CHAPTER 2

SURVEY OF LITERATURE

2.1 INTRODUCTION

The review of post and current researchers on CuInS$_2$, Sb, Zn, Bi doped and polyol assisted CuInS$_2$ thin films will give us better understanding of the various preparation methods, various studies and potential applications. Many researchers have reported the studies, characterizations and potential applications of CuInS$_2$, Sb, Zn, Bi doped and polyol assisted CuInS$_2$ thin films. In this chapter a review of works done by many researchers in their selected field has been carried out.

2.2 CuInS$_2$ THIN FILMS AND DOPED THIN FILMS

Takayuki Negami et al (1997) prepared CuInS$_2$ thin-films solar cells fabricated by sulfurization of Cu-In-O precursors in H$_2$S gas. X-ray diffraction patterns showed that In$_2$O$_3$ phases did not remain in the CuInS$_2$ films sulfurized in a HES and HE atmosphere, whereas In$_2$O$_3$ phase remained in the films sulfurized in a HES and Ar atmosphere. The performance of CuInS$_2$ solar cells were studied as a function of the H$_2$ gas pressure during sulfurization. The open-circuit voltage, short-circuit current and fill factor increased with increasing the H$_2$ gas pressure. The conversion efficiency of the CuInS$_2$ solar cells is strongly affected by the reduction of the Cu-In-O precursors.
Zribi et al (2008) studied post-growth annealing treatment effects on properties of Na-doped CuInS\textsubscript{2} thin films. Structural and optical properties of Na-doped CuInS\textsubscript{2} thin films grown by double source thermal evaporation method were studied. The films were annealed from 250 to 500°C in a vacuum after evaporation. X-ray diffraction pattern indicated that there are traces of Cu and In\textsubscript{6}S\textsubscript{7}, which disappeared on annealing above 350°C. Good quality CuInS\textsubscript{2}:Na 0.3% films were obtained on annealing at 500°C. Furthermore they found that the absorption coefficient of Na-doped CuInS\textsubscript{2} thin films reached 1.5×10\textsuperscript{5} cm\textsuperscript{-1}. The change in band gap of the doped samples annealed in the temperatures from 250 to 500°C was in the range 0.038–0.105eV.

Peza-Tapia et al (2005) studied the structural, electrical and optical properties of Na-doped CuInS\textsubscript{2} thin films grown by spray pyrolysis. These films crystallized in the sphalerite structure of CuInS\textsubscript{2}, and showed to contain traces of indium sulfide and CuIn\textsubscript{5}S\textsubscript{8} as impurity phases. All films were in-rich and showed p-type conductivity. The film conductivity was strongly affected by Na-doping, which decreased from 10\textsuperscript{-2} to 10\textsuperscript{-5} S/cm by increasing the [Na]/[Cu] ratio from 0.005 to 0.03 in the spray solution. The band gap energy was observed to increase, from 1.4 to 1.45 eV, with increasing the [Na]/[Cu] ratio.

Akaki et al (2003) studied structural, electrical and optical properties of Sb-doped CuInS\textsubscript{2} thin films grown by single source thermal evaporation method. The films were annealed from 100 to 500°C in air after the evaporation. The X-ray diffraction spectra indicated that polycrystalline CuInS\textsubscript{2} films were successfully obtained by annealing above 200°C. This temperature was lower than that of non-doped CuInS\textsubscript{2} films. Furthermore they found that the Sb-doped CuInS\textsubscript{2} thin films became close to stoichiometry in
comparison with non-doped CuInS₂ thin films. The Sb-doped samples annealed above 200°C have bandgap energy of 1.43-1.50eV.

