

## **Optical Properties of PbS Thin Films Prepared by Successive Ionic Layer Adsorption and Reaction Processes**

Pimsiri Tusamalee <sup>a,\*</sup>, Prathan Buranasiri <sup>a</sup>, Sutichai Chaisitsak <sup>b</sup>, Witoon Yindeesuk <sup>a</sup>

<sup>a</sup>*Department of Physics, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok, 10520 Thailand*

<sup>b</sup>*Department of Electronics Engineering, Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang, Bangkok, 10520 Thailand*

Received 13 March 2017; Revised 19 August 2017; Accepted 31 August 2017

### **Abstract**

This work aims to study lead sulfide thin films on glass slide by the successive ionic layer adsorption and reaction method (SILAR). The purpose of this research is to study the optical properties of PbS thin films on glass slide, which would lead to an understanding of the optical properties of each PbS thin films caused by the SILAR method. The growth of PbS thin films was found to be profoundly affected by number of SILAR cycles. This work uses Lead dinitrate and Sodium sulfide for creating PbS thin films. The PbS thin films on glass slide were investigated for the X-ray diffraction and the optical properties of the SILAR cycle effect. The X-ray diffraction image showed face center cubic structure. Moreover, we found that the transmittance of thin films depended on SILAR cycles. 60 and 80 SILAR cycles were lower spectral transmittance [below 40%] in wavelength of 400 – 900 nm. The films of 10 and 20 SILAR cycles of PbS thin films had very high transmittance though is used to contrast two statements. These two statements are not relevant. The PbS thin films were deposited by 40 SILAR cycles with transmittance between 40 – 90% in wavelength 400 – 900 nm. For SILAR method, the number of deposition cycles affect the optical properties of PbS thin films. Therefore, increasing the SILAR cycles leads to lower the transmittance of PbS thin film.

**KEYWORDS:** PbS; Thin films; SILAR method

---

\* Corresponding authors; e-mail: 58605061@kmitl.ac.th

### **Introduction**

Semiconductor nanoparticles or quantum dots (QDs) are intensive research efforts which have been undertaken to develop solar cells because QDs have excellent electronic properties and can be produced by low-cost methods. These include tunability of band gap energy, good photostability, narrow emission spectrum, broad excitation spectra, high extinction coefficient and multiple exciton generation [3–5]. With these advantages, researchers could be able to fabricate solar cells devices with high efficiency. [6]

The tactics to fabricate solar cells based on QDs is to use QDs as sensitizer in porous metal oxide nanostructure films. Mesoporous films consist of crystals with a diameter of tens of nanometers [7–8]. Mesoporous titanium dioxide was prepared by screen printing from paste and doctor blade method [9]. Sensitization of titanium dioxide was demonstrated into semiconductor

QDs. Among the various QD materials, PbS and PbSe are good candidates for solar cells, because they can be made to overlap the solar spectrum. By controlling their size, the adsorption wavelength of the first exciton peak can easily be extended in the infrared [10]. For mechanism of carrier multiplication in QDs, PbS and PbSe QDs are found to be the materials with dramatic indications of carrier multiplication with photon-to-exciton conversion efficiency up to 700% [11]. R.J. Ellingson and coworker focus on PbS quantum dots, they found that shows 300% quantum efficiency due to multiple exciton generation [12] and exhibit strong quantum size effects for relatively large sizes as compared to other semiconductors such as CdS, CdSe, ZnS, etc [13]. PbS QDs are interesting materials, which is possible to increase the light to electric power conversion efficiency. Nowadays, many researcher in the world have been studying properties of PbS QDs to construct solar cells.

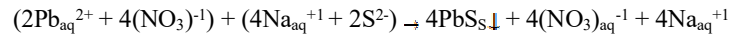
Lead sulfide is a IV-VI group of semiconductor, which has received considerable attention because, with a narrow direct energy band gap of 0.41 eV, PbS has a large exciton Bohr radius of 18 nm. It is not only PbS Quantum dot very interesting for solar cells applications but also PbS thin films because they are cheap and convenient to fabrication. Lead sulfide thin film have been synthesized using various method such as chemical bath deposition [2], spray pyrolysis [14] and the successive ionic layer adsorption and reaction (SILAR) method [15]. SILAR is most popular technique for deposition of thin film because the deposition rate and the thickness of the film can be easily controlled by changing the deposition cycles. Without using high power. inexpensive, simple and convenient for large area deposition [15].

