1.1 Introduction

Development of clean energy sources has become the most important task assigned to the science and technology in the 21st century and photovoltaics has emerged as the most promising candidate of the future energy technology. The importance of alternative energy sources has increased in significance both for energy supply and ecological conservation reasons. In spite of limitations due to short-term economic considerations, research and development of photovoltaic solar cell has increased and is playing an increasingly practical role all over the world. The industrial revolution started with coal as the main energy source, and later, it was shifted to oil and gas (LPG, LNG), owing to the mass-production technology, ease of transport as well as storage and also the [less] environmental issues in comparison with the coal. Today, electrical energy is identified as the most convenient form of energy and it is non-pollutant also. Everyday the Sun supplies energy to the Earth, which is several thousand times our requirement. The quantity of energy supplied by the Sun is more than five orders of magnitude larger than the present requirement of electric power for the whole world, to keep modern civilization going. Above all, solar photovoltaic power generation is almost maintenance free as well as clean technology.

The data given below (table 1.1) demonstrates the contributions to the global environmental issues by photovoltaics.
Table 1.1: Contributions to the global environmental issues by Photovoltaics

<table>
<thead>
<tr>
<th>Local Environment Global</th>
<th>(1) Solar PV power generation Clean sustainable energy sources</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(2) Cleaning of polluted air Ashing of pollutant gases by glow discharge</td>
</tr>
<tr>
<td></td>
<td>(3) Cleaning of water Electrochemical processing by PV</td>
</tr>
<tr>
<td></td>
<td>(4) Generation of Hydrogen Electrolysis of water by PV</td>
</tr>
<tr>
<td></td>
<td>(5) Stopping desertification PV water pumping at plantations</td>
</tr>
<tr>
<td></td>
<td>(6) Greening of deserts</td>
</tr>
</tbody>
</table>

Table 1.2: Pollutant emission factors for different energy sources

<table>
<thead>
<tr>
<th>Energy Source</th>
<th>( \text{CO}_2 )</th>
<th>( \text{NO}_2 )</th>
<th>( \text{SO}_2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal</td>
<td>322.8</td>
<td>1.8</td>
<td>3.400</td>
</tr>
<tr>
<td>Oil</td>
<td>258.5</td>
<td>0.88</td>
<td>1.7</td>
</tr>
<tr>
<td>Natural gas</td>
<td>178</td>
<td>0.9</td>
<td>0.001</td>
</tr>
<tr>
<td>Nuclear</td>
<td>7.8</td>
<td>0.003</td>
<td>0.030</td>
</tr>
<tr>
<td>Photovoltaic</td>
<td>5.3</td>
<td>0.007</td>
<td>0.020</td>
</tr>
<tr>
<td>Biomass</td>
<td>0.0</td>
<td>0.6</td>
<td>0.140</td>
</tr>
<tr>
<td>Geothermal</td>
<td>51.5</td>
<td>Trace</td>
<td>Trace</td>
</tr>
<tr>
<td>Wind</td>
<td>6.7</td>
<td>Trace</td>
<td>Trace</td>
</tr>
<tr>
<td>Solar thermal</td>
<td>3.3</td>
<td>Trace</td>
<td>Trace</td>
</tr>
<tr>
<td>Hydropower</td>
<td>5.9</td>
<td>Trace</td>
<td>Trace</td>
</tr>
</tbody>
</table>

Coal, oil and natural gas were/are still continuing to be the main sources of energy. From table 1.2, it is clear that Photovoltaics is a clean energy source. However, a large barrier impeding the expansion of the photovoltaic systems as a large scale power source has been the high cost of the modules. One of the solutions for the cost reduction is the
development of thin film solar cell, saving both material and energy in the production of cells and modules.

1.2 Discovery of photovoltaic effect

A physical phenomenon allowing light-electricity conversion - photovoltaic effect, was discovered in 1839 by the French physicist Alexandre Edmond Becquerel. Experimenting with metal electrodes and electrolyte he discovered that conductance rises with illumination.

1.3 First solar cells

Willoughby Smith discovered photovoltaic effect in Selenium in 1873 (fig 1.1). Later in 1876, with his student R. F. Day, William G. Adams discovered that illuminating a junction between Selenium and Platinum also has a photovoltaic effect. These two discoveries became the foundation for the first Selenium solar cell construction in 1877.

1.4 Theory of solar cell

The p-n junction is the classical model of a solar cell. This junction is created by doping different regions of the same semiconductor differently, so that there forms an interface between p type and n type layers of the same material. Since the work function of the p-type material is larger than the n type, the electrostatic potential must be smaller on the n side than p, and an electric field is established at the junction. Light absorption generates equal numbers of non-equilibrium electron-hole pairs, in concentrations much higher than equilibrium minority-carrier levels, but typically less than the equilibrium majority carrier concentrations. It is these non-equilibrium minority carriers and their potential energy changes that transform the absorbed photon energy into a DC voltage to drive DC current through the metal contacts for power delivery to an external electrical load. It is the majority carriers that finally flow through the two metal contacts to an external circuit. The junction region is always depleted of both electrons and holes and presents a barrier to majority carriers, and a low resistance path to minority carriers. It drives the collection of minority carriers which are photogenerated throughout the p and n layers, and reach the junction by diffusion.
Fig 1.1: Article published in *Nature* 1876 by Smith after the discovery of photovoltaic action in Selenium.
In a semiconductor, the effective field, existing between the two semiconductors [for separation of carriers] can be generated under the conditions of

(i) gradient in the vacuum level or work function

(ii) gradient in the electron affinity

(iii) gradient in the band gap

(iv) gradient in the band densities of states

The first three of these are exploited in photovoltaic devices and changes in these three can be achieved at the interface between two different materials (heterojunction) or through gradual changes in the composition of an alloy.2,3

1.5 Connection to an external load

Ohmic metal-semiconductor contacts are made to both the n-type and p-type sides of the solar cell, and the electrodes are connected to an external load. Electrons that are created in the n-type side, or have been collected by the junction and swept onto the n-type side, may travel through the wire, power the load, and continue through the wire until they reach the p-type semiconductor-metal contact. Here, they recombine with a hole that was either created as an electron-hole pair on the p-type side of the solar cell, or swept across the junction from the n-type side after being created there.

1.6 Equivalent circuit of a solar cell

![Equivalent circuit of a solar cell](image)
An ideal solar cell may be modelled as a current source in parallel with a diode. In practice, no solar cell is ideal, and hence, shunt resistance and series resistance components are added to the model. The result is the "equivalent circuit of a solar cell" shown in fig 1.2. Also shown (fig 1.3) is the schematic representation of a solar cell for use in circuit diagrams.

1.7 Solar cell efficiency factors

1.7.1 Maximum-power point

A solar cell may operate over a wide range of voltage (V) and current (I). By increasing the resistive load on an irradiated cell continuously from zero (short circuit condition) to a very high value (open circuit condition) one can determine the maximum-power point, i.e., the load for which the cell can deliver maximum electrical power at that level of irradiation, $V_m \times I_m = P_m \text{ in watts.}$

The quickest way to determine the optimal load for a given constant light condition (i.e. a stable quiescent point) is to measure the "Thevenin Equivalent Voltage" (i.e. open circuit), then using a potentiometer as a load, monitor the voltage across it. When the load voltage is exactly half of the Thevenin equivalent Voltage, disconnect the potentiometer and measure its resistance. By the maximum power theorem, the potentiometer resistance will be the optimal value of the load for maximum power transfer (due to the equal voltage division between internal Thevenin equivalent Resistance and the load).

The maximum power point of a solar cell varies with incident illumination. For systems large enough to justify the extra expense (say, ~1 kiloWatt), a 'power point tracker'
tracks the instantaneous power by continually measuring the voltage and current (and hence, power transfer), and uses this information to dynamically adjust the load so that the maximum power is always transferred, regardless of the variation in irradiation. A photovoltaic device optimally runs at 50% electrical efficiency (the point of maximum power transfer), as it is a now-or-never energy source.

1.7.2 Energy conversion efficiency

The energy conversion efficiency ($\eta$) of a solar cell is the percentage of power converted (from absorbed light to electrical energy) and collected, when a solar cell is connected to an electrical circuit. This term is calculated using the ratio of $P_m$, divided by the input light irradiance under "standard" test conditions ($E$, in W/m$^2$) and the surface area of the solar cell ($A_c$ in m$^2$).

$$\eta = \frac{P_m}{E \times A_c}$$

At solar noon, on a clear March or September equinox day, the solar radiation at the equator is about 1000 W/m$^2$. Hence, the "standard" solar radiation [known as the "air mass 1.5 spectrum(AM 1.5)"] has a power density of 1000 watts per square metre. Thus, a 12% efficiency solar cell having 1 m$^2$ of surface area in full sunlight at solar noon at the equator during either the March or September equinox will produce approximately 120 watts of peak power.

1.7.3 Fill factor (FF)

Another defining term in the overall behaviour of a solar cell is the 'Fill Factor (FF)'. This is obtained by dividing the maximum power point by the product of open circuit voltage ($V_{oc}$) and the short circuit current ($I_{sc}$):

$$FF = \frac{P_m}{V_{oc} \times I_{sc}} = \frac{\eta \times A_c \times E}{V_{oc} \times I_{sc}}$$
1.7.4 Quantum efficiency (QE)

'Quantum efficiency [QE]' refers to the percentage of absorbed photons that produce electron-hole pairs (or charge carriers). External QE includes the effect of optical losses such as reflection and transmission. Internal QE deals with photons that are not reflected or transmitted out of the cell.

1.7.5 Comparison of energy conversion efficiencies

Solar cell efficiency varies from 6% for amorphous Silicon-based solar cells to 40.7% [which is the efficiency of multiple-junction cells, produced in research labs]. Solar cell energy conversion efficiencies for commercially available micro crystalline Silicon [mc-Si] solar cells are around 14-16%. The highest efficiency cells have not always been the most economical — for example a 30% efficient multijunction cell, based on exotic materials such as Gallium Arsenide or Indium Selenide, and produced in low volume, will have a cost of about one hundred times that of an 8% efficient amorphous Silicon cell [which is having mass production], while only delivering about four times the electrical power.

![Best Research-Cell Efficiencies](image)

*Fig.1.4: Reported timeline of solar cell energy conversion efficiencies (from National Renewable Energy Laboratory, USA)*
To make practical use of the solar-generated energy, the electricity is most often fed into the electricity grid using inverters (grid-connected PV systems). In stand alone systems, batteries are used to store the energy that is not needed immediately. Fig 1.4 illustrates the best laboratory efficiencies obtained for various materials and technologies.

