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Fabrication of PbS/CZTS/PbS System Quantum Well Using Chemical Bath Deposition Method

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Abstract

Lead chalcogenides (PbS, PbSe, PbTe) quantum wells are ideal for fundamental studies of strongly quantum confined systems with technological applications. Tunable electronic transitions at near-infrared wavelengths can be obtained with these quantum wells. Applications of lead chalcogenides encompass quite a good number of important field viz. the fields of telecommunications, medical electronics, optoelectronics, etc. realized in nanoscale systems with coupled ionic and electronic transports are observed in many nanoscale electronic devices including semiconductor quantum well devices. This paper reports synthesis of PbS/CZTS//PbS quantum wells by chemical route. The fabricated samples are characterized by UV-Vis and FT-IR. Observed characteristics confirm QW formation.

1. Introduction

Semiconductor materials are always in focus due to their outstanding electronic and optical properties and potential applications in various devices including light-emitting diodes, single electron transistors and field effect transistors. The electronic and optical properties of semiconductor materials can be changed by changing their size and shapes. As an important IV-VI group semiconductor, Lead Sulphide (PbS) is an important direct narrow band gap semiconductor material (≈ 0.41 eV at room temperature), and has been widely used in many fields such as Pb^{2+} ion-selective sensors, IR detector, photography and solar absorption. Due to the non-linear optical properties, PbS nanoparticles have found extensive applications in optical devices such as optical switch. In addition, PbS has been utilized as photo resistance, diode lasers, humidity and temperature sensors, decorative and solar control coatings. In recent years, many researchers have studied PbS thin film properties for various nanodevice applications. Dan Li studied the nonlinear optical properties of PbS nanoparticles. Nanda investigated the band-gap tuning of PbS nanoparticles. Muscat studied the surface of galena PbS using the first-principles calculations. Sushil Kumar reported the characterization of vacuum evaporated PbS thin films. Preobrajenski reported the atomic and electronic structure of epitaxial PbS on InP and synthesized and characterized the PbS nanorods and nanowires. Gaiduk deposited PbS films on Si, Ge and GaAs substrate. Badir investigated the effect of PbS shell on the optical and electrical properties of PbSe as core nanoparticles [1].

These films can be obtained by several methods such as Molecular Beam Epitaxy (MBE), electrodeposition, spray pyrolysis, photo accelerated chemical deposition, microwave heating and chemical bath deposition (CBD). Among these methods the chemical bath deposition is used here because it is simple, low cost, the quality of the films and convenience for large area deposition. In recent years, we have been witnessing the rapid progress in nanoelectronics continuing the outstanding successes of microelectronics. This became possible among others, due to these deposition technologies and techniques which enables depositing thin layers of different materials, one on the top of another, with almost atomic precision, hereby forming a quantum well.

The classic model used to demonstrate a quantum well is to confine particles, which were initially free to move in three dimensions, to two dimensions, by forcing them to occupy a planar region. The concept of quantum well was proposed in 1963 independently by Herbert Kroemer and by Zhores Alferov and R.F. Kazarinov. The semiconductor quantum well was developed in 1970 by Esaki and Tsu, who also invented synthetic superlattices [2]. They suggested that a heterostructure made up of alternating thin layers of semiconductors with different band-gaps should exhibit interesting and useful properties. Since then, much effort and research has gone into studying the physics of quantum well systems as well as developing quantum well devices.

The theory surrounding quantum well devices has led to significant advancements in the production and efficiency of many modern components such as light-emitting diodes, transistors for example. Today, such devices are ubiquitous in modern cell phones, computers, and many other computing devices. Within the quantum well, there are discrete energy eigenstates that carriers can have. An electron in the conduction band with low energy can be trapped within the quantum well. Similarly, holes in the valence band can also be trapped in the top of potential wells created in the valence band. The states that confined carriers can be in are particle-in-a-box-like states. Quantum wells and quantum well devices are a sub field of solid-state physics that is still extensively studied and researched today. The theory used to describe such systems uses important results from the fields of quantum physics, statistical physics, and electrodynamics. Quantum wells can be studied using three models namely, Infinite well model, Finite well model and Superlattices.