Malle Krunks et al (1999) prepared polycrystalline CuInS₂ thin films by spray pyrolysis of aqueous solution of copper chloride, indium chloride and thiourea onto heated glass substrates. The parameters critical to structural and optical properties of sprayed CuInS₂ films are growth temperature and ion ratio of Cu/In in spraying solution. Excess of copper in starting solution promotes the recrystallization and growth of crystallites in the film. The X-ray diffraction patterns confirm that the use of copper-rich solutions reduces the temperature required for single-phase composition of CuInS₂ films from 380°C (Cu=In/1) to 290°C (Cu=In/1:25). Sprayed chalcopyrite CuInS₂ films have absorption coefficient, $10^5 \text{cm}^{-1}$ in visible and red region of spectra and optical band gap $1.45 \text{eV}$.

Baris Altiokka et al (2005) produced CuInS₂ semiconductor films by the spray pyrolysis method on to the glass substrates kept at different substrate temperatures. Optical characteristics of the CuInS₂ films have been analyzed using spectrophotometer in the wavelength range 400-900nm. The optical band gap energy has been obtained from the plot of $(h\nu)^2$ vs $h\nu$. The absorption spectra of the films showed that this compound is a direct band gap material and gap values varied between 1.51-1.80eV, depending on the substrate temperatures.

Chuchman et al (2008) analyzed emission spectra and the energy distribution of the excited-state population density of atoms and ions in erosion laser plasma from CuInS₂ with various crystal-structure orderings. It is shown that increased ordering of the target crystal structure causes the excited-state energies of indium atoms generated in the laser erosion plume to increase and that sulfur atoms always emit only in transitions from highly excited states. The ratio of relative ion concentrations in the laser plasma
plume is Cu+/In+/S+ = 0.3/0.08/2, which corresponds neither to the atomic ratio of Cu/In/S (1/1/2) in the target nor to the ratio of ionization energies. The results are explained by recombination processes for ions and by the atomization specifics of the CuInS₂ target exposed to long-wavelength radiation. The atomization consists essentially of dissociative processes expressed by CuInS₂ → CuInS + S and CuInS₂ → Cu + InS + S. The electron temperature of polycrystal (single-crystal) plasma at a distance of 1 mm from the target is 0.3eV (0.4eV) for atoms and 1.3eV (2.7eV) for ions and varies negligibly for plasma up to a distance of 7 mm from the target.

Agarwal et al (1998) reported the growth and properties of CuInS₂ thin films. Single phase copper indium disulphide (CuInS₂) thin films of thickness between 60nm and 650nm with the chalcopyrite structure are obtained on NaCl and glass substrates by flash evaporation. The films were found to be n-type semiconducting. The influence of the substrate temperature on the crystallinity, conductivity, activation energy and optical band gap was studied. An improvement in the film properties could be achieved up to a substrate temperature of 523 K at a molybdenum source temperature of 1873 K.

Chaffar akkari et al (2005) investigated the high absorbing CuInS₂ thin films growing by oblique angle incidence deposition in presence of thermal gradient. Oblique angle deposition technique can generate nanostructures and has attracted the interest of many researchers. The correlation between the obliquely angle deposition and the thermal gradient leads to an improvement in the optical properties of the films. Indeed high absorption coefficient (10⁵⁻³ - 10⁵ cm⁻¹) in the visible range and near-IR spectral range are reached for the small incident angles. Scanning electron microscopy shows that the films had a microstructure with columns that are progressively inclined as the incident angle was increased.
Juan Manuel Peza-Tapia et al (2009). determined the specific contact resistivity ($\rho_C$) for aluminum (Al), silver (Ag) and indium (In) metallic contacts on CuInS$_2$ thin films from I–V measurements, with the purpose of having the most appropriate ohmic contact (TLM) for the metallic contacts evaporated on CuInS$_2$ thin films deposited by spray pyrolysis with ratios $x$ $\frac{[Cu]}{[In]}$ ¼ 1.0, 1.1, 1.3 and 1.5 in the spray solution. The results show that In contacts have the lowest $\rho_C$ values for CuInS$_2$ samples grown with $x$ ¼ 1.5. The minimum $\rho_C$ was 0.26 ohm cm$^2$ for the In contacts. This value, although not very low, will allow the fabrication of CuInS$_2$ solar cells with a small series resistance.

