



Faculty of Sciences

Department of Physics and Astronomy

**INVESTIGATION OF COPPER IODIDE THIN FILMS AS A HIGHLY
TRANSPARENT *p*-TYPE MATERIAL FOR THERMOELECTRIC
APPLICATIONS**

by

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the Award of the Degree of Master of Science in Physics of BIUST

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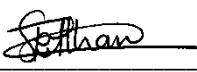
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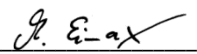
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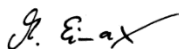
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The undersigned certifies that he has read and hereby recommends for acceptance by the college of Science a dissertation titled: **INVESTIGATION OF COPPER IODIDE THIN FILMS AS A HIGHLY TRANSPARENT p -TYPE MATERIAL FOR THERMOELECTRIC APPLICATIONS** in fulfilment of the requirements for the degree of Master of Science in Physics (MSc Physics) of the Botswana International University of Science and Technology.

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DEDICATION

This dissertation is dedicated to my late grandparents and also my mother. Thank you for making me the woman I am today.

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LIST OF ABBREVIATIONS AND SYMBOLS

SDGs – Sustainable Development Goals

UN – United Nations

kWh – Kilowatt-hour

W/m² – Watt per square metre

CO₂ – Carbon dioxide

nW – nanoWatts

MW – MegaWatts

TEG – Thermoelectric generator

TC's – Transparent conductors

LED – Light emitting diodes

RMS – Root mean square

ZT – Figure of merit

S – Seebeck coefficient

σ – Electrical conductivity

k – Thermal conductivity

k_e – Electronic thermal conductivity

k_l – Lattice thermal conductivity

PF – Power factor

V_{cu} – Copper vacancy

VBM – Valence band maximum

PLD – Pulsed laser deposition

CBD – Chemical bath deposition

SILAR – Successive ionic layer adsorption and reaction

PVD – Physical vapor deposition

XRD – X-ray diffraction

SEM – Scanning electron microscopy

EDS – Energy-dispersive X-ray spectroscopy

AFM – Atomic force microscopy

T – Transmittance

A – Absorbance

eV – Electron volts

S/cm – Siemens per centimetre

ABSTRACT

Thermoelectricity has been on focus for many years, because the world is investing in renewable energy and need energy sources that are environmentally friendly. The aim of thermoelectric technology is to convert heat into electrical energy which can be beneficial to people living in off-grid areas. Since transparent electronics has become an important field, the interest is on transparent *n*- and *p*-type thermoelectric materials. In recent years, different transparent thermoelectric *n*-type semiconductor thin films, such as, for example ZnO, SnO₂ or In₂O₃ have been found and studied extensively, however, the *p*-type transparent thermoelectric semiconductor counterparts in the low temperature regime have been missing for a while. At the current stage, *n*-type thermoelectric semiconductors have better efficiency as compared to *p*-type thermoelectric semiconductors near room temperatures. For this study, *p*-type CuI thin films were fabricated and optimised based on their structural, morphological, optical, electrical and thermoelectric (power factor) properties.

CuI powder was deposited on borosilicate glass substrates using thermal evaporation and electron-beam deposition techniques. The thickness of the films fabricated by both deposition methods was varied in the range of 210 nm to 380 nm. X-ray diffraction (XRD) results revealed that the deposited films for both deposition methods were polycrystalline zincblende structure with a cubic phase. All films are growing along the (111) plane, the crystallite size is increasing with thickness increase for electron-beam deposited films, however, it is decreasing with thickness increase for thermally evaporated thin films. Results obtained for the Raman spectroscopy revealed peaks at 122 cm⁻¹ and 124 cm⁻¹ for films deposited by electron-beam and thermal evaporation deposition techniques respectively. Both Raman peaks belong to the zincblende structure of CuI. The SEM micrographs showed well defined grains for both deposition techniques. The grains have a triangular shape which is expected of the zincblende structure. The grain size was increasing with an increase in thickness for both deposition methods but was higher for thermally evaporated films than thin films deposited by electron-beam method. This is in good agreement with the AFM results which showed higher values of Root Mean Square (RMS) roughness for thermally evaporated films than electron-beam deposited films.

All deposited films exhibited a high transparency of 60-90% in the visible range of the spectrum. The bandgaps obtained were lower than the expected value of 3.1 eV as they ranged between 2.85-3.03 eV. The carrier concentration of the CuI thin films was in the order of 10^{20} - 10^{21} cm⁻³ and the carrier concentration increased with an increase in thickness. The values obtained for the Hall coefficient were positive which meant that the grown CuI thin films were *p*-types. The electrical conductivity at room temperature was seen to increase with an increase in thickness from 59.1 S/cm to 104.4 S/cm and as the thickness increased further there was a slight decrease to 96.3 S/cm for electron-beam deposited thin films. Thermally evaporated CuI films showed a similar behaviour. The electrical conductivity for thermally evaporated CuI thin films increased with thickness increase from 79.0 S/cm to 110.2 S/cm and as the thickness increased further the conductivity value decreased to 105.3 S/cm. The designed home-made Seebeck measurement setup was used to measure the temperature difference between two points in the CuI thin films together with the Seebeck voltage formed due to the temperature difference. As a result, the Seebeck voltage was plotted against the applied temperature difference and the Seebeck coefficient was calculated. The measured Seebeck coefficient was in the range of 164.5 μ V/K to 203.8 μ V/K for both deposition methods. Finally, the power factor was determined to be ranging between 2.45 to 2.98 μ Wm⁻¹K⁻² for electron-beam deposited films and for thermally evaporated films it ranged between 2.98 and 3.38 μ Wm⁻¹K⁻².

CHAPTER 1: INTRODUCTION

Energy is required to support economic and social progress in the world, and developing countries require energy to build better quality of life. Energy is important because it is needed in everyday life to power communications, transportation, lighting, cooking and innovative medical equipment [1, 2]. But to provide this energy, we have a responsibility as the world to protect both people and the environment. This is guided by the Sustainable Development Goals (SDGs) that were published in 2015 by the United Nations (UN), the 17 SDGs have been adopted to end poverty and also deal with climate changes. For example, SDG 7 is interested in the supply of clean and affordable energy especially in African countries [3]. For developed countries, a reliable and affordable energy allows for products that extend and enrich life but for undeveloped countries, like African countries, it is fundamental to have reliable and affordable energy. In these countries, reliable energy improves and saves lives, improves transportation and communications, and helps people overcome poverty [4]. By far, Africa is the richest in renewable energy resources as it receives more hours of bright sunlight throughout the day according to the World Sunshine Map [5] and because of the continuous sunshine influence, Africa is known as the Sun Continent according to Griffiths [6].

The yearly energy demand around the world is higher than 10^{12} kWh and 75% of this energy demand is from non-renewable resources. Renewable resources only provide the remaining percentage towards that world energy consumption [7]. But because the world has a responsibility towards people and the environment, and most of the non-renewable resources are emitting greenhouse gases such as carbon dioxide (CO_2) into the atmosphere leading to global warming [8], which threatens the existence of human life, alternative energy resources may reduce environmental impacts [9, 10]. Therefore, renewable resources especially solar energy, is seen as the future for energy supply because it is the most sufficient source of energy, the world experiences on average solar radiation intensity of about 1000 W/m^2 emitted on a sunny day [11]. And since African countries receive the highest amount of solar radiation, this can be beneficial if these countries invest in harvesting solar energy to produce electricity. In the Sub-Saharan regions approximately 620 million people don't have access to electricity and depend on traditional methods such as firewood and solid biomass for cooking [4]. So new ways for harvesting energy

can be used so that electricity can reach people in off-grid areas. Energy harvesting directly converts energy extracted from ambient sources into electrical energy, and it can be used in off-grid areas to power small and medium electronic devices from nW to hundreds of MW [12]. The sources of energy used for harvesting energy are light energy, temperature gradient, chemical energy, motion energy and electromagnetic radiation. Energy harvesters mostly used are: thermal harvester, light harvester, electromagnetic harvester [13], piezoelectric harvester [14], chemical harvester and radio frequency harvester [15]. Thermal harvesters have received a lot of attention because they can convert waste heat into electrical energy by using thermoelectric technology which uses thermoelectric effect to generate electricity when a temperature difference exists [16]. Thermoelectric devices usually produce extremely low power because they have a conversion efficiency of about 5%, but this efficiency is suitable for low power requirement applications. Using thermoelectric generator (TEG) has many advantages because it is simple, reliable, has a power source that is flexible, it is non-toxic to the environment and it is highly durable to be installed under extreme conditions [17], which can be beneficial in African countries because they experience a lot of harsh conditions.

Table 1: TEG working temperatures and waste heat source examples

Temperature ranges (K)	TEG materials	Operating temperature (K)	Waste-heat source examples
Low temperature	Bi ₂ Te ₃ alloy [18, 19]	305-330 300-323	-Cooling water -Air compressors
Medium temperature	PbTe alloy [20, 21] TiO ₂ [22, 23]	425-650 425-650	-Catalytic crackers -Furnace
High temperature	Si-Ge [24, 25]	760-1100	-Copper-refinement furnace

TEG materials have many applications, for example, they can be used in spacecrafts in the form of radioisotope thermoelectric generators (RTGs) by exploiting the high temperature range found in the system [26]. TEGs are also seen as an alternative power supply for devices that require low power, and because of this, high-performance low temperature range thermoelectric devices are required so that they can utilize the low-grade heat waste. As it was revealed that almost 72% of

the primary energy is lost in the form of excess heat [27], the low-grade waste heat with a temperature below 200 K accounts for almost 63% of that excess heat which is mostly from transportation, industrial and power waste [28].

1.1 TRANSPARENT CONDUCTORS

Transparent conductors (TCs) have been the focus over recent years for being both transparent in visible light range and electrically conductive. Therefore, they have wide applications such as in LED displays, transparent transistors and solar cells [29-36]. However, the property of having high optical transparency and high electrical conductivity, contradicts the band structure theory because good electrical conductors such as metals, are opaque while the materials with good optical transparency, such as glass, are insulators. Transparent materials have a wide bandgap above 3 eV which makes visible light to pass through, because photons with energy below the bandgap value are not absorbed by these materials. The transmittance of the incident light is greater than 80% and they have a high carrier concentration ($>10^{19} \text{ cm}^{-3}$) and a mobility above $1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [37]. The semiconductors that have the majority of its carriers as holes are called *p*-types and the one that has majority of its carriers as electrons are called *n*-types. The first TC to be discovered was Cadmium oxide (CdO) which was used in solar cells but the challenges faced with it were the low bandgap energy, low thermal stability, and its high toxicity [38, 39]. The first TCs that made a ground break are the *n*-types. The commonly used *n*-type TCs are Indium oxide (In_2O_3), Tin (IV) oxide (SnO_2), Gallium Nitride (GaN), Fluorine doped tin oxide (FTO) [40-42]. Indium tin oxide (ITO) is among the known *n*-types first discovered in 1954 by Rupprecht [43], it has a transparency of 80-90% in the visible range and a high conductivity of $\sigma = 10^4 \Omega^{-1} \text{ cm}^{-1}$ [40]. But ITO is very scarce which makes it expensive, and because of indium it is toxic. This has led to more research to find TC alternatives with a high performance that are low cost, non-toxic, and durable.

P-type TCs on the other hand are very few in the semiconductor world, and they have a conductivity much lower than the *n*-types because they have low mobilities [37]. The reason for the limited variety of *p*-types is that to *p*-dope TCs is very difficult because of defect compensation [44, 45]. *P*-type TCs are very important for many applications like being used to make invisible *p-n* junction diode-based optoelectronics with low power consumption. A forecast shows that by

2025 a market of \$87.2 billion will be generated in transparent electronics [29]. Therefore, a lot of focus is being given to *p*-types because the important requirement of a TC is to be transparent and highly conductive, and a lot of ongoing research has been made to maximize the conductivity of *p*-type TCs because when compared to metals they are poor conductors. One of the adopted ways of improving the conductivity is by doping because doping increases the charge carriers.

1.2 STATEMENT OF THE PROBLEM

Transparent semiconductors are particularly useful to transparent optoelectronics because soon they will be an aspect of our lives, where windows can be turned into power generators because of transparent solar panels, but the application is limited to transparent electrodes in solar cells, flat panels display, touch panels and light emitting diodes [46]. The reason for the limitation in application is because of lack of the *p*-type conducting transparent conductor since TCs are mostly *n*-types, such as, ITO, GaN and SnO₂. But all this changed when Kawazoe et.al reported highly transparent *p*-type conducting films of copper aluminum oxide (CuAlO₂) in 1997 [46]. This *p*-type brought a lot of promise even though its conductivity was several orders of magnitude smaller than the transparent *n*-type conductors. After the discovery of CuAlO₂, attention has been given to copper-based oxides. They are promising candidates for the *p*-types because of their non toxicity, low costs and abundance [47]. Magnesium-doped Copper-Chromium oxide (Mg-doped CuCrO₂) was reported with the highest conductivity of ~220 S/cm, however, it had a transparency of 30% which is very low [48]. When *p*-type TCs maintain a high transparency above 70% in the visible spectral range and a band-gap energy (E_g) above 3.0 eV, the conductivity is usually several order of magnitude less than the conductivity of *n*-types. This is due to the valence-band carriers (holes) having lower mobility in comparison to the conduction-band carriers (electrons). Most of these TCs are synthesized at high temperatures (>400 °C) which is very costly and is not compatible with most device applications.

Researchers are now focused on producing high performing *p*-type thermoelectric materials that have a high conductivity, high optical transmittance and can operate at low temperatures. In particular, a lot of interest has been in the recovery of thermoelectric energy at room temperature because of the various uses of near room temperature range heat sources such as in wearable human

devices like smart watches, solar cells and home heating. The realization of highly transparent *p*-type thermoelectric materials could open many applications, for instance, smart windows that can harvest electrical energy even during the night, when photovoltaic devices do not produce electrical energy. So far, the discovered *p*-type TCs have poor conductivity compared to the *n*-type thermoelectric materials. This can lead to a poor thermoelectric performance at room temperature. Copper Iodide with a zincblende crystalline structure (γ -CuI) is a *p*-type non-oxide semiconductor that has a large exciton binding energy of 62 meV [49, 50] which makes it suitable for application in optoelectronics [51]. It was discovered to be a promising thermoelectric material at room temperature range, because it does not require high temperatures to be synthesized like most *p*-type thermoelectric materials. It is non-toxic, abundant and has a wide bandgap at room temperature which allows for high transparency in the visible range.

In this project both the optical and electrical properties of room temperature fabricated γ -CuI thin films will be investigated. The study of these properties is important because to have a good *p*-type TC, high transparency and high conductivity are a necessity. Since the sample preparation greatly affects the opto-electrical properties of thin films, two deposition methods were considered. By varying the thickness parameter, films with optimum properties were realized. Based on the chosen deposition methods good opto-electrical properties as well as the thermoelectric properties mainly the Seebeck coefficient and electrical conductivity (power factor) are expected.

1.3 AIMS AND OBJECTIVES

To fabricate highly transparent *p*-type thermoelectric γ -CuI thin films and to analyze the thermoelectric performance based on the power factor in the room temperature range.

