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Study of Structural, Optical and Electrical Properties of CuSe₂/CdS/ITO Thin Films Deposited by Thermal Evaporation Technique for Solar Cells Applications

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Dedication

To.....

The lights of my life

father & mother

The lights of my eyes

my brothers, sisters, relatives and friends

All faithful hearts who helped me

in the journey of my life

Roaa



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Abstract

In this study, first the alloy of copper selenide was prepared by quenching technique. After that copper selenide and cadmium sulphide thin films are prepared by using thermal evaporation technique. The thin films have been grown on clean glass and ITO substrates. The annealing effects on the structural, optical and electrical properties of the films which have been studied.

The results of XRD showed that the copper selenide alloy was polycrystalline in nature with multiphase of copper selenide, the dominate phase was CuSe_2 with cubic structure and preferred orientation (221). The cadmium sulfide films were single crystalline, have cubic structure with orientation (111) plane for as-deposited and annealed films. Copper selenide films show polycrystalline nature for as-deposited and annealed films, the Cu_3Se_2 phase with tetragonal structure and preferred orientation (101) plane was dominate in the as-deposited film while the CuSe_2 phase with cubic structure and preferred orientation (221) plan was dominate in annealed film. "Scherrer's formula" has been used to calculate the crystallite size and it is found increases after annealing for both films. AFM outcomes show that increase in surface roughness and (RMS) for both annealed films, in addition the grain size of cadmium sulphide film increases in annealing but decreases for copper selenide film. SEM results show that the copper selenide powder have a compact structure composed of single type.

The absorbance and transmittance curves were recorded in the range of (400- 1100) nm to investigate the optical characteristics. The results

have shown that the cadmium sulphide and copper selenide films have a good transmittance in visible and NIR region. The absorption coefficient and refractive index were calculated too. The energy gap for allowable direct electronic transition was estimated using Tauc's model. The energy gap was decrease from (2.45 eV) to (2.41 eV) for cadmium sulphide thin film when annealed and for copper selenide was increase from (2.27 eV) to (2.32 eV) after annealed.

The electrical properties included D.C, hall effect measurements, and (I-V) characteristic of solar cell. From D.C. measurements, It has found that the D.C conductivity of cadmium sulphide thin film was increase after annealing while decrease for copper selenide thin film after annealing. All films have two transport mechanisms of free carriers and there was two activation energies for as- deposited and annealed films. Hall measurement results showed that the thin films of cadmium sulphide are n-type while copper selenide thin films are p-type.

On the other hand, " V_{oc} , I_{SC} , R_s , R_{sh} , FF and efficiency" of the solar cell have been measured. The solar cell parameters were found by using (I-V) tester system under illumination. The results show that no efficiency found for copper selenide/ cadmium sulphide /ITO solar cell.

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List of Symbols

Symbol	Description	Unit
a	Lattice Constant	Å
D_{av}	Crystallite size	nm
d_{hkl}	Interplanar Spacing	Å
N_o	Number of crystallites per unit area	cm^{-2}
δ	Dislocation Density	cm^{-2}
I_o	Incident intensity	mW/cm^2
I_A	Absorbed light intensity	mW/cm^2
E_g	Energy gap	eV
E_u	Urbach energy	meV
E_a	Activation Energy	eV
E_v	Valence band energy	eV
E_c	Conduction band energy	eV
E_{ph}	Phonon energy	eV
λ	Wavelength of incident light	nm
λ_c	Cut off wavelength	nm
h	Planck's constant	J.s
n	Refractive index	-
T	Transmittance	-
A	Absorbance	-
R	Reflectance	-
α	Absorption Coefficient	cm^{-1}
K_o	Extinction coefficient.	-
θ	Diffraction angle	Degree

t	Thickness	nm
k_B	Boltzmann's constant	J/k
$h\nu$	Photon energy	eV
c	Speed of light	m/s
A'and B	Constants depending on properties of bands	-
ν	Frequency	s^{-1}
\vec{K}	Wave vector	cm^{-1}
J_{sc}	Short-circuit current density	A/m^2
V_{oc}	Open-circuit voltage	V
η	Conversion efficiency %	-
e	Electron charge	coul
V	Voltage	volt
J_m	Maximum current density	A / cm^2
V_m	Maximum voltage	V
P_{out}	Output power	W
P_{in}	Incident power	W
P_{max}	Maximum power	W
T	temperature	k
R_S	Series resistant	Ω
R_{Sh}	shunt resistant	Ω
μ_H	Hall mobility	$m^2 / (V.s)$
R_H	Hall coefficient	m^3/C
σ	Conductivity	$(\Omega.m)^{-1}$

List of Abbreviations

Abbreviation	Description
SEM	Scanning Electron Microscope.
AFM	Atomic Force Microscope.
UV	Ultra Violet.
XRD	X-Ray Diffraction.
RMS	Root Mean Square.
PV	Photovoltaic.
QE(E)	Quantum Efficiency.
FF	Fill Factor.
TFPV	Thin Film Photovoltaic Cell.
DSC	Dye-Sensitized Solar Cell.
AM	Air Mass.

Chapter One

Introduction

1-1 Introduction

The physics of thin films is considered as an important branch of solid state physics which then becomes an independent branch in physics. The expression (film) is used to explain a layer of tens of nanometers thickness. All researchers indicated that the thickness of thin film is very small and less than one micrometer [1].