1.7.6 Peak watt (or watt peak)

Since solar cell output power depends on multiple factors, such as the sun's incidence angle, for comparison purposes between different cells and panels, the “peak watt (Wp)” is used. It is the output power under the following conditions:

Solar irradiance = 1000 W/m²

Solar reference spectrum = AM1.5

Cell temperature = 25°C

1.8 Solar cells and energy payback

It is a fact that we have to spend energy for the production as well as transportation of solar cells. There is a controversy whether a solar cell can produce energy more than this. The energy payback time of a solar panel, [assuming the working lifetime to be around 40 years], is anywhere from 1 to 20 years (usually less than five) depending on the type and usage. This means that solar cells can be net energy producers only if they generate more energy during their lifetime, than the energy expended in producing them. According to some experts, studying this question, solar cells do generate positive net energy, when the energy consumption for manufacturing and distribution is taken into account.

1.9 Three generations of development

Photovoltaic devices have undergone three generations of development.

1.9.1 The First

The first generation of photovoltaic devices consists of a large-area, single layer p-n junction diode, which is capable of generating usable electrical energy from light source
having the wavelengths of sunlight. These cells are typically made of Silicon wafer. First
generation photovoltaic cells (also known as Silicon wafer-based solar cells) are still the
dominant technology in the commercial production, accounting for more than 86% of the
solar cell market.

1.9.2 The Second

The second generation of devices is based on the thin-films of semiconductors. These
devices were initially designed to be highly efficient multiple junction photovoltaic cells.
Later, as the major advantage of using a thin-film of materials was noted to be reducing
the mass of material required for cell design, leading to reduction of cost as well as
weight of the cells, there developed different technologies/semiconductor materials
suitable for mass production, such as amorphous Silicon, poly-crystalline Silicon, micro-
crystalline Silicon, Cadmium Telluride and Copper Indium Selenide/Sulfide. Even
though the efficiencies of thin-film solar cells are lower than that of crystalline Silicon
(wafer-based) solar cells, the manufacturing costs are much lower and hence lower cost
per watt can be achieved. Another advantage of the reduced mass is that less support is
needed for placing panels on rooftops and this allows fitting the panels on even flexible
materials.

1.9.3 The Third

Third generation photovoltaic devices are very different from the other two, and are
broadly defined as semiconductor devices which do not rely on a traditional p-n junction
to separate photogenerated charge carriers. These new devices mainly include
photoelectrochemical cells, polymer solar cells and nanocrystal/defect material solar
cells.

1.10 Current stage of development

24.7% efficient crystalline Silicon solar cell was developed at University of New South
Wales, Australia. NREL has developed a record-efficiency Cu(In,Ga)Se₂/CdS cell,
which possess the maximum among single junction, thin film solar cell of 19.9%.
Spectrolab fabricated 40.7% tandem cell with GaInP/GaInAs/Ge triple-junction. The efficiency was measured under the standard spectrum for terrestrial concentrator solar cell at 240 suns (24W/cm²). Organic solar cells have now reached an efficiency of 6% and Dye sensitized cell an efficiency of 11.1%.

Most widely used cells are made of crystalline Silicon, which require larger thickness because of the indirect band gap. Moreover, Silicon extraction process requires sophisticated technologies which increase the cost of Silicon solar cells. As an alternative to this, the Second Generation Technology, [i.e. Thin Film Technology] gained prominence. Thin film solar cells use layers of semiconductor materials having only a few micrometres thick.

Thin film technology has many advantages like,

1. A variety of techniques are available for depositing thin films of same material
2. Reduction in material costs
3. Fewer processing steps
4. Simpler device processing and manufacturing technology for large area modules and arrays
5. Higher power to mass ratio
6. A wide variety of shapes, sizes, areas and substrates are possible
7. Different types of electronic junctions, single and tandem junctions are feasible
8. Graded band gap, graded composition, graded lattice constants can be obtained to meet requirements for a designer solar cell
9. Surface and grain boundaries can be passivated with suitable materials
10. Weight of the modules becomes less

Thin film technology has made it possible to have solar cells functioning as rooftop shingles, roof tiles and building facades. The solar cell version of items such as shingles offer the same protection and durability as ordinary asphalt shingles.
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1.11 Important material properties for high efficiency cell

1. The band gap of the absorbing material must be small enough to allow absorption of an appreciable portion of a solar spectrum and at the same time large enough to minimize the reverse saturation current density $J_0$.

2. The diffusion length of minority carriers must be as large as possible so that carriers excited by light, even at some distance from the actual semiconductor junction, will be able to diffuse to the junction and be collected before they recombine with the carriers of opposite sign. The diffusion length of minority carriers $L_{\text{min}}$ is given by

$$L_{\text{min}} = (D_{\text{min}} \tau_{\text{min}})^{1/2} = \left[\frac{kT}{q} \left(\frac{\mu \tau}{q} \right)\right]^{1/2}$$

where $D_{\text{min}}$ is the diffusion constant, $\tau_{\text{min}}$ is the life time, $\mu_{\text{min}}$ is the mobility for minority carriers, $q$ is the electronic charge and $k$ is the Boltzmann constant. Hence it is desired to have a material in which the minority carriers have large mobility and life time.

3. The actual junction structure and composition determines the magnitude of the junction transport current density, $J_0$ and the ideality factor, $A$. Formation of semiconductor junction must be carefully controlled to produce junctions with a junction current as low as possible.

4. In an ideal solar cell, series resistance $R_s$ should be equal to zero and shunt resistance $R_{sh}$ equal to infinity. But in real solar cells, finite values of these resistances will be present and can be a major factor, particularly, in determining the effective values of the fill factor [FF]. Contributions to the series resistance can arise from the resistance of the semiconductor bulk and from contact resistance to the semiconductor to complete the circuit. The parallel resistance can be reduced by grain boundaries or other defects that enhance forward junction current and contributes to an increase in $J_0$ and a decrease in the voltage $\Phi_{oc}$. In polycrystalline thin film solar cells, grain boundaries at the junction interface can critically affect junction transport properties.
5. Solar cells are used in exposed areas for long periods of time without failure which means that a variety of phenomena that might lead to the decrease in cell efficiency with time of exposure must be carefully considered.

All these factors must be carefully considered while making a thin film solar cell so as to maximize the efficiency.

1.12 Materials for photovoltaic devices

1.12.1 Crystalline Silicon (c-Si)

Crystalline Si has almost an ideal band gap for solar energy conversion. It is one of the abundant materials on the earth’s crust and hence it has a dominant role in the development of solar cells over the last 50 years. In 1981, the Si p-n homojunction cell was the only widely available solar cell. Monocrystalline Si with a grain size greater than 10 cm and polycrystalline Si with grain size in the range of 1 μm to 1 mm are available. The cost of single crystal Si solar cells is greater than thin film multicrystalline Si solar cells. Single crystal Si solar cells require very high material quality, surfaces must be effectively passivated to reduce recombination there and the bulk properties must also be of high quality because of the long optical penetration distances associated with the indirect band gap of Si. Most of the solar cells exhibited in various simple demonstrations or applications are actually multicrystalline Si cells. Multicrystalline Si solar cells have been produced with efficiencies of ~ 17% and may be inexpensively produced from somewhat less pure starting materials using less expensive manufacturing methods.

1.12.2 Amorphous Silicon (a-Si)

Amorphous Silicon (a-Si) PV modules were the first thin-film PV modules to be commercially produced. a-Si has a high density of co-ordination defects (dangling bonds) corresponding to departures from the local tetrahedral coordination between four Si atoms. They act as recombination centres to greatly reduce the carrier lifetime, carrier diffusion and drift lengths. This also helps to pin the Fermi energy in such a way that the material can not be effectively doped as p or n type. But now it has been observed that
incorporation of 10% of Hydrogen reduces the density of defects from $10^{19}$ cm$^{-3}$ to $10^{16}$ cm$^{-3}$. Hydrogenated amorphous Si alloy [a-Si: H] has a higher energy absorption edge and larger optical absorption constant for solar radiation than crystalline Silicon. Only 1 - 2µm thickness of a-Si:H is required to absorb virtually all of the light above the absorption edge. However, the efficiencies of these modules have not yet reached levels that were predicted in the 1980's. To a significant degree this is due to the intrinsic degradation of a-Si under illumination. The use of multi-band gap multijunction devices (allowing the use of thinner absorber layers in the component cells) and the use of light-trapping appear to be the most powerful device design techniques to improve stabilized device performance. Presently, champion cells have stabilized efficiencies of 12% and champion modules (1 square foot) have stabilized efficiencies of over 10%. The use of multi-band gap multijunction devices (allowing the use of thinner absorber layers in the component cells) and the use of light-trapping appear to be the most powerful device design techniques to improve stabilized device performance.

1.12.3 Gallium Arsenide (GaAs)

The direct band gap of GaAs (1.43eV) is near the optimum for solar energy conversion and it leads to 97% absorption of AM1.5 radiation in a thickness of about 2µm. The carrier mobility of this material is higher than that of Si and it forms a variety of lattice-matched ternary compounds allowing for controlled variations of properties. Common dopants include S, Se, Te, Sn, Si, C and Ge as shallow donors and Zn, Be, Mg, Cd, Si, Ge and C as shallow acceptors. The dopants from column IV-C, Si, Ge and Sn are amphoteric in GaAs, behaving as donors or acceptors depending on whether they go onto Ga or As sub lattice and their electrical behaviour depends on the condition of the growth. Efficiencies of GaAs based solar cells are among the highest of any solar cells, lying between 20-30%. One of the major advantages of GaAs solar cell is its insensitivity to increase in temperature. Measurements indicate that there is only 0.033% decrease in efficiency per degree Centigrade. GaAs has better radiation hardness than Si. These factors mean that GaAs cells have been developed primarily for use in space. The most likely terrestrial application is for power generation under concentrated light. The
multijunction solar cell with GaInP/GaInAs/Ge structure has achieved a record efficiency of 40.7% at 240 suns, under the standard spectrum for terrestrial concentrator solar cells (fabricated at Spectrolab, USA).