- Fabricating γ -CuI thin films using both thermal evaporation and electron-beam deposition methods at different thicknesses.
- Study the structural, morphological, optical and electrical properties of the optimum γ -CuI thin film layers.
- Design a simple home-made system for measuring the Seebeck coefficient.
- Study the electrical conductivity and Seebeck coefficient and estimate the power factor.

1.4 SIGNIFICANCE OF STUDY

The absence of highly transparent *p*-type TCs has been a hinderance for an extensive range of applications in thermoelectric recovery at room temperature, such as in smart windows that harvest electrical energy and in transparent electronic devices. In addition, there is a challenge to find thermoelectric materials that are environmentally friendly, abundant, low cost and thermally stable with a high figure of merit in this temperature regime. A promising transparent and environmentally friendly *p*-type material is Copper Iodide. In this study γ -CuI is fabricated and optimized to obtain both a high conductivity and a high transparency at low temperature range. We analyse the thermoelectric performance based on the power factor. We consider industrially applicable deposition techniques inclusive of room temperature physical deposition by electron-beam and thermal evaporation method for thin film growth. The findings of this research will help to add to the existing knowledge of *p*-type thermoelectric materials in the applications at room temperature.

1.5 OUTLINE OF THE THESIS

The thesis is sectioned into five chapters: introduction, theory and background information, methodology, results and analysis, discussion and conclusion.

Chapter 1: Introduction

In this chapter the importance of energy was explained, ways of generating electrical energy using different energy harvesters, advantages of thermoelectric energy, transparent conductors were explained and the limitations experienced by thermoelectric materials at room temperature.

Chapter 2: Theory and Background Information

This chapter focuses on thermoelectric technology, its origin and current status. A brief explanation of the Seebeck effect is given. The different CuI phases are explained and the status of CuI as a transparent thermoelectric material is given. The structural properties, optical properties, electrical properties, and morphological properties of CuI are explained in detail. And the problems leading to poor thermoelectric performance of *p*-types is discussed. The deposition techniques that have previously been used to produce CuI thin films are explained in detail.

Chapter 3: Methodology

A detailed description of the preparation technique of the CuI thin films is given and the characterization techniques used on the thin films are described in detail. And the home made Seebeck setup model designed is explained in detail.

Chapter 4: Results and Analysis

The results obtained through the characterization techniques are thoroughly analyzed and the results obtained are discussed in depth.

Chapter 5: Conclusion

In this chapter the results are summarized and suggestions to improve the current work are given as a future perspective.

CHAPTER 2: THEORY AND BACKGROUND INFORMATION

2.1 THERMOELECTRICITY

Thermoelectricity is seen as an alternative for power generation because it uses thermoelectric effects to directly change heat energy into electricity due to the temperature difference between the environment and the thermoelectric materials. For years now, the world has been moving towards the use of alternative energy sources to reduce and hopefully avoid the use of non-renewable resources because of the many negative impacts they have on the environment. Thermoelectricity is seen as the most reliable green converter; it uses the thermoelectric effect. Part of the thermoelectric effect was discovered by Thomas J. Seebeck in 1821, it is called the Seebeck effect. The Seebeck effect is when electricity is generated from thermal energy directly from two semiconductors that have a difference in temperature [52]. This effect happens when the electrons move from low to high energy level regions, generating an electric voltage caused by the temperature differences at the two points [53]. The relationship between the temperature difference and the generated voltage is the Seebeck coefficient (also known as thermopower) as shown in equation (1) [54].

$$\Delta V = S(T_1 - T_2) \quad (1)$$

From equation (1), T_1 and T_2 are the temperatures at the two points of the material, ΔV is the potential difference (Seebeck voltage) and S is the Seebeck coefficient. The reverse of the seebeck effect is called the Peltier effect and it is the second part of the thermoelectric effect. It was first observed in 1834 by Jean Charles Peltier [55]. Practical thermoelectric generators are connected in series electrically and connected in parallel thermally [56, 57] as shown in Figure 1. Thermoelectricity is used in a vast range of applications like in electronics and optoelectronic devices. Thermoelectric generators (TEGs) are used for waste heat attaining applications and for specialized applications such as in temperature powered clothing and wristwatches at room temperature [58-60]. TEGs are very advantageous because they are reliable, simple, small in size, non-toxic and very durable to be used in harsh conditions [56, 61].

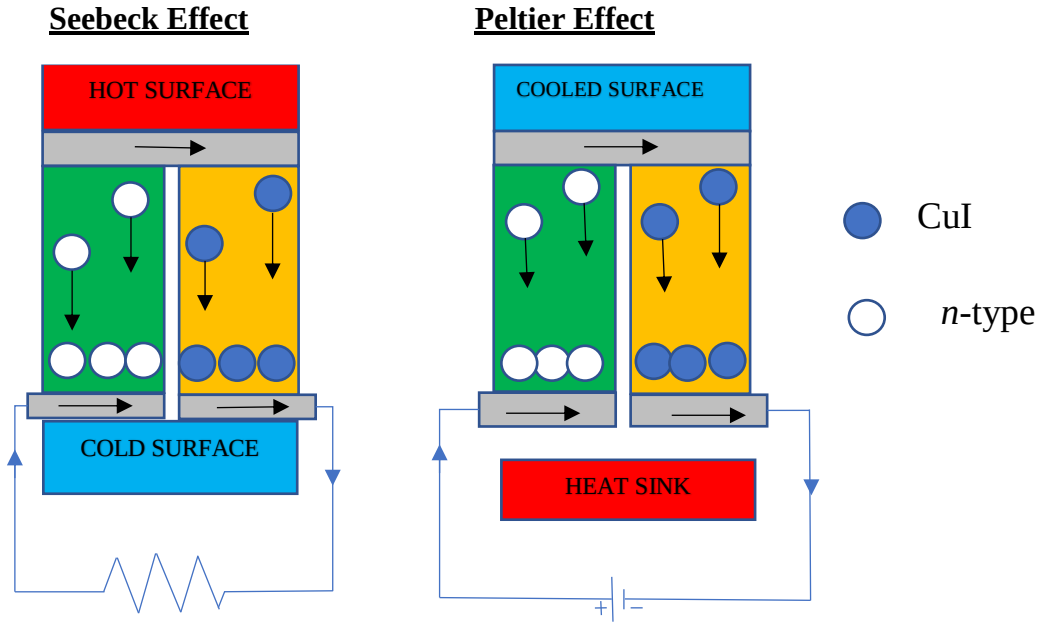


Figure 1: Thermoelectric effects

2.2 BEHAVIOUR OF A THERMOELECTRIC MATERIAL

The thermoelectric material's ability to convert temperature gradient into electrical energy is described by the Figure of merit (ZT) which is a dimensionless quantity. ZT is a measure to characterize the performance of the material. The ZT value is calculated as shown in equation (2), based on the Seebeck Coefficient (S), electrical conductivity (σ), thermal conductivity (k) and the average temperature in Kelvin (T) which is given in equation (3) [62-64]. The higher the ZT value the better the conversion efficiency of thermoelectric materials. This means that maximizing the ZT value is crucial for selecting and optimizing thermoelectric materials. For many years alloys based on bismuth telluride are known to have a ZT value slightly close to 1 [65].

$$ZT = \frac{\sigma S^2 T}{k} \quad (2)$$

$$T = \frac{T_1 + T_2}{2} \quad (3)$$

A thermoelectric material that is transparent is essentially a transparent semiconductor (TS) that has a high Seebeck coefficient value (S), a high electrical conductivity (σ) and a low thermal conductivity value (k). The thermal conductivity value (k) is usually the sum of lattice thermal conductivity (phonons moving through the lattice) (k_l) and electronic thermal conductivity (holes and electrons that transport heat) (k_e). These two parameters are related by equation (4) [66].

$$k = k_l + k_e \quad (4)$$

For a thermoelectric material to have a high ZT value, a number of parameters need to be optimized since it requires charge carriers with high mobility, low lattice thermal conductivity (low phonon mobility) and also a low effective mass as seen in crystalline semiconductors. From equation (2) it can be observed that the Seebeck coefficient and the electrical conductivity are directly proportional to the Figure of merit, the ZT value can be extrapolated from the Power factor (PF):

$$PF = \sigma S^2 \quad (5)$$

Crystalline materials are good thermoelectric materials because they can scatter phonons without significantly disrupting the electrical conductivity. As shown in Figure 2, for most thermoelectric materials when their carrier concentration is increased, the electrical conductivity and the thermal conductivity increase while the Seebeck coefficient decreases. This makes carrier concentration values between the order 10^{19} and 10^{20} the most ideal to attain high ZT values [67].

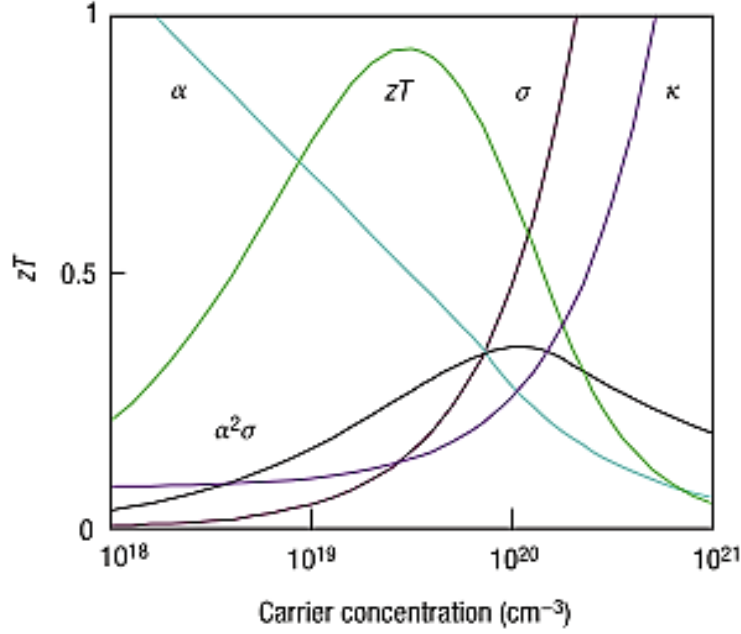


Figure 2: ZT vs carrier concentration, comprising of the seebeck coefficient (S denoted as α in this case), electrical conductivity(σ) and thermal conductivity(k) [31].

2.3 CURRENT TREND ON *P*-TYPE THERMOELECTRIC MATERIALS

As already outlined transparent conductors or semiconductors have a transmittance of the incident light greater than 80% and they have a high electrical conductivity. But since most research is focused nowadays on the recovery of thermoelectric energy in the room temperature range using invisible devices. This is because most materials that can be synthesized at low or room temperatures have more practical use such as in solar cells, consumer electronics, wearable human devices such as wristwatches and smart windows that can harvest energy. To fill the gap that exists, more researchers have been geared up in finding alternative *p*-type thermoelectric materials that can recover energy at room temperature but at the same time have a high conductivity. These thermoelectric materials should be inexpensive and be earth abundant elements so that they can be used for large area fabrication since the majority of thermoelectric materials commonly used are toxic and expensive elements [31]. Since the discovery of delafossite CuAlO_2 by Kawazoe [46], a lot of research was conducted on Cu(I)-based oxides like delafossite CuMO_2 ($M = \text{Ga, Cr, In, Y, Fe}$ and others) and non-delafossite SrCu_2O_2 and LnCuOCh ($\text{Ln} = \text{La-Nd}$, $\text{Ch} = \text{S and Se}$) [68-73],

however, it was hard to achieve a high conductivity and transparency. *P*-type thermoelectric semiconductors such as Copper (II) oxide (Cu₂O), Tin (II) oxide (SnO) and Nickel oxide (NiO) were seen as potential candidates but the challenge was their low mobility and low optical transparency [44, 68]. Most of the *p*-type thermoelectric materials exhibited poor electrical conductivity, which makes them to have a thermoelectric performance that is very poor at room temperature. For example, Perovskite Sr-doped LaCrO₃ (Strontium doped Lanthanide Chromite) has been reported as a new TC with the highest conductivity of ~ 54 S/cm and transparency of 42.3% which is very low [74]. Table 2 shows literature reported *p*-type TCs.

Table 2: Physical properties of various *p*-type thermoelectric materials at room temperature.

Material	Bandgap (eV)	$S^2 \sigma$ ($10^{-3} \text{ Wm}^{-1}\text{K}^2$)	k ($\text{Wm}^{-1}\text{K}^{-1}$)	ZT 300K	Reference
CuAlO ₂	3.50	0.01	3.50	0.001	[75]
CuCrO ₂	2.50-3.00	0.06	7.50	0.002	[76]
Ca ₃ Co ₄ O ₉	2.10	0.83	3.50	0.070	[48]
CuSe	1.23	0.60-0.80	0.80	0.200	[77]
PbTe	0.32	3.00	3.00	0.300	[78]
CuI	3.00	0.47	0.48	0.290	[79]

2.4 CUPROUS(COPPER) IODIDE

Copper Iodide (CuI) was first discovered in 1907 by Bädeker [80, 81]. It attracted a lot of focus as it has many unique features like a wide band gap, being temperature dependent, electrosensitivity and photosensitivity [82]. It also has a large exciton binding energy of 62 meV [83] and it is a semiconductor with a wide band gap of 2.3-3.1 eV [84]. It is known to exist in three polymorphic phases; (i) the zinc-blende structure (γ -CuI) which is stable at temperatures below 370 °C, (ii) the wurtzite structure (β -CuI) for temperatures from 370 °C to 390 °C and (iii) the rock salt structure (α -CuI) for temperatures above 390 °C as shown in Figure 3 [47]. Ions in the wurtzite and zinc-blende structure are tetrahedrally coordinated with a Cu-I distance of 2.338 Å. The α and β phases act as superionic conductors caused by the mobile Cu ions [85] while the γ -phase is a wide direct bandgap ($E_g = 3.1$ eV) *p*-type semiconductor at room temperature. Its *p*-type conductivity is

because of the vacancies at cation sites [86-88]. CuI is an eco-friendly material made of elements that are not toxic and are found in nature, which are Cu and I, respectively. Interestingly, since iodine is a heavy element, it leads to thermal conductivity that is low which is necessary to have a good thermoelectric performance. The wide direct bandgap ($E_g = 3.1$ eV) of γ -CuI allows for high transparency in the visible spectral range which bring possible applications in transparent electronics [88]. CuI usually appear as a reddish brown colour because of impurities. In its pure form it is colourless to white.