For solar energy to become the primary source of energy used in the world, a new approach is required that addresses the drawbacks of the current technologies: high material usage, high material costs and the use of toxic materials. Recently, the semiconductor Cu2ZnSn(S,Se)4 (CZTSSe) has attracted attention as a promising material for use in solar cells. It has a high theoretical efficiency (based on bandgap) and can be used as a thin film to limit material usage. It is formed entirely from earth abundant, inexpensive, non-toxic elements that are currently used to make thin film solar cells. The lowest abundant and highest cost element in the CZTS is Tin (Sn), which is still significantly better than the elements used in the current technologies (Cd, Te, In, Ga) [3].

Furthermore, the CZTS elements are mined in large quantities in many countries of the world. A large global production is necessary for the solar industry to continue to grow rather than be limited by material shortages. The CdTe industry is a prime example of an industry that is likely to be limited by material production. Tellurium (Te), one of the primary components of this material, has a very low annual production (250-300 tones/yr). At this production rate, if all the Te is converted directly into solar panels which no losses, the industry would only be able to produce 4-5 GW_p of solar panels per year.

The best CZTS devices are produced by Wang et al. using thermal co-evaporation. This process is similar to that used by Repins et al. to produce $CuInGaSe_2$ cells at efficiencies as high as 19.9%. However, the best CZTS devices are still limited to 6.8%. This is likely due to the added level of complexity in the CZTS system. Unlike the psuedo-ternary CIGS, CZTS is a quaternary compound which adds another set of possible detrimental defects. Recombination at these defects is the likely cause of the limited efficiencies that have been observed. If this is the case, a radical change in the device structure will be required to achieve efficiencies close to the theoretical maximum from this material [4.5].

One possible way to accomplish this is by nanostructuring the device to reduce the path length required for an electron to diffuse to the junction. There are multiple theoretical studies suggesting that this type of interdigitated structure can be used to improve efficiencies in materials with poor lifetimes. The ideal periodic spacing is dependent on material properties but in most cases ranges from 100-300nm. Initial experimental results of devices fabricated based on these studies have also been very promising. However, creating this type of nanostructure is generally a complicated process involving multiple steps and most of the techniques that have been attempted are not scalable to large areas. An ideal process would involve only one step and be capable of deposition over large areas in a short time [6].

Since the discovery of the quantum well, it has always been fabricated by the methods of molecular beam epitaxy and chemical vapor deposition. This signifies that chemical bath deposition method is a novel route to the fabrication of quantum wells. Chemical bath deposition (CBD) is a simple yet powerful technique that makes a significant contribution in solar cells fabrication industry. So far, its contribution in thin film solar cells has been mainly limited to growing n-type CdS and/or ZnS window layers for CdTe-based and CIGS-based solar cells. Meanwhile, most CBD, CdS thin films for example are grown using only ammonia as a complexing agent. In addition, optimization of CBD is mainly limited to maximizing growth rate.

The focus of this paper is to investigate the application of chemical bath deposition on quantum wells fabrication. The objective is to demonstrate that CBD is a simple and inexpensive alternative to other sophisticated more expensive techniques that are currently used in growing quantum wells for solar cells applications [7,8,9].

Chemical Bath Deposition requires supersaturated solutions, that is, the product of the concentrations of metal and chalcogenide must exceed the solubility product of the desired solid. In a closed system, growth cannot continue once the reactants have been depleted below this point. Thus, the maximum obtainable thickness is limited by the supply of reactants. Increasing the degree of supersaturation (for example by raising the pH, in the case of oxides) increases the rate of film growth, as reported by several groups under such conditions of rapid formation of solid, however, some of the solid forms powder, or relatively large particles that are only weakly adsorbed to the film. Thus, the films thickness if less than would be expected based on maximum utilization of the reactants. Solutions that are less heavily super saturated grow more slowly but ultimately provide thicker films.

Several workers have reported the effect of varying growth parameters such as deposition rate, bath composition and bath temperature on the various properties of their films. On a presensitized substrate surface, no incubation period for nucleation is observed, since nucleation centers already exist on the substrate. Also, when the substrates are suspended in the container before forming the complex in the solution, film thickness increases in a manner similar to that of the sensitized surface, thereby showing that the nuclei for the formation of the film are provided by the solution itself. If a change in metals' oxidation state occurs, it takes place in the bulk solution. The rate of deposition and the terminal thickness both depend on the number of the nucleation centers, super saturation of the solution (defined as the ratio of IP to SP), and stirring. The growth kinetics depend on the concentration of ions, their velocities, nucleation and growth processes on the immersed surfaces [9,10].