1.12.4 Indium Phosphide (InP)

Similar to GaAs, Indium Phosphide is a direct band gap material with an $E_g$ of 1.34 eV. Also like GaAs, homojunction cells are limited by surface recombination at the incident surface, but heterojunctions with good lattice matching. But ‘heterojunctions’ are much more efficient. InP based cells are more radiation resistant than GaAs cells. Hydrogenation of n−p InP solar cells has been shown to be increasing the efficiency to 17.5% at AM0 because of reduction in carrier concentration in the near-surface layer due to the formation of an acceptor-hydrogen complex. Due to the high cost of InP, only thin films with thickness $< 2\mu m$ were made. CdS/InP junction prepared on polycrystalline InP have shown an efficiency of 5.7%.

1.12.5 Cadmium Telluride (CdTe)

CdTe is again a direct band gap material, having an $E_g$ of 1.44 eV, strongly absorbing the solar spectrum within a few micrometres thickness. CdTe has a strong tendency to grow as highly stoichiometric, but p-type semiconductor film and can form a p-n heterojunction with CdS. CdTe have now reached up to an efficiency of 16.5%. Efficiencies up to 18% can be expected for the CdTe cell made under a mature technology. The maximum theoretical efficiency of CdTe solar cells is 27.5%.

1.12.6 Copper Indium Sulfide (CuInS₂)

CuInS₂ is particularly a promising candidate because of its optimum direct band gap of 1.5 eV for solar energy conversion. The conductivity type can be changed. This is one of the I-III-VI₂ type semiconductors that crystallize in chalcopyrite structure. Wider band gap of CuInS₂ compared to other widely used chalcopyrites, such as CuInSe₂, has an advantage of potentially higher open circuit voltages. Theoretically predicted efficiency of the homojunction of this material ranges between 27 and 32%. Recently CuInS₂ based cells has reached an efficiency of 11.4%.
1.12.7 Copper Indium Selenide (CuInSe₂-CIS)

With an efficiency of 19.9% on the laboratory scale and 13.4% for the power modules, CuInSe₂ has become the most efficient thin film technology today. The favourable properties of this material are listed below

1.13 Properties of CuInSe₂

1.13.1 Tetragonal chalcopyrite structure

Stable crystal structure of CIS is a subset of adamantine class and is named after the mineral chalcopyrite, CuFeS₂. Characteristic feature of the adamantine structure is the tetragonal arrangement of atoms in which each atom has four nearest neighbours. CIS crystallizes in this form at room temperature and reverts to the sphalerite structure (β phase) above 1073K. Bonding is mainly covalent because of the tetrahedral coordination. In general, various compound crystal structures are derived from the basic diamond close-packed structure. It has a sub lattice of anion in cubic close packing (as in the Zinc Blend (sphalerite) structure) or in hexagonal close packed type (as in the Wurtzite structure). CIS is obtained from the cubic Zinc blende structure of H-VI
materials like ZnSe by occupying the Zn sites alternately with Cu and In atoms. Each I(Cu) and III(In) atom has four bonds to the VI (Se) atom. In turn, each Se atom has two bonds to Cu and two to In. Because the strengths of the I-VI and III-VI bonds are in general different, the ratio of the lattice constants \( c/a \) is not exactly two. Instead, the quantity \( 2-c/a \) is a measure of tetragonal distortion in chalcopyrite materials.

1.13.2 Band gap of 1eV at room temperature

CIS has a relatively small band gap of 1.04 eV, which enables it to absorb a large portion of the solar spectrum. It also has a direct band structure thereby minimizing the requirements for large minority carrier diffusion length, since carriers are photoexcited close to the collecting junction. By partial substitution of In with Ga or Al [ie.\( \text{Cu(In,Ga)Se}_2 \), or Cu(In,Al)Se\(_2\)] and Se by S [\( \text{CuIn(S,Se)}_2 \)], the band gap value can be systematically shifted between 1.04 eV and 1.68 eV. This phenomenon allows for an optimum match with the solar spectrum.

1.13.3 High absorption co-efficient of \(10^5\) cm\(^{-1}\)

CIS has an absorption co-efficient (\(\alpha > 10^5\) cm\(^{-1}\)) which implies that 99% of the incoming photons are absorbed within the first micrometre of the material. As a result, only 1-2\(\mu\)m of this material is sufficient to effectively absorb the incoming photons compared to bulk Si, where at least 300\(\mu\)m of material is required.

1.13.4 Large structural tolerance to off-stoichiometry

A noticeable feature of CuInSe\(_2\), deposited by evaporation and several other techniques is the tendency to have average compositions to lie along a pseudo-binary composition line connecting the compounds Cu\(_2\)Se and In\(_2\)Se\(_3\) on the Cu-In-Se ternary phase diagram. However, the deposited layers are found to be predominantly single phase when stoichiometric or slightly In-rich, while two phase CuInSe\(_2\)+Cu\(_2\)Se has been reported for Cu-rich material.\(^{11}\)
1.13.5 Excellent stability and high radiation resistance

CIS-based solar cell devices have demonstrated good thermal, environmental and electrical stability. Preliminary tests have indicated that the radiation tolerance of CIS thin films is superior to that of single-crystalline Si or GaAs devices when tested under high energy electron and proton radiation.

1.13.6 Fabrication on variety of substrates

CuInSe₂ thin films are now prepared on lightweight flexible substrates which improves its suitability in space applications. CIS cells were already fabricated successfully on Molybdenum foil, Polymeric, metallic foils of Aluminium, Titanium, Stainless steel and Ni-alloys, Plastic and Polyimide foils.¹²⁻¹⁶

1.14 Milestones in the development of CIS based solar cells

1953: CIS was synthesized for the first time by Hahn

1974: CIS was proposed as a photovoltaic material with a power conversion efficiency of 12% for a single crystal solar cell

1976: L.L. Kazmerski et al. reported 5.7% efficiency polycrystalline solar cells

1983-84: Boeing Corp. reported efficiencies in excess of 10% from thin polycrystalline films obtained from a three source co-evaporation process

1987: Arco solar achieved a long-standing record efficiency of 14.1% for a thin film solar cell

1998: The first commercial Cu(In,Ga)Se₂ solar modules were available

1999: Conversion efficiency reached 18.8% (NREL, USA)

2003: Conversion efficiency reached 19.2% (NREL)

2008: Conversion efficiency reached 19.9% (NREL) on the laboratory scale and 13.4% on the commercial scale
1.15 Review on CIS thin films

CIS can be prepared using both vacuum and non-vacuum processes.

1.15.1 Vacuum processes

Vacuum processes include thermal, flash and electron beam gun evaporations, sputtering, laser ablation, rapid thermal processing (RTP) and molecular beam epitaxy (MBE).

(i) Evaporation

Vacuum evaporation is a commonly used technique in the deposition of CIS thin films which includes thermal evaporation, flash evaporation and electron beam evaporation. The record-breaking 19.9% CIGS cell was prepared using thermal evaporation (co-evaporation). The development of this method dates back to 1972 and currently it has become, one of the feasible methods for CIS preparation.

Neumann et al. prepared CIS epitaxial layers by single-source evaporation and found that source temperatures above 1400K were necessary for the deposition of single-phase and nearly stoichiometric CuInSe₂ films.¹⁷ Neelkanth et al. prepared CIS films using co-evaporation of constituent elements at a substrate temperature of 350°C. The band gap varied in the range 1.02-1.04eV. Thickness was in the range 0.15-1μm.¹⁸ Varela et al prepared CIS thin films using co-evaporation of Cu, In and Se. The films were deposited at different temperatures in the range 175-400°C.¹⁹ Mikihiko Nishitani et al. prepared CIS by co-evaporation of the elements under an ultrahigh vacuum by a molecular-beam deposition method. The process was found to be suitable for the fabrication of stoichiometric or slightly In rich films.²⁰ S. T. Lakshmikumar demonstrated gas phase selenization of vacuum deposited Cu and In thin films employing an elemental Se vapour source for the deposition of CIS thin films. The selenization reaction readily occurred at Cu and In films kept at 340–400°C. Lower selenization temperatures invariably led to the formation of Cu and In selenides with well defined crystalline microstructures.²¹ Guillen et al prepared CIS by sequential evaporation of stacked Cu and In layers and subsequent chalcopyrite formation using elemental Se within a closed-space graphite container.
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placed into a newly developed vacuum environment at 400°C in nitrogen atmosphere. These films showed smoother surface, higher grain size and uniformity when reactor pressure was increased during the selenization process. C Calderon et al. prepared CIS using sequential evaporation of Cu, In\textsubscript{2}Se\textsubscript{3} and Se.\textsuperscript{23} Mario Gossla et al. developed a new five-source PVD for the deposition of Cu(In\textsubscript{1-x}Ga\textsubscript{x})(Se\textsubscript{1-y}S\textsubscript{y})\textsubscript{2} absorber layers. By varying the sulfur contents (in Cu-poor samples), the band gap could be increased to 1.5eV and best cell showed an efficiency of 10%.\textsuperscript{24} Sung Chan Park et al. studied the electrical properties of CIS films prepared by evaporation of Cu-Se and In\textsubscript{2}Se\textsubscript{3} compounds. CIS film grown at 680°C had a smooth and dense microstructure with the grain size of 2 - 3 μm. H\textsubscript{2} post annealing was conducted to control the electrical resistivity and composition of CIS films. In H\textsubscript{2} atmosphere, the resistivity increased to about 100Ωcm by annealing at 350°C for 1 h. The resistivity decreased again when the annealing temperature was above 350°C.\textsuperscript{25}

T Schlenker et al. reported the initial growth behaviour of Cu(InGa)Se\textsubscript{2} prepared using co-evaporation on Molybdenum substrates. It was observed that the growth on polycrystalline Mo substrates fabricated by sputter process, a power law dependence between the island density and the deposition rate and an exponential dependence of the island density on substrate temperature. On electron gun evaporated Mo, the nucleation mechanism deviated from the model of homogeneous nucleation and strong island density fluctuations occurred.\textsuperscript{26} M J Romero et al. studied the surface widening in CuInGaSe\textsubscript{2} thin films prepared using three stage physical vapour deposition. This widening of the surface was confirmed using transmission electron microscopy and cathodoluminescence spectroscopy.\textsuperscript{27} Akhlesh Gupta et al. carried out studies on Cu-In precursor for the preparation of CIS thin films by the selenization technique. The effect of temperature on the degree of alloy formation between Cu and In layers was studied. The mechanism of alloy formation was different in bilayers annealed at temperatures lower and higher than the melting point of In, or prepared by deposition of Cu and In at 200°C and 150°C, respectively. While the annealing of the precursor up to 200°C
produced an alloy in the interface region of Cu and In layers, annealing at 500°C completely changed its morphology.\textsuperscript{28}