Being very thin, the film layer is deposited on certain substrates chosen according to the nature of study or scientific need, such substrate could be glass slides, silicon wafers, aluminum, quartz and others [2]. Extensive studies have shown that the properties of a thin film are different from those of bulk material [3]. Thin films are first made by (Busen & Grove) in 1852 by using (Chemical Reaction) and later in 1857; the scientist (Farady) had been able to obtain a thin metal film by means of (Thermal Evaporation) [4]. Furthermore, the properties of thin films depend on different parameters like the thickness and type of film and most of all on the evaporation conditions at which the films are prepared [2].

The thin films have many uses; they are rectifiers and junction diodes, integrated circuits industry, optical communications as light emitting diodes, semiconductors lasers and detectors, solar cells, light filters and special specifications mirrors [5]. They are also used mainly to protect the materials painted by thin films from corrosion and interaction with the atmosphere and the surfaces damage for various applications [6]. The wide varieties of semiconductor applications need high sensitive materials which are easy to fabricate, at the same time they have a broad range of electronic, optical, and optoelectronic properties. Thin films are

formed by depositing materials onto a clean supporting substrate to build up film thickness, rather than by thinning down bulk material [7].

1-2 Thin Films Preparation Methods

The methods of preparing thin films can be divided essentially into two main groups, namely, physical and chemical methods [8]. These methods are shown in figure (1.1).

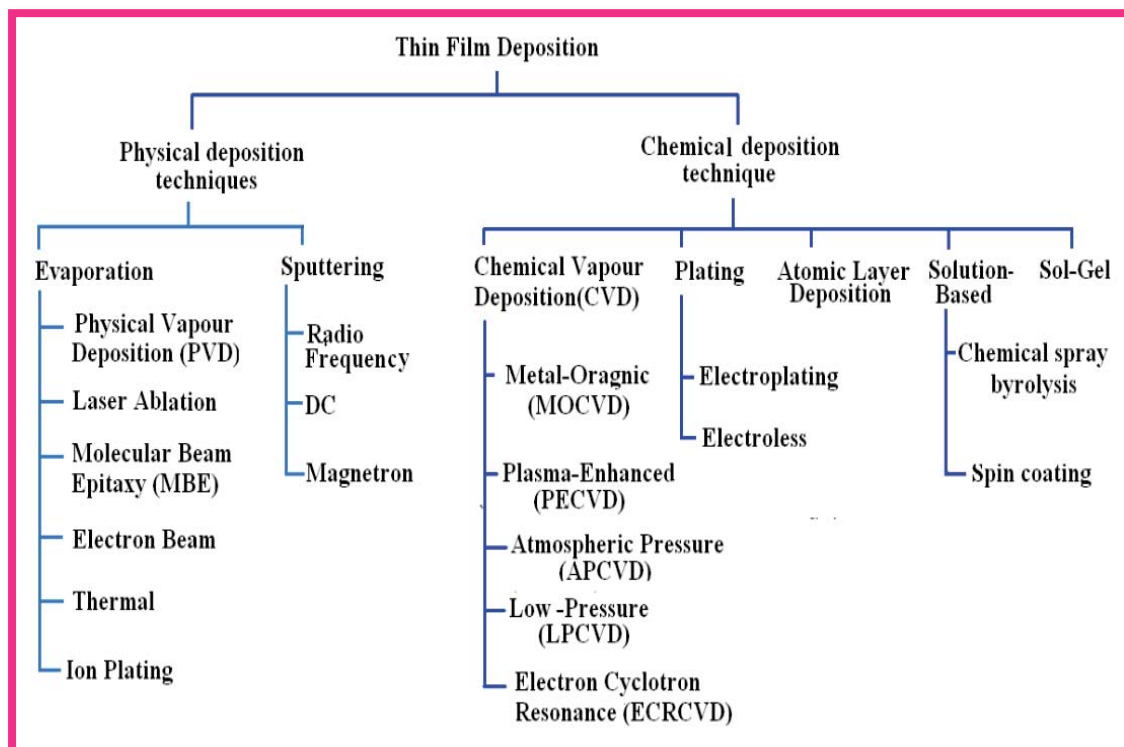


Fig. (1.1): Classification of thin film deposition techniques [9].

1-3 Thermal Evaporation Technique

Thermal evaporation is a common method of thin film deposition. In thermal evaporation technique, the material is heated by using a resistively heated filament or boat, generally made of high melting point and low volatility material such as tungsten or molybdenum to evaporate material in a vacuum (low pressures, about 10^{-6} - 10^{-5} Torr). The vacuum

allows vapor particles to travel directly to the target object (substrate), the mean free path of vapor atoms is the same order as the vacuum chamber dimensions, they condense back to a solid state, figure (1.2). The films grown by this method are usually amorphous and polycrystalline in nature[10,11]. There are many types of boats, as shown in figure (1.3).