Akaki et al (2003) studied the structural, electrical and optical properties of Sb-doped CuInS$_2$ thin films grown by single source thermal evaporation method. The films were annealed from 100 to 500ºC in air after the evaporation. The X-ray diffraction spectra indicated that polycrystalline CuInS$_2$ films were successfully obtained by annealing above 200ºC. This temperature was lower than that of non-doped CuInS$_2$ films. The Sb-doped samples annealed above 200ºC have bandgap energy of 1.43–1.50eV.

Ben Rabeh et al (2010) investigated the effect of antimony incorporation on structural properties of CuInS$_2$ crystals. CuInS$_2$ (CIS) single crystals doped with 1, 2, 3 and 4 atomic percent (at %) of antimony (Sb) were grown by the horizontal Bridgman method. The effect of Sb doping on the structural properties of CIS crystal was studied by means of X-ray diffraction (XRD), energy dispersive X-ray analysis (EDAX), scanning electron microscopy (SEM) and PL measurements. X-ray diffraction data suggests that the doping of Sb in the CIS single crystals does not affect the tetragonal (chalcopyrite) crystal structure. EDAX study revealed that Sb atoms can occupy the indium site and/or occupying the sulfur site to make an acceptor. PL spectra of undoped and Sb doped CIS crystals show two emission peaks at
1.52 and 1.62 eV, respectively which decreased with increasing atomic percent antimony.

Ben Rabeh et al (2009) studied the effect of antimony incorporation in CuInS$_2$ thin films. Structural, optical and electrical properties of undoped and Sb-doped CuInS$_2$ thin films grown by single source thermal evaporation method on corning 7059 glass substrates heated at 100°C were studied. The amount of the Sb source was determined to be in the range 0-4 Wt % molecular weight compared with the CuInS$_2$ alloy source. The films were annealed in vacuum at temperature of 200°C for 2h. The effect of vacuum annealing on the properties of the films was studied by means of X-ray diffraction, optical reflection and transmission and resistance measurement. All the CuInS$_2$/Sb films have relatively high absorption coefficient between $2 \times 10^4$ cm$^{-1}$ and $10^5$ cm$^{-1}$ in the visible and the near-IR spectral range.

Bollero et al (2009) reported the simplified modulated evaporation process for the production of CuInS$_2$ films with reduced substrate temperatures. CuInS$_2$ films with sub-micrometer thickness have been grown onto soda–lime glass substrates from the elemental constituents by a modulated flux deposition procedure. A reduced substrate temperature of about 350°C was used during the process. Morphological characterization of the films suggests the formation of an In-rich layer in a first step of the deposition process.

Sahal et al (2009) worked on CuInS$_2$ thin films obtained by spray pyrolysis for photovoltaic applications. In this work CuInS$_2$ thin films have been deposited by chemical spray pyrolysis onto glass substrates at ambient atmosphere, using different composition solutions at various substrate temperatures. Structural, chemical composition and optical properties of CIS films were analyzed by X-ray diffraction, energy dispersive X-ray spectroscopy and optical spectroscopy. X-ray microanalysis shows that a
chemical composition near to stoichiometry can be obtained. An optical gap of about 1.51 eV was found for sprayed CIS thin films.

Chidi Chukwuemeka uhuegbu et al (2008) reported thin films of CuZnS$_2$ were successfully deposited on glass substrates from aqueous solution of copper chloride in which EDTA and TEA were used as complexing agents. The optical and solid state properties were studied include: absorbance, transmittance, reflectance, extinction coefficient, refractive index, absorption coefficient, optical conductivity, dielectric constants. The direct and indirect band gaps obtained ranges from 2.2 eV to 2.4 eV for direct band gap and 0.4 eV to 0.9 eV for indirect band gap.