A Moharram et al. studied the optical and structural changes of thermally co-evaporated CIS films. Increasing In content on the expense of Se atoms, decreased the amount of Se phase which had higher energy band gap. Tetragonal CIS and hexagonal Cu\textsubscript{2}Se crystalline phases were resulted from thermal annealing.\textsuperscript{29} O Rodriguez et al. performed the chemical analysis of CIS prepared using evaporation through a multistage process. It was observed that the samples prepared using two stage processes are Cu-rich and that prepared using three stage process was Cu-poor. It was found that the films from three stage process were suitable for solar cell fabrication.\textsuperscript{30} A. Ashour et al. studied polycrystalline CIS thin film formation on glass substrates by preparing stacked elemental layers (SELs) of Cu, In and Se followed by annealing at 200, 250, 300 and 400°C for different times (from 15 to 240 min). It was concluded that a single phase of CIS film was obtained at a reaction temperature of 300°C for a heating time \(\geq 1\) h.\textsuperscript{31} C. Guillén et al. studied the Structure, morphology and photoelectrochemical activity of CIS thin films grown by the sequential evaporation of Cu and In layers, and subsequent reaction at 400°C with elemental selenium vapour. An improvement in the CIS quantum efficiency, related mainly to the increased homogeneity and smoothing of the sample surface, could be gained by using as precursors multiple stacked Cu–In bilayers evaporated onto unheated substrates.\textsuperscript{32} C. F. Kurdesau et al. performed in situ resistivity measurements during selenization of co-evaporated Cu–In layers in Se/N\textsubscript{2} gas mixture at atmospheric pressure. For selenization processes and in situ measurements a special container (a quasi-closed system) with mechanical contacts to the selenized film was constructed. The total resistance of the metallic layers and the contact system was approximately 10 \(\Omega\) before the reaction starts. During the selenization processes it increased to more than 10 k\(\Omega\), indicating the conversion of metals into CIS. The resistivity curve indicated the start and end point of the chemical reactions and identified three different stages of conversion.\textsuperscript{33} A. G. Chowles et al. carried out in situ RBS analysis of CIS prepared by sequential evaporation of the constituent elements onto Mo-
coated glass substrates and the layers were subsequently selenized in a closed graphite box at 400°C. For the Cu/In/Se structure, XRD performed after various anneals revealed that the Cu-In layer mixed with the Se layer to form a number of binary phases. For Cu/Se/In it was found that the Cu and Se had intermixed at room temperature. In both the structures the Cu-Se and In-Se binary phases formed below 200°C and upon annealing above this temperature interdiffused to form chalcopyrite CIS.\(^{35}\) A. Brummer et al. studied the formation of CIS by the annealing of stacked elemental layers. CIS crystallized from the direct precursors Cu\(_2\)Se (Cu\(_{2-x}\)Se, respectively) and InSe within a melt rich in selenium. Both, Na and Ga promoted the crystallization of Cu\(_2\)Se, the direct precursor phase for CIS. A comparison of the crystallographic structures of Cu\(_2\)Se and InSe showed that epitaxial growth of InSe (0001) on Cu\(_2\)Se (111) lattice planes was feasible.\(^{36}\) R. Caballero studied CIS formation by selenization of sequentially evaporated metallic layers. The selenization procedure was carried out within a partially closed graphite container. The CIS films showed single-phase chalcopyrite structure with preferential orientation in the (1 1 2) direction after 500°C selenization. The CIS surface morphology depended on the sequence used. The In/Cu/In seemed to be the best. An energy band gap above 0.95 eV and an absorption coefficient near 10\(^5\) cm\(^{-1}\) were obtained and similar optical properties were observed for all the prepared sequences.\(^{37}\) In the highest efficiency cell (Contreras et al.), CIGS was prepared by thermal co-evaporation which includes three stages. At the first stage, the composition was made Cu-rich, which aided the formation of high-quality, large-grained polycrystalline material. The second stage includes evaporation of In, Ga and Se to titrate the excess (Cu,Se) from the film aggregate. At the third stage, a small quantity In and Ga were added which assist the formation of a smooth surface and to facilitate the formation of a Cu-poor defect chalcopyrite that exist at the surface of CIS films.\(^{38}\) Flash evaporation and electron beam gun evaporation were also used to deposit CuInSe\(_2\) films. Joseph et al. prepared CIS using flash evaporation and samples were p-type. Activation energy of 75 meV was obtained for room temperature deposited (non-annealed) film, which was attributed to Se interstitials acting like acceptors. Activation
energy of 15 meV observed in film annealed at 50°C, was attributed to In$_{Cu}$ defect level while value of around 30 meV observed in other films annealed up to 200°C, was attributed to Cu$_{In}$ defect level. Akl et al performed structural study of flash evaporated CIS thin films. M. Klenk et al. studied the properties of flash evaporated chalcopyrite absorber films and solar cells. C. Guillen et al studied structure, morphology and photoelectrochemical activity of CIS thin films as determined by the characteristics of evaporated metallic precursors. An improvement in the quantum efficiency, related mainly to the increased homogeneity and smoothing of the sample surface, could be gained by using multiple stacked Cu-In bilayers evaporated onto unheated substrate as precursors.

(ii) Sputtering

I Martil et al. prepared CIS films by rf sputtering in Ar/H$_2$ atmosphere. Measurements of resistivity at various temperatures indicated a hopping conduction mechanism through gap states for films grown at low temperature (100-250°C), the existence of three acceptor levels at about 0.046, 0.098 and 0.144 eV above valence band for films grown at intermediate temperature (250-350°C) and a pseudo-metallic behaviour for films grown at high temperatures (350-450°C). P Menna et al. performed the study of Selenium incorporation in sputtered Cu-In alloys. Selenium incorporated in the ternary compound assumed a constant value around 48% while the Cu/In ratio ranged between 0.8 and 1.2. As the copper content was further lowered, Selenium decisively increased up to almost 51% when Cu/In is 0.6. The inversion point in the Se-Cu/In diagram was correlated to the formation of a secondary phase identified as the chalcopyrite vacancy-variant compound CuIn$_3$Se$_5$(OVC). Sang Deok Kim characterized CIS thin films grown by selenization of co-sputtered Cu-In alloy layers, which consisted of only two phases, CuIn$_2$ and Cu$_{11}$ln$_9$. The CIS films selenized in vacuum had large grain sizes, smooth surfaces and dense microstructures. J. Schmidt et al. prepared thin films of CIS by selenizing co-sputtered Cu-In films with selenium vapour. The conductivity types were p-type for Cu-rich and n-type for near-stoichiometric and ln-rich films. All samples showed a thermally activated conductivity for higher temperatures and the
variable-range hopping conduction mechanism in the lower temperature range. The
dependence of the absorption coefficient on incident photon energy indicated allowed
direct transitions with energies in the range 0.96-1.01 eV. F. O. Adurodija et al. carried
out the characterization of co-sputtered Cu-In alloy precursors for CIS thin films
fabrication by close-spaced selenization. The co-sputtering technique for producing Cu–
In alloy films and selenization within a close-spaced graphite box resulting in quality CIS
films was developed. Very In-rich films yielded the ODC compound with small crystal
sizes whilst slightly In-rich or Cu-rich alloys yielded single phase CIS films with dense
crystals and sizes of about 5 µm. Film resistivity varied from $10^{-2}$ to $10^{8} \Omega \text{cm}$. The films
had compositions with Cu/In of 0.40-2.3 and Se/(Cu+In) of 0.74-1.35. All CIS films
with the exception of very Cu-rich ones contained high amount of Se (>50%).
Tooru Tanaka et al. studied the effect of substrate temperature on properties of thin films
prepared by RF sputtering from CIS target with Na$_2$Se. The copper content was found to
decrease with increasing the substrate temperature, and the band gap of the thin films
became large, suggesting the formation of CuIn$_3$Se$_5$ structure. The reduction of copper
content was presumed to be due to the surface reaction during the growth. The effect of
8 MeV electron irradiation on electrical properties of CIS thin films were also studied.
The n-type CIS films in which the carrier concentration was about $3 \times 10^{16} \text{cm}^{-2}$, were
epitaxially grown on a GaAs(0 0 1) substrate by RF diode sputtering. No significant
change in the electrical properties was observed under the electron fluence $<
3 \times 10^{16} \text{e cm}^{-2}$. As the electron fluence exceeded $10^{17} \text{e cm}^{-2}$, both the carrier
concentration and Hall mobility slightly decreased. The carrier removal rate was
estimated to be about 0.8 cm$^{-1}$, which was slightly lower than that of III–V compound
materials. J. Müller et al. studied the composition, structure and optical properties of
sputtered thin films of CIS. Results of EDAX analysis revealed that the sputtered films
were near to stoichiometry for substrate temperatures $T_{\text{Sub}}$ not exceeding 200°C XRD
patterns indicated that the films exhibited some pattern similar to that of bulk crystals of
tetragonal chalcopyrite, predominantly (112) oriented. The band gap $E_g$, estimated from
optical absorption data, was between 0.6–1.08 eV, depending on sputtering conditions
such as substrate temperature and bias voltage. High optical absorption coefficients (> 10^4 cm^-1) were found.

(iii) Laser ablation

Yoshida et al. prepared CIS thin films with large grain by XeCl excimer laser ablation on glass substrates. The deposition was carried out at 550°C and the target-substrate distance was changed from 15 to 60 mm. All films showed the single-phase and stoichiometric chalcopyrite structure, independent of the distance. The deposition rate was large with the small distance. The electrical conductivity measurements gave p-type conduction, and the mobility was improved with the smaller distance. V. V. Kindyak et al. studied the optical transitions in laser-evaporated CIS thin films. The optical absorption coefficients of highly oriented laser-evaporated thin films were determined from the measured reflectance R(λ) and transmittance T(λ) in the wavelength range 400–1700 nm. The optical absorption spectrum of CIS thin films showed three energy gaps, which were associated with the fundamental edge and valence band splitting by the tetragonal crystal-field and spin-orbit effects, and four optical transitions from the Copper d levels to the conduction bands. S. Kuranouchi et al. studied the annealing effects of CIS films prepared by pulsed laser deposition. The composition of annealed films was Cu-rich and no significant loss of Selenium was observed. The liquid (Cu_xSe)_solid (CIS) growth mechanism was suggested and the CIS grain growth was enhanced. A. Tverjanovich et al. prepared CIS thin films by UV laser ablation.