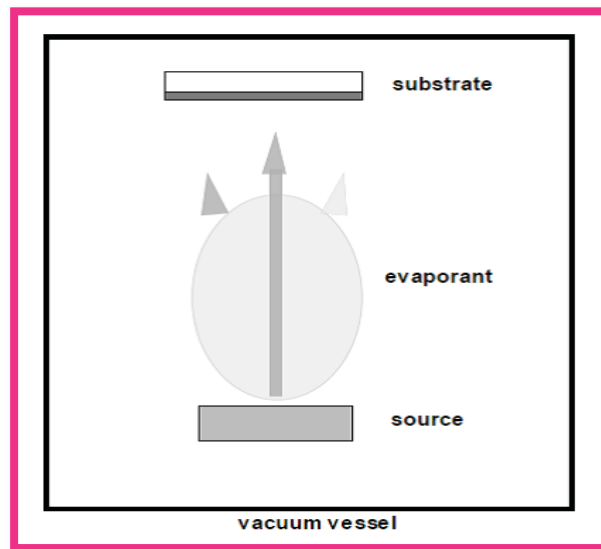


Fig. (1.2): The three basic steps in any physical vapor deposition process: evaporation from the source, transport of evaporation, and condensation of the evaporate [11].

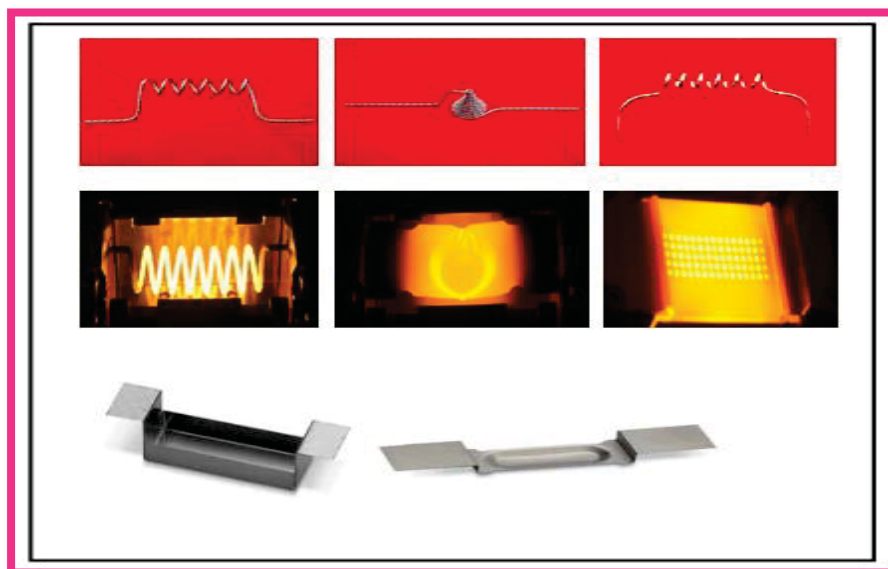


Fig. (1.3): Configurations for filaments used in electrical resistance heated thermal evaporation[12].

1-4 Solar Cells

A solar cell device converts the sunlight directly into electricity through the photovoltaic. In principle, it depends on two parameters. The generation of current by absorbed incident illumination and the loss of charge carriers via so-called recombination mechanisms[13].

The radiant power per unit area perpendicular to the direction of the sun outside the earth's atmosphere but at the near earth-sun distant is essentially constant. This radiation intensity is referred to as the solar constant or, alternatively, air mass zero (AM0) radiation. The presently accepted value of the solar constant in photovoltaic work is 1.353 kW/m^2 this value has been determined by taking a weighted average of measurements made by equipment mounted on balloons, high-altitude aircraft, and spacecraft. A knowledge of the exact distribution of the energy content in sunlight is important in solar cell work because these cells respond differently to different wavelengths of light [14].

Conventional semiconductor solar cells are based on p-n junctions. In a p-n junction, two semiconductors with different majority charge carriers and doping concentrations an n - doped and a p - doped material are in close contact, as show in figure(1.4)[15].

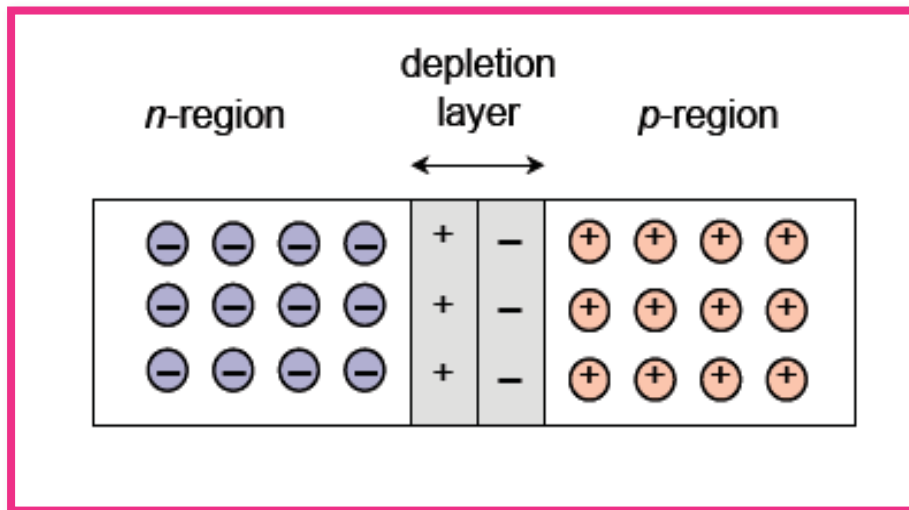


Fig. (1.4): p-n junction of solar cell [15].

