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

***Arthur I I Ejere, Aghore Desmond Erhumwwunse**

*Department of Physics Faculty of Physical Sciences, University of Benin, Benin city, Nigeria.
Department of Science Laboratory Technology, Edo Polytechnic, Edo state, Nigeria.

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Abstract

Quantum wells have attracted so much attention in solar cells due to their high photovoltaic ability as they are able to trap and control electrons in their structure. Properties of quantum-well (QW) structures have proved useful in providing enhanced device characteristics and even in generating new device applications. The experimental and novel method of chemical bath deposition is used in this work and to fabricate quantum well. Deposition times were varied to see how difference in deposition time will affect the properties and functionality of the quantum well. UV-Vis and FT-IR spectroscopy were the measurements used to characterize the QW.

1. Introduction

The advances in nanotechnology over the years have made nanostructures potential targets of the industries due to their unique characteristics that influence the physical, chemical, electrical, and optoelectrical attributes of nanomaterials. The band gap, high exciton binding energy, piezoelectricity, biocompatibility, and pyroelectrical characteristics of nanomaterials such as ZnS, CuS, PbS, CZTS and Bi_2S_3 have made them suitable for innovative sensors, anodes for lithium-ion batteries, photoanodes, and nanogenerators for electricity harvesting. Nanostructures such as nanowires, nanotubes, nanobelts, nanosprings, nanoribbons, nanorings, nanosheets, and nanoparticles have found applications in non-linear optical devices, flat panel displays, light-emitting diodes, lasers, logic gates, and transistors. These nanostructures have been able to acquire their distinctive characteristics via modifications in the morphology, sizes, and shapes, through the fabrication process that involves the application of temperature, pressure, and chemicals such as catalyst substrates. Hence, the influence of temperature and pH on fabrication of nanomaterials has been done by different physical, chemical, and mechanical methods that used temperature, pressure, and phase transformation to create nanostructures. Different fabrication techniques such as chemical bath deposition, physical vapor deposition, molecular beam epitaxy, pulsed laser deposition, sputtering, metal organic deposition, electrode position, and electrospinning have predominated the nanostructures' fabrication [1,2].

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 effects of quantum confinement take place when the quantum well thickness becomes comparable to the de Broglie wavelength of the carriers (generally electrons and holes), leading to energy levels called "energy sub-bands", i.e., the carriers can only have discrete energy values. A quantum well is a particular kind of heterostructure in which one thin "well" layer is sandwich between two "barrier" layers. Both electrons and holes see lower energy in the "well" layer, hence the name (by analogy with a "potential well"). This layer, in which both electrons and holes are confined, is so thin (between 1Å to 100 Å, or about 40 atomic layers) that we cannot neglect the fact that the electron and hole are both waves. In fact, the allowed states in this structure correspond to standing waves in the direction perpendicular to the layers. Since only particular waves are standing waves, the system is quantized, hence the name "quantum well".

A wide variety of electronic quantum well devices have been developed based on the theory of quantum well systems. These devices have found applications in lasers, photodetectors, modulators, and switches for example. Compared to conventional devices, quantum well devices are much faster and operate much more economically and are a point of incredible importance to the technological and telecommunication industries. Quantum well devices are currently replacing many, if not all, conventional electrical components in many electronic devices.

Quantum wells can be formed with semiconductors by having a material, like Copper Zin Tin Sulphide (CZTS), sandwiched between two layers of a material with a wider bandgap, like Copper Sulphide. Consider, as an example, two layers of CuS with a large bandgap surrounding a thin layer of CZTS with a smaller band-gap. Let’s assume that the change in material occurs along the z-direction and therefore the potential well width is along the z-direction (no confinement in the x–y plane.). Since the bandgap of the sandwiched material is lower than the surrounding CuS, a quantum well (Potential well) is created in the CZTS region.

