to 658 nm for 15 to 50 cycles. Figure 5 shows optical spectra of refractive index $n$ (solid line) and extinction coefficient $k$ (dashed line). Those spectral behavior qualitatively follow the corresponding curves of the bulk material, but the values have trend to get down, essentially even when the deposited film have a considerable high thickness, all of them present this characteristic. For instance, in 15 cycles film the $n$ is around 4 at most for the wavelength 450 nm, whereas for the bulk material, the corresponding value is 4.3. As for extinction coefficient $k$, the maximum of $\sim 3.5$ approximately is achieved close to the wavelength of 350 nm, with the corresponding bulk value of 3.3 (Vorobiev et al 2012). This reduction of the values of ‘$n$’ and ‘$k$’ in our samples in relation to the bulk material is evidently due to the samples porosity; here, contrary to the case examined in (Vorobiev et al 2012) the crystallites shape is spherical, which is suggested by the SEM images. Analyzing the films of 15 cycles having the highest optical constant, we take the size of spherical crystallites of 22 nm that agrees with the roughness of 10 nm (table 1). The pores have a shape defined for a 3D-space between four adjacent balls, and can be approximated by a tetrahedral pyramid formed by triangular pyramid planes as mentioned in (Willars-rodríguez et al 2018).

Another important observation is, that CBD technique assisted by UV illumination promotes a growth of porous material. As previously our group reports the effect porosity fraction upon band gap in different
semiconductor materials. In this avoid, the theoretical assumptions were made with a set of 4 atoms in tetrahedral and spherical crystal structure being the last one the most accurate approximation. This theoretical analysis is reported in detail in (Willars-Rodríguez et al 2018). Thus, in this paper we discuss a pore that can be looked as some model of a spherical array of 4 atoms. In this case is possible observed a tiny blue shift of the absorption edge which one correspondingly of the band gap value is described by the relation:

$$\hbar \omega_{\text{min}} = E_g + \frac{h^2}{2ma^2}$$  \hspace{1cm} (1)

where $m$ is the reduced exciton effective mass, and $a$ the length of a pyramid base (pore is considered the space between tetrahedral pyramid form by stacking of 4 atoms). Furthermore, PbS exciton reduced mass 0.0425 m0, we get from figure 3 the band edge shift experimental data ($\hbar \omega_{\text{min}} - E_g$) is estimated on 0.23 to 0.27 eV approximately, the values of a range from 10–14 nm. The relation between a and the spherical balls radius $R$ can be found from identical treatment of close stacking atoms problem (Pérez-García et al 2015) the spheres occupy around of 74% of the total volume. Considering that a sphere there is one octahedral and two tetrahedral pores, we estimate the pore ratio value of $a$ is close to 1.5 $R$. Then, for $a = 12$ nm, we get $R = 8$ nm and thus sphere diameter (crystallite size) of 16 nm, which is rather close to experimental value of 22 nm.

For the average crystallite dimension of ∼22 nm the pore fraction, thus, would be $(12/22)^3 \approx 16\%$. It is important to mention that PbS has a high dielectric constant and the excitation radio is ∼22 nm. It means that this particle is the same order in size that the crystal size of PbS. Therefore, it is accurate to assume that quantum
confinement effect even without considering the porosity effects are not neglected. The case of spherical Quantum Dot was considered in (Vorobiev et al 2010) the corresponding blue shift for the dimensions discussed is smaller than that given by the porosity.

3.4. Electrical characterization
The resistance of the films was obtained from the slope of the I versus V curves. Using the area and thickness of the films, the resistivity (\( \rho \)) was calculated as (Göde and Ünlü 2019),

\[
\rho = \frac{xW}{L}R
\]  

where, \( L \) is the distance between the contacts, \( x \) is the length of the contact and \( W \) is the thickness of the film. We obtained a resistivity of 13.6 \( \Omega \)cm\(^{-1} \) for all samples, this result corresponds to the semiconductor resistivity value.

3.5. Solar cell application
Figure 6 displays the current density voltage (J-V) curves of the solar cells for 20, 40 and 50 cycles, inset shows the configuration of the device. From the J-V curves, short circuit current density (Jsc), open voltage (Voc), fill factor (FF) and efficiency (\( \eta \)) values were calculated and reported in table 2, following the relations:
Were $P_{in}$ is the incident power, and for obtained $FF$, the following equation were used:

$$\eta = \frac{FF \cdot V_{OC}J_{SC}}{P_{in}}$$

(3)

Where $V_m I_m$ is the maximum power of the product of voltage and current.

The major efficiency was observed in 40 cycles solar cell, this is due to material band gap which has a lower energy getting a decrease in the electron transition barrier, so the current increases resulting in a high photovoltaic conversion efficiency, but compared with (Mohamed 2014), the efficiency was lower, this could be explained due losses between semiconductor layers attributed to structure, morphology and optical properties of each layer (CdS/PbS) and leakage current in ohmic contacts.

4. Conclusions

In this work we synthesized and compared good quality PbS films grown by SILAR at different cycles. We observed that films deposited by this condition are optimal for obtain higher thickness layers with a room temperature electrical resistivity of 13.6 Ωcm$^{-1}$ from a simple and cost-effective technique, this is a great advantage for using these PbS films as p-type semiconductor in a heterojunction solar cell, because it does not require high temperatures and sophisticated equipment. The PbS films shown gradual increase in absorption with the increase of thickness and roughness. Also we have produced devices using two different simple and cheap methods, CBD and SILAR in order to obtain solar cell structures of ITO/CdS/PbS/C.