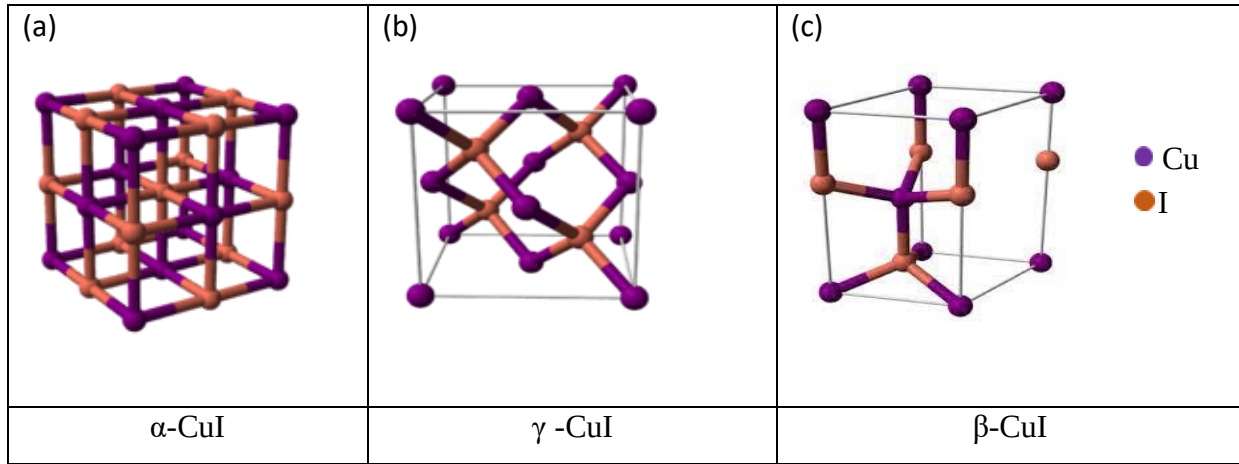


Figure 3: Polymorphic phases of CuI (a) rock salt structure, (b) zincblende structure and (c) Wurtzite structure [47].

Structural properties: The zincblende structure has different diffraction planes as shown in Figure 4. The most preferred orientation in γ -CuI thin films is the (111) plane because its surface energy is the lowest and therefore, the growth rate is fastest along this plane.

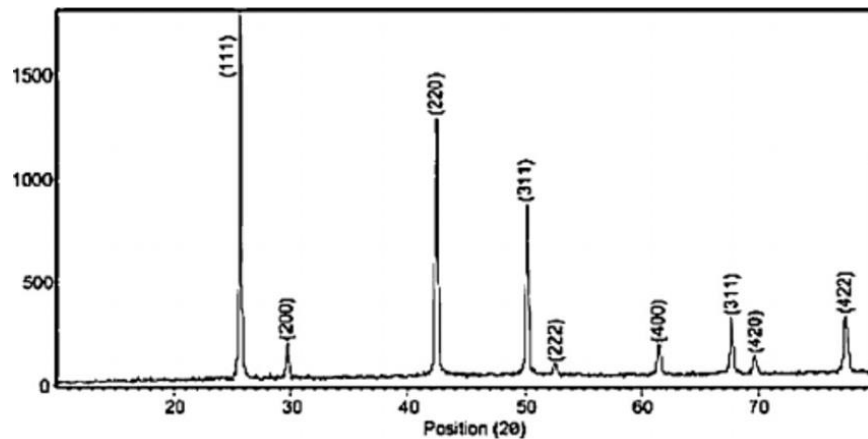


Figure 4: Typical X-ray diffractogram of γ -CuI thin films [89].

Electrical properties: The γ -CuI with hole concentration (p) of $5 \times 10^{18} \text{ cm}^{-3}$ is reported to have hole mobility (μ) of $40 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ for bulk material and $6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ as a thin film. Moreover, it has a high conductivity of 280 S/cm at room temperature [90]. At 300 K and for a hole concentration of $p = 10^{20} \text{ cm}^{-3}$, the Seebeck coefficient value of $237 \text{ } \mu\text{V/K}$ was obtained, based on theoretical prediction with Boltzmann transport theory combined with first-principles calculations [91]. Looking at the γ -CuI structure, the valence band maximum (VBM) consists of Cu 3d states and I 5p states. The copper vacancy (V_{Cu}) forms shallow acceptor states above the VBM [92]. Because the I 5p states are spatially spread they lead to a small hole effective mass of $0.3m_e$ [90]. The easy formation of the V_{Cu} makes the zincblende CuI thin films very conductive with hole carrier concentration in the range 10^{17} - 10^{21} cm^{-3} [93]. Because of the large ionic radius difference between Cu^+ and I^- , Cu^+ is the stable state in CuI unlike oxide-based materials that favor the Cu^{2+} [94]. CuI can be synthesized in the low temperature range unlike all the other p -type TCs which need high deposition temperatures. In addition, the stable cubic structure of γ -CuI makes it possible for it to be fabricated using different physical vapor and chemical solution deposition techniques.

Optical properties: The γ -CuI has a wide direct band gap which allows it to have a transparency of 60-85% in the visible range of the spectrum. In Figure 5, an absorption edge(hump) is observed at 409 nm and it could be because of electrons from sub-bands in the valence band being excited to the conduction band, corresponding to an optical band gap of 3.01 eV . The thin films of CuI from Figure 5 are grown with varying N_2 : Ar gas ratios of 3:2, 4:2 and 5:2 and they exhibited a transmittance at 60, 70 and 75% respectively, in the visible region. This may be due to the surface roughness, because at low surface roughness, light scattering is weak, and this leads to a higher transmittance [95].

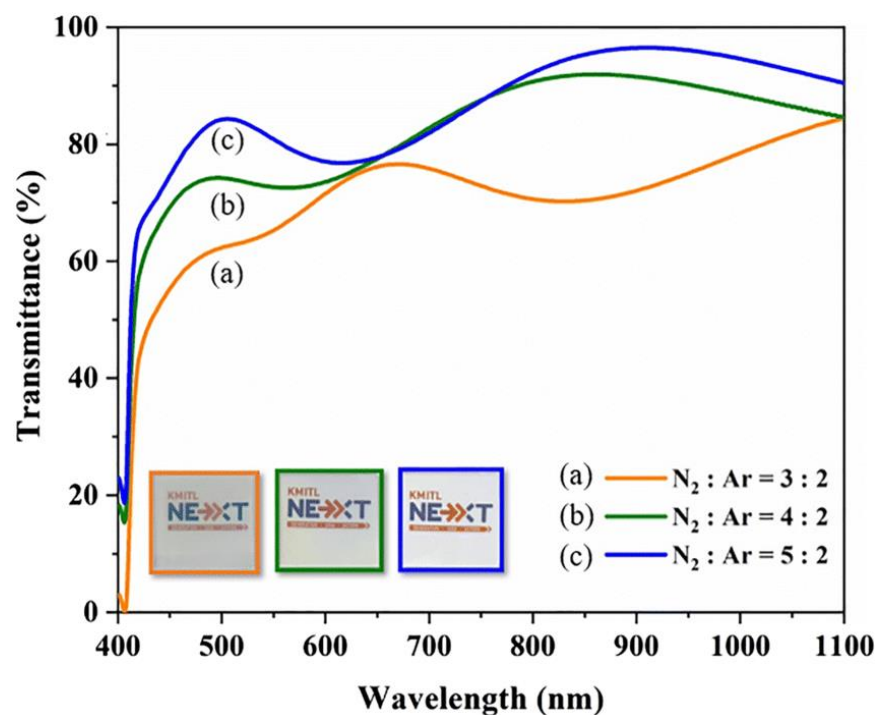


Figure 5: Typical transmittance graph of γ -CuI thin film of γ -CuI grown at different N_2 : Ar gas ratios [96].

2.5 METHODS OF GROWING γ -CuI THIN FILMS

To obtain CuI thin films with a good quality, several deposition methods have been used. And the methods are divided into two categories being physical and chemical depositions and they are summarized as seen in Table 3.

Table 3: Physical and chemical deposition methods [97].

Physical deposition	Chemical deposition
Electron beam evaporation	Sol-gel technique
Thermal evaporation	Spray pyrolysis technique
Molecular beam epitaxy	Chemical vapor deposition
Laser beam evaporation	Electroplating technique
Sputtering	Chemical bath deposition

Physical vapor deposition (PVD) methods produce thin films by vaporizing the desired material and it condenses onto the substrate to form a thin film layer while chemical deposition (CVD) methods vaporize the target material and decompose it into atoms and molecules by a heat source and as it reacts with other gases and liquids near the substrate, it culminates in the formation of thin films [98]. Even though PVD methods are expensive they lead to thin films with a high-power conversion efficiency and can be used at low temperature ranges as compared to low and cost-effective chemical methods which tend to require high temperatures [98]. The deposition method chosen has an impact on the physical and chemical properties of γ -CuI [99] thin films. Therefore, choosing the right technique is vital for thermoelectric materials. Since 1907, when Bädcker reacted sputtered Cu thin films with iodine vapor and produced a transparent γ -CuI with a hole mobility of $6 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and carrier concentration of $5 \times 10^{18} \text{ cm}^{-3}$ was discovered for the first time [100-102]. A lot of researchers have been reacting sputtered Cu thin films with iodine vapor until recently, they changed to a solution iodination approach which was used by dipping Cu thin films in iodine dissolved in an ethanol solution at room temperature [103]. The CuI thin films produced by this solution iodination approach exhibited a high transparency of $>70\%$, a low resistivity of $0.02 \text{ }\Omega\text{cm}$ and a high mobility of $34 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [104]. Later on, Grundmann et al, used thermal evaporation method at room temperature and obtained thin films with a surface roughness of 2 nm [85]. The spin coating method was also used and the CuI thin films obtained have shown a high transparency above $>90\%$ and a smooth surface with a surface roughness 0.6 nm and a hall mobility of $5.1 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ [105]. Physical methods are the most promising choices for thermoelectrics, because they tend to grow CuI thin films with a high electrical conductivity and also evaporation and sputtering are usually preferred for industrial mass production. CuI synthesized from precursor solution deposition methods such as spray pyrolysis, contains a certain number of impurities and tends to exhibit poor transparency and insufficient electrical conductivity. As already stated, the method chosen for deposition of the CuI thin films has a great influence on the opto-electrical properties of the films which is summarized in Table 4. When dealing with thermoelectric materials it is very important to carefully choose the method that will produce samples that have a high conductivity and also a high transparency in order to be a good TC.

Table 4: Optical and electrical parameters of γ -CuI thin films fabricated using different deposition techniques.

Method	Hall mobility ($\text{cm}^2\text{V}^{-1}\text{s}^{-1}$)	Carrier concentration (cm^{-3})	Growth temperature ($^{\circ}\text{C}$)	Transmittance At 500nm (%)	σ (S/cm)	Ref.
Evaporation	2-25	10^{19} - 10^{20}	RT=200	>60	75	[85]
Vapor iodination	6	10^{18} - 10^{19}	120	50	5	[100-102]
Solution iodination	34	10^{18} - 10^{19}	RT	60	50	[104]
Spin coating	0.5-7	10^{16} - 10^{19}	RT=150	>70	0.025-3.5	[105]
Ink-jet coating	10.5	2.2×10^{16}	60	>80	-	[106]
Solid iodination	9-21	10^{17} - 10^{18}	120-150	70	1	[47]
Pulsed laser deposition	8-20	10^{16} - 10^{19}	70-240	80	100	[107]
Sputtering	3-9	10^{19} - 10^{20}	RT	>60	156-283	[108-110]

The next chapter gives a detailed description of the methods used for fabricating γ -CuI thin films and this chapter is sectioned into: substrate cleaning, CuI powder preparation, deposition technique of CuI thin films and the characterization techniques used.

CHAPTER 3: METHODOLOGY

3.1 SUBSTRATE CLEANING

Borosilicate glass substrates were used in this study and firstly before being used for deposition, they were cleaned to remove any dust, oil or dirt that may cause uneven layers or poor adhesion of the film to the substrate. This is done because any of these impurities can have a negative impact on the film quality and film adhesion and this will lead to poor results obtained from the experiment. The Branson Sonerex Ultrasonic tank was used for cleaning as shown in Figure 6. This ultrasonic tank uses high frequency sound waves transmitted through the liquid to clean the surfaces of substrates. The high frequency causes formation of tiny bubbles which form when the sonic energy creates a cavity that then gets trapped as a bubble in the liquid solution. And the tiny bubbles then implode with so much force that causes the dirt or grease adhered to the surface of the substrates to be removed. The ultrasonic tank was filled with water and the substrates were each sonicated for 10 minutes using acetone and distilled water. The substrates were then dried using compressed air.



Figure 6: The ultrasonic tank used to clean the glass substrates

3.2 CuI POWDER PREPARATION

CuI powder was prepared from copper II chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) and potassium iodide (KI) as received from Sigma Aldrich. 3.40 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ salt was added to 200 ml of double distilled water in a beaker and a magnetic stirrer was placed into the beaker. The blue solution was left for 10 minutes on the magnetic hotplate under stirring. This was done so that the salt fully dissolves into the double distilled water. The same process was used to dissolve 6.64 g of KI in 400 ml double distilled water. Aqueous solutions of 0.1 M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and KI were separately made using double distilled water as a solvent. The KI was added to the $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and a precipitate formed, the precipitate had a reddish-brown colour. The precipitate was allowed to rest for 10 minutes and the excess liquid was removed using a filter paper. Double distilled water was used to wash the precipitate several times to improve the purity of the CuI powder and it changed from reddish-brown colour to white. The obtained white CuI powder was dried for 2 hours in an Labotec EcoTherm Digital oven at 100 °C as shown on Figure 7. After drying it was crushed into a fine powder using a mortar and stored in an airtight bottle.

CuI powder formed using $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and KI can be explained by the chemical reaction below:

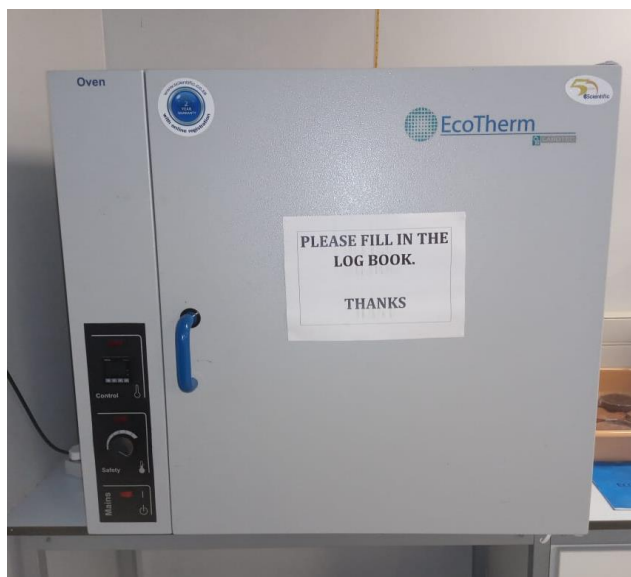
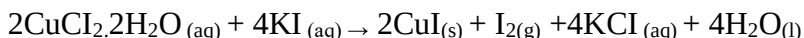


Figure 7: Labotec EcoTherm Digital oven used for drying the powder.

3.3 DEPOSITION OF γ -CuI THIN FILMS

Different techniques of deposition were previously used for fabricating CuI thin films such as magnetron sputtering [111], thermal evaporation [112], pulsed laser deposition (PLD) [113], laser assisted molecular deposition [114], successive ionic layer adsorption and reaction (SILAR) [115], chemical bath deposition (CBD) [116], solvent evaporation [117], electron-beam evaporation [118] and spray pyrolysis [119]. In this research project, the CuI film was deposited on clean borosilicate glass substrates using the HHV TF500 thin film coating machine shown in Figure 8. The HHV TF500 machine is a combination of three different deposition methods: (i) thermal evaporation, (ii) electron-beam evaporation and (iii) RF magnetron sputtering. This thin film coating machine has a vacuum capability of 5×10^{-7} mbar. In this study thin films of CuI were synthesized by thermal evaporation and electron-beam evaporation methods of deposition. Both methods are physical vapor deposition (PVD) methods.