Copper zinc tin sulfide (CZTS) is a quaternary semiconducting compound which has received increasing interest since the late 2000s for applications in thin film solar cells. The class of related materials includes other such as copper zinc tin selenide (CZTSe) and the sulfur-selenium alloy CZTSSe. CZTS offers favorable optical and electronic properties similar to CIGS (copper indium gallium selenide), making it well suited for use as a thin-film solar cell absorber layer, but unlike CIGS (or other thin films such as CdTe), CZTS is composed of only abundant and non-toxic elements. Concerns with the price and availability of indium in CIGS and tellurium in CdTe, as well as toxicity of cadmium have been a large motivator to search for alternative thin film solar cell materials. The power conversion efficiency of CZTS is still lower than CIGS and CdTe, with laboratory cell records of 11.0 % for CZTS and 12.6 % for CZTSSe [3,4].

CZTS (Cu_2ZnSnS_4) offers to alleviate the material bottlenecks present in CIGS and CdTe (the two most promising thin-film solar cells). CZTS is similar to the chalcopyrite structure of CIGS but uses only earth-abundant elements. Raw materials are about five times cheaper than those for CIGS, and estimates of global material reserves (for Cu, Sn, Zn and S) suggest we could produce enough energy to power the world with only 0.1% of the available raw material resources. In addition, CZTS is non-toxic, unlike CdTe and to a lesser extent CIGS (although selenium is sometimes alloyed with CZTS and CdS is sometimes used as the n-type junction partner). In addition to these economic and environmental benefits, CZTS exhibits much greater radiation hardness than other photovoltaic materials, making it an excellent candidate for use in space [3].

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 and novel route to the fabrication of quantum wells. Chemical bath deposition 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. Therefore, the aim of this paper is to investigate the effect of chemical bath deposition on quantum wells. The main objective of this paper 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. The effect of difference in deposition times for the as-deposited QW.

Chemical bath deposition is a technique in which thin semiconductor films are deposited on substrates immersed in dilute solutions containing metal ions and a source of hydroxide, sulfide or selenide ions. The earliest reported work dates back to 1919 and dealt with the deposition of PbS thin films. There is a high feasibility of producing multilayer films by this technique [5].

The chemical bath deposition technique is ideally suited for the production of large area thin films as required for solar energy applications. The basic advantages of chemical bath deposition have been highlighted by various authors. The technique is applicable for the deposition of highly insoluble compounds. For example, the solubility of CuS at room temperature in water is estimated to be $10^{\sim 36}$g/dm^3, or in other words, the product of the ionic concentrations of the Cu^{2+} and the S^{2-} ions in the saturated aqueous solution of CuS is 10^{-36}mol^2/dm^6. This is the solubility product (SP). If in an arbitrarily constituted aqueous solution of Cu^{2+} and S^{2-} ions, the product of their ionic concentration (IP) is $>10^{-36}$ mol^2/dm^6, the excess ions will be precipitated as CuS. The details of these concepts are given in standard sources.

In the above-mentioned event, if the precipitation is controlled through the use of suitable complexing agents such as triethanolamine for the metal ions (so as to reduce the amount of free metal ions) and the amount of sulfide, selenide, or hydroxo ions in the bath is controlled through setting up of appropriate chemical equilibria, thin-film deposition can take place. A further condition to be satisfied is the availability of nucleation centers over the substrate. Such centers are normally formed through the adsorption of metal hydroxo species over the surface. The hydroxo- group would be substituted by the sulfide or selenide ions which would thereby form an initial layer of the metal chalcogenide. The deposition of the thin film takes place through the condensation of the metal and sulfide/selenide ions on this initial layer, which acts as a catalytic surface [6].