In this work we report an experimental study on optical properties of PbS thin films. The absorbance, along with X-ray diffractometer and uv-vis spectroscopy measurements, indicate transmittance range of PbS thin films. The meaning of these results for each of thin films will be discussed.

## Materials and Methods

### *PbS thin films preparation*

Lead dinitrate ( $\text{Pb}(\text{NO}_3)_2$ ) and sodium sulfide ( $\text{Na}_2\text{S}$ ) aqueous solution were used as the lead source and sulfide source for PbS thin films. PbS thin films was prepared by successive ionic layer adsorption and reaction (SILAR) method. Here, thin films were immersed in two solutions for 1 minute each. The glass slide was dipped in  $\text{Pb}(\text{NO}_3)_2$  solution and following by dipping into methanol. After that the films were thoroughly cleaned with methanol and dried with hot air.



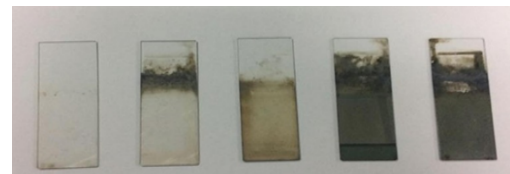
Next, glass slide was dipped in  $\text{Na}_2\text{S}$  solution and following by dipping into methanol. Finally, the films were thoroughly cleaned with methanol and dried with hot air. By repeating these cycles, PbS thin films of different thicknesses could be obtained.

Successive ionic layer adsorption and reaction (SILAR) method was called the modified generation of chemical bath deposition (CBD) method. SILAR is solution method for the deposition of thin films. The facts affecting the growth phenomena of thin films are the quality of the precursor solution, pH values, concentrations, counter ions, complexing agent and pretreatment

of substrate have been shown to affect the SILAR growth [15]. The crystal structure and orientation of the PbS thin films were examined by Bruker AXS : D8 Advance X-ray diffractometer using  $\text{CuK}\alpha$  radiation. Transmittance measurements were carried out using the UV-vis spectrometer : Avantes avaspec-EDU, which is the tungsten light source (MEGALIGHT 100 from SCHOTT Nippon k.k. Fiber Optics). The probe beam which was white light can be tuned in the 400 – 900 nm wavelength region using a software.

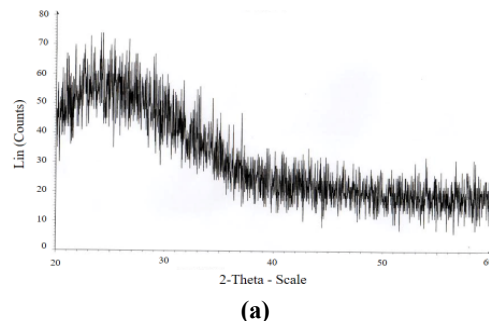
In this research we studied PbS thin films by concentration of precursor at 0.02 M. SILAR cycles were used 10, 20, 40, 60 and 80 cycles for measurement the optical properties of PbS thin films. The SILAR deposition cycles affect the properties of thin films. According to the X-ray diffraction image in Fig. 2 the PbS thin films grown on glass slide with 10, 20, 40, 60 and 80 SILAR cycles were face centered cubic structure. In Fig. 2(a) 10 SILAR cycles, the peak still not clearly. In Fig. 2(b), 20 SILAR cycles, the peak is strong at (111) and preferential orientation of (200) in Fig. 2(c), 2(d) (40 and 60 SILAR cycles respectively) and the most obvious in Fig. 2(e) which is the PbS thin films that deposition by 80 SILAR cycles.