Tetsuya Yamamoto et al (2000) investigated the electronic structures of Na-incorporated In-rich CuInS$_2$ based on electronic band structure calculations and X-ray photoelectron spectroscopy. Mobile Na will act as a passivator of donor states, such as In at Cu sites and interstitial Indium, leading to good P-type conductivity of CuInS$_2$ films. On the other hand, we conclude that the formation of the ionic chemical bonds of Na at Cu sites - S atoms near the surface are energetically favorable due to a decrease in the Madelung energy. This results in the stabilization of ionic charge distributions of CuInS$_2$:NaCu with a shift in the energy levels of S3 $p$ orbitals in the vicinity of the Na atoms towards lower energy regions.

Tetsuya Yamamoto et al (2000) investigated the electronic structures of $n$-type doped CuInS$_2$ crystals with chalcopyrite structures using Zn or Cd species, Cu-substituting species, as donor dopants based on ab initio electronic band structure calculations. The strongly localized impurity states for $n$-type CuInS$_2$ doped with Zn with small decrease in Madelung energy compared with that for N-type CuInS$_2$ crystals doped with Cd species. The formation of Cu vacancy in the vicinity of Zn sites, donor-impurity sites, is energetically favorable for Zn-doped CuInS$_2$. 
Ben Rabeh et al (2007) reported the role of oxygen in enhancing N-type conductivity of CuInS$_2$ thin films. Post-growth treatments in air atmosphere were performed on CuInS$_2$ films prepared by the single-source thermal evaporation method. The structural, optical and electrical property of the films was studied by means of X-ray diffraction (XRD), scanning electron microscopy (SEM), optical reflection and transmission and resistance measurements. The films were annealed from 100 to 350$^\circ$C in air. Annealing temperatures above 200$^\circ$C the N-type conductivity is stable. The samples after annealing have direct bandgap energies of 1.45–1.50 eV.

Zribi et al (2006) structural, morphological and optical properties of Sn-doped CuInS$_2$ thin films grown by double source thermal evaporation method were studied. Firstly, the films were annealed in vacuum after evaporation from 250 to 500$^\circ$C for Sn deposition time equal to 3mins. Secondly, the films deposited for several Sn evaporation times were annealed in vacuum after evaporation at 500$^\circ$C. The X-ray diffraction spectra indicated that polycrystalline Sn-doped CuInS$_2$ films were obtained and no Sn binary or ternary phases are observed for the Sn evaporation times equal to 5 min. Scanning electron microscopy observation revealed the decrease of the surface crystallinity with increasing the Sn evaporation times and the annealing temperatures. The Sn-doped samples after annealing have bandgap energy of 1.42–1.50 eV.

Takayuki Watanabe et al (1997) investigated the influence of sodium on the properties of CuInS$_2$ thin films and solar cells. The controlled incorporation of sodium into the absorber layer of CuInS$_2$ solar cells improved cell performance. Without toxic KCN treatment, conversion efficiencies of over 6% were achieved by sulfurization of sodium-containing precursors. The ternary compound semiconductor of NaInS$_2$ was found to form mainly on the surface of each of the CuInS$_2$ films.
Kijatkina et al (2003) CuInS$_2$ sprayed films on different metal oxide underlayers. CuInS$_2$ films as absorbers for solar cells were deposited by the spray pyrolysis method onto commercial ITO and TCO glasses and two different types of TiO$_2$ and ZnO electrodes—flat and porous. Structural, morphological and electrical properties of metal oxidey CuInS$_2$ structures have been studied. CuInS$_2$ crystallite sizes of 6–10 nm on flat electrodes and of 20–30 nm on randomly orientated porous underlayers have been calculated. Doped large band gap oxides are found to be appropriate conductive electrodes for CuInS$_2$ deposited with the spray process. The penetration of CuInS into microporous and columnar structures has been confirmed by scanning electron microscopy studies.

Klenk et al (2005) CuInS$_2$ has emerged as a promising absorber material for thin film photovoltaic modules. A pilot production line for full size (120-60 cm$^2$) modules is currently being established. CuInS$_2$ preparation, material properties, and cell structure are in many aspects comparable to those of the more widely researched selenium-containing chalcopyrite absorbers but there are also unique features of each of the material systems. In this contribution, we give an overview of the historical development, current status, and near to mid-term future of CuInS$_2$-based devices.