The electrons diffuse from the n-type side to the p-type side. Similarly, holes flow by diffusion from the p-type side to the n-type side. If the electrons and holes were not charged, this diffusion process would continue until the concentration of electrons and holes on the two sides were the same, as happens if two gasses come into contact with each other. However, in a p-n junction, when the electrons and holes move to the other side of the junction, they leave behind exposed charges on dopant atom sites, which are fixed in the crystal lattice and are unable to move. On the n-type side, positive ion cores are exposed. On the p-type side, negative ion cores are exposed. An electric field forms between the positive ion cores in the n-type material and negative ion cores in the p-type material. This region is called the "depletion region" since the electric field quickly sweeps free carriers out, hence the region is depleted of free carriers. A "built in" potential due to electric field is formed at the junction [16,17].

1-4-1 Photovoltaic (PV)

The history of photovoltaics goes back to the nineteenth century. The term photovoltaic (derived by combining the Greek word for light, photos, with voltaic) is the most direct way to convert solar radiation into electricity and is based on the photovoltaic effect, which was first observed by Henri Becquerel in 1839, when he found that two different brass plates immersed in an electrolytes liquid produced a continuous current when illuminated with sunlight his theory then sparked the idea of using semiconductor material as a source to convert solar power to electrical energy [16,18,19].

The 20th century witnessed the discovery of the photoelectric effect by Albert Einstein and others [19]. The first silicon solar cell was thereafter developed by Chapin et al. also from Bell laboratories, in 1954. The cell, using silicon as its raw material, initially yield an efficiency of 6%, which was rapidly increased to 10% [20]. In 1941, Russell Ohl invented the silicon solar cell. With his discovery the efficiency of solar cells began to increase [21]. Furthermore, the first photovoltaic effect in an organic crystal was observed by Kallman and Pope in 1959 [22]. Dewald's (1959, 1960) lucid expositions of the principles of semiconductor electrochemistry laid the foundation for rapid experimental advances in the sixties, when many important concepts were established: the relation between the sign of the photo potential and the conductivity type of the electrode (Williams, 1960) [23].

The PV cell is a smallest building block of a photovoltaic system, and it is made of materials called semiconductors, which have weakly bounded electrons occupying a band of energy called the valence band.

When energy exceeding a certain threshold, called the band gap energy, is applied to a valence electron, the bonds are broken and the electron is somewhat “free” to move around in a new energy band called the conduction band where it can “conduct” electricity through the material. For each negatively charged electron, a corresponding mobile positive charge, a hole, is created. Thus, the free electrons in the conduction band are separated from the valence band by the band gap (measured in units of electron volts or eV). This energy needed to free the electron can be supplied by photons, which are particles of light [16]. See figure (1.5).

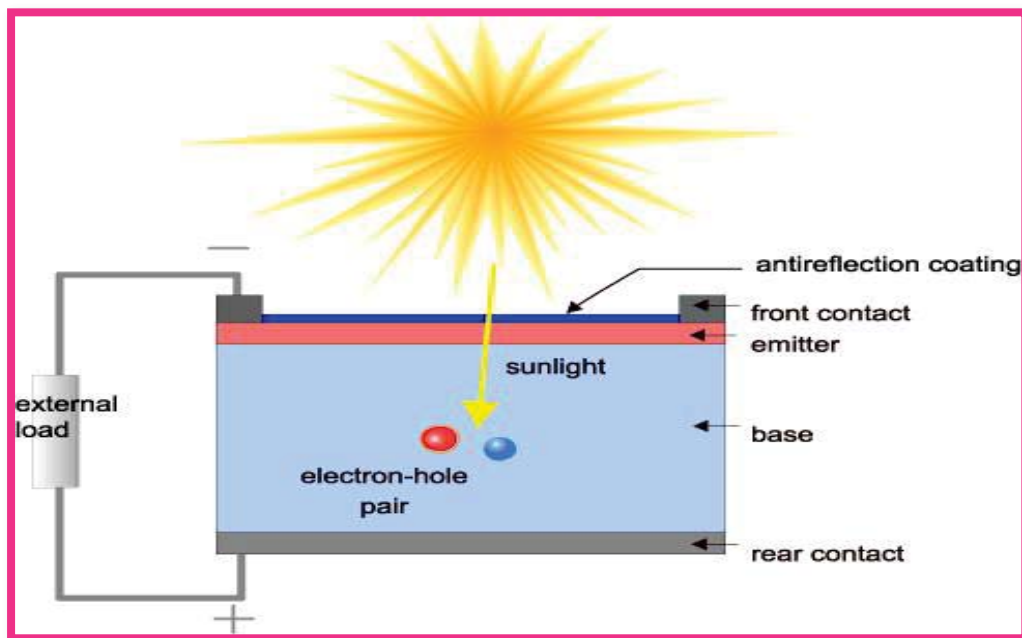


Fig. (1.5): Structure of a PV cell [24].

Figure (1.6) shows the scheme of solar cell. When the solar cell is exposed to sunlight, photons hit valence electrons, breaking the bonds and jumping them to the conduction band. There is a specially made selective contact that collects conduction-band electrons drives such electrons to the external circuit. The electrons lose their energy by doing work in the external circuit such as pumping water, spinning a fan,

powering a sewing machine motor, a light bulb, or a computer. The movement of these electrons in the external circuit and contacts is called the electric current. The potential at which the electrons are delivered to the external world is slightly less than the threshold energy that excited the electrons [25].