2. Methodology

The CBD process enables the deposition of thin films on substrates submerged in solutions containing chalcogenide source, metal ions, and chelating agent. The latter is used to limit the hydrolysis of the metal ion and impart some stability to the bath. The deposition rate may be controlled by adjusting temperature of the bath, pH, stirring rate and relative concentration of the reactants within the solution (chalcogenide source, chelating agent and/or metal ions).

This section provides a precise explanation on the reagents used, bath formulation, substrate preparation, important formulae used and a description of the films deposition process.

2.1. Chemical Reagents

A list of the reagents used, their chemical formula and their sources is provided in table 1.

Table 1: Reagents.

Name	**Formula**	**Source**
Lead(II)acetate trihydrate	$Pb(CH_3COO)_2.3H_2O$	Kermel
Triethanolamine 98%	$C_6H_{15}NO_3$	CDH (P) Ltd
Sodium Hydroxide	$NaOH$	CDH (P) Ltd
Thiourea	CH_4N_2S	Kermel
Copper(II)Sulphate pentahydrate	$CuSO_4.5H_2O$	Pyrex-IG
Stannous Sulphate	$SnSO_4$	CDH (P) Ltd
Zinc Sulphate heptahydrate	$ZnSO_4.7H_2O$	Pyrex-IG
Sodium Thiosulphate pentahydrate	$Na_2S_2O_3.5H_2O$	Pyrex-IG

All chemicals were of analytical (AR) grade and used without further purification.

2.2. Apparatus

Different apparatus and materials were used for the deposition process. A list of the apparatus and materials are provided below.

Glass microscope slides
Glass apparatus (beakers, measuring cylinders and flat bottom flasks)
pH strips
Masking tape
Digital weighing balance
Laboratory gloves
Surgical masks
Stop watch
Rubber pipettes
Chemical bath

2.3. Substrate Preparation

Glass microscope slides of dimension 25.4mm×76.2mm×1.2mm were used as substrates for the deposition of the films. The slides were first washed with detergent and rinsed with water. They were then left in concentrated hydrochloric acid for 48 hours to remove other impurities left after the use of detergent. Finally, the substrates were rinsed distilled water and dried in air before they were used for the deposition.

2.4. Experimental Set-Up

A typical set-up for CBD deposition is shown in the figure below: a beaker filled with aqueous solution of precursors for deposition is in a water bath placed on a hot plate that controls temperature and stirring process. The substrate is immersed into the solution and kept there for a determined time period. Stirring is continuous from room temperature. The beaker with solution is covered with a cap to avoid evaporation of ammonia.

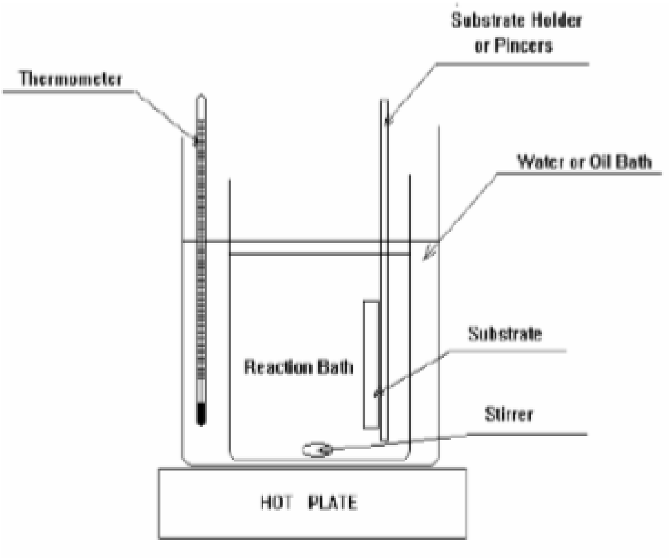

Figure 1: Schematic of Chemical bath deposition set-up

2.5. Experimental Procedure

2.5.1. Deposition of PbS thin film layer

PbS thin films were prepared by consecutively stirring 1M lead(II)acetate trihydrate, 1M triethanolamine, 1M sodium hydroxide and 1M thiourea in total volume. Distilled water was added to obtain total solution volume of 100 ml. Previously cleaned glass microscope slides were placed vertically in solution. Deposition was held at room temperature for 0.5h, 1h, 1.5h, 2h, 2.5h and 3h for six different substrates. Obtained films were rinsed with distilled water, then dried in air.