Figure 8: The HHV TF500 thin film coating machine.

3.3.1 Thermal evaporation technique

A high current is passed through the source in vacuum in order to evaporate the desired material into its vapor, and it condenses on the substrate surface to form a thin film as shown in Figure 9. The evaporation boat is made of tungsten and this boat keeps the desired material to be evaporated, and for evaporation resistive heating method is used. Borosilicate glass substrates of length 75 mm by 25 mm were cleaned as explained earlier, there were placed on rotating substrate holders 25 cm above the evaporation boat so that the source material (CuI powder) and the substrate distance is large enough to avoid solid particles reaching the substrate. CuI powder was measured and placed onto the tungsten boat and the deposition chamber was evacuated to a base pressure of 3.70×10^{-5} mbar before the deposition, the power was ramped from 5% -34% at 10 s intervals and the thin film was deposited at a coating vacuum level of 1.35×10^{-4} mbar. Several CuI thin films of different thicknesses were produced by changing the time range from 548 s to 1160 s and the CuI powder masses from 0.50 g to 0.80 g.

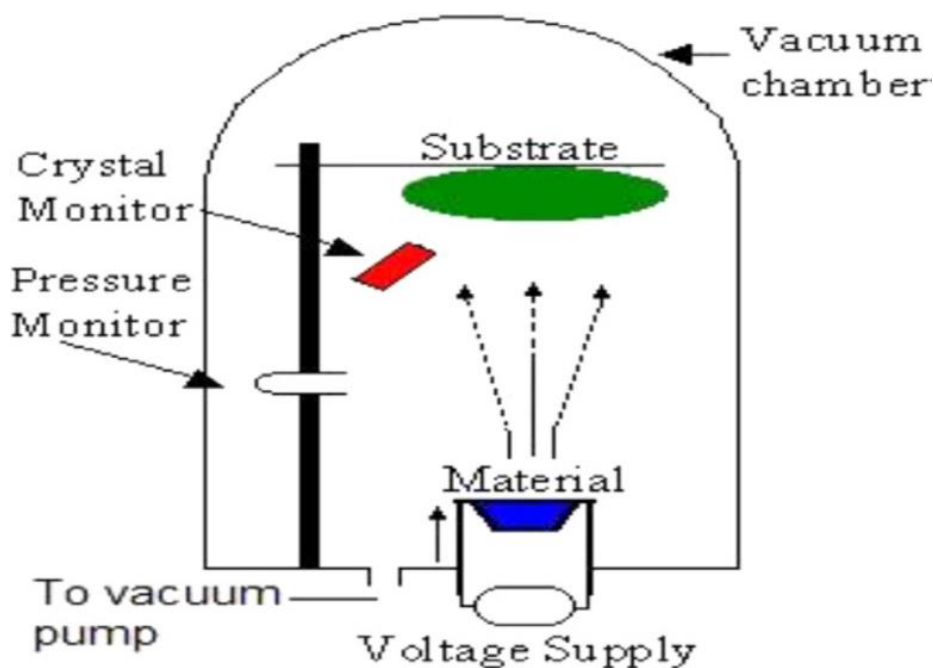


Figure 9: Thermal evaporation method used for thin film deposition [120].

3.3.2 Electron-beam evaporation technique

A beam of electrons hits the source material (CuI powder) in the graphite crucible as shown in Figure 10, to generate a vapor at a current of 40 mA. The graphite crucible was placed inside the crucible holder in the vacuum chamber with a measured amount of CuI powder and evacuated to 4.02×10^{-5} mbar. From the filament, the electron beam is guided to the target material by the magnetic field and the electron beam is directed by the electric field over the substrates to ensure uniform vapor formation. The vapor reaches the substrates and forms a thin film, the deposition time ranged from 99 s to 130 s to be completed. The process was repeated using different masses ranging between 0.15 g to 0.30 g of CuI powder to produce different CuI thin film thicknesses.

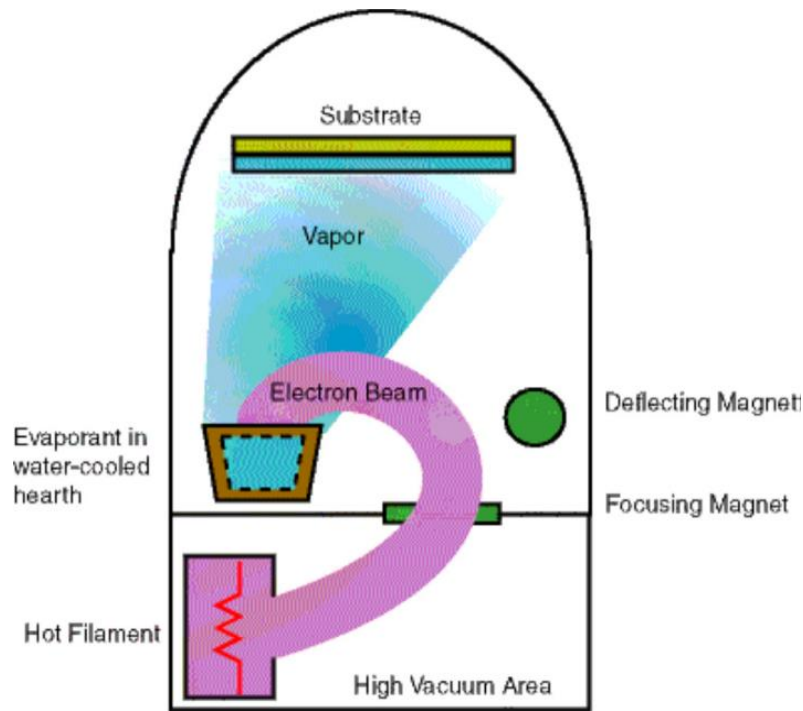


Figure 10: Electron-beam evaporation method used for thin films fabrication [121].

3.4 CHARACTERIZATION TECHNIQUES

The structural, optical, morphological, electrical properties as well as the thickness and sample composition of CuI thin films were characterized by different techniques. All these properties were studied using Stylus Profilometry, X-ray Diffraction (XRD), Raman Spectroscopy, Energy-Dispersive X-Ray Spectroscopy (EDS) and Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), UV/VIS/NIR Spectroscopy, Hall Measurement and the Four Point Probe system. These techniques are explained below:

3.4.1 Stylus Profiler

A stylus profiler is an instrument that is used to measure step height, film thickness and the roughness of the surface. This instrument has a sample stage, diamond stylus and a detector. Before any measurements are made, the sample was scratched with a metal pin to create a step or etched with hydrochloric acid, this is done to provide a difference between the substrate and film height. The sample is put on a sample holder and the stylus tip is placed directly above the sample so that it can be lowered and come into direct contact with the sample. The stylus scans over the sample surface across the step made in order to obtain the film height. The step profile displayed in the computer is then used to obtain the film thickness.

When making a step it is very important to make sure that the scratching does not go deep into the substrate by using a blunt metal pin, otherwise, it will provide the wrong thickness values. Background vibrations may affect the profiler measurements so it's vital to fit shock mountings and rigid support that will help minimize any vibrations occurring around the profiler from interfering with the results. For this study the thickness of the CuI thin films was measured using the KLA Tencor D-100 surface profiler shown in Figure 11. This instrument has a height sensitivity range of 10 nm to 1 mm.



Figure 11: KLA Tencor D-100 Surface Profiler.

3.4.2 X-Ray Diffraction (XRD)

XRD is a technique that uses x-rays to study the structures of materials. It verifies the structure and crystallinity of a sample but information about its chemical nature is not given. XRD patterns are fitted to permit for calculation of the materials lattice parameters, stresses in crystalline regions, the orientation of the crystal (or grain) and secondary phases in the sample. It is in general a bulk characterizing technique that makes an average diffraction pattern for the measured area. The instrument used is called an X-ray diffractometer, it has an x-ray tube which is a vacuum glass enclosing the electrode pair; the anode and cathode. A cathode is a heated tungsten filament that gives out electron through a process called thermionic process. The anode is made mainly from one of the heavy elements such as Cu, W, Ga, Mo and many others. X-rays are produced when high speed electrons bombard a metal target in the anode, so a high voltage has to be applied across the anode and cathode to speed up the motion of electrons from the cathode towards the anode. Only about 1% of the electron's kinetic energy is converted to x-rays when the electrons reach the

anode. The rest of the 99% is converted to heat energy, therefore, the x-ray tube has to be submerged in a coolant so that it cools and does not overheat.

In this study, the structural properties of the CuI thin films were studied using the Bruker D8 Advance X-ray Diffractometer shown in Figure 12. The X-ray diffractometer is fitted with LynxEye detector and equipped with $\text{CuK}\alpha$ radiation of wavelength $1.54060 \text{ \AA}$. The current and voltage were set to 40 mA and 40 kV respectively. The scan type and scan mode used are Couple Two Theta and Continuous Position Sensitive Detector (PSD) Fast.



Figure 12: Bruker D8 Advanced X-ray diffractometer.

X-rays interact with crystalline solids to give a unique diffraction pattern for a particular material. The particular material will always give the same diffraction pattern which is more like its own unique print. When the substances are mixed together each will produce its own unique diffraction pattern independent of the others. Because x-rays are electromagnetic waves, they have a wavelength ranging from 0.01 nm to 10 nm. This wavelength is the same for the spacing between the atoms in most solids, and so this makes x-rays very suitable to study the interatomic distances of crystal lattices.

When an x-ray beam penetrates a material, the beam gets dispersed in different directions by the atoms of the crystal by either specular or diffuse reflection. When the x-rays scatter in specular reflection, constructive interference occurs and this interference is explained by Bragg's law.

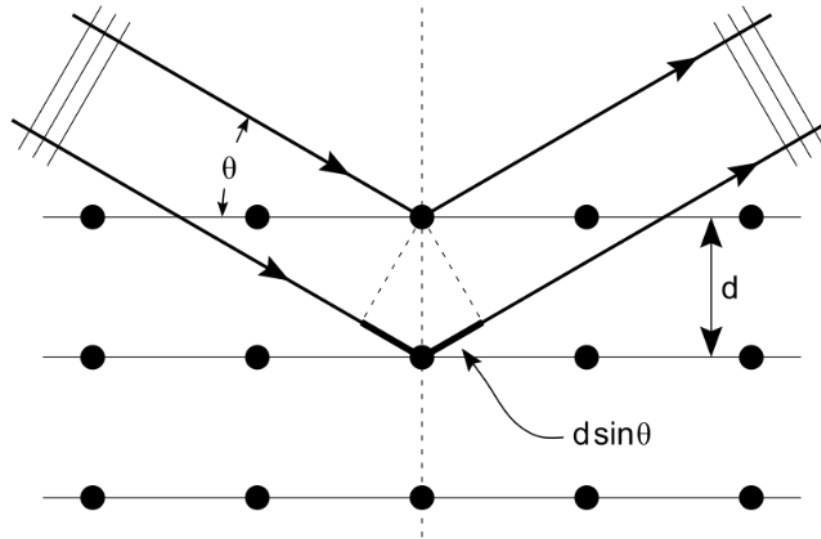


Figure 13: Bragg's scattering [122].

According to Figure 13, constructive interference due to the path difference between successive crystal planes being equal to an integral number of wavelengths of the electromagnetic radiation. Bragg's law of diffraction can be mathematically expressed as [123];

$$n\lambda = 2d_{hkl}\sin\theta \quad (6)$$

where d is the path difference, θ is the incidence angle, λ is the wavelength of the incident x-ray beam and n is an integer called the order of diffraction.

Solids can be amorphous or crystalline. Amorphous solids have atoms disorderly arranged and crystalline solids have atoms arranged in a regular order. The smallest repeating pattern of crystalline solids is called the unit cell, it extends in three dimensions and is defined in terms of lattice points a , b , c and the angles α , β , and γ , respectively. There are seven units cell shapes that can fill all 3-D space and they are cubic, hexagonal, tetragonal, orthorhombic, monoclinic, and triclinic.

3.4.3 Raman Spectroscopy

Raman spectroscopy is a non-invasive method that uses scattered light to measure the sample's vibrational energy modes and it then provides structural and chemical information by detecting the Raman scattering from the samples. It was named after an Indian Physicist C.V Raman who first observed Raman scattering in 1928. The radiation incident upon a sample always scatters in different direction because of the vibrating molecules within the sample. In the majority of the scattering the scattered radiation wavelength is equal to that of the incident radiation this is called elastic or Rayleigh scattering and it is the dominant process. In few cases, Raman Scattering occurs, which is an inelastic scattering process where the radiation scatters at less (stoke-shift Raman scattering) or greater (anti-stoke shift Raman scattering) wavelengths than that of the incident radiation. Because Raman scattering is less intense than Rayleigh scattering, to obtain the Raman spectra, Rayleigh scattering should be prevented from overpowering the weaker Raman scattering.

Raman spectroscopy uses an equipment called Raman spectrometer. The equipment uses excitation lasers, it illuminates the laser onto a sample and detects the scattered light passed through the spectrometer. The energy difference between the incident light and the scattered light is called the Raman shift. It is associated with two energy bandgaps. When the shift is at wavelengths higher than the incident light it is called stokes scattering and at wavelengths lower than the incident light it is called anti-stokes scattering, Raman scattering is therefore very dependent on the incident light. For this study, the structural properties of the CuI thin films were further studied using the Horiba Labra HR Evolution Raman Spectrometer shown in Figure 14.



Figure 14: The Horiba LabRAM HR Evolution Raman Spectrometer.

3.4.4 Atomic Force Microscopy (AFM)

The AFM was developed in 1985 by Quate, Binnig and Gerber, it is a high-resolution method that is used for surface analysis. The AFM is used for accurate measurement of topographical imaging.

A standard AFM is made up of the probe, tip, cantilever, piezoelectric scanner, laser beam, photodetector and many more. During the operation of the AFM system, the probe that has a sharp tip (made of silicon or silicon nitride) is scanned in a raster pattern over the sample surface. Usually, the tip is at one end of the cantilever. The piezoelectric scanner controls the lateral and vertical position of the probe in respect to the surface of the sample. As the tip moves over the sample surface creating different heights, the cantilever deflection changes. And the reflected laser beam from the back of the cantilever traces this deflection. This reflected laser beam is directed into the photodetector which is position sensitive. The coordinates made by the tip are combined and used to produce three-dimensional topographic images of the surface.

The AFM has two basic imaging modes which are dynamic mode and contact mode, and the dynamic mode is divided further into non-contact mode and tapping contact mode, depending on the forces of interaction between the surface and the tip. In the contact mode the probe tip maintains constant surface contact while being scanned, the forces found between the tip and the surface are repulsive and soft cantilevers with force constant of ≤ 1 N/m are the most suitable for contact mode [124]. As for the tapping mode the probe tip makes periodic surface contact as the tip moves up and down as it travels over the sample and the forces found between the tip and surface are repulsive, stiff cantilevers with force constant of 10-100 N/m are the most suitable [125]. And lastly the non-contact mode probe tip has no contact with the sample surface as the distance between the two is usually a few nanometers to tens of nanometers. The forces in this interaction are attractive and the most suitable cantilever is the one that has a high force constant [126].