Although CBD has a number of advantages over other more intensive methods of film deposition, it also has limitations. It has been claimed that in the case of CBD cadmium sulfide, only approximately 2% of the initial cadmium concentration is used in film formation, resulting in high levels of cadmium waste. This, along with the volatility of ammonia (commonly used in bath solutions) in larger scale CBD operations, lead to a significant environmental hazard if not addressed. Homogeneous precipitation and deposition of the chalcogenide material on the walls of the reactor vessel are also limitations of the method, which have the effect of depleting the chemical bath of vital reagents which, in turn, leads to a reduction in both film thickness and film quality. The presence of contaminants, introduced during the deposition process can also result in a reduction in film quality and performance.

In order to make the CBD process more economical, not only financially but also in terms of maximum yield, various methods have been employed. These methods serve to minimise the extent of particulate growth within the solutions. To achieve this aim, techniques such as the careful spacing of substrates in the bath solution and the minimisation of the initial concentrations of reagents have been reported in literature. In an attempt to minimise the environmental impact of cadmium residues from CBD baths, a method was developed whereby excess cadmium could be recovered and the reagents recycled. It was also noted that by keeping the bath solution at a lower temperature and heating only the substrate, both homogeneous precipitation and deposition onto the walls of the reaction chamber could be minimized ([7,8].

2. Materials and Method

The effective study of the deposition process of CBD thin films requires a range of techniques in order to investigate the early stages of growth as well as the resultant product. The techniques that can detect that growth can be either in-situ or ex-situ techniques. 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 begins with information on the reagents used. It then provides a precise explanation on the 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**
Copper(II)chloride	$CuCl_2$	Merck Schuchardt
Triethanolamine 98%	$C_6H_{15}NO_3$	CDH (P) Ltd
Ammonium Hydroxide	NH_4OH	Griffin & George
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
Thioacetamide	C_2H_5NS	CDH (P) Ltd

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

Apparatus

Many different apparatus and materials were used before, during and after 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 and so on

2.2. 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.

2.3. Experimental Set-Up

A typical set-up for CBD deposition is shown in the Figure 1. 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.

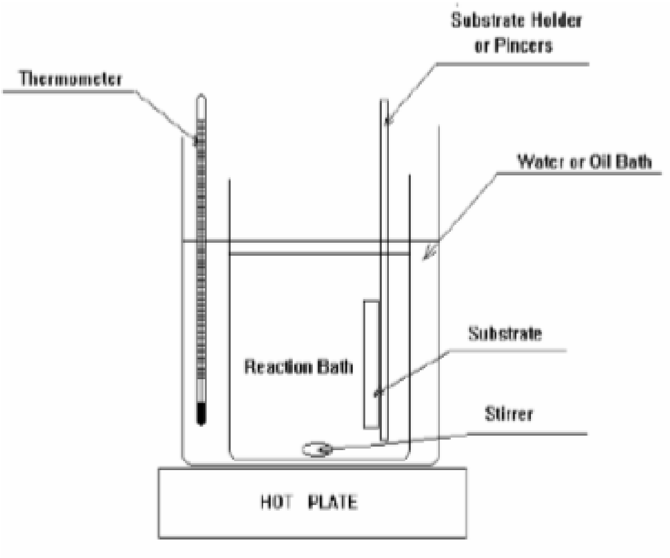

Figure 1: Schematic of Cemical bath deposition set-up

2.4. Experimental Procedure

2.4.1. Deposition of CuS thin films

CuS thin films were prepared by consecutively stirring 0.75M copper(II)chloride, 50% triethanolamine, 25% ammonia, 1M sodium hydroxide and 1M thiourea in total volume. Distilled water was added to obtain total solution volume of 100 ml. Glass microscope slides, with previously deposited ZnS films, were placed vertically in solution. Deposition was held at 65C for 0.5h, 1h, 1.5h, 2h, 2.5h and 3h for six different substrates. Obtained films were rinsed with distilled water, then dried.

2.4.2. 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 CuS films, were placed vertically in solution. Deposition was held at 40C for the six substrates. Obtained films were rinsed with distilled water, then dried.

The last deposition of the CuS thin film was made using the previously explained procedure resulting in three layers and the result was spread out to be dried.