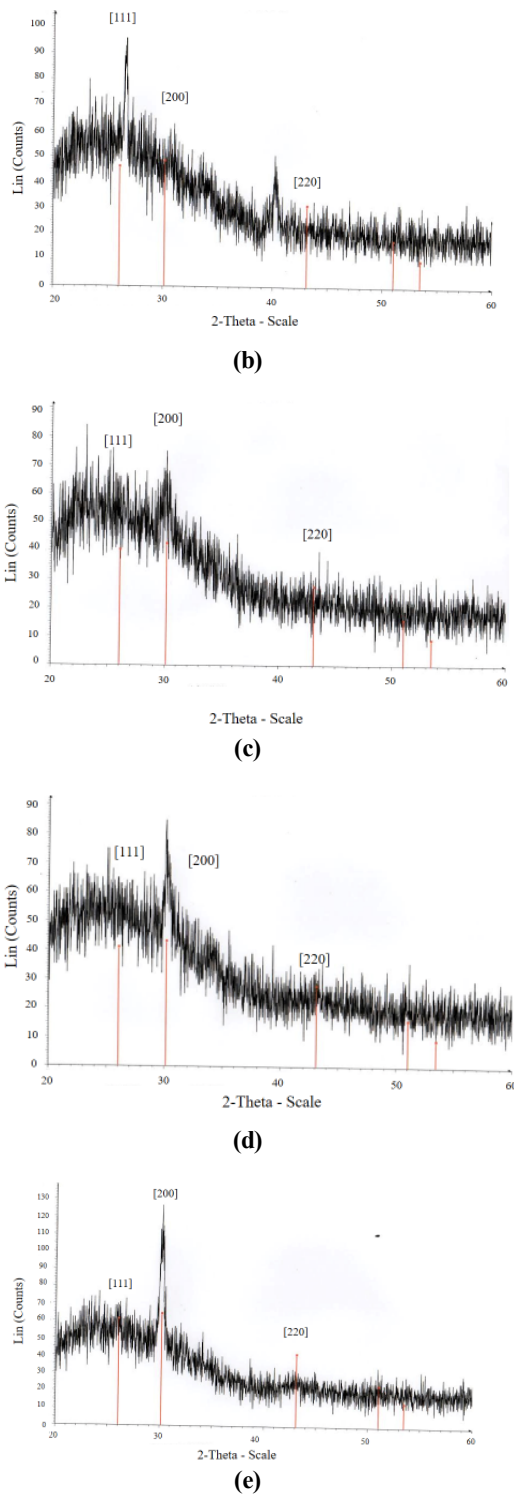
## Results and Discussion



**Fig. 1** PbS thin films of the deposition thin films by SILAR method 10, 20, 40, 60 and 80 cycles respectively.

### *Optical properties of PbS thin film XRD pattern*

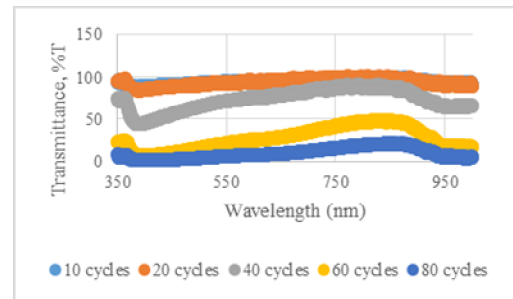




**Fig. 2** (a) X-ray diffraction pattern of 10 SILAR cycles, (b) 20 SILAR cycles, (c) 40 SILAR cycles, (d) 60 SILAR cycles and (e) 80 SILAR cycles.

According to the X-ray diffraction pattern in Fig. 2 the PbS thin films grown on glass slide with 10, 20, 40, 60 and 80 SILAR cycles were face centered cubic structure. In Fig. 2(a) 10 SILAR cycles, the peak is not clear. In Fig. 2(b), 20 SILAR cycles, the peak is strong at (111) and is preferential orientation of (200) in Fig. 2(c), 2(d) (40 and 60 SILAR cycles respectively) and the most obvious in Fig. 2(e) which is the PbS thin films that deposition by 80 SILAR cycles.

*Transmittance of PbS thin films*



**Fig. 3** The Transmittance as the function of SILAR cycles of PbS thin films

Fig. 3 shows the transmittance of PbS thin films using SILAR method of difference cycles. The SILAR cycles of films showed different trends in transmittance all of the films. 60 and 80 SILAR cycles were lower spectral transmittance (below 40 %) in wavelength of 400 – 900 nm. The films of 10 and 20 SILAR cycles of PbS thin films obtained high transmittance. The PbS thin films were deposited by 40 SILAR cycles with transmittance between 40 – 90% in wavelength 400 – 900 nm. For growth of PbS by SILAR methods, the number of deposition cycles affect the optical properties of PbS thin films. Therefore, increasing the SILAR cycles leads to lower the transmittance of PbS thin films.

**Conclusion**

The properties of PbS thin films glass slides substrate which was prepared by successive ionic layer adsorption and reaction (SILAR) method were measured by X-ray diffractometer. The characteristics of PbS thin films showed face centered cubic structure. For 20 SILAR cycles of PbS thin films, the peak is strong at (111). 40, 60 SILAR cycles of PbS thin films the peak is strong at (200) and the most obvious in 80 SILAR cycles of thin films. For the spectra analysis of the data were done to obtain the transmittance. It was found from the spectra measurement that

PbS thin films can be possible as good absorbers in 40 SILAR cycles.