(iv) Rapid Thermal Processing (RTP)

W Riedl et al. analyzed the surface microstructure of CIS thin films produced by rapid thermal processing by scanning tunneling microscopy and spectroscopy in ambient air. Although the bulk material of all samples investigated was p-conductive, abrupt changes of the conductivity type of the surfaces from p- to n-type were observed as a function of the overall Cu/In ratio. The dominant current flow direction in slightly Cu-rich thin film bulk material was associated with p-type conduction, whereas In-rich samples exhibited largely n-type conductivity at the surface. V Alberts et al. studied the material
properties of CIS prepared by rapid thermal treatment of metallic alloys in $\text{H}_2\text{Se}/\text{Ar}$. Selenization at temperatures around 400°C resulted in a sharp increase in Cu/In atomic ratio due to the loss of Indium from the samples. Homogeneous and dense films were formed without Cu-rich binary phases in the case of samples which were rapidly heated and selenized at temperatures around 400°C.\textsuperscript{56} J. Keranen et al. studied the effect of sulfurization on the microstructure of chalcopyrite thin-film absorbers. Rapid thermal processing in $\text{H}_2\text{S}$ atmosphere with processing temperatures ranging from 350 to 550°C was used to sulfurize the absorber. A non-uniform and porous surface reaction layer was evident in the CIS and CIGS structures after the RTP. The CIGS structure had a tendency towards a phase separation, whereas, the CIS films exhibited mixed sulfoselenides, $\text{CuIn(Se}_{1-x}\text{S}_x)\text{2}$, where $x$ varies. In order to improve the device performance, the formation of two distinct phases should be avoided during the sulfurization processing.\textsuperscript{57}

(v) Monocrystalline CIS

CIS single crystals were also well studied. S. Niki et al. studied the effects of annealing on CIS films grown by molecular beam epitaxy on GaAs (0 0 1) at substrate temperatures of $T_s = 450\text{–}500°C$ and the effects of annealing under various atmospheres. An epitaxially grown $\text{In}_2\text{O}_3$ phase was found both in Cu-rich and In-rich films annealed at $T_A = 350°C$, which was not observed in the films annealed in Ar atmosphere. Thermodynamic calculations based on the Cu-In-Se-O-N system showed $\text{In}_2\text{O}_3$ to be the most stable phase in good agreement with the experimental results.\textsuperscript{58} K. Yoshino et al. studied the temperature dependence of photoacoustic spectra in CIS thin films grown on (0 0 1)-oriented GaAs substrate by molecular beam epitaxy (MBE) at substrate temperature of $T_s = 450°C$. The samples were characterized by means of piezoelectric photoacoustic (PPA) measurements between liquid helium (4.2 K) and room temperature (300 K). Two distinct PPA signals due to band gap of CIS and GaAs were observed in the whole temperature range from 4.2 to 300 K and the PPA signals of CIS decreased at the temperature range. Since the PPA signals of CIS thin films could be obtained up to room temperature, the PPA measurements were quite effective to obtain the optical characterizations, especially for the non-radiative recombination processes.\textsuperscript{59} A. N.
Tiwari et al. carried out a review on heteroepitaxy of CuIn_xSe_y. Molecular beam epitaxy has been used to grow heteroepitaxial CuIn_xSe_y layers on Si and GaAs substrates. Layers of different Cu/In ratios have been grown to study the formation of different phases such as CIS chalcopyrite (α-phase) and defect-chalcopyrite/stannite phases (β-phase) in this material system. An interfacial CuSexSi_y layer is formed during the growth of CuIn_xSe_y on Si. In the case of GaAs substrates, Ga from the substrate diffuses into the CuIn_xSe_y and a quaternary compound Cu(In,Ga)_xSey is formed at the interface. James H. Ely et al. characterized epitaxial Cu–In–Se thin films using Raman spectroscopy. Epitaxial chalcopyrite alloys (CIS (001) and CuIn_3Se_5 (001)) were fabricated with varying compositions and thicknesses on GaAs (001) substrates using a simple physical vapour deposition method. All of the spectra were dominated by the A_t(Γ_{11}) [W_{1}] non-polar optical mode at 172 cm^{-1} for CIS and 152 cm^{-1} for the CuIn_3Se_5 phase. In addition, Raman spectra for the thinner layers indicated that these films were under compressive stress due to the lattice mismatch between the films and the substrate. Tooru Tanaka et al. prepared CIS by epitaxial growth and studied the effect chlorine ion implantation on electrical properties. The conductivity type in all implanted films was n-type and the carrier concentration was increased with increasing Cl concentration in the films. Cl acts as a donor in CIS.

A. Zegadi et al. performed photoacoustic study on the effect of Se content on defect levels in CIS single crystals. Champness et al. prepared monocrystalline CIS by vertical Bridgman technique with non-stoichiometric proportions of the starting elements Cu, In and Se. With stoichiometry or an excess of Se the ingots were p-type. With a deficiency of Se, n-type conductivity was obtained but with binary phases such as InSe present in the last zone of the ingot. H. P. Wang et al. reported studies on monocrystalline CIS and CuIn_3Se_5 in photovoltaic cells using monocrystalline CIS as a substrate. Pre-annealing the substrate in argon at 350°C for about 2 h improved photovoltaic performance. Measurements of Auger profiles in the first 200Å or so of annealed and unannealed monocrystalline samples indicated no evidence of the formation of an OVC near the surface during the heat-treatment process. Champness et al. also studied the effect of
annealing of monocrystalline CIS samples. In monocrystalline p-type CIS samples, with a room temperature hole concentration of approximately $10^{17} \text{ cm}^{-3}$, partial type-conversion was observed to take place after heat-treatment at 500°C in argon at atmospheric pressure. The depth of the outer n-layer in the original p-type material, as determined by hot probing and etching, increased approximately as the square root of the annealing time.\textsuperscript{66} K. Timmo et al. studied CIS monograin growth in the liquid phase of potassium iodide. All the grown powder materials with narrow-disperse granularity were chalcopyrite CIS. The grown crystallites had tetrahedral shapes and homogeneous composition. Particle size distribution was used to describe the growth process. The activation energy of linear growth of crystals was $E_d = 0.25 \pm 0.05 \text{ eV}$, and the power of time dependence of the crystal growth was $\ln t = 0.26 \pm 0.06$. The solubility of CIS in KI at 990 K was $0.17 \pm 0.05 \text{ wt. %}$. The solubility of potassium and iodine in CIS at 990 K was $0.094 \text{ wt. %}$, and $0.0086 \text{ wt. %}$, respectively. As a result, homogeneous p-type CIS monograin materials were synthesized in KI solvent.\textsuperscript{67}

1.15.2 Non-vacuum processes

Non-vacuum processes are attractive for reducing the high initial cost of physical vapour deposition processes. CBD, electroless deposition, ink coating, CSP, MOCVD and SILAR are considered as the non-vacuum processes in CIS deposition.

(i) Chemical Bath Deposition (CBD)

P.K. Vidyadharan Pillai fabricated CIS/CdS solar cell completely by CBD and characterization was performed. An efficiency of 3.1% was obtained for this CBD cell.\textsuperscript{68} Bindu et al. prepared CIS thin films combining CBD and PVD in which Se was deposited using CBD and Cu and In using PVD. In this work, Se precipitate remaining in the bath after deposition of Se film was recovered for the use as starting material for further deposition process.\textsuperscript{69}

(ii) Electrodeposition

Pankaj Garg et al. studied the growth and characterization of electrodeposited CIS thin films from seleno-sulphate solution. The films deposited at a deposition current density
of $J= 1.1$ mA/cm² with InCl₃ (15.12 mM) content in the bath mixture and at $J= 0.8$ mA/cm² with InCl₃ (18.6 mM) content have a stoichiometric chalcopyrite structure with $c/a - 1.97$. Electrical measurements showed that deposited films were p-type and had a resistivity of about $5 \times 10^3 \ \Omega \ \text{cm}$.⁷⁰ N Khare et al. studied the photoelectrochemical, electrolyte, electroreflectance and topological characterization of electrodeposited CIS films. n-type CIS thin films were obtained by electrodeposition from a chloride bath containing SeO₂ and annealed at different temperatures in N₂ plus either 5% H₂ or a few parts per million O₂. When the heat treatment temperature was increased, the band gap decreased from about 1.07 to 0.98 eV.⁷¹ S. R. Kumar et al. developed a nonaqueous method to electrodeposit Cu-In alloy precursor for n-CIS films. Flash annealing of the stacked Cu-In alloy/Se layers had been used to prepare CIS films and the flashed n-CIS films had a chalcopyrite structure with strongly oriented (112) planes.⁷² A. N. Molin et al. prepared CIS thin films by electrodeposition from citric aqueous solutions containing Cu, In and Se. It was shown that the chemical reaction determining the common rate of electrodeposition was $\text{SeO}_2^2^−$ reduction by metallic copper.⁷³ H. P. Fritz et al. developed a novel method for the electrodeposition of the metallic grey hexagonal modification of selenium using the system. $\text{Se[(EtO)₂PS}_2]_2/n-\text{Bu}_4\text{NBF}_4/\text{chlorobenzene}$ with simultaneous illumination of the cathode.⁷⁴ R. Pal examined the variation of trap state density and barrier height with Cu/In ratio in CIS films. The density of trap states in the intercrystalline region of the films was found to increase with increasing Cu/In ratio. The effect of illumination on the grain boundary barrier height was studied and this indicated that the grain boundary charges are depleted by sub-band gap photons resulting in the reduction of the barrier height with increase of illumination level.⁷⁵ S. Jost et al. studied the formation of CIS thin-film solar cell absorbers by laser annealing of electrodeposited precursors. All absorbers processed with laser or furnace annealing consisted of crystalline CIS in the chalcopyrite crystal structure with a high degree of cation disorder. Laser annealing did not lead to unintentional selenium loss during the semiconductor formation process.⁷⁶ S. Nakamura et al. studied the electrodeposition of Cu-In-Se films
with an aqueous solution containing CuCl₂, InCl₃ and SeO₂, in terms of composition control of deposited films for the preparation of CIS.⁷⁷