3. Results and Discussion

The optical transmittance and absorbance of the CuS/CZTS/CuS 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. The results from the characterization is shown in the diagram below.

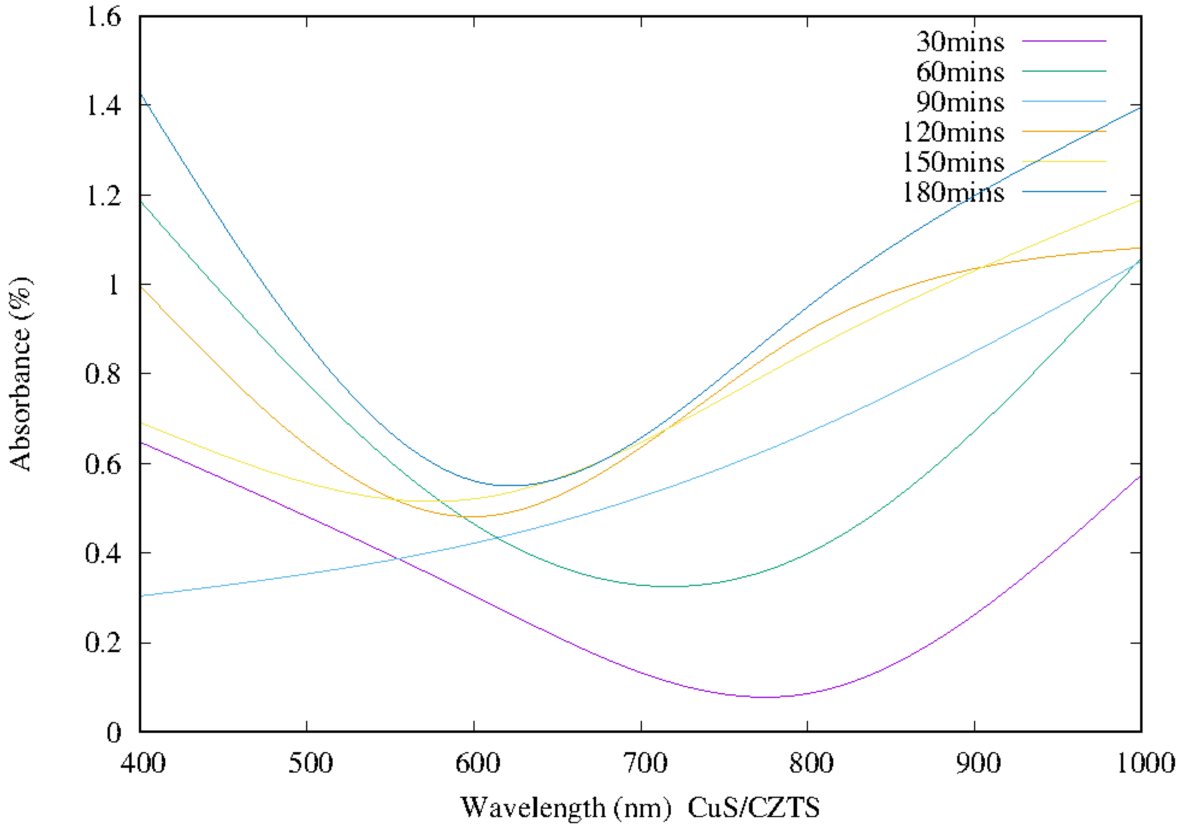

Figure 2: UV-Vis Absorbance spectroscopy of CuS/CZTS/CuS Quantum well

It can be seen from the graphical representation above that the CuS/CZTS/CuS quantum well exhibited good absorbance with its highest minimum peak at about 0.6 for the film deposited at 60mins. This is an essential characteristic showing the QW to be used in a photovoltaic 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 to Figure 8.