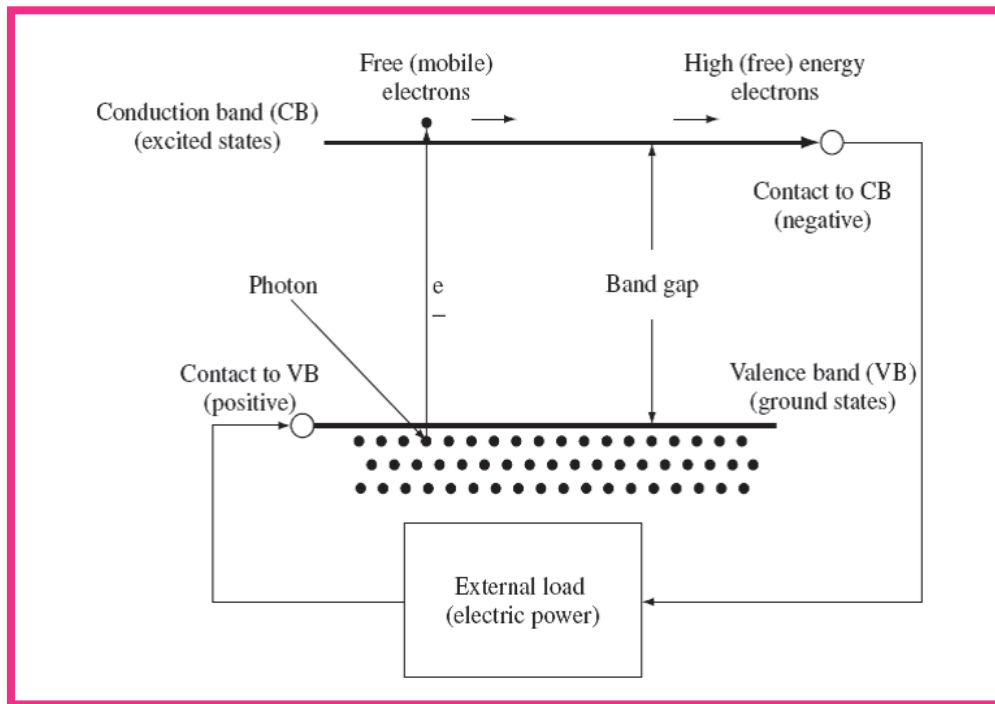


Fig. (1.6): Schematic of a solar cell. [25].

A typical PV system consists of a large number of individual PV cells typically contains (28-36) cells and are interconnected and encapsulated into units called PV modules[26,27], see figure (1.7) which is the product usually sold to the customer. They produce DC current that is typically transformed into the more useful AC current by an electronic device called an inverter.



Fig. (1.7): Some typical PV systems[27].

1-5 Generations of Solar Cells

Solar cells can be classified into four generations; which are:

- First Generation

First generation solar cells are the dominant technology in the commercial production of solar cells. These cells are made using a crystalline silicon wafer; they consist of large area, single layer p-n junction devices. They are characterized by broad spectral absorption range and high carrier motilities, but they require expensive manufacturing technologies [28].

- **Second Generation**

Second generation of thin-film solar cell devices are based on low energy preparation techniques such as vapor deposition and electroplating [28]. Thin-film solar cells are cheaper but less efficient [29].

- **Third Generation**

Third generation photovoltaic refers to cell concepts that overcome the 31% theoretical upper limit of a single junction solar cell as defined by Shockley and Queisser [30]. Third generation PV technologies may overcome the fundamental limitations of photon to electron conversion in single-junction devices and, thus, improve both their efficiency and cost [31]. The third generation photovoltaics are very different from semiconductor devices. These new devices include photo-electrochemical cells, polymer solar cells, and nano-crystal solar cells [32].

- **Fourth Generation**

In the fourth generation composite photovoltaic technology with the use of polymers with nanoparticles can be mixed together to make a single multi-spectrum layer. Then the thin multi-spectrum layers can be stacked to make multi-spectrum solar cells more efficient and cheaper based on polymer solar cell and multi-junction technology [32].

1-6 Literature Review

The previous studies involving the CdS, copper selenide thin films showed their structural, optical and electrical properties.

In (1999) García et al. [33] have reported on the structural, optical and electrical properties of thin films of copper selenide obtained from chemical bath deposition and the changes brought about in these properties during thermal treatment at (200 °C – 400 °C) in air and vacuum. CuSe thin films deposited using N,N-dimethylselenourea transformed to Cu_{2-x}Se during vacuum annealing at 400 °C, whereas, the composition of chemically deposited Cu_{1.85}Se films obtained using sodium selenosulfate remained practically stable during such annealing. The high near infrared reflectance (30-80%) and low transmittance of the films were related to a high p-type electrical conductivity $\sim(1-5)\times 10^3 (\Omega.\text{cm})^{-1}$ of these films.

In (2000) Oladeji et al. [34] have used Rutherford backscattering spectrometry (RBS), X-ray diffraction (XRD), Raman, and photoconductivity to characterize CdS thin films grown by single, continuous, and multiple dip chemical processes. XRD has shown, that grown CdS films, independent of the process, in an almost homogeneous reaction free basic aqueous bath have a zinc blende crystal structure where reflections from (111), (200), (220), and (311) planes were clearly identified. RBS, Raman, and photoconductivity confirm the high stoichiometry and excellent structural properties with low optically active trap state density of single and continuous dip CdS films. However, they collectively suggest that multiple dip CdS films suffered from defects that act as carrier traps and lead to prolong photoconductivity decay in these films.