The BRUKER Atomic Force Microscope shown in Figure 15 below characterized the morphological properties of the CuI thin films in this study.



Figure 15: The BRUKER Atomic Force Microscope.

3.4.5 Scanning electron microscope (SEM)

An SEM is designed to study the surface morphology and film composition of samples by projecting electron beam over the surface of a sample to create an image. Electron microscope gives better resolution compared to other microscopes such as light because electrons have a shorter wavelength. The main components found in an SEM include an electro gun which is a source of electrons, sample chamber, electromagnetic lenses, electron detector and computer to view images. Electrons are produced in the electron gun and accelerated down at energies of 1-30 keV and the electrons go through a combination of apertures and lenses for a focused electron beam to be produced, which then strikes the sample surface. The scan coils that are above the objective lenses are the ones that control the electron beam position on the sample. The scanning beam allows information to be collected about the sample. As the beam of electrons hits on the sample surface it probes to depth of a few microns depending on the density of the sample and the accelerating voltage, so this interaction between the sample and the beam of electrons produces signals such as secondary electrons, backscattered electrons and characteristic X-rays. The backscattered electron signals are captured by the detectors to form images which are then displayed on the computer screen to give information about the surface morphology and chemical composition of the sample. SEMs provide a resolution of about 1-20 nm depending on several factors such as interaction of the electron beam with the sample and electron spot size. In this study the surface morphology of γ -CuI thin film was studied using the JEOL JSM-7001F Field Emission Scanning Electron Microscope (FESEM) shown in Figure 16. This instrument has an Electron Backscatter Diffraction (EBSD) system and an Energy-dispersive X-ray spectroscopy (EDS) detector which is used for analyzing the chemical composition of the CuI thin films. The EDS detector separates the characteristic X-rays of different elements into an energy spectrum and uses the EDS system software to determine the specific elements by analyzing the energy spectrum therefore giving the chemical composition of the sample.



Figure 16: JEOL JSM-7001F Field Emission Scanning Electron Microscope.

3.4.6 UV/VIS/NIR Spectrophotometer

UV/VIS/NIR Spectrophotometry is an analytic technique used to measure light absorbed in the visible and ultraviolet ranges of the electromagnetic spectrum. The incident light can be transmitted or absorbed when the light hits material depending on different properties such as spectral composition, sample thickness and many more. When light is absorbed in the ultraviolet or visible range it causes atomic excitation, so for an atom to change excitation states it has to absorb enough amount of radiation in order for the electron to move to higher orbits.

The UV/VIS/NIR spectrophotometer is the instrument used in UV/VIS/NIR spectrophotometry to measure the light intensity passed through a sample in comparison to the reference measurement of the incident light source. This instrument has different components such as a light source

(usually a twin tungsten halogen and deuterium lamp source), monochromators which separates light into narrow band of wavelengths, this machine uses holographic diffraction grating to provide precise measurements. Light is then transmitted through a sample and the light detector converts the light into readable signal by using the sample and reference signals, the reference is imperative because it is used by the instrument to help in obtaining accurate absorbance values of the sample. the readable signals are presented as graphs of transmittance (T) or absorbance (A) as a function of wavelength.

Transmittance is the ratio of the intensity of light after passing through the sample (I) to the intensity of light before passing the sample (I_0). Mathematically it is expressed as [127]:

$$T = \frac{I}{I_0} \quad (7)$$

Absorbance refers to the logarithm involving absorbance of the intensity light before passing the sample (I_0) to the intensity of light after passing the sample (I). which states how much light has been absorbed by the sample. Mathematically it can be expressed as [128]:

$$A = \log \left(\frac{I_0}{I} \right) \quad (8)$$

Equation (8) expressed in terms of transmittance it is written as:

$$A = -\log T \quad (9)$$

In this research, the absorbance and transmittance of CuI thin films were measured using the Perkin Elmer 750 UV/VIS/NIR Spectrophotometer shown in Figure 17. The wavelength range of 300 nm to 1100 nm with data interval of 1nm was used and the scan speed was 1200 nm/min.



Figure 17: The Perkin Elmer 750 UV/VIS/NIR Spectrophotometer.

3.4.7 Hall effect Measurement system

Hall effect measurement is vital for the characterization of the electrical properties of semiconductor materials. It uses the Hall effect phenomenon discovered in 1879 by Edwin Herbert Hall. The Hall effect occurs when a Hall voltage is produced across an electrical conductor when a magnetic field is applied perpendicular to the current flow, and the sign of the Hall voltage produced is the one used to determine whether the charges carrying the current are positive or negative. In semiconductors the Hall voltage sign is used to show the type of charge carriers (*p*-type or *n*-type) that are dominant. Since the Hall voltage is the primary parameter determined using the Hall effect, it can be used to derive other parameters, such as, Hall coefficient, carrier mobility, carrier concentration and magnetoresistance.

A basic Hall measurement system is made up of different components such as a sample holder that is gold or nickel coated, a constant current source that accommodates both low and high resistivity samples, a permanent magnet and also since Hall measurement depends highly on sample temperature, there is a temperature controller. The ECOPIA HMS5500 Hall measurement system, shown in Figure 18, was used for measuring the CuI thin film's electrical properties. This system

has two sub systems which were used, being the AMP55T and the AHT55T5. The AMP55T measures parameters at a temperature range of 80 K to 350 K, while the AHT55T5 measures at a temperature range of 350 K to 773 K. These sub systems use the 0.55 Tesla permanent magnet and also have gold coated sample holders.



Figure 18: The ECOPIA HMS5500 Hall Effect Measurement System.

3.4.8 The Four Point Probe System

The electrical conductivity and resistivity of semiconductor samples was determined using the Four-point probe method. This method uses four equally spaced probes that are colinear, to make contact with the material that is being characterized. The two outer probes (1 and 4) pass current through the length of the sample, this is done using a power supply. The voltage across the sample is measured using the two inner probes (2 and 3) as seen in the schematic diagram in Figure 19. Each probe has a probe contact resistance (R_{cp}), spreading resistance (R_{sp}) and probe resistance (R_p). Since the voltage measurements draws very small current, all the resistances can be neglected.

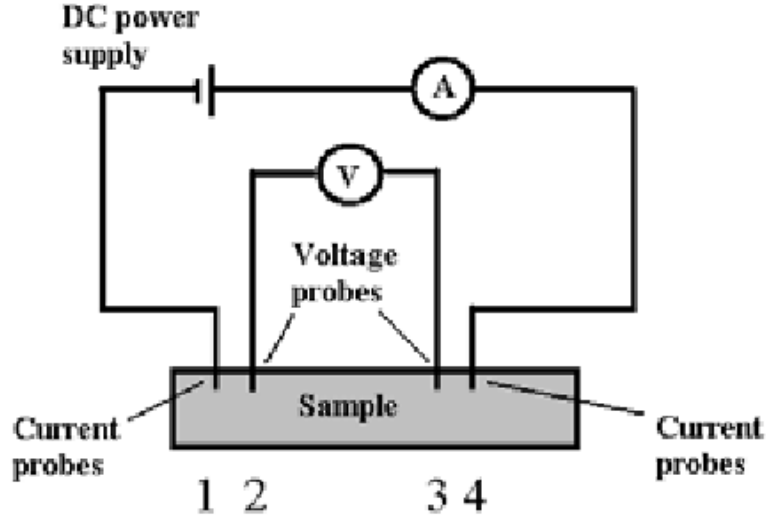


Figure 19: The circuit for the Four point probe setup [129].

Sheet resistance is a measure of the lateral resistance per square area of a thin film which has a uniform thickness. The probe readings of voltage and current are used for the sheet resistance, R_s , calculation using the following equation (10) [130].

$$R_s = \frac{\pi}{\ln 2} \left(\frac{V}{I} \right) \quad (10)$$

where R_s is the sheet resistance in Ω/sq , I is for current in Amperes and V is for voltage in volts.

The resistivity is reported by using the sample thickness as shown in equation (11) [131]:

$$\rho = \frac{\pi}{\ln 2} \left(\frac{V}{I} \right) t \quad (11)$$

$$\rho = R_s t \quad (12)$$

Where t is the sample thickness in cm and ρ is the volume resistivity in Ωcm . The electrical conductivity was calculated using the resistivity obtained. The relation in equation (13) was used [132]:

$$\sigma = \frac{1}{\rho} \quad (13)$$

where σ is the electrical conductivity in S/cm.

3.4.9 The Seebeck Measurement Setup

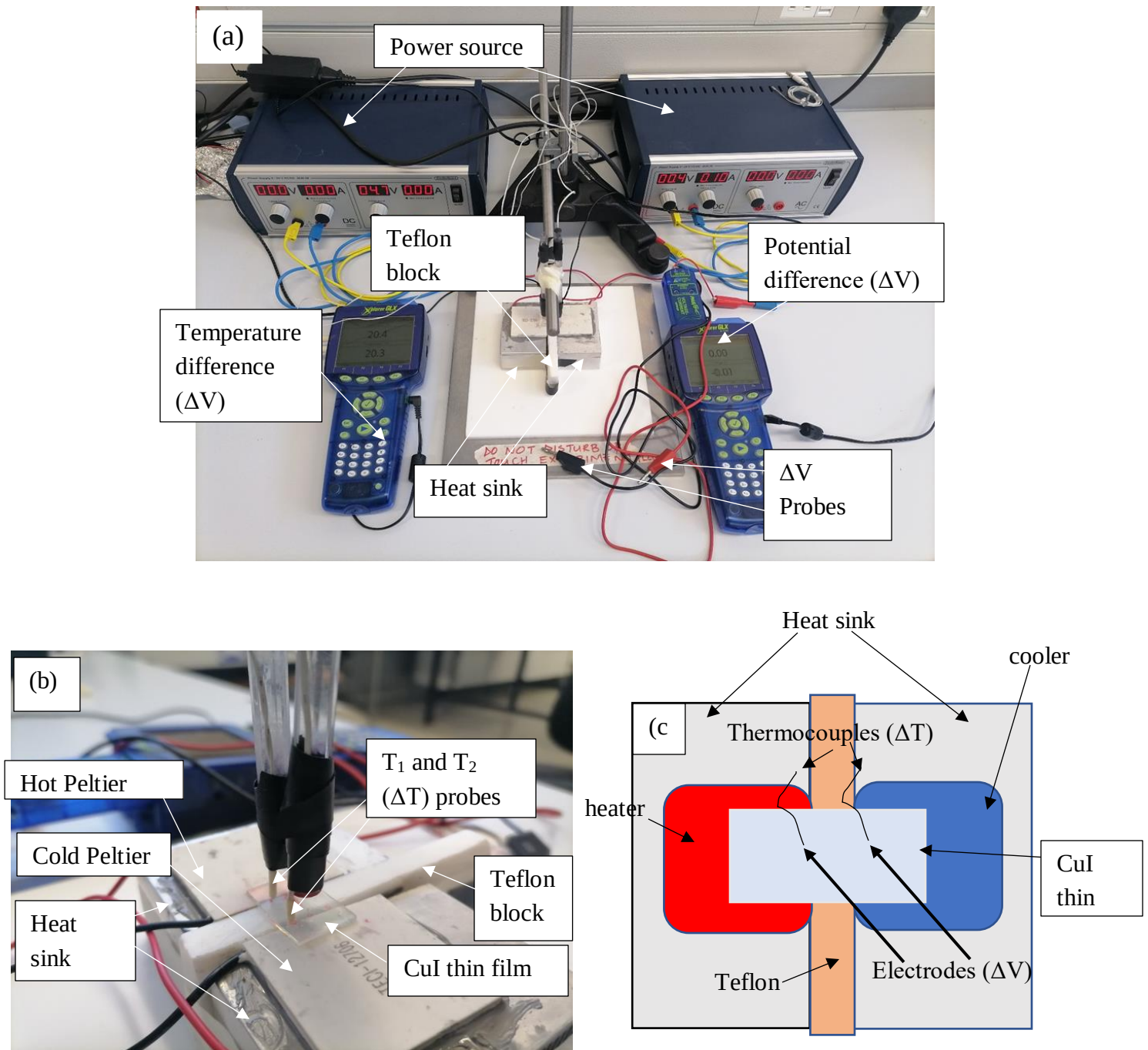


Figure 20: Home-made Seebeck measurement setup (a) full view, (b) zoom in of the contact on the thin films and (c) a schematic diagram of the probes.

The Seebeck Coefficient was measured using a home-made setup as illustrated in Figure 20. A sample of length 20 mm by 25 mm was put on top of two Peltier modules (TEC1-12706) and silver conductive paste contacts separated by 1 cm were deposited onto the film. An equal length of the γ -CuI thin film was over both the hot and cold Peltier elements which were powered by two different power sources. The equal length was done in order to avoid an unbalanced heating or cooling of the sample. Each Peltier was attached to a heat sink by applying a thermal paste. The thermal paste allows for an efficient transfer of heat from the Peltier to the heat sink which is used to dissipate the heat as it provides an efficient path to transfer heat into the air and away from the device. A Teflon block was placed between the two heat sinks so that it acts as an insulator to avoid heat transfer between the two Peltier's as seen from Figure 20b. Two PASCO Xplorer GLX were used for collecting the results. One was used for measuring the temperatures T_1 and T_2 using two thermocouples so that the temperature difference can be calculated using equation (14). While the other was used to measure the Seebeck voltage created across the cold and hot side. The results were varied by changing the temperatures of the two Peltier modules creating different temperature differences (6 °C, 12 °C, 18 °C). The Seebeck voltage (ΔV) was measured for each temperature difference using the probes connected to the other PASCO Xplorer GLX. The temperature differences were chosen in such a way that the average temperature (calculated using equation (3)) was 27 °C. Plotting the Seebeck voltage as a function of the temperature reveals the Seebeck coefficient of the thin films as a slope of the curve according to equation (1).

$$\Delta T = T_1 - T_2 \quad (14)$$

CHAPTER 4: RESULTS AND ANALYSIS

The results of γ -CuI thin films synthesized by thermal evaporation and electron-beam deposition method are presented and explained in depth.

4.1 THICKNESS: STYLUS PROFILOMETER

The thickness of a sample affects many of its properties such as its structural, optical and electrical properties. In this study γ -CuI thin film thicknesses were measured using a KLA Tencor D-100 surface profiler. The scanned length for all samples was 4mm and the range used for scanning was 10 microns. The results obtained are summarized in Table 5.