From these structures J-V characteristic curves under illumination condition was studied to estimate some important parameters finding that the optimal conditions for a maximum solar cell efficiency in a CdS/PbS heterojunction was for 40 cycles SILAR PbS due to material band gap energy. There is not a direct relation of the efficiency with thickness and number of cycles.
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References

Abbas M M et al 2011 Effect of deposition time on the optical characteristics of chemically deposited nanostructure PBS thin films Energy Procedia 6 241–50
Arreola-Jardón G, Jiménez-Sandoval S and Mendoza-Galván A 2014 Growth and characterization of CuCdTeO thin films sputtered from CdTe–CuO composite targets Vacuum Elsevier Ltd 101 130–5
Gaiduk A P, Gaiduk P I and Larsen A N 2008 Chemical bath deposition of PbS nanocrystals: effect of substrate Thin Solid Films 516 3791–5
Gao X-D, Li X-M and Yu W-D 2004 Deposition of polycrystalline ZnO thin films by successive ionic layer adsorption and reaction process (SILAR) Wujj Calliao Xuebao/Journal of Inorganic Materials 19 85–111
Góde F and Unlu S 2019 Synthesis and characterization of CdS window layers for PbS thin film solar cells Mater. Sci. Semicond. Process. 90 92–100
Hernández-Borja I, Vorobiev Y V and Ramírez-Bon R 2011 Thin film solar cells of CdS/PbS chemically deposited by an ammonia-free process Sol. Energy Mater. Sol. Cells 95 1882–8
Kannaiiian T et al 2000 Structural and topographical studies of SILAR-grown highly oriented PbS thin films Mater. Res. Bull. 35 1045–51
Mane R S and Lokhade C D 2000 Chemical deposition method for metal chalcogenide thin films Mater. Chem. Phys. 65 1–31
Mohamed H A 2014 Theoretical study of the efficiency of CdS/PbS thin film solar cells Sol. Energy Elsevier Ltd 108 360–9
Nair P K and Nair M T S 1990 PbS solar cell coatings: safety, cost and optimisation J. Phys. D: Appl. Phys. IOP Publishing 23 150
Najdoksi M et al 1995 Optical properties of thin solid films of lead sulphide J. Mol. Struct. 349 85–8
Orozco-Terán R A and Sotelo-Lerma M 1999 PbS-CdS bilayers prepared by the chemical bath deposition technique at different reaction temperatures Thin Solid Films 343–344 387–90
Pathan H M and Lokhade C D 2004 Deposition of metal chalcogenide thin films by successive ionic layer adsorption and reaction (SILAR) method Bull. Mater. Sci. Springer India, in co-publication with Indian Academy of Sciences 27 85–111
Patil R S et al 2006 Characterization of chemically deposited nanocrystalline PbS thin films J. Mater. Sci. 41 5723–5
Popa A et al 2006 Crystallite size effect in PbS thin films grown on glass substrates by chemical bath deposition J. Optoelectron. Adv. Mater. 8 43–5
Preetha K C et al 2012 Effect of cationic precursor pH on optical and transport properties of SILAR deposited nano crystalline PbS thin films Curr. Appl. Phys. Elsevier 12 1826–9
Preetha K C and Remadevi T L 2013 Behavior of chemically deposited PbS thin films subjected to two different routes of post deposition annealing Mater. Sci. Semicond. Process. Elsevier 16 605–11
Puisio J et al 2002 Growth of PbS thin films on silicon substrate by SILAR technique Thin Solid Films 403–404 457–61
Pérez-García C E, Ramírez-Bon R and Vorobiev Y 2015 PbS thin films for photovoltaic applications obtained by non-traditional chemical bath deposition Mater. Sci. Semicond. Process. 26 5–7
Pérez-García C E, Ramírez-Bon R and Vorobiev Y V 2015 PbS thin films growth with CBD and PCBD techniques: a comparative study Chalcogenide Letters 12 579–88
Saikia D and Phukan P 2014 Fabrication and evaluation of CdS/PbS thin film solar cell by chemical bath deposition technique Thin Solid Films Elsevier B.V. 562 239–43
Valenzuela-Jauregui J I et al 2003 Optical properties of PbS thin films chemically deposited at different temperatures Thin Solid Films 441 104–10
Vorobiev Y V et al 2010 Effect of boundary conditions on the energy spectra of semiconductor quantum dots calculated in the effective mass approximation Physica E 42 2266–7
Vorobiev Y V et al 2012 The effects of porosity on optical properties of semiconductor chalcogenide films obtained by the chemical bath deposition Nanoscale Res. Lett. 7 483
Watanabe S and Mita Y 1972 Electrical properties of CdS–PbS herejunctions Solid-State Electronics 15 5–10
Willars-rodríguez F J et al 2018 Effects of tin-doping on cadmium sul de (CdS : Sn) thin- films grown by light- assisted chemical bath deposition process for solar photovoltaic cell Thin Solid Films Elsevier 653 341–9