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Synthesis of Some Ternary Metal Oxides and Sulphides Nanostructures Thin Films For Photovoltaic Applications

A thesis
Submitted to the Council of the College of Science
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for the Degree of Doctor of Philosophy in Physics sicences

By

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هُو الَّذِي جَعَلَ الشَّمْسَ ضِيَاءً وَالْقَمَرَ نُورًا

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Dedications

To

The first teacher who gave me the strength and patience and diligence.

(My father)

To

My way candle that lit up my life and stayed up nights to my care.

(My late Mother)

To:

The lights of my life

My wife and my children

To:

The lights of my eyes

Brothers and sisters

To:

My beloved country Iraq

The martyrs of Iraq with all the love and appreciation

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Abstract

In this study, thin films of prepared materials (Cd_2SnO_4 and Zn_2SnO_4) were deposited via spray pyrolysis at temperatures (450, 500, and 550 ℃), while thin films of prepared materials (Cu_2SnS_3 and CuZnS) were deposited using spin coating at temperatures (2000, 250, and 300 ℃). The materials NPs (Cd_2SnO_4 and Zn_2SnO_4) were prepared at temperatures of (550 ℃) while the materials (Cu_2SnS_3 and CuZnS) were prepared at temperatures of (300 ℃) using the autocombostion sol-gel method.

The structural, optical, and electrical (Hall effect) properties of the obtained thin films were investigated. X-ray diffraction (XRD) results demonstrated that the films prepared by spray pyrolysis method Cd_2SnO_4 and $Zn_2SnO_4$are polycrystalline with a cubic structure (Spinel), whereas the films prepared by spin coating Cu_2SnS_3 are polycrystalline with a tetragonal structure and a hexagonal structure of CuZnS, and that an increase in substrate temperature increased the crystal size. Using the Scherer formula, the crystal sizes of (Cd_2SnO_4, Zn_2SnO_4, Cu_2SnS_3, and CuZnS) were determined to be 43.8 nm, 22.0 nm, 22.5 nm, and 37.2 nm, respectively. The X-ray diffraction results further revealed that all sol-gel-prepared films of Cd_2SnO_4, Zn_2SnO_4, Cu_2SnS_3, and CuZnS are polycrystalline with a cubic structure. The FTIR spectra indicated the formation of the materials and the presence of broad vibration peaks (O-H) via spray pyrolysis and spin coating methods.

The existence of nanostructures in the thin films prepared with (XRD, AFM and FE-SEM) techniques was confirmed as the results of atomic force

microscopy (AFM) measurements demonstrated a clear temperature dependence in the values of grain size, surface roughness, and the square root of the mean roughness with the substrate. Through the use of thermal evaporation and spin coating methods . The optical characteristics were investigated by recording the spectrum absorbance and transmittance over a range of wavelengths (300-900 nm).

Thin films of Cd_2SnO_4 and Zn_2SnO_4 demonstrated a decrease in absorption with rising transmittance values and an increase in wavelength. The results also demonstrated an increase in the values of the absorption coefficient with an increase in the substrate temperature, an increase in the absorption of the films with a decrease in the transmittance values, and an increase in the wavelength of Cu_2SnS_3 and CuZnS. For the films prepared by spin coating method. It showed that the energy gap values increase with the increase in the substrate temperature of the films prepared by spray pyrolysis method Cd_2SnO_4 and Zn_2SnO_4 their energy gap values were 2.75 eV and 3.30 eV at 550 ^oC, respectively. The energy gap of each of Cu_2SnS_3.and.CuZnS was.also measured, and it was found to be equal to eV1.65 and eV1.80, respectively, at a temperature of 300 ^oC, which was prepared by spin coating method.

The Hall effect results demonstrated that increasing the substrate temperature improves the electrical properties of all films, with Cu_2SnS_3 having the highest electrical conductivity at 1.001×10^6 $(\Omega .cm)^{-1}$, which was offset by an increase in the concentration of charge carriers of 1.23×10^{23} $(cm)^{-3}$ and a decrease in electrical resistivity of 9.987×10^{-7} $(\Omega .cm)$.

Cd_2SnO_4 and Zn_2SnO_4 were subsequently deposited on porous silicon by the spray pyrolysis method, while Cu_2SnS_3 and CuZnS were deposited via the spin coating method. And Cd_2SnO_4, Zn_2SnO_4, Cu_2SnS_3, and CuZnS were deposited using the drop-casting method (1μm thick porous silicon). Then, using spray pyrolysis, aluminum was deposited as a conducting electrode on the back face of the silicon cell. The features of the solar cell and photodetector were

subsequently evaluated. The parameters of the photovoltaic current density (I-V) curves of manufactured solar cells were measured under 100mW/m^2 of simulated solar light. The parameters (open-circuit voltage V_{OC}), (closed-circuit current I_{SC}), (fill factor FF %), and (solar cell efficiency η %) were determined.

The thin films that were deposited by spin coating method offered the maximum performance, and its value was (4.7%).For heterogeneous junctions (CuZnS)/PSi/n-Si/Al, and the results indicated that the drop-casting approach had a major role in enhancing the performance of the solar cell. The heterojunctions (Cu_2SnS_3)/PSi/n-Si/Al produced the greatest efficiency value (7.80 %). The spectral response measurements of the prepared photodetectors revealed that they performed within the range of (400-900) nm, which is the maximum spectral response value for heterogeneous junction (CuZnS) PSi / n-Si / Al that can be employed for near-infrared photodetector applications. The red and visible spectrum, where the spectral response (Rλ) and specificity detection (D*) of CuZnS/PSi/n-Si/Al photodetectors are approximately (0.60A/W) and ($9.2x10^{12}$ cm Hz1/2 W^{-1}) at λ~ 450 nm, respectively.