2.5.2. Deposition of CZTS thin films

CZTS thin films were prepared by consecutively stirring 0.05M copper(II)sulphate pentahydrate, 0.1M zinc sulfate heptahydrate, 0.05M stannous sulphate, 0.2M sodium thiosulfate pentahydrate and drops of ammonia in 100ml total volume. Glass microscope slides, with previously deposited PbS films, were placed vertically in solution. Deposition was held at 40C for 1h for the six substrates. Obtained films were rinsed with distilled water, then dried.

The last deposition of the PbS layer was made using the previously explained procedure resulting in three layers and the result was spread out to be dried [11,12].

3. Results and Discussion

The optical transmittance and absorbance of the PbS/CZTS thin films were determined from the variation of optical absorbance with UV-Vis light wavelength λ at room temperature in the range of 400 nm–1000 nm with a Visible Spectrophotometer Labtech – 722.

It can be seen from the graphical representation above that the PbS/CZTS/PbS quantum well exhibited good absorbance profile for the films deposited at 30mins and 60mins deposition time. This is an essential characteristic of QW device. If the material's absorbance falls below zero, such material will be so poor in trapping and converting solar energy to electrical energy. Fourier Transform Infrared (FT-IR) Spectroscopy is used to perform qualitative and quantitative analysis of organic compounds and to determine the chemical structure of many inorganic compounds. FTIR, when combined with proper sample handling, elemental analysis, the use of appropriate reference standards, and a simple separation step, has proven superior to other techniques in the identification of many inorganic compounds. The spectral system used was the Thermo-Scientific FT-IR Spectrophotometer (iD1 Transmission – Nicolet iS5). The results for the different deposition times are displayed in Figure 3.

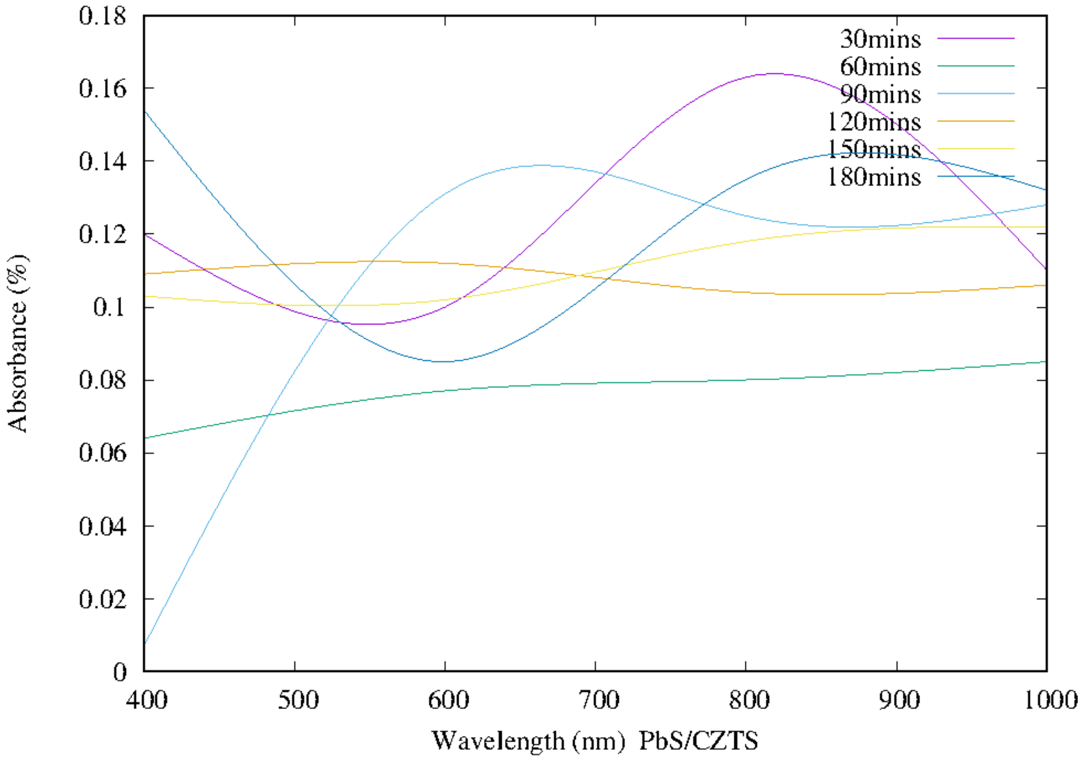

Figure 2: UV-Vis Absorbance spectroscopy of PbS/CZTS/PbS Quantum well.