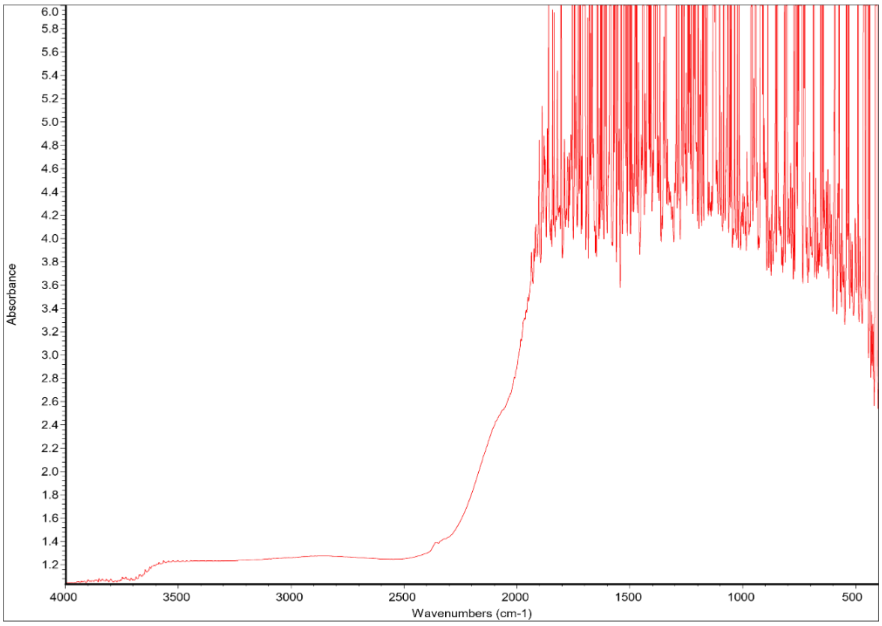

Figure 3: FTIR Absorbance spectroscopy of CuS/CZTS/CuS Quantum well for 30mins.

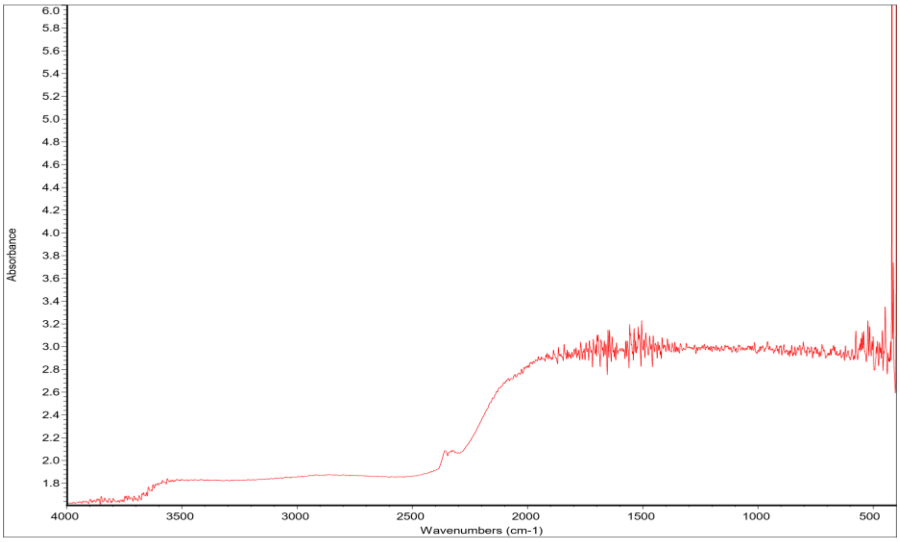

Figure 4: FTIR Absorbance spectroscopy of CuS/CZTS/CuS Quantum well for 60mins.