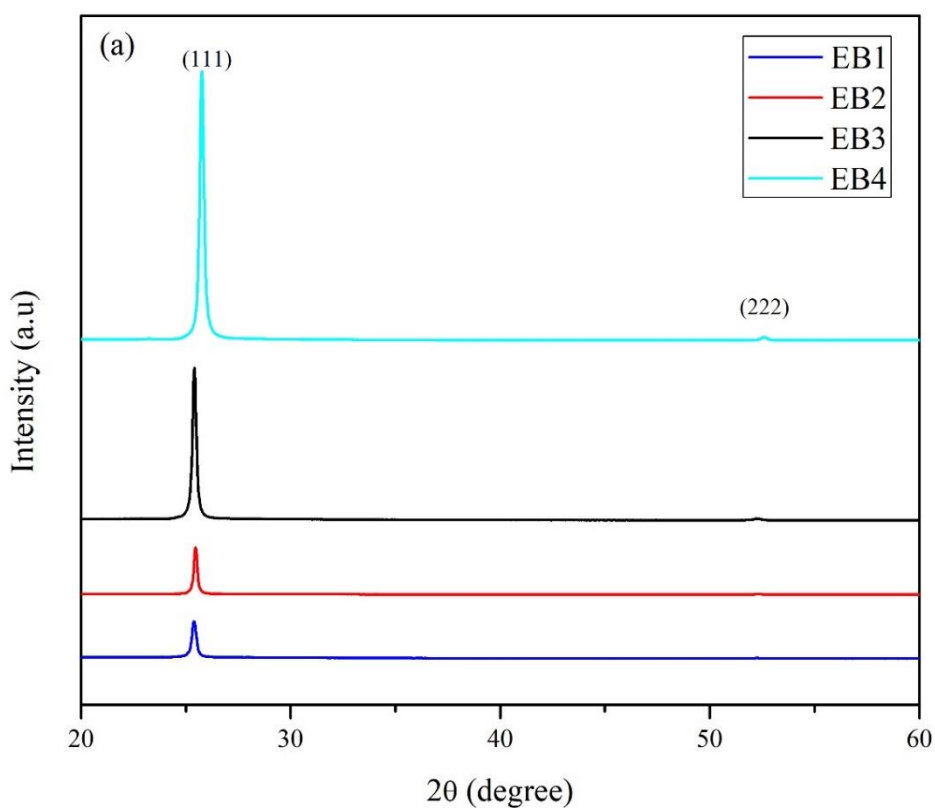
From Table 5 the thickness values for all the γ -CuI thin films are in the range of 210 nm to 380 nm for all deposition methods used. The thicknesses produced are in the range of 200-300 nm [80]. In addition, EB4 and TE4 are produced beyond 300 nm to estimate sample properties at a larger thickness.

Table 5: Thickness of γ -CuI thin films for different deposition methods

Deposition method	Sample Name	Sample Thickness (nm)
Electron-beam Evaporation	EB1	219.7
	EB2	268.0
	EB3	312.9
	EB4	366.5
Thermal Evaporation	TE1	249.0
	TE2	294.6
	TE3	327.3
	TE4	374.1

4.2 STRUCTURAL PROPERTIES: X-RAY DIFFRACTION

X-ray diffraction (XRD) measurements were used to identify crystal phases and analyze the composition, microstructure and purity of the γ -CuI thin films. The thin films were studied using the Bruker D8 Advance XRD. The Bruker D8 Advance XRD uses $\text{CuK}\alpha$ radiation of $1.54060 \text{ \AA}$ and operating current and voltage of 40 mA and 40 kV respectively. The 2θ range from 20° to 60° with an increment of 0.02157° and time per step of 0.650 s were used. Scan type and mode used were Coupled Two Theta and Continuous PSD Fast respectively. XRD profiles of γ -CuI thin films fabricated with different deposition techniques are shown in Figure 21.



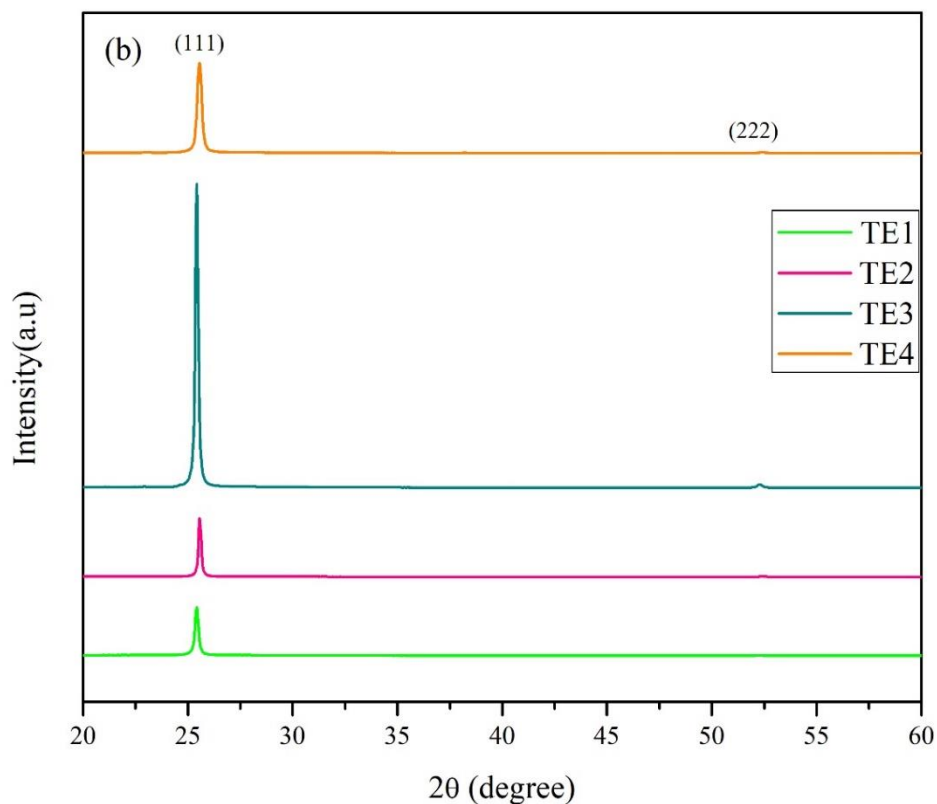


Figure 21: XRD patterns of γ -CuI thin films at different thicknesses (a) Electron-beam evaporation method and (b) Thermal evaporation method.

Figure 21 shows XRD patterns of γ -CuI thin films deposited with different deposition methods. It is observed that the main phase of the prepared thin films is polycrystalline γ -CuI. The main diffraction peaks are identified as the (111) and (222) peaks. All the samples show X-ray diffraction peaks in agreement with literature, i.e., maximum diffraction peaks at 25.76° and 52.64° corresponding to the (111) and (222) peak planes of zinc-blende structure [133], respectively. They are all indexed to JCPDS data file #060246 [134]. Several XRD peaks typical of CuI in literature are missing from Figure 21, this may occur sometimes because some of the scattered x-rays from some set of planes may cancel out due to the scattered rays from another plane. The observed patterns show that the thin films crystallized in cubic phase of the zinc blende structure. All the samples seem to favor the (111) as it is the most dominant peak for all samples which indicates a

well-preferred orientation of (111). This is associated to the low surface energy at this particular orientation for cubic γ -CuI [135, 136]. The direct deposition of the (111) oriented γ -CuI has already been reported by solution method [137, 116] as well as PVD [138, 139]. All the peaks are sharp indicating a high level of crystallinity and no other impurity phases were identified such as peaks of Cu_2O and CuO . That means there was no copper oxidation that took place during sample fabrication [140]. The (111) plane is a close-packed plane that has the lowest energy [141] and the rate of growth along this (111) plane is the fastest. Figure 21(a) shows that the (111) peak intensity increases with thickness increase. This may be because the degree of crystallinity is shown by peak intensity. Figure 21(b) shows the highest intensity of the (111) peak at thickness of 327.3 nm compared to other thicknesses which may mean it is the most crystalline. Both figures show that the thickness has no effect on the phase compositions as all the thin films have the same peaks found in a zincblende structure. The (111) peak is showing a shift in the peak position to the higher side as the thickness increases for all the samples by 0.01° . At lower thicknesses for both deposition methods, EB1, EB2, TE1 and TE2 it can be observed that there is only the (111) peak, which means it is the most crystalline.

The crystallite sizes (D) of the γ -CuI thin films were determined by equation (15), which is the Debye-Scherrer's formula and considers the Full width at half maximum (FWHM) of the most intense diffraction (111) plane [142].

$$D_{hkl} = \frac{k\lambda}{\beta \cos\theta} \quad (15)$$

where D_{hkl} is the crystallite size(nm), λ is the wavelength of the X-ray source ($1.5406\text{\AA}$ CuK α radiation), $k= 0.9$ is the Scherrer constant, β is the Full width at half maximum (FWHM) of the diffraction peak and θ is the Bragg diffraction angle. According to Table 6, the crystallite size of the thin films deposited by electron-beam deposition method increases with an increase in thickness (range from 28.41 nm to 32.92 nm). For the thin films prepared by thermal evaporation method it can be observed that the crystallite size is showing a decrease with an increase in thickness (36.18 nm to 29.55 nm). This may be caused by the crystal defects that are increasing with thickness increase. Comparing both deposition methods, sample EB3 and TE1 have the highest crystallite sizes which indicates that they have the best crystalline structure in comparison to other samples.

Table 6: The structural properties of γ -CuI thin films

Sample	Sample Thickness	Lattice parameter, a (Å)	FWHM (°)	Crystallite size, D_{hkl} (nm)	Dislocation density $\times 10^{-3}(\text{nm}^{-2})$	Microstrain in the a-axis $\times 10^{-3}$
EB1	219.7	6.070	0.287	28.41	1.24	5.55
EB2	268.0	6.058	0.279	29.22	1.17	5.39
EB3	312.9	6.067	0.247	32.92	0.92	4.79
EB4	366.5	6.021	0.264	30.82	1.05	5.05
TE1	249.0	6.063	0.225	36.18	0.76	4.35
TE2	294.6	6.022	0.247	32.92	0.92	4.75
TE3	327.3	6.062	0.237	34.33	0.85	4.58
TE4	374.1	6.032	0.276	29.55	1.15	5.30

In addition, the dislocation density is the measure of the dislocations in the unit volume of a crystalline material and is estimated from equation (16) [143].

$$\delta = \frac{1}{D_{hkl}^2} \quad (16)$$

where D is the crystallite size and the calculated dislocation densities are shown in Table 6. The dislocation density shows a decrease with an increase in thickness for samples prepared by electron-beam deposition method except for EB4 which shows a slight increase and the thermally evaporated samples show an increase in the dislocation density with thickness increase. This means they are less crystalline as compared to the EB3 and TE1. Both EB3 and TE1 samples have the lowest dislocation density which means that they have the best crystalline structure. Since γ -CuI is a cubic phase the lattice constant $a=b=c$. The lattice constants can be determined by analytic method [144] using equation (17) [145].

$$\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad (17)$$

where (h, k, l) are miller indices, d is the d-spacing or inter-atomic distance in Å and a is the lattice parameter. The (111) plane was used to determine the lattice parameter a . For the (111) peak the miller indices h, k, l are 1, 1, 1 respectively. Substituting them into equation (17) yields:

$$a = \sqrt{3d^2} \quad (18)$$

The lattice constants were calculated and given in Table 6. It is found that the lattice parameter a , is in the range from 6.021-6.070 Å for all the samples. For both deposition methods the lattice parameter a , decreases with thickness increase. Moreover, the lattice parameter a , of the samples was found to be almost equal to the bulk CuI from JCPDS data file 060246 which reads 6.063 Å [134]. The difference between the measured lattice parameters and the bulk CuI lattice parameter may be caused by strains in the thin film.

Nanocrystals usually have an intrinsic strain found in them because of grain boundary, point defect and stacking faults [146], however, the Scherrer equation fails to address this. Therefore, lattice strain values are calculated considering the peak broadening due to the microstrain (ϵ) using the FWHM [147] in equation (19).

$$\epsilon = \frac{\beta}{4\tan\theta} \quad (19)$$

where ϵ is the microstrain, θ is the Bragg's angle and β is the FWHM of the diffraction peak. The microstrain calculated are given in Table 6. The microstrain decreases with an increase in crystallite size. We have found that the formation of defect free and highly oriented films can be favoured for samples prepared by electron-beam deposition method, while thermally evaporated thin films show a contradiction as the strain is increasing with a decrease in the crystallite size. This may be due to an increase in defects in the films at increased thickness.

4.3 COMPOSITION: RAMAN SPECTROSCOPY

The Raman spectra of γ -CuI thin films shows a resolved peak at 122 cm⁻¹ and at 124 cm⁻¹ as observed in Figure 22(a) and (b) respectively. These Raman peaks correspond to transverse optical modes (TO) for Cu-I bonding vibration in CuI thin films [148]. The Raman peaks obtained in this study, are higher than the literature Raman peak value of 120 cm⁻¹ [148]. This red shift from the

literature values may be due to the crystallinity of the films that has improved [149]. and this is in agreement with the XRD results as the peaks were seen to shift to a higher angle. No peaks that can be associated with CuO and Cu₂O are observed in both graphs which shows no oxidation had taken place during the preparation of the thin films and this is in agreement with the XRD results.