Shalini et al. developed a novel approach to prepare CIS-based thin-film photovoltaic cells. Cells were constructed using n-type CIS with a concentrated effort on the synthesis of n-CIS thin-film absorber. They also aimed at the electrochemical conversion of CIS surface to a semi-insulating, lattice-matched CuInₓSeᵧI₂ transition layer and a semi-conducting p-CuISe₃ window.⁷⁸ C. Guillen et al. analyzed the improvement of the optical properties of electrodeposited CIS thin films by thermal and chemical treatments. In order to eliminate the semi metallic phases and to improve the semiconductor behaviour of the electrodeposited material, thermal and chemical treatments were performed. After heat-treatment of the samples at 400°C in flowing argon, elemental Selenium loss has been detected together with an enhancement of the allowed direct optical transition. The subsequent chemical etching of the layers in a KCN solution showed to be successful in eliminating the copper selenide phases which were responsible of the remaining sub-band gap absorption.⁷⁹ P.P. Prosini et al. carried out electrodeposition of Copper-Indium alloy under diffusion-limiting current control. The relationship between the ratio of Cu²⁺ to In³⁺ in the solution and the metal ratio in the deposited film was investigated. In order to avoid the use of complexing agents, the stoichiometry of the Copper-Indium alloys was controlled by electrodepositing them under diffusion-limiting current.⁸⁰ S.N. Qiu et al. carried out the diffusion length measurements on electrodeposited CIS cells. The diffusion length of the CIS with an acceptor concentration less than 2 × 10¹⁶ cm⁻³ was not very sensitive to the variation of concentration. The diffusion length of the order of 0.52 μm was obtained at 1.2 μm wavelength which was closer to the value 0.6 μm for evaporated CIS.⁸¹ A. M. Fernandez et al., performed the characterization of co-electrodeposited and selenized CIS (CIS) thin films. As-deposited as well as selenized films exhibited a compact or a granular morphology depending on the composition. The film stoichiometry was improved after selenization at 550 °C in a tubular furnace.⁸² A.M. Fernandez et al characterized co-electrodeposited and selenized CIS thin films. The films were formed with a mixed composition of binary as well as ternary phases.⁸³ E.
Tzvetkova et al. prepared CIS thin films by one-step electrodeposition process. The deposition was done in potentiostatic regime from an original electrolyte containing Cu', In^3+, Se^4+ ions and thiocyanate as a complexing agent. It was established that Se treatment was more effective than the annealing in Ar in addition to crystallite size. N. Stratieva et al. prepared CIS by electrodeposition from a thiocyanate electrolyte with a complexing agent. The annealing in Ar ambient did not influence the composition of the layers considerably but improved the crystalline structure. R. P. Raffaelle et al. carried out scanning tunneling microscopic analysis of electrodeposited CIS nanoscale multilayers. Alternating layers of two different compositions based on the Cu_in_2-xSe_2 system were potentiostatically deposited. These nanometer-scale layers were used to form reduced-dimensionality structures such as superlattices that could be used in concentrator solar cells. A. M. Fernandez et al. on the characterization of electrodeposited and selenized CIS thin films. The selenization process was carried out using chemical vapour transport by gas (CVTG). The film stoichiometry improved after selenization at 550°C. A.A.I. Al-Bassam prepared CIS by electrodeposition. A structural transition from chalcopyrite to sphalerite was observed on the electrodeposited CIS, when the composition of the thin films was varied from a quasi-stoichiometry to In rich. Quasi-stoichiometric CIS thin films were obtained in the chalcopyrite structure with grain sizes of the matter of 0.06μm. L. Zhang et al. studied the formation of CIS and Cu(In,Ga)Se_2 films by electrodeposition and vacuum annealing treatment. All the as-deposited films were annealed in vacuum at 450°C for a short time to improve the crystalline properties. The crystallization of the films was greatly improved after annealing. Further more, a CIGS film with 23 at% Ga was obtained.

J.L.Xu et al studied influence of vacuum annealing process on electrodeposited CIS films. Crystallization of the films was greatly improved by fast annealing process without significant change in composition. The samples were p-type. Annealing after electrodeposition was proved to be useful method to prepare polycrystalline CIS films for solar cell application. M. E. Calixto et al. performed the Depth profile analysis of CIS thin films grown by the electrodeposition technique. The electrodeposited CIS film had a
Cu-rich bulk region and an In rich surface, which led to the formation of an n-layer (CuIn$_2$Se$_{3.5}$) on the top of the p-type CIS phase. R. Ugarte prepared CIS polycrystalline thin films by electrodeposition on titanium and conducting glass substrates from an aqueous solution containing CuCl$_2$, InCl$_3$, SeO$_2$ in a glycine acid medium, pH around 2 adjusted with HCl. M. C. F. Oliveira et al. performed a voltammetric study of the electrodeposition of CIS in a citrate electrolyte. The electrode reactions occurring on a Mo surface and on a Mo-modified surface, i.e. presenting indium-compound nucleation sites (Cu$_x$In$_y$Se or In$_y$Se) were not the same. The presence of these nucleation sites was responsible for the non-reduction of Cu$_x$Se on the electrode. The effect of the CIS substrate on the reduction potential of Cu$^{2+}$, In$^{3+}$ and Se$^{4+}$ in separate citrate solutions was examined. Evidence was given for the copper and indium deposition by a surface-induced deposition mechanism and for the Cu$_x$Se formation by a co-deposition mechanism. J. L. Xu et al. studied the influence of the vacuum annealing process on electrodeposited CIS films. The crystallization of the films was greatly improved by the short time vacuum annealing process without significant change in composition. The capacitance–voltage measurement showed characteristic p-type behaviours. This annealing process after electrodeposition was proved to be a useful method to prepare the polycrystalline CIS films for solar cell application. M. E. Calixto et al. studied the compositional and optoelectronic properties of CIS and CIGS thin films formed by electrodeposition. As-deposited as well as selenized films exhibited a compact or a granular morphology depending on the composition. The film stoichiometry was improved after selenization at 550°C in a tubular furnace. The films were formed with a mixed phase composition of CIS and CuIn$_2$Se$_{3.5}$ ternary phases. J. Huang et al. studied the Formation of CIS thin films on flexible substrates by electrodeposition (ED) technique. Ternary compounds were co-deposited on Au coated plastic substrate from an aqueous acidic solution containing 1 mM CuCl$_2$, 5 mM InCl$_3$ and 1 mM SeO$_2$ adjusted to pH=1.65. It was found that the film stoichiometry improves when the growth solution consisted of 1 M triethanolamine (TEA) and 0.1 M Na-citrate. The optimal ED-CIS film was obtained after annealing at 150°C for 1 h in a nitrogen (N$_2$) atmosphere. Optical
absorption study showed that the energy gap of the annealed material was 1.18 eV. Good and reliable quality ED-CIS film was grown with the potential use in fabricating flexible solar cells. K. T. L. De Silva et al. carried out electrodeposition and characterization of CIS for applications in thin film solar cells. Cu composition remained the same within the deposition potentials used in this investigation. The deposited layers were polycrystalline and annealing at 350°C for 30 min improves the crystallinity. The film quality deteriorated due to dissociation when annealed at temperatures above 350°C. Excessive annealing resulted in a surface which was depleted in Cu and rich in In and Se. C. Guillen et al. studied the recrystallization and components redistribution processes in electrodeposited CIS thin films. The obtained data reveal the importance of oxygen interaction with CIS layers at temperatures above 400°C, by resulting in a crystalline \( \text{In}_2\text{O}_3 \) phase which remains in the film near-surface region and a poor crystalline \( \text{Cu}_x\text{Se} \) which migrates towards the bulk. Such components redistribution allows overall stoichiometric layers to approach the characteristics of global Cu-rich ones and achieve the highest CIS recrystallization.

J. Kois et al. carried out Electrodeposition of CIS thin films onto Mo-glass substrates. It was found that the value of indium and copper ratio (In/Cu) in the films electrodeposited in the potentials area from \(-0.2\) to \(-0.6\) V (vs. SCE) was independent of the concentration ratio of \( \text{Cu}^{2+}/\text{In}^{3+} \). At the same time, the concentration of Indium in the films obtained was determined both by the deposition potential and the ratio of Se(IV)/Cu\(^{2+}\) in the solution.

(iii) Electroless deposition

P. J. Sebastian et al. studied the Formation of CIS thin films by selenization, employing CVTG, of electroless deposited Cu-In alloy. This process consisted of Cu-In alloy deposition by electroless followed by high temperature selenization of the alloy employing CVTG. The alloy phase consisted mainly of \( \text{Cu}_{11}\text{In}_9 \) alloy. Selenization of the alloy at 400°C resulted in the formation of cubic CIS with alpha-\( \text{Cu}_2\text{Se} \) as the secondary phase. Philip A. Jones et al. carried out the plasma enhanced chemical vapour deposition of CIS. Thin films with compositions around the Cu:In:Se stoichiometric ratio 1:12 were grown using a glow discharge enhanced CVD process. B Ghosh et al.
introduced a novel back-contacting technology for CIS thin films. Electroless deposition of a Nickel-Molybdenum alloy on chromium-coated glass substrates was carried out.\textsuperscript{102} Manjunatha Pattabi et al. carried out preparation and characterization of CIS films by electroless deposition. The deposition bath consisted of aqueous solutions of copper chloride, indium chloride, selenous acid and lithium chloride. The pH of the bath was adjusted to 2.2 by adding dilute HCl. The Mo substrate was short-circuited with the aluminum counter electrode for the electroless deposition.\textsuperscript{103}

(iv) Ink coating

G. Norsworthy et al. prepared CIS film by metallic ink coating and selenization. The technique used an ink formulation containing sub-micron size particles of Cu-In alloys. A metallic precursor layer was first formed by coating this ink onto the substrate by spraying. The precursor film was then made to react with Se to form the CIS compound.\textsuperscript{104} M. Kaelin et al. prepared CIS and CIGS layers from selenized nanoparticle precursors. The chemical conversion (selenization) of nanosized precursor materials into CIS and Cu(In,Ga)Se\textsubscript{2} compounds and microstructural properties of these layers were investigated. Three categories of nanoparticles, namely metal-oxides, metal-selenides and elemental metal particles were selenized in selenium vapour. Using two different reactor designs, the influence of the selenium vapour pressure was investigated. While oxide and selenide precursors showed limited sintering and chemical conversion, dense CIS layers with large grains (1–2 \( \mu \text{m} \)) were obtained with metal precursors.\textsuperscript{105}