Ben Rabeh et al (2005) studied structural and optical properties of non-doped and Sn-doped CuInS$_2$ thin films grown by double source thermal evaporation method. Sn deposition time is taken between 0 and 5 min. The films were annealed at 250°C for 2hs in vacuum after evaporation. The X-ray diffraction spectra indicated that polycrystalline CuInS$_2$ films were successfully obtained after annealing and no Sn binary or ternary phases are observed for the Sn time depositions less or equal to 5 min. The Sn-doped samples after annealing have bandgap energy of 1.45–1.49 eV.
Krunks et al (2000) studied the composition and structure of CuInS$_2$ prepared by spray pyrolysis of an aqueous solution of CuCl$_2$, InCl$_3$ and thiourea onto heated glass substrates. The effect of the composition of starting solutions on the phase and chemical composition and the structure of sprayed is studied. In-rich and S-rich solutions lead to the multiphase with poor crystallinity according to X-ray diffraction. Organic secondary phases could be responsible for the formation of molten phase which together with copper sulphide act as recrystallisation agent during the growth of copper-rich.

Mauricio Ortega-LoÂpez et al (1998) investigated the characterization of CuInS$_2$ thin films for solar cells prepared by spray. The chemical composition, the electrical, optical and the structural properties of polycrystalline CuInS$_2$ thin films prepared by spray pyrolysis to be used for thin film solar cells. The material is p-type with grains preferentially oriented in the direction of the sphalerite structure. The electro-optical properties show a very strong dependence on the [Cu]/[In] ratio in the solution. Films with copper excess have smaller resistivity and better crystallinity than those which are stoichiometric or have indium excess.

Oja et al (2005) studied the crystal quality of CuInS$_2$ films prepared by spray pyrolysis Raman spectroscopy and XRD methods were applied to determine the phase composition and crystal quality of copper indium sulphide (CIS) films grown by spray pyrolysis. The A1 phonon modes at 290 and 300 cm$^{-1}$ in Raman spectra show that CIS films deposited at 370°C consisted of chalcopyrite (CH) and Cu–Au (CA) ordered phases of CuInS$_2$. Both XRD and Raman studies showed the presence of an extra phase in as-deposited films using Cu/In=0.8–1.0, which could belong to CuIn$_5$S$_8$. Thermal treatments reduced the amount of secondary phase and improved the crystallinity of the films.
Bouzouita et al (1998) reported the spray pyrolysis of CuInS. Spray pyrolysis is a low cost method of depositing thin films and is economically more attractive than other methods that have been used to produce stable CuInS thin films. The electrical optical and structural properties of the films as prepared are presented together with their evaluation and with a variation of some fabrication parameters the fabrication temperature and the ionic ratio Cu In S in the solution.

Mere et al (2003) worked on the electrical properties of sprayed CuInS$_2$ films for solar cells. CuInS$_2$ films and superstrate configuration ZnO/CdS/CuInS$_2$ solar cells were prepared by cost-effective spray pyrolysis technique using the Cu/In molar ratios of 0.9, 1.0 and 1.1 in spray solution. Appropriate metal chlorides and thiourea were used as starting chemicals to prepare the absorber layer. XRD, scanning electron microscopy, current–voltage, capacitance–voltage and frequency-swept admittance spectroscopy methods have been used to characterize sprayed absorber and solar cell.

Malle Krunks et al (1999) reported the growth and recrystallization of CuInS$_2$ films in spray pyrolytic process. It is shown that the structure, composition and surface morphology of chemically sprayed CuInS$_2$ films depend on the growth temperature and copper to indium ratio in the spraying solution. The use of Cu-rich initial solutions leads to single-phase films with the rough surface morphology. The important role in the formation of these films plays segregation of molten phase of thermal decomposition products on the surface during the spray process.