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List of Symbols

Symbol	Meaning	Units
λ	The wavelength of the incident X- ray	nm
θ	Bragg's angle	degree
n	Integer number	-
D	crystallite size	nm
k	Shape factor	-
a ,b and c	Lattice constants	Å
hkl	Miller indices	-
d_{hkl}	Inter planar spacing	Å
β	Full width at half maximum	Degree
δ	Dislocation Density	cm^{-2}
$N_{\circ}$	Number of crystallites per unit area	cm^{-2}
T	Transmittance	-

I_o	Incident light intensity	mW/cm^2
I_T	Transmitted light intensity	mW/cm^2
R	Reflection	-
I_R	Reflectance light intensity	mW/cm^2
n	Refractive Index	-
A	Absorbance	-
ε	Micro strain	-
A′ and B	Constant depending on properties of bands	-
h	Planck 's constant	J.s
hν	Photon energy	eV
E_g	Optical Energy Gap	eV
V.B	Valence band	eV
C.B	Conduction Band	eV
r	Exponential coefficient depends on the type of transition	-
α	Optical absorption coefficient	cm^{-1}
E_u	Urbach energy	meV
$\vec{k}$	Wave vector	cm^{-1}
E_{ph}	Phonon energy	eV
t	Film Thickness	nm
R_s	Series resistance	Ω
R_{Sh}	Shunt resistance	Ω
μ_H	Hall mobility	$m^2/(V.s)$
n_H	Concentration of charge carriers	$(cm)^{-3}$
R_H	Hall coefficient	m^3/C
σ	Conductivity	$(\Omega.m)^{-1}$
V_H	Hall Voltage	V
B_Z	magnetic field strength	Tesla
V	Voltage	V

V_a	Applied Voltage	V
K_B	Boltzmann constant	J/K
q	Electron charge	C
I_{ph}	The light-generated current density	mA
I_L	Light induced current	mA
I_d	Dark current	mA
ṅ	The diode ideality factor	-
T	Temperature	K
I_o	The saturation current density	mA
I_E	Electric current	mA
I_{max}	Maximum current	mA
I_{sc}	Short circuit current	mA
I_{sh}	Shunt current	mA
V_{max}	Maximum voltage	V
V_{OC}	Open-circuit voltage	V
J_{max}	Current density at maximum power point	mA/cm^2
J_{sc}	Short- circuit current density	mA/cm^2
F.F	Fill Factor	-
ɳ	Efficiency	-
P_{in}	The incident power	mW/cm^2
p_{max}	Maximum power	mW/cm^2
R_λ	Responsivity	$A.W^{-1}$
$D_\lambda{}^*$	Spectral Detectivity	$cm.Hz^{1/2}.W^{-1}$
G	Photocurrent Gain	-
$\mathcal{A}$	The active surface area of the cell	cm^2

List of □bb□e□iations

□bb□e□iation	□efinition
AFM	Atomic Force Microscope
FE-SEM	Field emission scanning electron microscopy
FTIR	Fourier Transform-Infrared Spectroscopy
FWHM	Full Width at Half Maximum
hkl	Miller Indices
I-V	Current-Voltage
J-V	Current density–Voltage
P	Porosity
PCE	Power Conversion Efficiency
PD	Photodetector
PL	Photoluminescence
PSi	Porous Silicon
PV	Photovoltaic
RMS	Root Mean Square
UV	Ultra violet
Vis	Visible
W-H	Williamson-Hall
XRD	X- ray Diffraction

Chapter One

Overview of Nanomaterials and Literature Review

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When a material's size is lowered to the nanoscale, its chemical and physical characteristics are radically altered. Nanoscience focuses on controlling the formation of nanostructures and morphology, whereas nanotechnology studies the link between matter's size and function [1]. Thin-film physics is a subfield of solid-state physics that will ultimately become a discipline. A layer with a thickness of tens of nanometers is referred to as a nanolayer (film). Thin film has a thickness of less than one micron, according to a published [2]. Because the film layer is so light, it is only placed on the specific type of substrates depending on the study's nature or scientific requirement necessity. Glass slides, silicon wafers, aluminum, quartz, and other substrates are among them. Properties of a thin film vary from bulk material depending on the kind of significant research. Thin films were produced for the first time in 1852 by (Busen & Grove) by a chemical reaction, and a thin metallic film was obtained in 1857 by the scientist (Farady) using thermal evaporation [3].Furthermore, various factors influence the characteristics of thin films, including the thickness and kind of film utilized, as well as the evaporation conditions employed to make the films. Thin films have a wide range of applications, including rectifiers then junction diodes, integrated circuits, optical communications as light-emitting diodes, semiconductor lasers and detectors, light filters, solar cells, and special-purpose mirrors [4]. In addition, they are used in a range of applications to protect thin-film-painted materials from corrosion, environmental contact, and surface deterioration [5]. The sensitive materials that are convenient for manufacture using a variety of electrical, optical, then optoelectronic possessions are required for a broad area of semiconductor applications. Rather than thinning down bulk material, thin films are generated by depositing ingredients onto a clean, supporting substrate to build up film thickness[6].