In (2003) Enríquez et al. [35] have deposited cadmium sulfide films of different thicknesses by chemical bath deposition (CBD) from a bath containing cadmium acetate, ammonium acetate, thiourea and ammonium hydroxide. The XRD patterns showed that the films were of hexagonal phase with preferred (0 0 2) orientation and the grain size increased with the thickness of the film. The band gap of the films was calculated from the transmittance data and it was found that the band gap decreased as the film grew in thickness.

In (2005) Al-Shammari [36] prepared CdS thin films with different thicknesses (1000-2300Å) using chemical bath deposition technique. Also CdS thin films were prepared using high vacuum evaporation techniques with different thicknesses (1000-3000Å). The films have been annealed at different annealing temperatures (250-400 °C). The diffraction peak existed at $2\theta=26.6^\circ$ for chemical bath deposition prepared films and at $2\theta=26.5^\circ$ for high vacuum evaporation ones corresponding to either the (002) hexagonal or the (111) cubic planes. The resistivity of as-deposited CdS films using chemical bath deposition and high vacuum evaporation techniques were in the range of 10^6 and $10^3 \Omega\text{-cm}$ respectively. It was found that the resistivity decreased as the film thickness increased and as the annealing temperature was increased for CdS films prepared by both chemical bath deposition and high vacuum evaporation techniques. It has been observed that the transmission of chemical bath deposition CdS thin films decreased as the film thickness was increased. high vacuum evaporation CdS thin films exhibit high transmissions (70-90%) in the visible range. The band gap decreases with the increased film thickness and annealing temperature.

In (2006) Patidar et al. [37] have prepared cadmium sulphide by using Chemical method using cadmium, hydrochloric acid and H_2S . The energy band gaps of these films have been calculated from reflection spectra. It was found that the energy band gap of both films was same as 2.41 eV. It was indicated that energy band gap of these films does not change. This value of band gap was in good agreement with the value reported by other workers. The films show high photosensitivity and high photocurrent decay. Thus, the obtained films were suitable for fabrication of photodetectors and solar cells.

In (2007) Devi et al. [38] have deposited cadmium sulphide thin films on glass substrates and found to be polycrystalline having hexagonal type structure. The photocurrent-light intensity characteristics showed sub-linear and super-linear behavior which were attributed to the defects. The defect characterization was done from the temperature dependence of dc photoconductivity and rise and decay characteristics of the photo current. Shallow levels (0.06 to 0.34eV) arising from interstitial cadmium or Sulphur vacancies were found to cause extrinsic photoconductivity near room temperature whereas the deep levels dominated the rise and decay characteristics and super linearity.

In (2008) Gosavi et al. [39] have grown copper selenide (CuSe) thin films onto amorphous glass substrate from an aqueous alkaline medium using solution growth technique (SGT) at room temperature. The preparative parameters were optimized to obtain good quality of thin films. X-ray diffraction (XRD) pattern revealed that the films are polycrystalline in nature. Energy dispersive analysis by X-ray (EDAX) showed formation of stoichiometric CuSe compound. Uniform deposition of CuSe thin films on glass substrate was observed from scanning

electron microscopy (SEM) and atomic force microscopy (AFM) micrographs. Average grain size was determined to 144.53 ± 10 nm using atomic force microscopy. The band gap was found to be 2.03 eV with direct band-to-band transition. Semi-conducting behavior was observed from resistivity measurements. Ohmic behavior was seen from I–V curve with good electrical conductivity.

In (2008) Murali et al. [40] have deposited cadmium sulphide (CdS) thin films by the flash evaporation technique using the CdS powder synthesized by a chemical precipitation method in the laboratory from AR grade cadmium acetate and thiourea. This powder was used as a source material for the deposition of thin films on glass and titanium substrates. The substrate temperature was varied in the range of 30-250 °C. XRD patterns indicated that the films were polycrystalline exhibiting peaks corresponding to the hexagonal phase. Optical absorption studies indicated a direct band gap of 2.39 eV. Photo-electrochemical measurements were made on the films deposited at different substrate temperatures. The as deposited films exhibited weak photo-activity, due to the annealing in argon atmosphere.

In (2009) Elawi et al. [41] prepared CdS films by thermal evaporation at pressure (10^{-6} torr) of $1 \mu\text{m}$ thickness onto glass substrate by using (Mo) boat. The optical properties of CdS films, absorbance, transmittance and reflectance were studied in wavelength range of (300-900)nm. The refractive index, extinction coefficient, and absorption coefficient were also studied. It's found that CdS films had allowed direct and forbidden transition with energy gap 2.4eV and 2.25eV respectively with high absorption coefficient ($\alpha > 10^4 \text{ cm}^{-1}$).

In (2010) Khan et al. [42] deposited cadmium sulfide polycrystalline thin films of different thickness on ultrasonically cleaned glass substrates using thermal evaporation technique in a vacuum of about 2×10^{-5} torr. XRD study showed that, all the films have the hexagonal wurtzite structure, with lattice constants $a=b=4.142$, $c=6.724 \text{ \AA}$. Crystallite sizes calculated from Scherrer relation are in the range of 49-68 nm and the grain size of the thin films are observed to increase with the increase in the thickness of the sample. The band gap of the thin films is found to be direct allowed transition and increases with the increase of thickness of films in the range of 2.35- 2.46 eV.

In (2011) Okereke and Ekpuobi [43] have prepared copper selenide thin films by chemical bath deposition method on a glass substrate at room temperature. The XRD patterns indicated that the films were crystalline in the structure. The band gap energy was found to be both direct and indirect.