Guezmir et al (2006) reported the optical properties of sprayed CuInS$_2$ thin layers thin layers of copper indium disulphide. They were prepared on Pyrex glass substrate at 320ºC by the chemical reactive pray process from an aqueous solution containing cuprous and indium chlorides, and thiourea. Films bulk and surface were analyzed by X-ray diffraction
(XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM) in order to understand the effect of layers microstructure on their optical properties. The optical spectral profiles of such material are highly related to the optical scattering of light.

Catelijne Grassoa et al (2005) studied the electron transport in CuInS$_2$-based nano structured solar cells. Three-dimensional solid state solar cells, or 3D-cells, are based on nano structured n-type TiO$_2$ electrodes as known from dye-sensitized solar cells, and completed with a p-type solid state semiconductor absorber CuInS$_2$ which is absorber and hole conductor in one. The photocurrent response of the 3D-cell turns out to be four orders of magnitude faster than the response of nano structured dye-sensitized solar cells. No voltage dependency is found for the time constants. An increase in illumination intensity results in a decrease in time constant.

Joris Hofhuis et al (2010) How multiple decay paths affect the photoluminescence intensity in CuInS$_2$. The influence of the excitation power on the photoluminescence (PL) intensity of spray-deposited CuInS$_2$ has been studied. Above a certain threshold power, the PL intensity decreases when the excitation power increases, this is a new phenomenon for the semi materials. There combination model that we developed earlier to explain the transient absorption behavior of CuInS$_2$ is modified to simulate the power-dependent PL measurements. The model includes state-to-state recombination path ways. It is found that saturation of deep defect state sat 1.1 eV inhibits there combination from the conduction band to defect states at 0.15 and 0.2 eV, when state-to-state coupling is enabled.

Mi Sun Park et al (2010) Synthesis and Characterization of Polycrystalline CuInS$_2$ Thin Films for Solar Cell Devices at Low Temperature Processing Conditions Polycrystalline CuInS$_2$ thin films were deposited on glass substrates using a novel solution based continuous flow micro reactor
process for the first time. A series of analysis was performed to characterize the CuInS$_2$ thin films using UV-visible spectrophotometer, scanning electron microscope, X-ray diffraction spectrometer, and X-ray photoelectron spectroscopy. The estimated optical band gaps of CuInS$_2$ thin films were in the range of 1.52~1.60 eV. The structural and chemical binding information indicated that CuInS$_2$ thin films with a tetragonal chalcopyrite structure were successfully deposited. Dense film with a thickness around 1_m could be obtained with a 5 minute deposition time. This study demonstrates the solution-based continuous flow micro reactor process is a promising low cost alternative for thin film PV manufacturing.

Simona Manolache et al (2007) The influence of the precursor concentration on CuSbS$_2$ thin films deposited from aqueous solutions. The paper discusses the influence of precursor concentration on the morphology and the structure of CuSbS$_2$ thin films obtained from aqueous solutions and used as absorber for three-dimensional (3D) solar cells. CuSbS$_2$ films are obtained by Spray Pyrolysis Deposition, varying the precursor weight ratio ($\text{CuCl}_2 \cdot \text{H}_2\text{O}$: $\text{H}_2\text{NCSNH}_2$: $(\text{CH}_3\text{COO})_3\text{Sb}$) between 2.57: 1: 5.71–6.86: 1: 5.71, at 240ºC. The films were analyzed by XRD, I–V dark measurements and SEM. Enriching the films in antimony proved to be a control method of the films morphology and structure.

Tina Sebastian et al (2009) Role of substrate temperature in controlling properties of sprayed CuInS$_2$ absorbers. Optimization of substrate temperature of spray pyrolysed CuInS$_2$ absorber is discussed along with its effect on the photo activity of junction fabricated. For CuInS$_2$ thin films, properties like crystallinity, thickness and composition showed progressive behavior with substrate temperature. X-ray photoelectron spectroscopic depth profile of all the samples showed that the concentration of copper on the surface of the films is significantly lesser than that in the bulk thus avoiding
need for toxic cyanide etching. Interestingly, samples prepared at 623 K had higher conductivity compared to those prepared above and below this temperature. Also, the low energy transition, in addition to the direct band gap which was observed in other samples were absent in films prepared at 623 K. From thermally stimulated conductivity studies it was seen that shallow levels present in this sample contribute to its improved conductivity. Also, CuInS$_2$/In$_2$S$_3$ bi-layer prepared at this substrate temperature showed higher photo activity than those prepared at other temperatures.