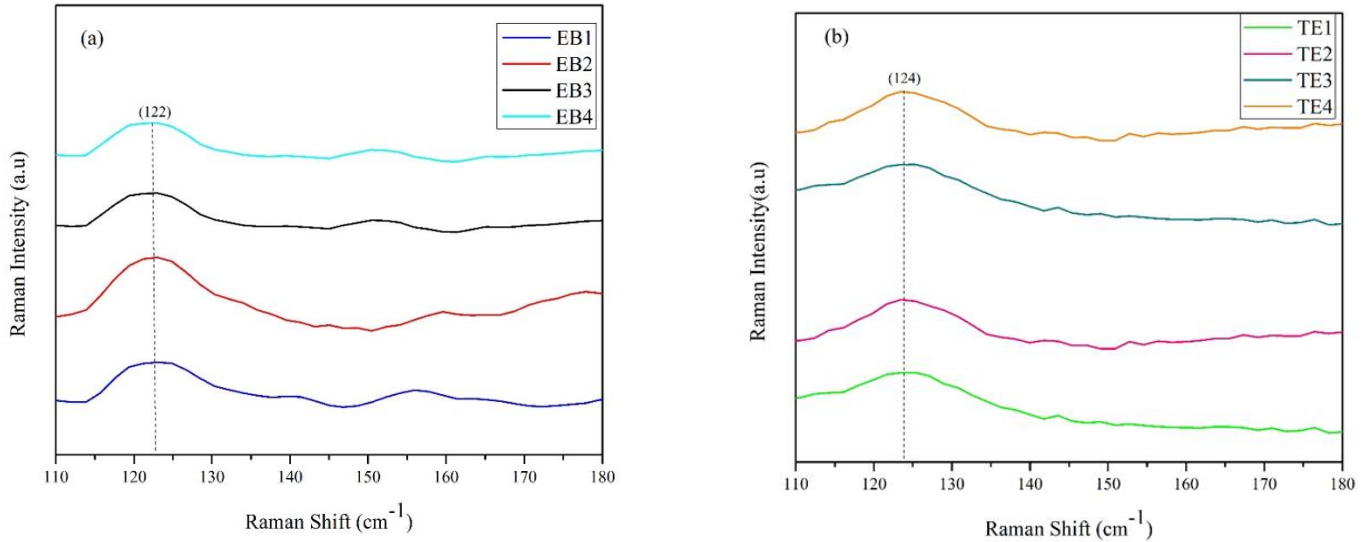
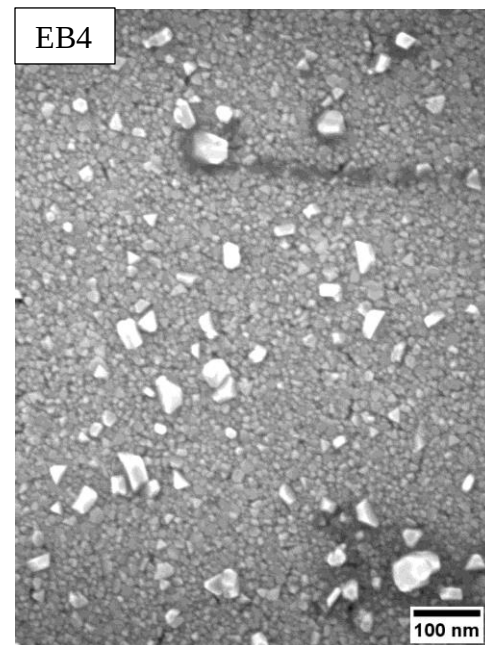
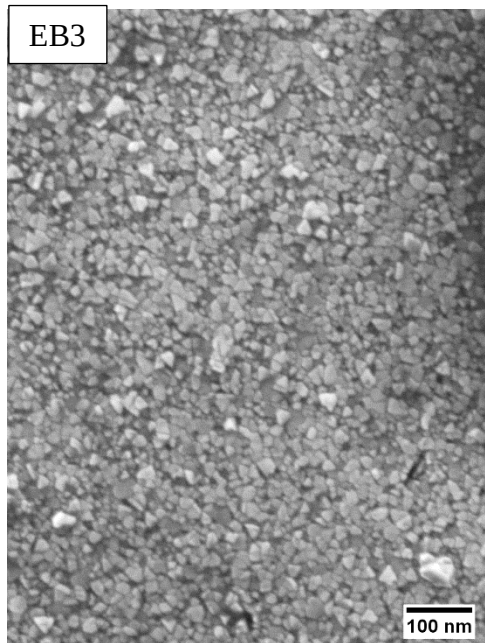
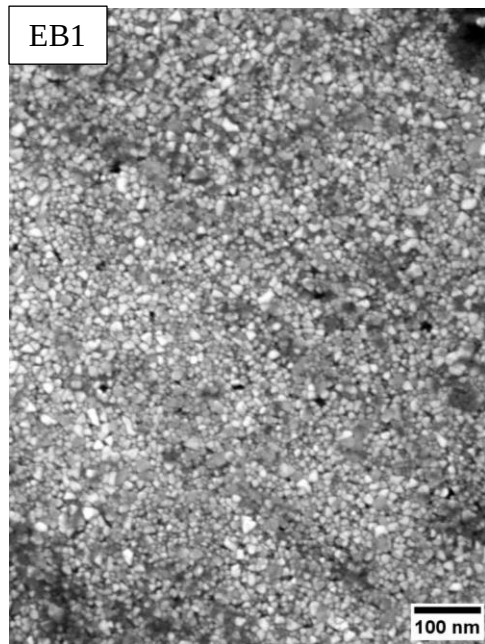


Figure 22: Raman Spectra for γ -CuI thin films at different thicknesses (a) Electron beam evaporation method and (b) Thermal evaporation method

4.4 MORPHOLOGY: SCANNING ELECTRON MICROSCOPY

The surface morphology of the γ -CuI thin films was studied using the JEOL JSM-7001F Field Emission Scanning Electron Microscope (FESEM). The obtained results in Figure 23, show 2D micrographs at X 35000 magnification for all the samples. The grains are uniformly distributed over the surface, and this close packed structure of the films allows for holes and electrons not to travel long distances. This means that the surface energy between the substrate and grain aggregation favours the formation of triangular nanostructures. The triangular shape was reported by Grundmann et al, for γ -CuI thin films deposited by sputtering [150, 151]. It was also reported for solution deposited γ -CuI thin films [108, 152], as well as for CuI thin films obtained by electrochemical deposition method [153]. This triangular shape is in agreement with XRD results as it confirms the (111) oriented γ -CuI.

Figure 23 reveals that the grain size increases with an increase in thickness as seen in Table 7. Thin films prepared by thermal evaporation deposition method have a larger grain size when compared to those prepared by electron beam evaporation method. The increase in grain size is associated with an increase in the surface mobility [154].



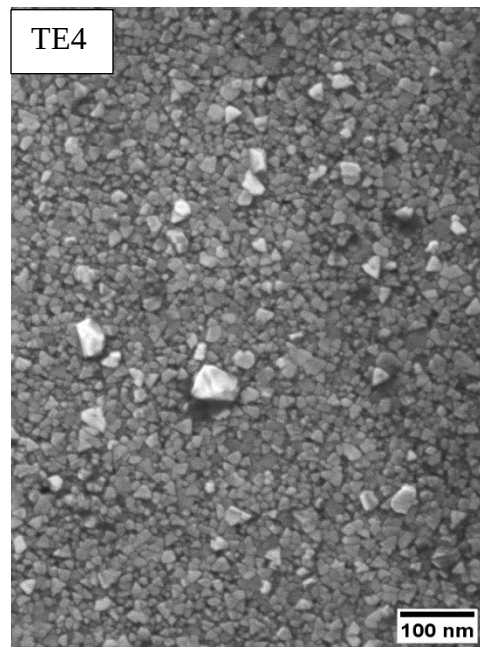
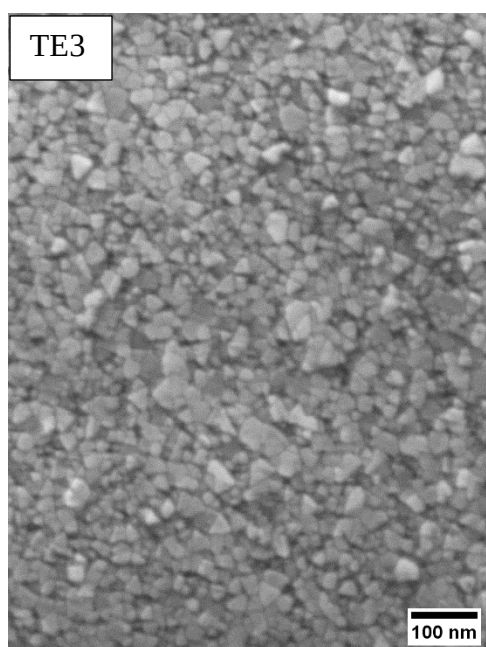
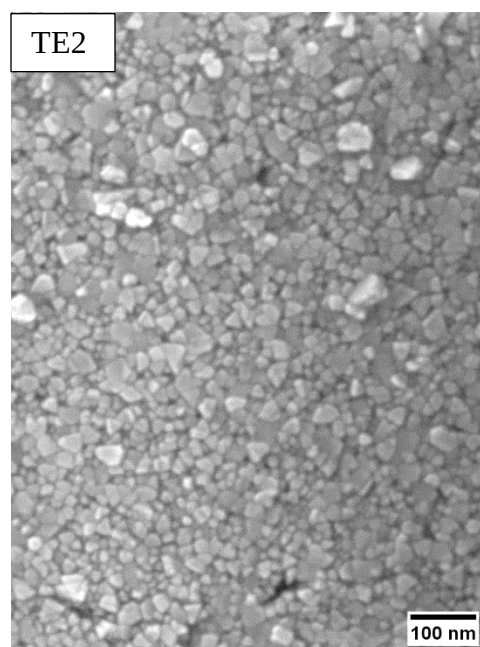
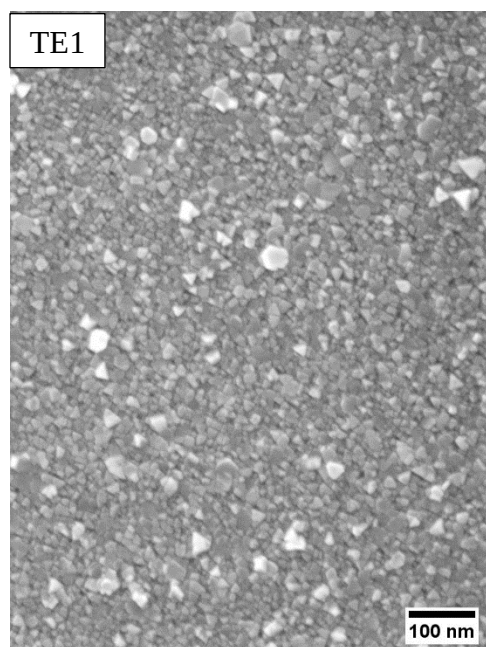


Figure 23: SEM images for samples deposited by Electron beam evaporation technique; EB1, EB2, EB3, EB4 and samples deposited by Thermal evaporation technique; TE1, TE2, TE3, TE4.

Table 7: The average grain size for γ -CuI thin films prepared by thermal evaporation and electron beam deposition method.

Sample Name	Average grain size (nm)
EB1	12.1
EB2	13.9
EB3	15.2
EB4	18.2
TE1	20.5
TE2	21.4
TE3	23.8
TE4	25.1

4.5 ENERGY DISPERSIVE X-RAY SPECTROSCOPY

The elemental distribution and atomic percentage of Cu and I were measured for all samples using the Energy Dispersive X-Ray Spectroscopy (EDS). The elementary composition of the samples is summarized in Table 8. For samples prepared by electron-beam deposition method, the atomic percentage of Cu cation decreases from 56.68% to 49.45% with thickness increase, while the atomic percentage of I anion is increasing from 43.32% to 50.55% with an increase in thickness. As a consequence, the stoichiometry between Cu and I in the formed CuI nanoparticles changes significantly with the thickness of the CuI thin films. On the other hand, for samples prepared by thermal evaporation method it can be observed that Cu cation increases with an increase in thickness from 48.48% to 57.24% and the I anion is decreasing with an increase in thickness from 51.52% to 42.76%. This may be caused by facile diffusion of iodine vapors over a thermally evaporated CuI thin film surface.

Table 8: Elemental composition of the γ -CuI thin films.

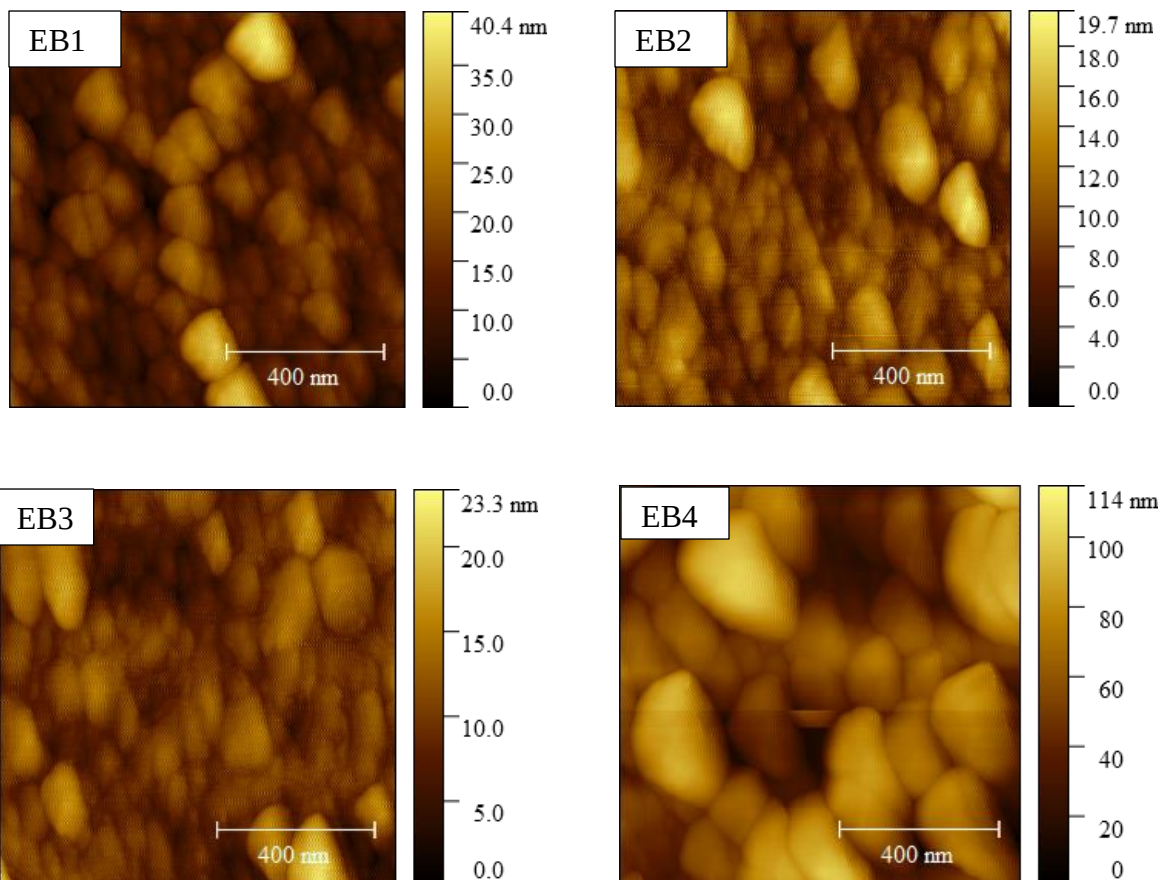
Sample Name	Cu (at. %)	I (at. %)
EB1	56.68	43.32
EB2	53.87	46.13
EB3	51.34	48.66
EB4	49.45	50.55
TE1	48.48	51.52
TE2	50.76	49.24
TE3	54.55	45.45
TE4	57.24	42.76

4.6 SURFACE MORPHOLOGY: ATOMIC FORCE MICROSCOPY (AFM)

AFM measurements are performed to get insight into the film topography of the γ -CuI thin films fabricated by both electron-beam and thermal evaporation deposition techniques. The AFM microscopy revealed that the root mean square (RMS) surface roughness for both methods increase with an increase in thickness. This phenomenon may be caused by the surface undulation due to increase in thickness [155], which may be due to an increase in the number of particles see Table 9. It is observed that films prepared by thermal evaporation are rougher (5.76 nm to 27.67 nm) when compared to films prepared by electron beam deposition method (2.64 nm to 19.15nm). This is in agreement with SEM results shown in section 4.4. We found larger grain sizes with thickness increase in CuI thin films prepared by thermal evaporation method compared to grain sizes in CuI thin films prepared by electron beam deposition method. The topographic maps are shown in Figure 24. The images show columnar-like structure. The bright to dark region variations reflects the height variation of the order of magnitude of the film thickness.

Table 9: Surface roughness values of CuI thin films fabricated by electron-beam and thermal evaporation method at varied thicknesses.