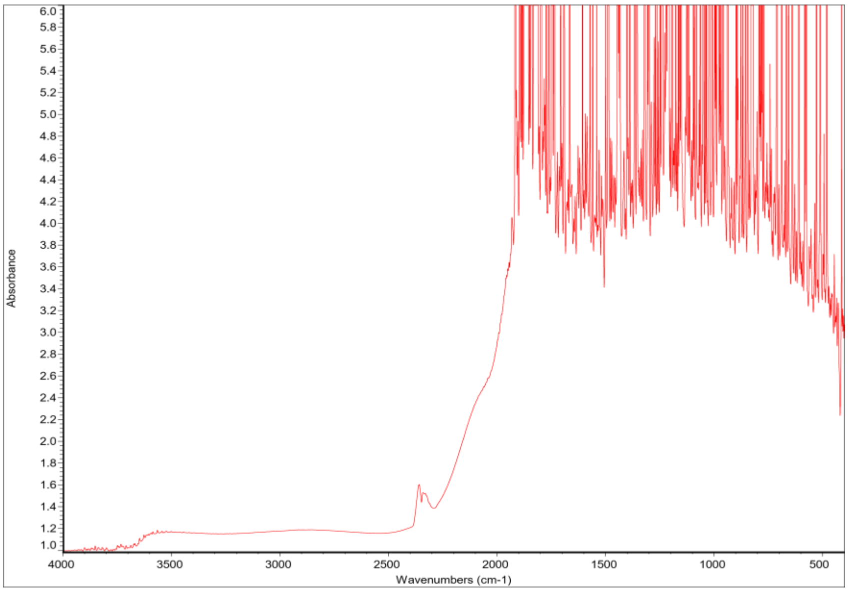

Figure 5: FTIR Absorbance spectroscopy of CuS/CZTS/CuS Quantum well for 90mins.

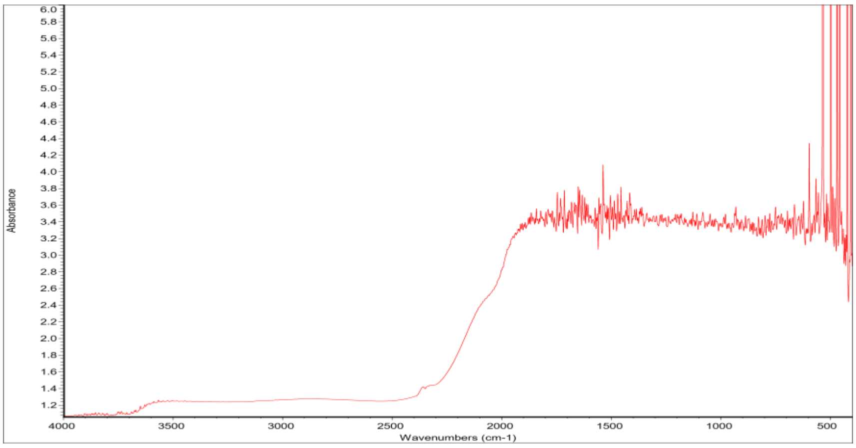

Figure 6: FTIR Absorbance spectroscopy of CuS/CZTS/CuS Quantum well for 120mins.