□□□ □□in □ilms □□e□a□ation Met□o□s

Thin film properties are quietly sensitive to the preparation method. Different techniques have been developed to deposion thin film on alloys, polymers, superconductors, and metals on several kinds of substrate materials. Indeed, no technique can deposit thin films that cover all the desirable aspects like equipment cost, deposition conditions, substrate material nature, etc. The broad types of thin-film materials, their deposition methods, processing,spectroscopic characterization, fabrication technologies, optical characterization investigations, physical and chemical properties, and structure-property relationships are the main features of these devices and the basis of thin-film technologies. The achievement and economics of thin-film components are the industrialization techniques used to produce the devices.Several techniques are valuable and available to enhance nanostructure thin film in a wide range of potential applications. The production techniques of nanostructured thin film are usually classified into two categories, as shown in figure 1.1:

(i) Physical techniques, such as the evaporation or sputtering of the material from source and deposition on a substrate, etc. [7].

(ii) Chemical techniques like a chemical reaction between volatile/non-volatile compounds of the material and deposition on the various substrates etc. [8].

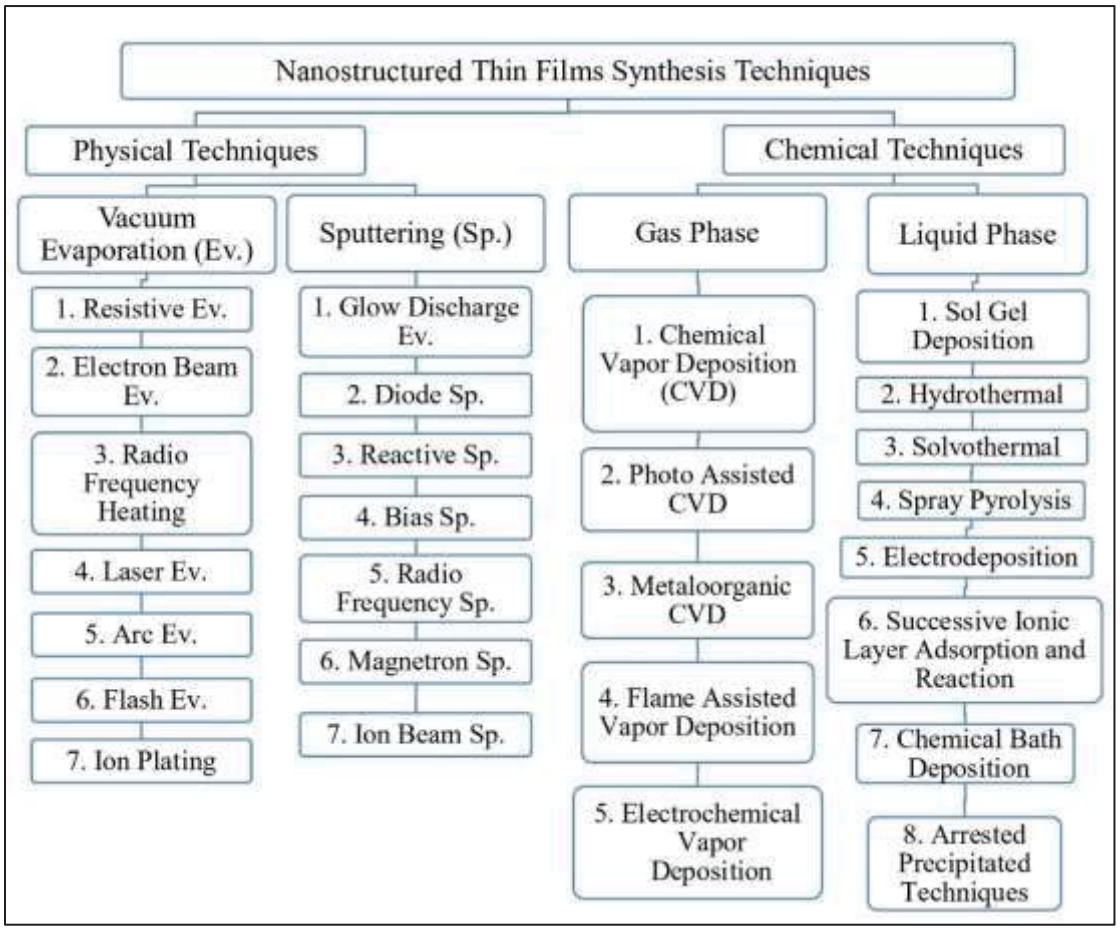

Figure □ □ □Various nanostructured thin film syntheses techniques [9].

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One of the most common processes for generating big area homogeneous coatings is Chemical Pyrolysis by spraying. Chemical Pyrolysis by spraying. is particularly beneficial in the fabrication of conventional and thermal mirrors and very competent filters plus solar cells [10]. One of the most frequent depositings of .a wide-ranging of materials in thin-film form. It Chemical Pyrolysis by spraying . For manufacturing high-quality thin films, variables such as substrate temperature, spray rate, and solution concentration, among others, must be fine-tuned. Atomization pyrolysis have on the other hand, get a lot of interest [11]. Spray pyrolysis involves spraying an aqueous solution containing soluble salts of the constituent atoms of the desired compounds to the heated substrates onto a

techniques like ultrasonic nebulization, better Pyrolysis by spraying. Coronas Pyrolysis by spraying., electronic Pyrolysis by spraying., and microprocessor-based spray pyrolysis have on the other hand, get a lot of interest [11]. Particles of the required chemicals are dissolved in water and then sprayed over heated surfaces that are held at high temperatures for spray pyrolysis. This is done in order to break down the compounds in question. When the sprayed droplets reach the hot substrate, they undergo pyrolysis breakdown and produce a single crystal or cluster of crystallites. In the vapor phase, various volatile byproducts and excess solvents escape [12]. Despite its flaws, this approach has numerous advantages [13, 14].