Camus et al (2008) Properties of Spray ILGAR CuInS$_2$ thin films. CuInS$_2$ thin films were prepared by using the recently presented Spray Ion Layer Gas Reaction (Spray ILGAR). Originally designed for buffer layer deposition this process has now been significantly modified in order to deposit absorber layers for thin film solar cells with thicknesses in the micrometer range. Several post deposition treatments are applied to these films. In this report the CuInS$_2$ films are characterized regarding structure, bulk and surface composition. X-Ray Diffraction (XRD), X-Ray Fluorescence Spectroscopy (XRF), X-Ray Photoemission Spectroscopy (XPS), and Elastic Recoil Detection Analysis (ERDA) were employed to compare the composition of these films to reference CuInS$_2$ films, which were prepared by Rapid Thermal Processing (RTP). It is shown that in terms of composition and surface chemistry the ILGAR films are very similar to device grade reference samples.

Ben Rabeh et al (2009) the influence of Zn and Sb impurities on the structural, optical and electrical properties of CuInS$_2$ thin films on corning 7059 glass substrates was studied. Undoped and Zn or Sb doped CuInS$_2$ thin films were deposited by thermal evaporation method and annealed in vacuum at temperature of 450°C Undoped thin films were grown from CuInS$_2$ powder using resistively heated tungsten boats. Zn species was evaporated from a
thermal evaporator all together to the CuInS$_2$ powder and Sb species was mixed in the starting powders. The amount of the Zn or Sb source was determined to be in the range 0-4 wt % molecular weight compared with the CuInS$_2$ alloy source. The films were studied by means of X-ray diffraction (XRD), Optical reflection and transmission and resistance measurements. The films thicknesses were in the range 450 – 750 nm. All the Zn:CuInS$_2$ and Sb:CuInS$_2$ thin films have relatively high absorption coefficient between 104 cm$^{-1}$ and 105 cm$^{-1}$ in the visible and the near-IR spectral range. The bandgap energies are in the range of 1.472 – 1.589 eV for Zn: CuInS$_2$ samples and 1.396 – 1.510 eV for the Sb:CuInS$_2$ ones. The type of conductivity of these films was determined by the hot probe method. Furthermore, we found that Zn and Sb-doped CuInS$_2$ thin films exhibit P type conductivity and we predict these species can be considered as suitable candidates for use as acceptor dopants to fabricate CuInS$_2$-based solar cells.

Joris Hofhuis et al (2010) the influence of the excitation power on the photoluminescence (PL) intensity of spray-deposited CuInS$_2$ has been studied. Above a certain threshold power, the PL intensity decreases when the excitation power increases, this is a new phenomenon for these materials. There combination model that we developed earlier to explain the transient absorption behavior of CuInS$_2$ is modified to simulate the power-dependent PL measurements. The model includes state-to-state recombination pathways. It is found that saturation of deep defects $t$atesat1.1 eV inhibits there combination from the conduction band to defect states at 0.15 and 0.2 eV, when state-to-state coupling is enabled.

Atanas Katerski et al (2008) CuInS$_2$ films were deposited by spray pyrolysis method at 350ºC. Films were characterized by XPS, AFM and electrical resistivity. The effect of chemical etchings in KCN and (NH$_4$)$_2$S$_2$O$_8$ solutions and thermal treatment at 530ºC in flowing hydrogen sulphide on the
film surface composition has been studied. Indium oxide as main secondary phase in surface region of KCN-etched films is probably responsible of high surface conductivity and failure to prepare substrate configuration solar cell. Oxygen bounded to metal is present in the film bulk revealed by O1s BE of 530.0eV of Ar⁺ sputtered profile. Hydrogen sulfide treatment transforms indium oxide into indium sulfide. Etching in ammonium persulfate solution has found to be effective to remove conductive upper layer resulting in surface with composition Cu:In:S=28.3:22.5:49.3. According to XPS, sprayed films show phase composition grading from the film surface to depth.