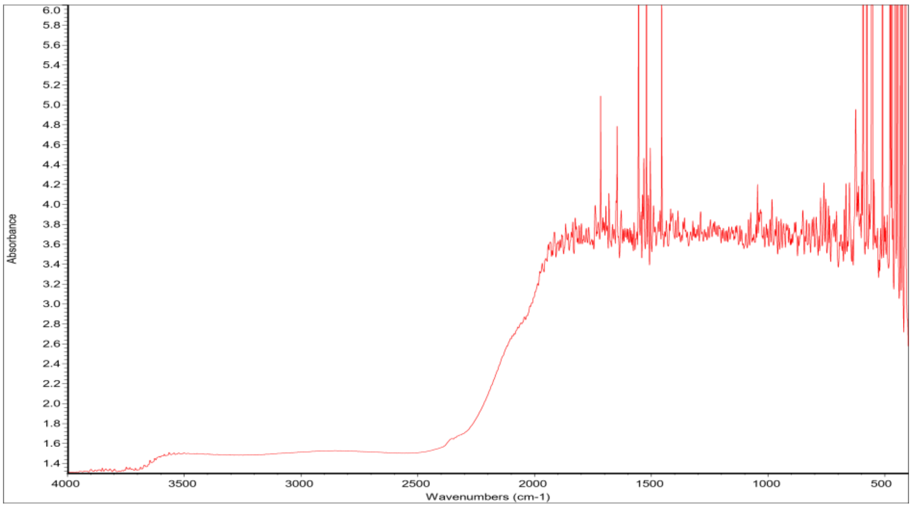

Figure 7: FTIR Absorbance spectroscopy of CuS/CZTS/CuS Quantum well for 150mins.

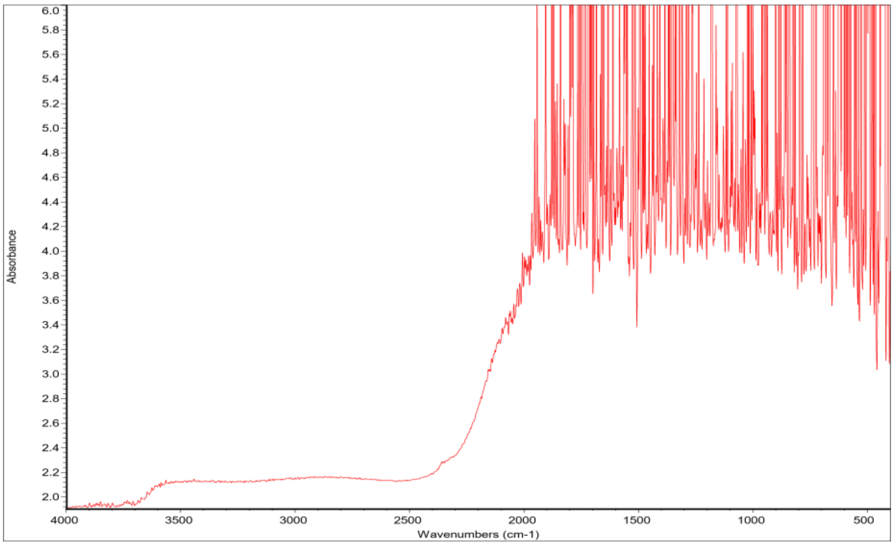

Figure 8: FTIR Absorbance spectroscopy of CuS/CZTS/CuS Quantum well for 180mins.

The graphs above are the results from the FTIR spectroscopic characterization of the as-deposited CuS/CZTS/CuS semiconductor thin film quantum wells. They all exhibited the same properties within wavenumber range of 1800cm^{-1} – 500cm^{-1} with so much noise in the readings but within wavenumber range of 4000cm^{-1} – 1800cm^{-1}, the different thin films with their difference in deposition times exhibited different absorbance peaks with respect to wavenumbers. The values were 1.0-3.8, 1.6-2.9, 1.0-3.8, 1.0-3.3, 1.3-3.5 and 1.9-4.0 for the 30mins, 60mins, 90mins, 120mins, 150mins and 180mins depositions respectively.

From the results above, it is obvious that the ultrathin film that was deposited at 60mins had the feature for best performance, followed by the 120mins deposition time.

4.0. Conclusion

CuS/CZTS/CuS thin film quantum wells have been deposited at temperatures of 65^{o}C 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. They all showed optical absorbance with definite values above unity. From this paper, it can be seen that Chemical bath deposition, is a cheap and not-so-technical alternative that 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. The variation in deposition times also showed that at 60mins, the CuS/CZTS/CuS ultrathin film will have the best performance. Therefore, variation in deposition time helps to know which deposition time that will be best for application in ultrathin film solar cells. Lastly, the results have significantly shown that CuS and CZTS can be brought together to fabricate semiconductor quantum wells with photovoltaic abilities.

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