1- Safe low-cost and simple technique.
2- The necessary equipment cost and raw materials are inexpensive.
3 -Using high-quality targets and substrates is not essential.
4 -Spray settings can be adjusted to manage film thickness and uniformity.
5- It can be used in any type of weather.
6- It has the ability to manufacture thin film materials with a high melting point.
7- It has the ability to produce thin-film materials with excellent homogeneity and enormous dimensions.

□□□S□in □oating □e□□ni□□e

A Spin coating is a fast and most commonly utilized chemical deposition method for producing thin and homogenous organic or inorganic sensing from solution. This method enables the creation of very repeatable and homogeneous films. Two forces act on the solution during spin coating: adhesive forces at the solution substrate contact and centrifugal forces induced by the high-speed spinning. These two opposing forces will cause a considerable shearing action at the interface, leading the solution to create a thin film of varying thickness,

determined by rotating velocity, solution concentration, and a viscosity [15]. Several factors must be considered to generate homogeneous films, including solvent evaporation rate, fluid viscosity, solution concentration, angular velocity (rotation speed), and spinning time. The advantage of the spin coating technique is its high ability to provide thin films with thickness ranging from a few nanometers to a few microns in an easy, quick and economical way, the film thickness can be easily changed by changing spin speed, and it is considered a low-cost operating system [16].

□□□ □a□mi□m Stannate □□ □□Sn□ □□□□o□e□ties

Cd_2SnO_4 films have a spinel cubic polycrystalline structure as shown in fig 1.2. The cations ratio of Cd and Sn has an essential role in achieving a homogeneous structure of thin-film without any secondary phases, and the lattice parameters have an approximate value of a=b=c=0.9174 nm [17, 18]. Cadmium tin oxide is a n-type semiconductor [17]. It has high carrier mobility, with n-type doping, The visible absorption edge goes to considerably higher energy [19]. Cadmium stannate has a low electrical resistivity, good transmittance in the visible light spectrum, and low reflection in the near IR range. Spray pyrolysis was used to make thin films of Cd_2SnO_4 with a 3eV energy bandgap [20]. Cd_2SnO_4 thin films were demonstrated. It has been several essential advantages of the CdTe/CdS-based solar cells. In contrast, they have the best adhesion to the CdTe/CdS solar cells with respect to tin oxide (SnO_2)[21].

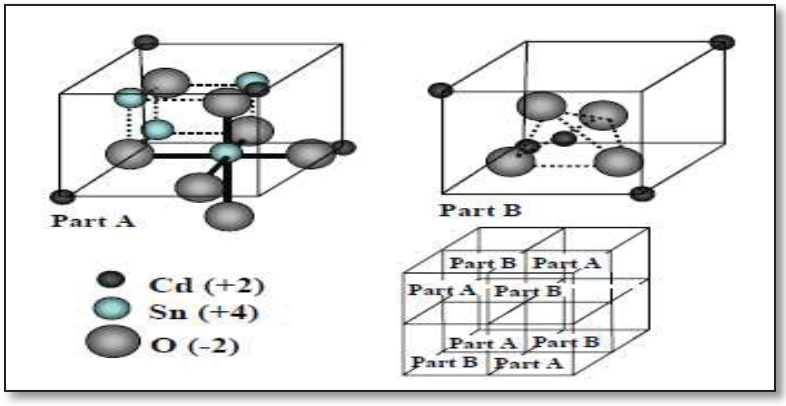

Figure □ □ □Crystalline structures of Cd_2SnO_4(Cubic spinel) [17].

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Because of their unique features in optics and electronics, ZnO and SnO_2 have gotten a lot of attention in recent years. However, ternary semiconductors Zn_2SnO_4 may have received better properties and are still less studied and investigated. As it has high-electron mobility, high-electrical conductivity, and significant optical properties, all of these properties make it to be appropriate for solar cell, dye sensitized solar cell, gas sensor Li-ion battery and photodtectors applications [22, 23]. Fig 1.3 Zn_2SnO_4 has a polycrystalline crystal structure (cubic spinel) [24], with the lattice parameters a=b=c= 8.657 nm [25]. has a lot of electron mobility . Pyrolysis by spraying was used to make thin film. Of high electrical, an n-type transparent conductive oxide with a conductivity of 3.7 e V and a large [24].