In (2011) Ehsani and Dizaji [44] fabricated CdS thin films with thicknesses 40 and 800nm using flash evaporation technique on ITO coated glass substrates at RT in vacuum chamber. CdS powder was evaporated from a molybdenum boat heated up to the temperature about 1500K appropriate to evaporate the CdS powder, the deposition rate was about 5 \AA/s , and then annealed at 300°C . The structural characterization indicated that both of the films showed preferential growth of film crystallites at $2\theta=26.84^\circ$ which coincides with (002) diffraction line of the CdS hexagonal phase and cubic (111) planes. The band gaps of the as-deposited 40 nm and 800 nm CdS films were found to be about 2.42 and

2.36 eV and the same for the annealed films were found to be about 2.39 and 2.31 eV respectively.

In (2012) Güzeldir et al. [45] have studied CuSe thin films which directly formed on n-type Si by means of Successive Ionic Layer Adsorption and Reaction (SILAR) method, at room temperature. The SEM and XRD studies showed that films covered well n-type Si substrates and exhibit polycrystalline phase. The EDAX spectra showed that the expected elements exist in the thin films. Some of the thin film with equal distribution of grains, mostly falling in nanometer regime, was clearly seen. Additionally, Cu/CuSe/n-Si/Au-Sb structures are prepared by the SILAR method at room temperature. The characteristics parameters such as ideality factor (η), barrier height (Φ_b) and saturation current (I_0) were obtained from current- voltage (I-V) measurement by applying a thermionic emission theory. According to the optical and electrical characterizations, it was concluded that, these structures can be used for solar-cell studies, rectifying contacts, integrated circuits, other electronic devices and so on.

In (2012) Thomail [46] prepared CdS thin films with a different thicknesses on glass substrates by using thermal vacuum evaporation technique at substrate temperature of 150°C. The optical characteristics of the prepared thin films had been investigated by UV-VIS spectrophotometer in the wavelength range (300-1100 nm) . The films had a direct allow electronic transitions and the optical absorption were shifted to the low energies by increasing the thickness. Also the optical energy gap (E_g) had decreased from 2.47 eV to 2.22 eV by increasing the thickness value.

In (2013) Ezenwa et al. [47] have chemically deposited copper selenide (CuSe) thin films onto a glass substrate. They studied optical properties which include absorbance, reflectance, transmittance, refractive index. A bandgap of 2.2eV and refractive index of 2.5 was obtained for CuSe thin film.

In (2013) Al-Shaikley [48] have deposited CdS thin films of 100 ± 10 nm thickness onto glass substrate maintained at room temperature using thermal evaporation technique. The effect of annealing temperature on the electrical and some optical properties were investigated. The annealing process in air for 1h was found to decrease the optical band gap energy and to increase the conductivity and Hall mobility of the investigated thin films. The optical band gap values were varied between 2.4 and 2.3 eV with allowed direct transition. Urbach energy was found to be decreased for air-annealed films up to 623K then it increased with further elevation in annealing temperatures up to 723K. On annealing process, the dark DC electrical conductivity at room temperature and Hall mobility of the films increased from 1.67×10^{-6} to 3.93×10^{-4} ($\Omega\cdot\text{cm}$)⁻¹ and from 0.31 to 42.35cm² /V.s respectively. These physical behavior made prepared films good candidate for solar cells fabrication. All the investigated films have n-type conduction with their carrier concentration were to be in the order of 10^{13} cm⁻³. The activation energy as a function of the annealing temperature was found to be in the range 0.776-0.375 eV.

In (2013) Durdu et al. [49] deposited copper selenide thin films, by chemical deposition technique on glass substrates. Sodium selenosulphate was used as a selenide ion source in an alkaline solution. The X-ray diffraction patterns showed that the Cu₃Se₂ film has a tetragonal structure.

In (2014) Yadav [50] has deposited copper selenide thin films by spraying a mixture of aqueous solutions (0.50 M) of copper chloride hydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) and selenourea [$\text{H}_2\text{-NC(Se)NH}_2$] on preheated fluorine doped tin oxide coated glass substrates at various substrate temperatures. The cell configurations copper selenide were used for studying the capacitance–voltage (C–V) characteristics in the dark, current–voltage (I–V) characteristics in dark and under illumination, photovoltaic power output and spectral response characteristics of the as deposited films. Photo-electrochemical study recorded that as deposited copper selenide thin films were of p-type. The spectral response characteristics of the films at room temperature showed a prominent, sharp peak at 550 nm. The measured values of efficiency (η) and fill factor (FF) were found to be 0.99 % and 0.51 respectively for film deposited at 350°C.

In (2014) Awodugba et al. [51] have deposited cadmium sulfide polycrystalline thin films on glass substrates using chemical bath technique at deposition temperature of 60°C from a bath containing cadmium chloride, ammonium chloride, ammonium hydroxide and thiourea.

In (2014) Chizomam et al. [52] have deposited CuSe thin films on glass slides from alkaline bath employing chemical bath deposition method. Films were annealed at 573K to study their properties. Both the as-deposited and annealed films were found to be amorphous which was detected by the SEM microscopy and confirmed by the X-ray diffraction. Peak values of 96.10%, 46.43% were observed for absorbance and reflectance which increased on annealing while transmittance decreased.