(v) Chemical Spray Pyrolysis (CSP)

Tomoaki Terasako et al. studied the structural and optical properties of In-rich Cu–In–Se polycrystalline thin films prepared by chemical spray pyrolysis. Structural and optical properties of In-rich Cu–In–Se polycrystalline thin films (0.54<In/(Cu+In)<0.78) prepared by chemical spray pyrolysis (CSP) on glass substrate were systematically studied in terms of In/(Cu+In) ratio. Lattice constants a and c of the films decreased with increase of \( \text{In/}(\text{Cu+In}) \) ratio. The films exhibited a characteristic Raman peak shifting higher frequencies as the \( \text{In/}(\text{Cu+In}) \) ratio increases. Optical band gap energy was
approximately 1.22 eV for 0.54<In/(Cu+In)<0.67, but increased from 1.22 to 1.36 eV when the In/(Cu+In) ratio increased from 0.67 to 0.78. Photo acoustic measurements revealed the existence of high concentration of non-radiative centers introduced by the deviation from the stoichiometric composition.\textsuperscript{106} Tomoaki Terasako analyzed the three-stage growth of Cu–In–Se polycrystalline thin films by chemical spray pyrolysis. The films grown at substrate temperature ($T_s$) of 420 °C exhibited larger grains in comparison with the Cu–In–Se films grown by the usual CSP method. Optical gap energy was approximately 1.06 eV for 360 °C and 420 °C, but increased dramatically from 1.06 to 1.35 eV when the substrate temperature rose from 420 to 500 °C. Conductivity type was p for $T_s<420$ °C, but n for $T_s>420$ °C.\textsuperscript{107} It is obvious that, in this technique band gap can be increased up to 1.36 eV without alloying Al, Ga or Sulfur.

**(vi) Metal Organic Chemical Vapour Deposition (MOCVD)**

Seok Hwan Yoon et al. prepared CIS thin films through MOCVD using di-$\mu$-methylselenobis(dimethylindium) and bis(ethylisobutyrylacetato) copper(II) precursors. First, phase pure InSe thin film was prepared on molybdenum substrate by using a single-source precursor, di-$\mu$-methylselenobis(dimethylindium). Second, on this InSe/Mo film, bis(ethylisobutyrylacetato) copper(II) designated as Cu(eiac)$_2$ was treated by MOCVD to produce CIS films. The thickness and stoichiometry of the product films were found to be easily controlled in this method by adjusting the process conditions. Also, there were no appreciable amounts of carbon and oxygen impurities in the prepared CIS films.\textsuperscript{108}

**(vii) Successive Ionic Layer Absorption and Reaction (SILAR)**

Yong Shi et al. studied the effects of post-heat treatment on the characteristics of chalcopyrite CIS film deposited by SILAR method. XRD results showed that the proper post-annealing process can lead to a complete formation of chalcopyrite structure CIS with high degree of preferred orientation towards (112) reflection. After annealing process, the composition of annealed films was close to the standard stoichiometry and O, Cl impurities decreased. The direct band gap increased from 0.94 to 0.98 eV and resistivity showed a big decrease with the increase of annealing temperature.\textsuperscript{109} Jingxia
Yang et al. investigated the effect of cationic precursor solutions on formation of CIS thin films by SILAR method. SILAR deposition of CIS films was performed by using Cu\textsuperscript{2+}–TEAH\textsubscript{3} (Cupric chloride and triethanolamine) and In\textsuperscript{3+}–CitNa (Indium chloride and sodium citrate) chelating solutions with weak basic pH as well as Na\textsubscript{2}SeSO\text sub{3} solution at 70 °C. Well-crystallized, smoothly and distinctly particular CIS films could be obtained after annealing in Ar at 400 °C for 1 h by using the mixed cationic solution mode.\textsuperscript{110}

1.15.3 Defect studies

Defect plays an important role in governing the opto-electronic properties of CIS. Defect analysis was mainly done using Photoluminescence and temperature dependant conductivity studies.

C.Rincon et al. made studies on luminescence and impurity states in n-type CIS and three peaks were observed at 0.98\textsubscript{eV}, 0.99\textsubscript{eV} and 1.013\textsubscript{eV}. The main peak at 0.98\textsubscript{eV} was due to the donor-acceptor pair recombination. Peak at 1.013\textsubscript{eV} was due to Se vacancy and at 0.99\textsubscript{eV} due to In vacancy. Acceptor ionization energy was 33±2 meV and donor ionization energy was 10±2 meV.\textsuperscript{111} S Zott et al. identified the observed luminescence as due to the donor-acceptor pair transition including the acceptor \textit{V}_{\text{Cu}} and two donors \textit{V}_{\text{Se}} and \textit{In}_{\text{Cu}} from excitation-intensity and temperature dependant measurements.\textsuperscript{112} J. H. Schön et al. demonstrated sharp transitions for Cu-rich films compared to broad emission lines for In-rich materials. Cu-rich materials were characterized by four relatively sharp emission lines at 1.036 eV, 0.993 eV, 0.971 eV and 0.942 eV at 6 K. As the composition was gradually changed from Cu rich to stoichiometric compositions only one broad emission line could be observed at 0.964 eV, which corresponds to a donor–acceptor pair transition. In the case of In-rich material (Cu/In atomic ratio=0.3–0.6), three dominant transitions were observed at 1.10 eV, 0.975 eV, and 0.89 eV. The observed spectra are explained by considering the formation energies of the defects and the composition of the specific film.\textsuperscript{113} O. Ka et al. investigated post-growth Cu-diffusion in In-rich CIS films through photoluminescence and explained a transition from the commonly observed broad band around 0.94 eV to a much sharper peak around 0.985 eV under low excitation.
density. This recombination appeared at a slightly but definitely larger energy than the recombination usually reported around 0.96 eV. The excitation power dependence led to ascribe the peak observed to a donor–acceptor be [Cu_in–Cu_i] pair band, as evidenced by the 2.5 meV/decade shift of the peak-energy and the temperature-dependence of the photoluminescence signal. S. Niki et al. studied the anion vacancies in CIS. The presence of the Cu–Se surface phase, the post-growth air-annealing and the Na incorporation all provided significant changes in photoluminescence spectra. Decrease in positron lifetime and reduction of twin density were found to occur simultaneously, along with the changes in photoluminescence spectra. Change in photoluminescence spectra and the corresponding decrease in positron lifetime indicated the annihilation of Se-vacancies; the control of Se-vacancy is a key issue to be addressed for improving the electrical, optical and structural properties of CIS films.

Shigeru Niki et al. measured the photoluminescence of CIS film prepared using molecular beam epitaxy. PL spectra of Cu-rich CIS epitaxial films showed well-defined emission lines. A broad peak at $\lambda = 1.45 \mu m$ became dominant in In-rich films, and excitation power dependence of such a broad emission indicated a pair-type radiative recombination, most likely the emission due to donor-acceptor pair or their complex. K. Timmo et al. studied the effect of sodium doping to CIS monograin powder properties. Sodium was added in controlled amounts from $5 \times 10^{16} \text{ cm}^{-3}$ to $1 \times 10^{20} \text{ cm}^{-3}$. The photoluminescence spectra of Na-doped stoichiometric CIS powders had two bands with peak positions at 0.97 and 0.99 eV. The photoluminescence bands showed the shift of peak positions depending on the Na doping level. Peak positions with maximum energy were observed if added sodium concentration was $1 \times 10^{19} \text{ cm}^{-3}$. This material had the highest carrier concentration $2 \times 10^{17} \text{ cm}^{-3}$. In the case of stoichiometric CIS (Cu:In:Se = 25.7:25.3:49.0), Na doping at concentrations of $3 \times 10^{17} \text{ cm}^{-3}$ and higher avoided the precipitation of Cu-Se phase. Solar cells output parameters were dependent on the Na doping level. Sodium concentration $3 \times 10^{18} \text{ cm}^{-3}$ resulted in the best open-circuit voltage. K. Puech et al determined minority carrier lifetimes in CIS thin films. Luminescence at two distinct spectral positions was observed: A high energy emission.
attributed to free carrier or free exciton recombination (depending on composition), that
decayed extremely fast with a lifetime of tens of picoseconds to a few nanoseconds; a
lower energy emission from defect related recombination that decayed much more
slowly, with typical lifetimes greater than tens of nanoseconds.\textsuperscript{118}

R. Trykozko studied photoelectrical properties of CIS thin films prepared using flash
evaporation and beam evaporation. Films showed p-type conductivity. Activation energy
of photoconductivity did not exceed 30 meV. But in the dark conductivity curve, there
were two regions with activation energies of 81 and 190 meV respectively. These were
attributed to an acceptor level due to In vacancies or interstitial Se.\textsuperscript{119} Wasim et
al. prepared CIS from vacuum fusion of the stoichiometric mixture of highly pure
elements. Both n and p-type samples were prepared. Three donor levels at 8, 80 and
180 meV were attributed to In\textsubscript{Cu}, V\textsubscript{Se} and In\textsubscript{i} respectively. The acceptor levels around 30,
80 and 400 meV were due to V\textsubscript{Cu}, V\textsubscript{In} or Cu\textsubscript{In} and Fe\textsuperscript{2+}\textsubscript{In} respectively.\textsuperscript{120} Datta et al.
calculated activation energies from TSC measurements. They obtained three energy
levels 35, 45 and 100 meV and were associated with intrinsic defects. Room temperature
resistivity was $10^5 \Omega$ cm.\textsuperscript{121} Masayuki et al. studied photoluminescence of CIS films
prepared using selenization technique with solid or vapour-phase selenium. PL spectra
could be explained by the levels: the donor level of Se vacancy (V\textsubscript{Se}), 70 meV below the
conduction band, the acceptor levels of the copper vacancy (V\textsubscript{Cu}), 40 meV and 85 meV
above the valence band, the In vacancy (V\textsubscript{In}) 40 meV above the valence band and copper
on the antisite at indium (Cu), 40 meV above the valence band.\textsuperscript{122} J. H. Schön et al.
carried out a comparison of point defects in CIS and CuGaSe\textsubscript{2} single crystals grown by
chemical vapour transport. V\textsubscript{Cu} and V\textsubscript{Se} showed similar properties and activation energies
in both materials. Ga\textsubscript{Cu} levels in CuGaSe\textsubscript{2} are much deeper than In\textsubscript{Cu} in CIS, and
furthermore, the formation of In\textsubscript{Cu} is much easier compared to Ga\textsubscript{Cu}.\textsuperscript{123} A. V. Mudryi et
al. carried out optical characterization of high-quality CIS thin films synthesized by two-
stage selenization process. For near stoichiometric films, intense band-to-band
recombination generated a room temperature PL peak at 1.028 eV with full width at half
maximum (FWHM) of approximately 50 meV. At 78 K, the A and B free exciton peaks
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appeared, in both PL and OA spectra, merged into a band at approximately 1.044 eV. The 4.2 K-PL spectrum contains a number of features. The A and B excitonic peaks shift to 1.0409 eV (A) and 1.0444 eV (B) and were well resolved in both the PL and OA spectra, with their FWHM reduced to 2.5 meV. Their spectral positions and FWHM are approaching those in high quality CIS single crystals.124