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Agarwal et al (1998) Single phase copper indium disulphide (CuInS₂) thin films of thickness between 60 nm and 650 nm with the chalcopyrite structure are obtained on NaCl and glass substrates by flash evaporation. The films were found to be n-type semiconducting. The influence of the substrate temperature on the crystallinity, conductivity, activation energy and optical band gap was studied. An improvement in the
film properties could be achieved up to a substrate temperature of 523 K at a molybdenum source temperature of 1873 K.

Kai Siemer et al (2001) CuInS$_2$-based solar cells are prepared by a rapid thermal process (RTP). We use a sequential preparation with metallic layers of Cu and In rapidly heated in elemental sulfur vapor. Absorber layers from this process show good crystallinity, as seen from XRD and SEM. For further analysis of the defect chemistry, photoluminescence and admittance spectroscopy measurements are carried out. Solar cells prepared from these RTP absorbers have reached 11.4% total area efficiency ($A=0.5\, \text{cm}^2$), which is to our knowledge the best CuInS$_2$-based solar cell so far.

El-Sayed (2006) Thin films of bismuth with different thicknesses were produced by thermal evaporation from a molybdenum boat source onto cleaned glass substrates at room temperature. The material has been characterized using X-ray diffraction, electrical and optical measurements. A polycrystalline transition phase was observed. The resistivity was calculated for different film thicknesses and found to vary with thickness and temperature. An anomalous dependence of resistivity on temperature was observed during heating. The optical constants were determined from the transmission and reflection data of these thin films for normal incidence. The absorption coefficient revealed the existence of an allowed direct transition with energy gap ($E_g$) values ranging from 3.45 to 3.6 eV.

Biljana Pejova et al (2005) Electrical and photoelectrical properties (including both the stationary photoresponse and the photocarriers’ relaxation dynamics) of nanocrystalline semiconducting bismuth (III) sulfide thin films were investigated. The experimental design of photoelectrical properties was achieved by controlling the chemistry of the deposition process (varying the reagent concentration in the reaction system) and also by physical means (controlling the crystal dimensions by post-deposition
annealing). The band gap energy of thin films characterized by most pronounced photoelectrical properties was calculated, on the basis of measured photoconductivity spectral response curves, by several approaches. All of the obtained values are in very good agreement with the corresponding ones obtained from optical spectroscopy data within the framework of parabolic approximation for dispersion relation. On the basis of measured temperature dependence of dark electrical resistivity of nanocrystalline bismuth(III) sulfide films, the thermal band gap energy and the ionization energy of the impurity level (of donor type) were calculated. The corresponding values are 1.50 and 0.42 eV. Dynamics of non-equilibrium charge carriers’ relaxation processes was studied with the oscillographic method. By analysis of the photoconductivity decay kinetics data it is found that recombination of non-equilibrium charge carriers is carried out according to the linear mechanism. The calculated relaxation time of photoexcited charge carriers is 1.58 ms, the relaxation processes occurring via local trapping centers. Recombination processes occurring via a single-type trapping center can be described within the framework of the Schockley–Read model. The practically linear regimes detected in the measured lux–ampere characteristics of the studied films indicate as well a linear recombination mechanism of the photo excited charge carriers.

Akaki et al (2006) Structural, electrical and optical properties of Bi-doped CuInS$_2$ thin films prepared by a single-source thermal evaporation method were investigated. The as-deposited films were annealed in the temperature range between 100 and 500°C for 10 min in air. The film of chalcopyrite CuInS$_2$ single phase was obtained by annealing at 200°C successfully. It was found that Bi atoms enhanced the growth of CuInS$_2$ single phase at lower temperature. Furthermore, the crystalline quality of doped films was higher compared with the non-doped ones.