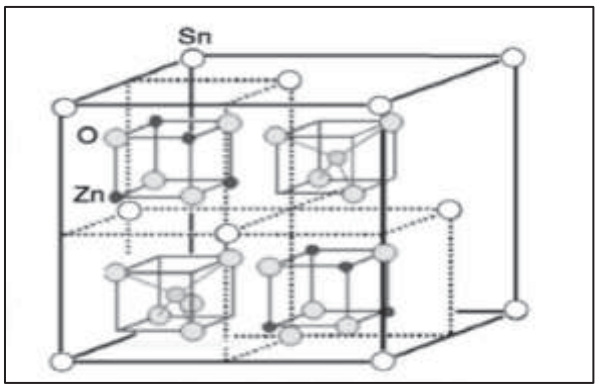

Figure □ □ □The cubic spinel structure of Zn_2SnO_4 [24].

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Since 1960, the Cu–Sn–S system has been considered. Cu_2SnS_3, Cu_3SnS_4, and Cu_4SnS_4 are the three phases in this system Cu_2SnS_3 exhibits polymorphs such as monoclinic, cubic, tetragonal, and triclinic as shown in figure 1.4 structures in Additionally, Cu_2SnS_3 crystallizes in wurtzite and hexagonal nanocrystalline form . They've been discovered to be an important absorbent for solar cell use. The (Cu–Sn–S) system is part of the (I–IV–VI) group, and it contains non-toxic, abundant, and inexpensive elements. Due to its usefulness in a wide range of applications, the ternary Cu_2SnS_3 (CTS) semiconductor has recently gained a lot of attention. This system's optoelectronic features make it ideal for this application. As photovoltaic devices, the electrical conductivity of the p-type with band gap may be controlled in an optimal range from (1.0 to 1.5 eV). A high optical absorption value of ~10^5 cm^{-1} is also seen. CTS thin films have been tried as absorbers solar cells using thin films (TFSCs) by a variety from approaches such as evaporation, sputtering, electro-deposition, pulsed laser deposition and chemical bath deposition [26-28].

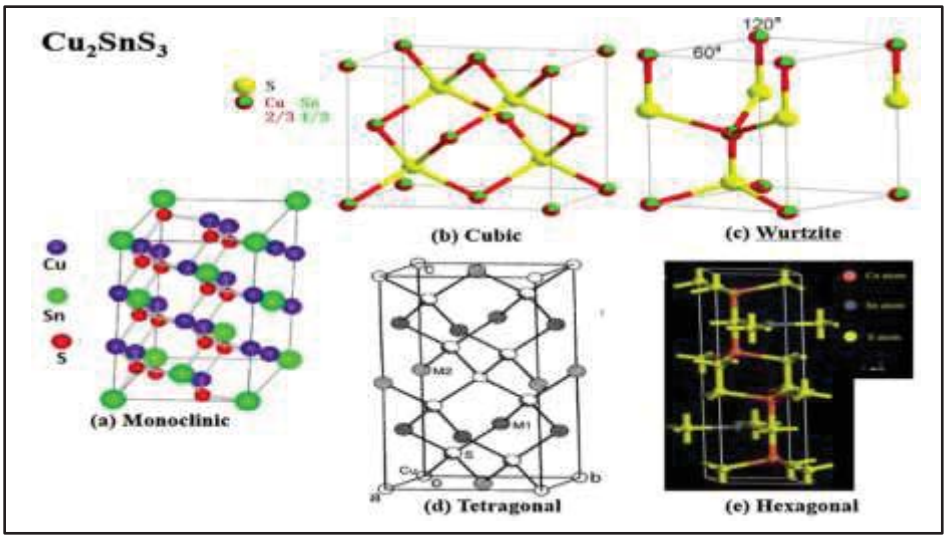

Figure □ □ □Crystallographic structures of Cu_2SnS_3 (a) Monoclinic, (b) Cubic, (c) Wurtzite, (d) Tetragonal and (e) Hexagonal [27].

□□□ □o□e□□□in□S□l□□i□e □□ □□nS□□□o□e□ties

CuS is an essential semiconductor with unique electrical, chemical, and optical characteristics and a wide range of solar cell applications. CuS thin films have recently exposed ability in applications for example gas-sensor materials [29] .2.36 eV and 2.03 eV it direct bandgap has CuS with a hexagonal structure, according to structural and optical analysis [30] .The most significant rate of all (II–VI) composite semiconductors with n-type semiconductor and broad direct bandgep is (ZnS), which has on energy bandgep of (3.65 eV). It can therefore be utilized in optoelectronics and as an anti-reflective coating for heterojunction solar cells [31].

Nanocomposites thin films' structural, morphological, optical, and electrical properties have recently become an interesting topic due to their unique techniques. CuZnS ternary compounds are a promising nanostructured material for electroluminescent and photoconductor devices, as well as photovoltaic cells. The nano-composite films can also be used as a solar cell absorber. Improvements in the characterisation of copper-zinc sulphide (CZS) are of particular importance since these spectacular p-type inorganic materials have a large direct band gap and are crucial in solar cell applications [29].

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□i□a□i et al□□□□□□□□□ Direct liquid coating (DLC) was used to precipitate thin films of tetragonal Cu_2SnS_3 (CTS) made of a metal-thiourea compound methanolic precursor solution. X-ray Diffraction confirms the formation of tetragonal Cu_2SnS_3. AFM and scanning electron microscopy demonstrated that the films are soft and uniform with a roughness (RMS) of 1–2 nm energy band gap (Eg) for Cu_2SnS_3 1.12 eV plus 10^5 cm^{-1} for absorption coefficient (α), according to optical measurements. The films are p-type, with a 0.5 s/cm

electrical conductivity(s), rendering to hall measurements, The concentration and mobility of holes are around (10^{18} cm^{-3} and $1cm^2/V/s$), respectively. DLC developed non-toxic thin-film solar cells (TFSC) made from graphite/Cu_2SnS_3/ZnO/ITO/SLG with a power transformation efficiency PCE of 2.10 % and voltage in the open circuit., current in a short circuit, and the fill factor 0.816 V, $6.14mA/cm^2$, pluse 0.42, respectively [32].