M. V. Yakushev et al. studied the effects of deviation from stoichiometry on excitons in CIS single crystals. The Cu/In ratio of the crystals varied from 0.8 to 1.2. At 4.2 K free-exciton peaks A and B as well as a number of bound-exciton peaks were observed well resolved in the PL spectra. Deviations from Cu/In=1 resulted in shifts of the free-exciton peaks to lower energy and an increase in their full width at half maximum. The A–B separation energy was found to be strongly influenced by the Cu/In ratio and temperature suggesting that the valence band B is less sensitive to the tetragonal distortion in the lattice than the uppermost valence band A.125 N. Rega et al. analyzed the defect spectra in epitaxial CIS grown by MOVPE on GaAs (0 0 1) wafers. The photoluminescence spectra for p-type Cu-rich ([Cu]/[In]>1.05) CIS were dominated by one donor acceptor pair transition at 0.972 eV. For slightly Cu-poor and stoichiometric samples a free to bound transition at 0.992 eV is observed. Also an exciton emission could be detected at $E_{\text{FX}}=1.032$ eV indicating a band gap of $E_g=1.038$ eV at 10 K. These results could be combined in a defect model for CIS containing two acceptors states with 40 and 60 meV and a compensating 6 meV donor state.126 A. V. Mudryi et al. studied the free and bound exciton emission in CIS. New values were determined for the band gap energy $E_g=1.0459$ eV and for the excitonic binding energy 5.1 meV in CIS at 4.2 K.127 Zeenath et al. studied the trap levels of p-type CIS samples. As prepared samples had two trap levels of activation energies 70.72 meV and 40.5 meV due to presence of Se vacancy and Cu vacancy. For vacuum annealed samples, activation energies of 70.29 meV and 414 meV were obtained due to the existence of Se vacancy and Fe impurity. In the case of air annealed samples 40.5 meV and 103 meV were obtained due to Cu vacancy.128 Jochen Klais et al. performed calculation and experimental characterization of the defect physics
in CIS. This led to the assumption that the single defects $V_{Se}$, $V_{Cu}$, $Cu_{In}$ and the defect pair $(2V_{Cu}-In_{Cu})$ occur in the investigated specimens in considerable concentrations.\footnote{129}

**Table 1.4: Defect activation energies**

<table>
<thead>
<tr>
<th>Defect</th>
<th>Activation energy (meV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V_{In}$</td>
<td>33, 40</td>
</tr>
<tr>
<td>$In_{Cu}$</td>
<td>8</td>
</tr>
<tr>
<td>$V_{Se}$</td>
<td>80, 70</td>
</tr>
<tr>
<td>Ini</td>
<td>180</td>
</tr>
<tr>
<td>$V_{Cu}$</td>
<td>30, 40, 85</td>
</tr>
<tr>
<td>$Cu_{In}$</td>
<td>80</td>
</tr>
<tr>
<td>$Fe^{2+}_{In}$</td>
<td>400</td>
</tr>
</tbody>
</table>

Table 1.4 gives a summary of the activation energy of the defects mainly observed in CuInSe$_2$ thin films, derived from the above review.

**1.15.4 Effects of Na and O**

Incorporation of Na and O was found to produce beneficial effects in CIS solar cells, by passivating grain boundaries and increasing conductivity. Hence the effect of Na and O on CIS has been the subject of study of many researchers.

Su-Huai Wei et al. studied the effect of Na on the electrical and structural properties of CIS. It was showed that the main effect of sodium, either via direct substitution $Na_{In_{Cu}}$ or via the release of oxygen radicals and the subsequent $O_{V_{Se}}$ occupation, was to reduce intrinsic donor defects in CIS. When Na concentration was small, Na first eliminated $In_{Cu}$ defects, thus increased the effective hole densities. As the Na concentration increases to the level that most of the $In_{Cu}$ defects have already been eliminated, it will start to remove the acceptor $V_{Cu}$, therefore reduces the hole density.\footnote{130} David W Niles et al. observed the Na and O impurities at grain surfaces of CIS. It was proved that Na and O reside at grain surfaces and not in the grain interiors of CIS and improved the efficiency of CIS solar
Ryuhei Kimura et al. studied the photoluminescence properties of sodium incorporation in CIS and CuIn$_3$Se$_5$ thin films. Enhanced grain growth and preferred (1 1 2) grain orientation as well as a decrease in resistivity with respect to undoped films were observed with sodium incorporation. Compensation was reduced due to the suppression of donor-type defects by the presence of Na. Yoshinori Nagoya, studied the role of sulfur incorporation into the surface of Cu(InGa)Se$_2$ thin film absorber. The incorporated S was concluded to be elective to improve the p-n heterojunction quality due to the passivation of surface and grain boundary of CIGS absorber through the formation of a thin CIGSS surface layer.

Table 1.5: Properties of CIS.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Formula</strong></td>
<td>CuInSe$_2$</td>
</tr>
<tr>
<td><strong>Molecular weight</strong></td>
<td>336.28</td>
</tr>
<tr>
<td><strong>Density</strong></td>
<td>5.77 g/cm$^3$</td>
</tr>
<tr>
<td><strong>Colour</strong></td>
<td>Grey</td>
</tr>
<tr>
<td><strong>Transition to sphalerite structure</strong></td>
<td>810°C</td>
</tr>
<tr>
<td><strong>Melting temperature</strong></td>
<td>986°C</td>
</tr>
<tr>
<td><strong>Symmetry</strong></td>
<td>Chalcopyrite</td>
</tr>
<tr>
<td><strong>Space group</strong></td>
<td>$I42d$ - $D_{2d}$</td>
</tr>
<tr>
<td><strong>Lattice parameters</strong></td>
<td></td>
</tr>
<tr>
<td>(a)</td>
<td>5.789 Å</td>
</tr>
<tr>
<td>(c)</td>
<td>11.62 Å</td>
</tr>
<tr>
<td><strong>Thermal expansion co-efficient (at 273K)</strong></td>
<td></td>
</tr>
<tr>
<td>((a) axis)</td>
<td>8.32 x 10$^{-6}$ K$^{-1}$</td>
</tr>
<tr>
<td>((c) axis)</td>
<td>7.89 x 10$^{-6}$ K$^{-1}$</td>
</tr>
<tr>
<td><strong>Thermal conductivity</strong></td>
<td>0.086 W cm$^{-1}$ K$^{-1}$</td>
</tr>
<tr>
<td><strong>Specific heat</strong></td>
<td>7.67 x 10$^{-4}$ K$^{-1}$</td>
</tr>
<tr>
<td>Property</td>
<td>Value</td>
</tr>
<tr>
<td>----------------------------------------------</td>
<td>----------------------------------------</td>
</tr>
<tr>
<td>C2</td>
<td>$4.06 \times 10^{-6} \text{K}^{-2}$</td>
</tr>
<tr>
<td>C3</td>
<td>$4.3 \times 10^{-9} \text{K}^{-3}$</td>
</tr>
<tr>
<td>Debye temperature</td>
<td>$221.9 \text{K}$</td>
</tr>
<tr>
<td>Microhardness (112 face)</td>
<td>$3.2 \times 10^{9} \text{N/m}^{2}$</td>
</tr>
<tr>
<td>Compressibility</td>
<td>$1.4 \times 10^{-11} \text{m}^{2} \text{N}^{-1}$</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td></td>
</tr>
<tr>
<td>Low frequency</td>
<td>$13.6\pm2.4$</td>
</tr>
<tr>
<td>High frequency</td>
<td>$8.1\pm1.4$</td>
</tr>
<tr>
<td>Sound velocity (longitudinal)</td>
<td>$2.2 \times 10^{5} \text{cm}^{-1}$</td>
</tr>
<tr>
<td>Electrical resistivity (polycrystalline films)</td>
<td></td>
</tr>
<tr>
<td>Cu-rich</td>
<td>$0.001\Omega \text{cm}$</td>
</tr>
<tr>
<td>In-rich</td>
<td>$&gt;100\Omega \text{cm}$</td>
</tr>
<tr>
<td>Mobility</td>
<td></td>
</tr>
<tr>
<td>Electrons ($n = 10^{14} - 10^{17} \text{cm}^{-3}$)</td>
<td>$100$-$1000$(at 300K)$\text{cm}^{2} \text{V}^{-1} \text{s}^{-1}$</td>
</tr>
<tr>
<td>Holes ($p = 8 \times 10^{15} - 6 \times 10^{16} \text{cm}^{-3}$)</td>
<td>$50$-$180$(at 300K)$\text{cm}^{2} \text{V}^{-1} \text{s}^{-1}$</td>
</tr>
<tr>
<td>Effective mass</td>
<td></td>
</tr>
<tr>
<td>Electrons</td>
<td>$0.09 \text{m}_{e}$</td>
</tr>
<tr>
<td>Holes (heavy)</td>
<td>$0.71 \text{m}_{e}$</td>
</tr>
<tr>
<td>(light)</td>
<td>$0.092 \text{m}_{e}$</td>
</tr>
<tr>
<td>Energy gap (In-rich polycrystalline films)</td>
<td>$1.02 \text{eV}$</td>
</tr>
<tr>
<td>Temperature dependence of gap</td>
<td>$-2\pm1\times10^{4} \text{eV} \text{K}^{-1}$</td>
</tr>
<tr>
<td>Pressure dependence of gap</td>
<td>$2.8\times10^{11} \text{eV} \text{Pa}^{-1}$</td>
</tr>
</tbody>
</table>
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