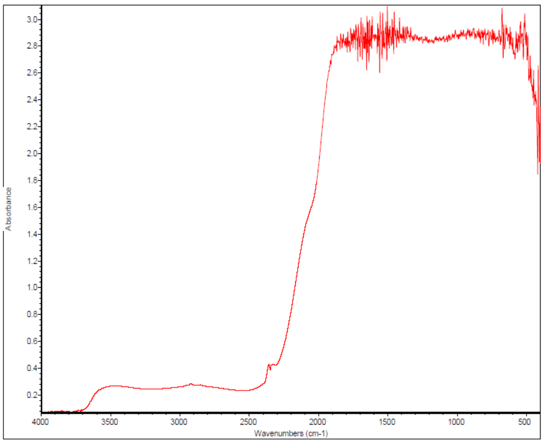

Figure 3: FTIR Absorbance spectroscopy of PbS/CZTS/PbS Quantum well for 30mins

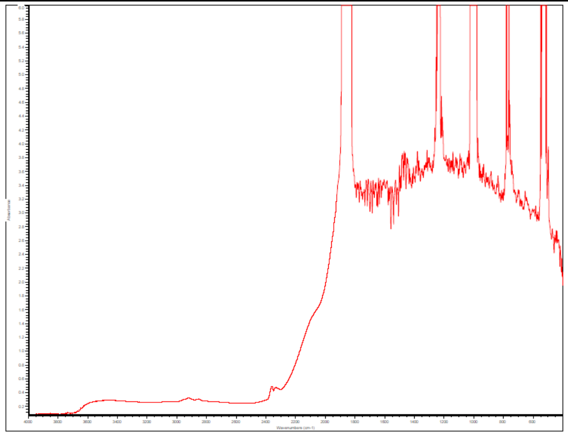

Figure 4: FTIR Absorbance spectroscopy of PbS/CZTS/PbS Quantum well for 60mins

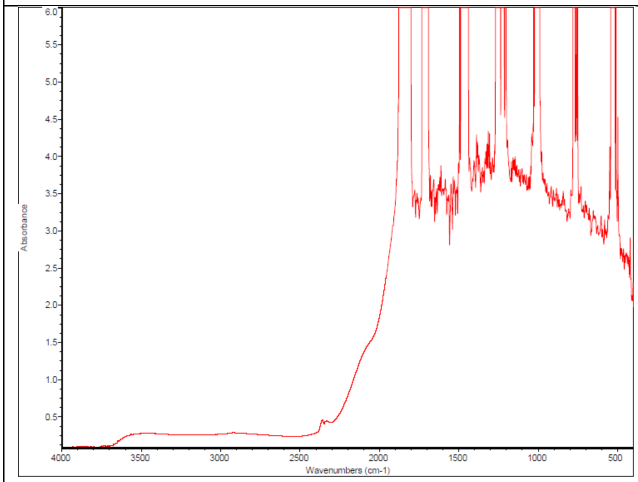

Figure 5: FTIR Absorbance spectroscopy of PbS/CZTS/PbS Quantum well for 90mins

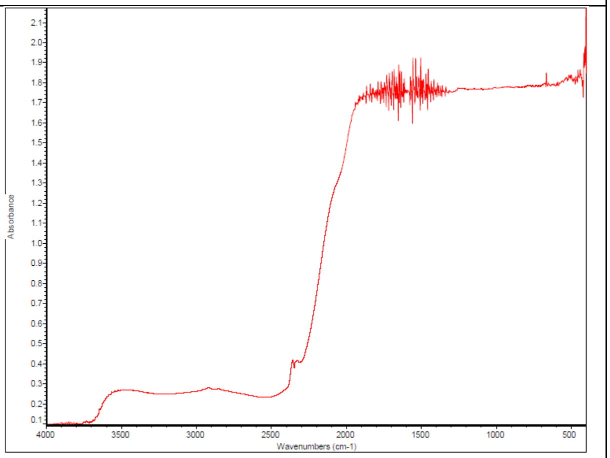

Figure 6: FTIR Absorbance spectroscopy of PbS/CZTS/PbS Quantum well for 120mins

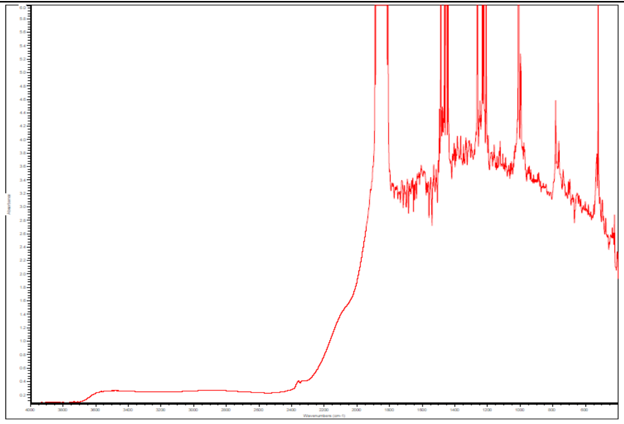

Figure 7: FTIR Absorbance spectroscopy of PbS/CZTS/PbS Quantum well for 150mins

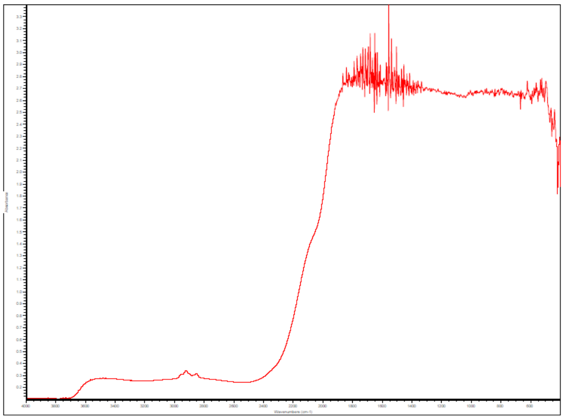

Figure 8: FTIR Absorbance spectroscopy of PbS/CZTS/PbS Quantum well for 180mins

The graphs above are the results from the FTIR spectroscopic characterization of the as-deposited PbS/CZTS/PbS semiconductor thin film quantum wells. They all exhibited the same properties within wavenumber range of 500cm^{-1} – 1800cm^{-1} with so much noise in the readings but within wavenumber range of 1800cm^{-1} – 4000cm^{-1}, the different thin films with their difference in deposition times exhibited different absorbance peaks with respect to wavenumbers. The values were 0.0-2.75, 0.0-3.35, 0.0-3.5, 0.1-1.7, 0.1-3.4 and 0.1-2.7 for the 30mins, 60mins, 90mins, 120mins, 150mins and 180mins depositions respectively.

From the results above, it is obvious that the thin film that was deposited for 90mins had the highest range of 3.5 while the highest peak of absorbance of infrared light was exhibited at 6.0 by the 60mins, 90mins and 150mins depositions.

4. Conclusion

PbS/CZTS/PbS thin film quantum wells have been deposited at room temperature and 40^{o}C respectively using chemical bath deposition at different deposition times on microscope glass slides as the substrates. The films were characterized using UV-Vis and FT-IR Spectroscopy. The important property tested in the different substrates is the optical absorbance of the thin films as the deposition times are varied.

Firstly, they all showed optical absorbance with definite values above unity. This is an evidence that quantum wells deposited using chemical bath deposition technique also have the qualities exhibited by those deposited using molecular beam epitaxy and chemical vapor deposition. From this, it can be seen that Chemical bath deposition, as a cheaper and not-so-technical alternative to its counterparts, can be used to fabricate quantum wells, though with a slight difference in result efficiency, but with a cheaper and simple approach without altering the properties of the quantum well as was feared before.

Secondly, the variation in deposition times also showed that at 30mins, the PbS/CZTS/PbS thin film had the best absorbance for the UV-Vis spectrum while that of 90mins had the best absorbance for the infrared spectrum. Therefore, variation in deposition time helps to know which material and what deposition time will be best for application in thin film solar cells.

Lastly, the results have significantly shown that PbS and CZTS can be brought together to fabricate semiconductor quantum wells with excellent photovoltaic abilities.

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