S□ee□it□ et al□□□□□□□□Chemical spray pyrolysis was used to make CuZnS thin films. Rendering to the findings, the material may be transformed of n-type to p-type with a 4-order improvement in electrical conductivity by just increasing the Cu content. In comparison, increasing Cu content causes the band-gap to decrease from 3.4 - 1.8 eV. High Cu concentration films are more absorbent, but low Cu concentration films can be employed as a buffer/window layer in solar cells. The absorber layer was CuZnS, and the buffer layer was In_2S_3. The J-V possessions from the cell were measured by Ag as the highest electrode. V_{oc} =0.451 V, J_{sc} =5.47 mA/cm^2, *FF* = 42.2 %, and η= 1.04% were the parameters obtained for the optimal doped cell [33].

□o□ines et al□□□□□□□□On glass substrates, the researcher developed Cd_2SnO_4 polycrystalline thin films with cubic phase using the sol-gel process. Commencing with a combination of two simple CdO and SnO_2 precursor solutions and thin films formed at room temperature. In the precursor solution, the atomic concentrations of Sn (x) in relation to Cd (1-x) were x=16, 25, 29, 32, 35, and 40. After the annealing operations, Cd_2SnO_4 films retained their spinel-type crystalline structure. The Cd/Sn ratio of the Cd_2SnO_4 compounds was closest to that of the Cd_2SnO_4 compounds at x=29 at % without annealing. Cd_2SnO_4 films demonstrated good optical transmission ~85% in the 500 nm <λ<

1500 nm range, both with and without annealing. For Cd_2SnO_4 films (x=33 at%) annealed in a vacuum at 550 °C, a minimum resistivity of roughly 2×10^{-3} Ω cm was found, by a direct band gep energy of 3.55 eV [34].

□□ao et al□□□□□□□□□ A method for producing high-quality, homogenous, and band-gap-adjustable Zn_2SnO_4 nanotubes has been published. By altering the heat treatment temperature, These nanotubes can be autologous-assemble inside a range from different nanofilms by changeable.Gaps in optical bands ranging of 3.54 to 3.18 eV. The Zn_2SnO_4 nanotube-nanofilm-based UV-light photo detectors have been successfully produced and show much greater photocurrent and a bigger photocurrent to dark current part than separate nanostructure-founded UV-light photodetectors. Top-showing photo detectors, solar cells, plus Li-ion battery electrode materials could all benefit from it [35].

□anai et al□□□□□□□□□ According to experts, Cu_2SnS_3 is a p-type semiconductor that has an coefficient of absorption of over 10^4 cm^{-1} and a bandgap energy of 0.92 to 1.77 eV. As a result, it has proven to be a highly absorbent layer to thin-film solar cells. According to this study, CTS thin films made via deposition and annealing of primary films made via co-evaporation of Cu,Sn,S. The photovoltaic properties of solar cells with CTS films as absorbent layers were then studied in relation to the annealing temperature. A solar cell with the voltage in an open circuit of 248 mV a 570°C annealed CTS thin film. A current density in a short circuit of 33.5 mA/cm^2, the factor of fill 0.439, and a transformation efficiency of 3.66% [36].

Dong et al., (2015): Cu_2SnS_3 Sulfurizing stacked metallic precursors yielded CTS thin sheets. and sputtering them by a radio frequency magnetron, according

to this study. The synthetic, structural, morphological, optical, plus electrical characteristics of Cu_2SnS_3 thin films formed up soda-lime glass substrates are influenced by the sulfur temperature. The synthetic study reveals totally of the samples remain Sn- rich. Within increasing sulfurization temperatures, the Cu/Sn ratio approaches the stoichiometric composition of CTS. According to structural characterization, Cu_2SnS_3 thin films sulfurized by upper sulfur temperatures exhibit greater crystalline kind. At 550 °C for sulfurization, the CTS thin film has a greater amount of crystallization and a bigger average grain size. bandgap is roughly 1.0 eV,as shown by the transmission plus reflectance spectra, compatible with the projected estimate based on outer quantum efficiency. The photoelectric characteristics from solar cells improve as the sulfurization temperature rises. For an area of 0.16 cm^2,the solar cell produced by the Cu_2SnS_3 absorber stratum annealed by 550 °C achieves a 0.28% efficiency [37].

ana et al., (2015): Cu_2SnS_3 thin films have been characterised as the result of annealing after co-evaporation of Cu, Sn, and cracked sulphur. Now a quick thermal treating oven supplied by N_2 gas on air pressure, the as-deposited films by annealed at 570 °C for 5 minutes in the of attendance 100 mg of sulphurion lumps. After that, the CTS films were utilised such as absorber layers in solar cells, then their efficiency was measured for various Cu/S ncompositional rate . Films through a considerably Sn-rich composition had the largest grain size. The use of a CTS thin film in solar cells by a (Cu/Sn) rate of nearly 1.9 had the best performance. The voltage across the open circuit of cell by a Cu/Sn rate of 1.87 was 258 mV, the current density in a short circuit was 356mA/cm^2, the factor of fill was 0.467 plus power transformation efficiency was 4.29 % [38].