Average values of refractive index which ranged between 2.14 – 2.62 increased to 2.16 – 3.33 on annealing. As-deposited band gap which ranged between 2.35 eV and 2.60 eV were found to reduce on annealing to the range 2.10 eV – 2.40 eV. Films could be used as absorber materials in solar cells and as window layer in photovoltaic cells.

In (2014) Ramesh et al. [53] have deposited copper selenide thin films on indium doped tin oxide coated glass substrates. X-ray diffraction analysis revealed that the deposited films possess polycrystalline in nature. Optical absorption analysis showed that the deposited films possess band gap value around 2.1 eV.

In (2015) Demir and Gode [54] have prepared cadmium sulfide thin films on glass substrates at 82 °C for 1 hour by chemical bath deposition. After deposition, the films are annealed at 480 °C for 1 hour in air atmosphere. The X-ray diffraction patterns of deposited films showed the formation of polycrystalline of CdS with both cubic and hexagonal structure. Moreover, after the thermal treatment of 480 °C, they mostly turned into polycrystalline CdO with cubic structure. The grain size of the deposited film decreased approximately from 10–20 nm to 2-3.5–5.5 nm by annealing. The band gap energy of the films was determined for the direct transitions of 2.15 eV and increased to 2.25 eV by the thermal treatment. After thermal process, the electrical conductivity of the films was calculated from the current–voltage characteristic in the dark increased from $5.482 \times 10^{-10} (\Omega \text{ cm})^{-1}$ to $5.304 \times 10^{-8} (\Omega \text{ cm})^{-1}$.

In (2015) Thirumavalavan et al. [55] have prepared copper selenide (CuSe) thin films by chemical bath deposition (CBD) method. The AC electrical conductivity study revealed that the conduction depended both

on the frequency and the temperature. The temperature dependent conductivity study confirmed the semiconducting nature of the films. Photoconductivity measurements were carried out in order to ascertain the positive photoconductivity of the CuSe thin films.

In (2016) Danu et al. [56] An investigation has been carried out to determine the annealing-induced variation in the optical properties and possible phase changes that may occur in CBD synthesised CuSe thin films. Structural analysis of the copper selenide samples showed the presence of several phases in the as-deposited sample. After annealing, the diffraction pattern showed the presence of a single phase, krutaite with preferred orientation along the (111) plane. No diffraction peaks from other species could be detected in the annealed copper selenide sample. The as-deposited copper selenide films possessed two band gaps of 1.20 and 1.33 eV which could be attributed to the presence of several phases. After annealing, the band gap changed to 2.20 eV. There was an increase in the average grain size of copper selenide samples after annealing suggesting a further growth in grain size at this temperature.

In (2016) Gilic et al. [57] described the structural and optical properties of Cu-Se thin films. Formation of Cu–Se thin films was concluded to proceed unevenly, in the form of islands which later grew into agglomerates. The presence of two-phase system was observed, one is the solid solution of Cu in Se and the other is low-pressure modification of CuSe₂. The Raman spectroscopy was used to identify and quantify the individual phases present in the Cu–Se films. Red shift and asymmetry of Raman mode characteristic for CuSe₂ enable us to estimate nanocrystal dimension.

In (2016) Beggas et al. [58] prepared CdS thin films by chemical bath deposition (CBD) technique. The bath solution was a mixture of Cadmium carbonate CdCO_3 and thiourea as source of Cadmium and Sulfur respectively, ammonia was used as complexing agent. In order to investigate the deposition time; films were prepared with two deposition times 45 and 90 min. Hexagonal CdS thin films were obtained with (002) preferred orientation and having crystallite size in the range of (14.3–30.4 nm) for the two deposition times. CdS thin films transmittance was above 70% in visible region. Band gap energy was 2.46 and 2.42 eV for both samples.

In (2016) Muthukannan et al. [59] presented first report on Al doped CuSe_2 thin films deposited on to the glass substrate using elemental precursors Cu, Al and Se by thermal evaporation method. The XRD study of the annealed film showed polycrystalline nature. The predominant orientation along (101) direction corresponding to orthorhombic structure of CuSe_2 with an additional phase of Al_2Se_3 along $(\bar{3}14)$ and (331) direction. The SEM and AFM images of the annealed film showed densely packed grains and the surface roughness was found to be about 21.16 nm respectively. The direct band gap and resistivity was decreased in annealed film when compared to the as-deposited film. Which could be attributed to the influence of annealing process.

In (2017) Singh et al. [60] fabricated CdS thin films on soda lime glass (SLG) substrates using vacuum thermal deposition method in the presence of hydrogen sulphide (H_2S) atmosphere. The consequence of ambient H_2S on the growth, quality and structure-property relationship of vacuum deposited CdS thin films has been investigated. The deposited films have been characterized by XRD, SEM with EDX analysis, AFM,

XPS and optical spectroscopy. The physical characterization of as-deposited CdS films reveals that the films deposited in controlled H₂S ambient are more crystalline, highly uniform and stoichiometric in comparison to films deposited without H₂S atmosphere.

1-7 The Aims of Study

The present study aims at:-

- 1- Preparation copper selenide alloy.
- 2- Preparing CdS and CuSe₂ thin films on glass substrates by thermal evaporation technique at thickness 200 and 500 nm respectively.
- 3- Studying the effect of annealing on structural ,optical and electrical properties of CdS and CuSe₂ thin films.
- 4- Fabricating CuSe₂/CdS/ITO solar cell and studying their properties.