### Acknowledgements

The authors acknowledge helpful discussions with Witoon Yindeesuk, and Prathan Buranasiri in Department of Physics, King Mongkut's Institute of Technology Ladkrabang (KMITL). This work was supported by Sutichai Chaisitsak of Department of Electrical Engineering, King Mongkut's Institute of Technology Ladkrabang (KMITL). The author would also like to thank Asst.Prof.Dr. Pattareeya Damrongsak for UV-vis spectrometer: Avantes avaspec-EDU.

### References

- [1] R.S. Patil, H.M. Pathan, T.P. Gujar, C.D. Lokhande, Characterization of chemically deposited nanocrystalline PbS thin films. *J. Mater Sci.* 41 (2006) 5723 – 5725.
- [2] K.M. Gadave, S.A. Jodgudri, C.D. Lokhande, Chemical deposition of PbS from an acidic bath, *Thin Solid Films.* 245 (1994) 7 – 9.
- [3] H.K. jun, M.A. Careem, A.K. Arof, Quantum dot-sensitized solar cells perspective and recent development A review of Cd chalcogenide quantum dots as sensitizers, *Renew. Sustain. Energy Rev.* 22 (2013) 148 – 167.
- [4] S. Ruhle, M. Shalom, A. Zaban. Quantum-Dot-Sensitized Solar Cells. *Chemphyschem*, 11 (2010) 2290 – 2304.
- [5] W.W. Yu, L. Qu, W.Z. Guo, X. Peng. Experimental Determination of the Extinction Coefficient of CdTe, CdSe and CdS Nanocrystals. *Chem. Mater.* 15 (2003) 2854 – 2860.
- [6] H. Alexander, S. Thon, S. Hoogland, O. Voznyy, D. Zhitomirsky, R. Depnath, Hybrid passivated colloidal quantum dot solids. *Nat. Nanotechnol.* (2012) 577 – 582.
- [7] S. Dor, Th. Dittrich, A. Ofir, L. Grinis, A. Zaban, Postpressing dependence of the effective electron diffusion coefficient  $n$  electrophoretically prepared nanoporous ZnO and TiO<sub>2</sub> films. *J. Mater. Res.* (2008) 975 – 980.
- [8] A. Ofir, S. Dor, L. Grinis, A. Zaban, T. Dittrich, J. Bisquert, Porosity dependence of electron percolation in nanoporous TiO<sub>2</sub> layers. *J. Chem. Phys.* 128 (2008) 064703.
- [9] S. Ito, T.N. Murakami, P. Comte, P. Liska, C. Grätzel, M.K. Nazeeruddin et al., Fabrication of thin film dye sensitized solar cells with solar to electric power conversion efficiency over 10 %, *Thin Solid films.* 156 (2008) 4613 – 4619.
- [10] B.R. Hyun, Y.W. Zhong, A.C. Bartnik, L. Sun, H.D. Abruna, Frank W et al., Electron Injection from Colloidal PbS Quantum Dots into Titanium Dioxide Nanoparticles. *ACS NANO.* 2 (2008) 2206 – 2212.
- [11] R.D. Schaller, M. Sykora, J.M. Pietryga, V. I. Klimov. Seven Excitons at a Cost of One: Redefining the Limits for Conversion Efficiency of Photons into Charge Carriers, *Nano Lett.* 6 (2006).
- [12] R.J. Ellingson, M.C. Beard, J.C. Johnson, P. Yu, O.I. Micic, A.J. Nozik et al., Highly Efficient Multiple Exciton Generation in Colloidal PbSe and PbS Quantum Dots, *Nano Lett.* 5 (2005) 865 – 871.
- [13] J.D. Patel, T.K. Chaudhuri, Synthesis of PbS/poly (vinyl-pyrrolidone) Nanocomposite, *Mater. Res. Bull.* 44 (2009) 1647 – 1651.
- [14] B. Thangaraju, P. Kaliannan, Spray pyrolytically deposited PbS thin films. *Semiconductor Science and Technology*, 15, 2000.
- [15] H.M. Pathan, C.D. Lokhande, Deposition of metal chalcogenide thin films by successive ionic layer adsorption and reaction (SILAR) method, *Bull Mater Sci.* (2004) 85 –111.