□□□ **et al., (201□):** in this research demonstrates the use of small -cost metal stannate-founnded nanostructures as fast materials for great- fulfillment UV photodetectors. Thin-film devices embrance of amorphous $ZnSnO_3$ nanotubes and/or polycrystalline Zn_2SnO_4–SnO_2 nanoparticles by diverse optical plus electrical architectures were successfully produced using a durable, affordable, and scalable drop-casting approach. Thermal treatment from amorphous $ZnSnO_3$ nanocubes resulted in the formation of Zn_2SnO_4–SnO_2 heterojunction nanoparticles. Big-area, regular, and continuous film photodetectors by clear plus quick responses, with rise and decay durations smaller than 1.0 s, have been developed when subjected to UV irradiation 370 nm. When compared to their predecessors, these two stannate nanostructures have more benefits, for example ZnO, SnO_2, Zn_2SnO_4, ZnO–SnO_2 single nano structures or film photo sensors, containing photo-sensitivities that are extremely high ($S>10^2$ and $\sim10^3$ existed completed for ($ZnSnO_3$) and Zn_2SnO_4–SnO_2 photodetectors, respectively then excellent responsivite (as great as 0.5 A W^{-1} at 5.0 V bias of the Zn_2SnO_4–SnO_2 photo sensors) below short light intensity [39].

D□a□an□ □ □□□an□□□(201□): Have successfully synthesized Cu_2SnS_3 (CTS) thin-film deposition employing a spin coating method. The films feature a tetragonal crystal structure, according to XRD. The film form and particle size were then determined using SEM. The crystal's various planes were examined using TEM. Its excellent absorption coefficient of 10^4 cm^{-1} and optimum band gap of 1.23 eV enable its use as photoactive material. The visible and infrared (IR) photoresponses were examined at various light intensities. At 3V applied bias, the current increased from a dark current of 0.31 A to 1.78 A at 1.05 suns and 8.7 A under 477.7 m W/cm^2 IR illumination intensity. At 1.05 lights, the responsivity, sensitivity, outer efficiency in quantum, Then it was revealed

that specific detectivity exists. (10.93 mA/W, 5.74 and 2.47) %, plus 3.47× 10^{10}, respectively, while at 477.7 m W/cm^2 IR illumination, they were 16.32 mA/W, 27.16 and 2.53 percent, and 5.10× 10^{10} Jones, respectively. The transient photoresponse was measured using visible and infrared illumination [40].

□□ee□t□ et al., (201□): CuZnS is a novel potential element for thin-film photovoltaics that is plentiful and ecologically kindly, according to the report. Copper and Zinc atom ratios may be changed to control electrical and optical characteristics, making it suitable for use as an absorber or window layer. This material's conductivity may be altered of n to p by changing the Cu/Zn rate. The current study shows that raising the Cu to Zn ratio in CuZnS improves the cell characteristics of the CuZnS/In_2S_3 hetero junction significantly. Current density rise of 5.4 mA/cm^2 to 10.7 mA/cm^2, improving transformation efficiency of 1% to 1.95%. Results are clear based by the enhancement from several band structures [41].

□ □□ et al., (201□): have reported that extremely crystallized CTS thin films by prepared via sputtering-based on deposition. Furthermore, the impact from various annealing temperatures by the crystallographic, electrical, Cu_2SnS_3 thin films were investigated for their optical characteristics. XRD from the (112), (220), and (312) planes reveal such the produced Cu_2SnS_3 thin films include a monoclinic structure. Extrapolating from external quantum efficiency (EQE) measurements, the direct bandgap energy of Cu_2SnS_3 thin film annealed at 580 °C is 1.03 eV. The CTS-based thin-film solar cells (TFSCs) are invented by a structure of Mo/CTS/CdS/i-ZnO/AZO/Al. 1.35% of initial power-transformation efficiency with a (28.3 mA/cm^2) of current density in a short circuit was

obtained. An voltage in the open circuit. and the factor of fill were found to be 147.5 mV and 32% , respectively [42].

□e□□e□ et al., (201□): Reported a mono-crystalline CdTe/MgCdTe binary - CuZnS hole contact in a heterostructure solar cell an ITO electrode had been published. Other contact materials, such as a-Si:H or ZnTe, have been used in similar devices to achieve highet open-circuit voltages and low circuit current densities. Cu_x Zn_{1-x} S is a tunable material system that was synthesized by chemical bath deposition (a low-cost deposition process) and offered a variety of band gaps, conductivity, and band offsets. Devices with x = 15%, 25%, and 65% copper compositions have been created and analyzed, producing a top active-area power transformation efficiency of 12.9 %, an voltage in an open circuit of 956 mV, the factor of fill 63.5%, and a low current density in the circuit from 21.2 mA/cm^2 [43].

□□ et al., (201□): In this research. A thin coating of (CZS) for a solar cell was successfully prepared using a pyrolysis by spray preparation process. XRD, UV, SEM, and the J–V tester were used to study the impact of changing the spray temperature of the substrate on the structural, optical, compositional, morphological, and photovoltaic characteristics of the generated CZS film. Under ideal conditions, our unique CZS thin films include a perfect crystallinity phase with a band gap of 2.21 eV and transformation efficiency of 0.84 % , as evidenced by the results [44].

□□e□□an□□. □□anaat□□oa□, (201□): In this work, a transparent conductive made an (oxide/mesoporous) Zn_2SnO_4.Thermal evaporation is used to place various types of metal oxide semiconductor thin films (such as SnO_2, TiO_2, and ZnO) on the FTO substrate to reduce charge recombination at the synthesized

material interface and increase photovoltaic performance. The results show that, compared to SnO_2 and (ZnO), the TiO_2 thick layer is the best effective obstructive layer to suppressing recombination of charges and boosting the constructed devices current density in a short circuit and power conversion efficiency. Furthermore, the creation of an energy barrier at the FTO/Zn_2SnO_4 contact results in the formation of an energy barrier, The device with the TiO_2 blocking layer achieves With a current density of 7.36 mA/cm^2 in a short-circuit and a voltage in the open circuit of 664 mV, the highest power conversion efficiency is 3.02%. According to this study, Charge recombination at boundary is one of the major problems limiting the power conversion efficiency of dye-sensitized solar cells [45].

□ □**et al., (201□):** Using the sol-gel solution approach, they created monoclinic Cu_2SnS_3thin films. The influence of the Cu/Sn atomic ratio on structure and morphology have been investigated. The CTS films grew more compact when the Cu/Sn atomic ratio rise from 1.6 to 2.0, minor phases for example SnS faded away, then the grain size of the films reduced. The Cu/Sn ratio of 1.9 in the CTS film resulted in a monoclinic structure and homogenous morphology plus a band gap of 1.12 eV, resulting in a power transformation efficiency of 0.58%. Then, Cu_2SnS_3 (CTS) can be considered a possible thin-film solar-cell material [46].

□□o□o □□□e□**a et al., (2020):** The application of heterogeneous Cd_2SnO_4/ CdS/Cu_2O/Ag in solar cells was researched by the researcher. Chemical procedures were used to deposit the heterostructure on the glass substrate: (1) Sol-gel synthesis of Cd_2SnO_4 as TCO, (2) Chemical bath deposition of CdS as an n-layer, and (3) Cu_2O as the player via pyrolysis by spray . The Cd_2SnO_4 and CdS layers have thicknesses of 290 and 135 nanometers, respectively. Cu_2O (τ)

of various thicknesses was used to investigate the impact of this parameter on solar cell performance (135, 185, 220, 350, and 800 nm). Photovoltaic values at their best remained VOC = 346 mV, JSC = 1.57 mA/cm^2, FF = 33.4 and = 0.18 percent for = 220 nm. Gaps in the Cu_2O plus CdS bands. The current donating is mostly due to flaws in the Cu_2O lattice, which result in an energy level source inside the band gap [47].

□**a**□□□ □ **et al., (2021**): Using the co-precipitation approach, high-quality Zn_2SnO_4 nanoparticles were generated, and they were able to improve the degree of crystallization as well as a pure phase of the final nanopowders by varying pH, Temperatures of annealing plus concentrations of precursors. The porous layer was then modified with MgO and Al_2O_3 passivation layers, after which Zn_2SnO_4 crystalline nanoparticles by an average size of nearly 35 nm existed utilized as a porous layer. Controlling the solution concentration and spin coating operation speed enhanced the thickness of these barrier layers, which was critical in reducing recombination by significantly improving the showing of DSSCs. The electronic settings with the highest values were obtained for J_{SC} = 8.59 mA/cm^2, V_{OC} = 0.66 *V*, and *FF* = 0.51 for the MgO-treated device with a rotational speed of 4000 rpm, which exhibited a 40% increase in efficiency from 2.07% to 2.90 %as compared to the untreated sample. All of the treated samples showed a reduction in VOCs. Electrochemical resistance spectroscopy, The transport and recombination mechanisms were subsequently investigated using, voltage in open-circuit decay, and the dye loading procedure, which confirmed a higher transfer ratio and slower electron recombination in the greatest modified devices [48].

Dee□, an□ □e□□□, (2021): Zinc Stannite Zn_2SnO_4 nanoparticles were synthesized using a solvent and heat technique, according to the study. XRD analysis reveals that the nanoparticles generated have a face-centered cubic spinel shape. According to TEM pictures, the produced Zn_2SnO_4 nanoparticles are roughly 20 nm in size. To prepare photoanodes for use in semi-transparent dye sensitized solar cells, a paste incorporating synthetic Zn_2SnO_4 nanoparticles was developed. Semi-transparent dye-sensitized solar cells based on dye adsorbed Zn_2SnO_4 photoanodes have a photoconversion efficiency of 0.86% [49].

1.10 □□□ o□t□e □ o□□:

1-Synthsis of some different ternary metal oxides and sulfied Cd_2SnO_4 (CTO), Zn_2SnO_4 (ZTO), Cu_2SnS_3 (CTS), and CuZnS (CZS) thin films using different method (chemical spray pyrolysis, spin coating , sol-gel and drop-casting methods)

2-Study effect of substrates temperature on the structure ,Morphological ,Optical and electrical properties of prepared thin film.

3-Synthsis of Cd_2SnO_4 (CTO), Zn_2SnO_4 (ZTO), Cu_2SnS_3 (CTS), and CuZnS (CZS) nanoparticle by sol-gel method.

4-Applications of prepared thin films in photovoltaics applicable such as solar cell and photodetectors.