Sample name	Sample Roughness (nm)
EB1	2.64
EB2	5.19
EB3	5.64
EB4	19.15
TE1	5.76
TE2	13.75
TE3	17.38
TE4	27.67



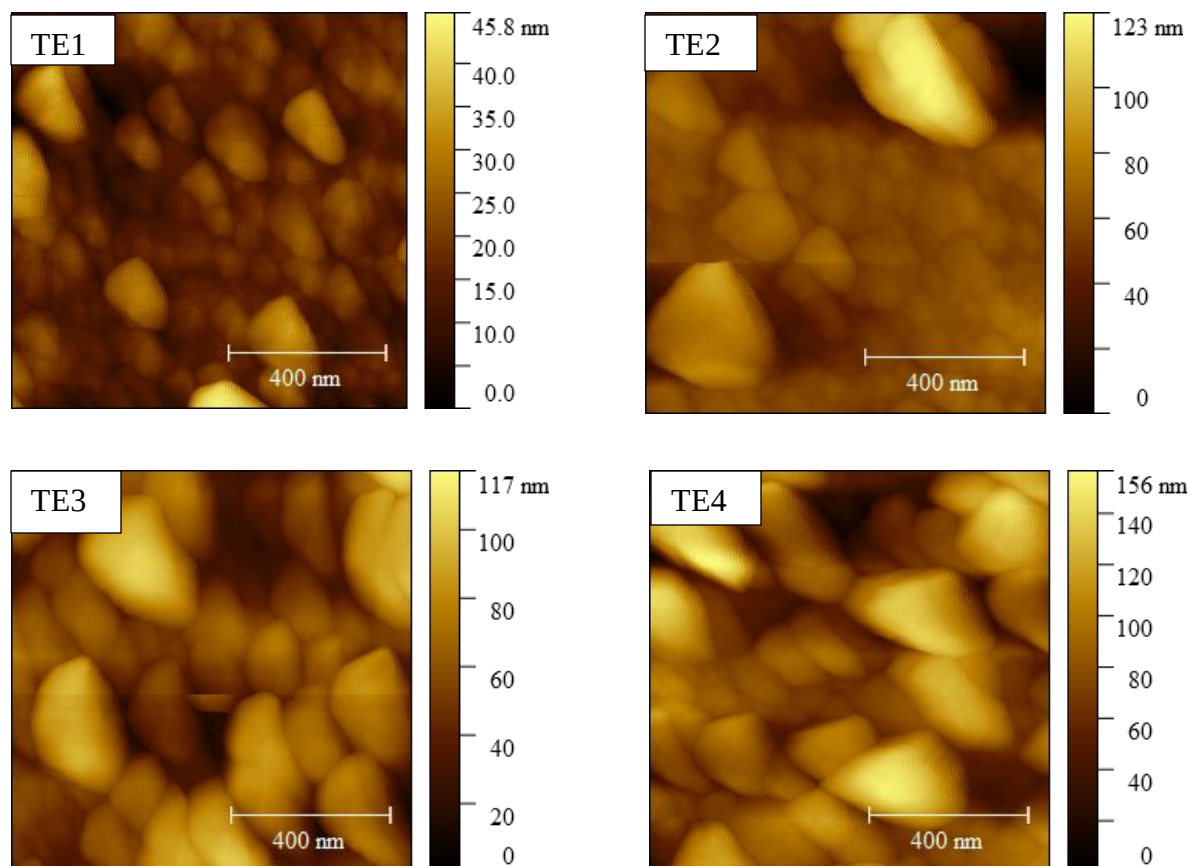


Figure 24: AFM results of the γ -CuI thin films fabricated by Electron-beam evaporation (EB1, EB2, EB3,EB4) and thermal evaporation method (TE1, TE2, TE3,TE4).

4.7 OPTICAL CHARACTERIZATION: UV/VIS/NIR SPECTROPHOTOMETER

Figure 25 shows the transmittance spectra of all the γ -CuI thin films deposited by electron-beam and thermal evaporation deposition methods, respectively. All the thin films show a high transparency of 60-90% in the visible range between 300-1000 nm of the optical spectrum. The transparency is slightly below that of *n*-types (80-90%) because of the significant reflection at the film surface and also at the substrate/film interface [156]. The observed sharp hump at 406 nm on Figure 25(a) and 405 nm on Figure 25(b) may be due to excitation of electrons from sub-bands in the valence band to the conduction band [138]. A slight fluctuation in the transmittance spectra of both graphs may be because of the interference of the thin film layers [157], which means the film surface and thickness are uniform [134]. The thermally evaporated γ -CuI thin films are slightly

less transparent than the transparency obtained in literature. In reference [95] an optical transmission above 80% in the visible range is reported. Apart from this, it can be observed from Figure 25(b) that samples prepared by thermal evaporation method show transparency lower than those in Figure 25(a) prepared by electron-beam evaporation method. This reveals that the deposition method has an impact on the optical transparency of γ -CuI thin films. Moreover, both graphs in Figure 25 show a decrease in transparency with an increase in thickness since the passage of light is reduced as thickness increases. The results obtained are in accordance with the AFM results obtained in Chapter 4.6, because lower surface roughness results in weaker light scattering and thus a higher light transmittance [134].

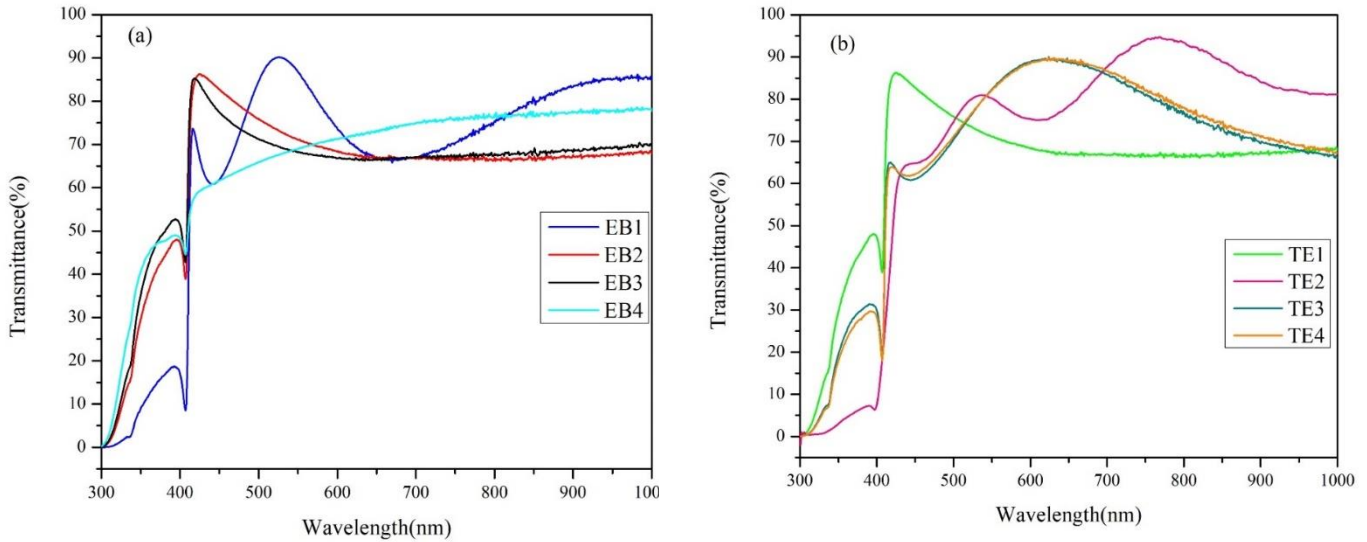


Figure 25: Transmittance spectra of γ -CuI thin films with varying thicknesses deposited by (a) Electron-beam evaporation method and (b) Thermal evaporation method.

The absorbance spectra of γ -CuI thin films prepared by electron-beam and thermal evaporation deposition methods is recorded from 300 nm to 1000 nm. Figure 26(a) shows samples EB2, EB3 and EB4 exhibiting a lower absorbance in the visible range when compared to EB1. The absorption maximum in the visible region at 406 nm for EB2, EB3 and EB4 ranges between 0.41 to 0.35 and EB1 has the highest absorbance of 0.99. Figure 26(b) shows samples TE1 and TE2 which have the lowest absorbance maximum (0.41 and 0.37 respectively) in the visible region at 405 nm, while

TE3 and TE4 have the highest absorbance in the visible range (0.72 and 0.74 respectively). EB samples decrease with an increase in thickness from 0.99 to 0.35. This is because the increase in thickness reduces the intensity of light rays passing through a material and this is seen to affect the bandgap of the thin films as seen in Table 10. The absorbance of TE samples increases with an increase in thickness from 0.41 to 0.74 that means film thickness increases the absorption light in the visible range. Therefore, different deposition methods impact the optical properties of γ -CuI thin films.

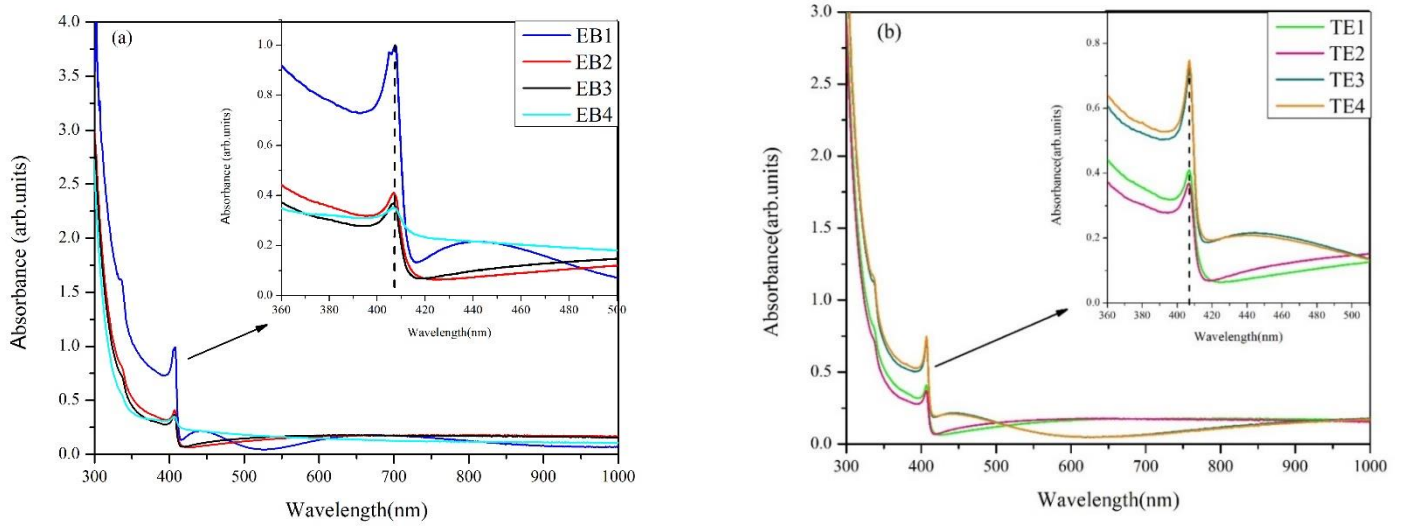


Figure 26: Absorbance spectra of γ -CuI thin films prepared by (a) Electron-beam and (b) Thermal evaporation deposition method

Optical transitions can either be direct or indirect transitions between the valence band and conduction band. The semiconductor bandgap energy is determined using the Tauc's Plot [158].

$$\alpha h\nu = A(h\nu - E_g)^m \quad (20)$$

where α is the absorption coefficient, A is a constant, $h\nu$ is the photon energy and E_g is the bandgap energy and m is $\frac{1}{2}$ for direct band transitions, while $m = 2$ for indirect band transitions [158]. To determine bandgaps using the Tauc plot, $(\alpha h\nu)^2$ vs $h\nu$ was plotted as shown in Figure 27. The linear parts of the plots were extrapolated to zero absorption coefficient ($\alpha=0$) in order to give the energy

bandgaps of the γ -CuI thin films. The absorption coefficient (α) was determined using the relation in equation (21) [159]:

$$\alpha = \frac{2.303A}{t} \quad (21)$$

where t is the thickness of the sample and A is the absorbance.

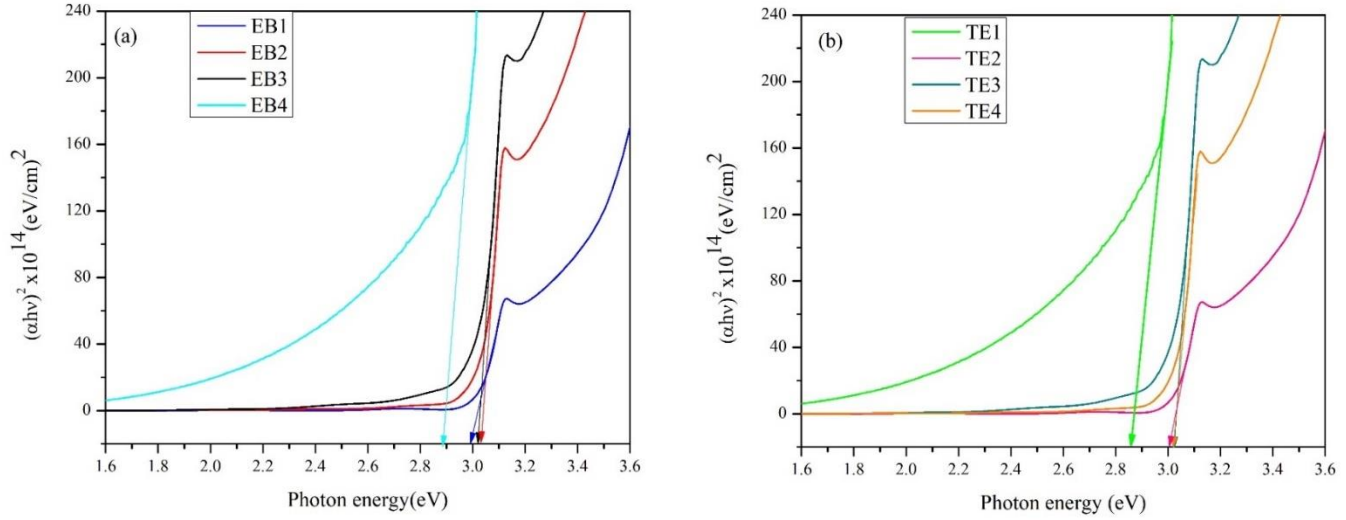


Figure 27: Tauc plot for γ -CuI thin films (a) Electron-beam deposition method and (b) Thermal evaporation deposition method.

The energy bandgap values obtained for the γ -CuI thin films were determined using the Tauc Plot shown in Figure 27. The values for each sample are shown in Table 10. They are in a range between 2.85 eV to 3.03 eV for all samples. This bandgap values for the thin films prepared by both electron-beam and thermal evaporation method are smaller than the previously reported value for γ -CuI of 3.1 eV by Yang et al [160]. Lower bandgaps help for better energy utilization of longer wavelength found at the blue part of the solar spectrum. It can also be seen from Table 10 that the bandgap decreases with thickness increase as already explained that thickness reduces the passage of light rays. The obtained bandgaps are in the same range with those obtained by Sankapal et al. [116] and Dhere et al. [99]. Those findings are in agreement with the transmittance measurements because highly transparent materials have a wide bandgap compared to the samples with lower transmittance.

Table 10: Energy bandgaps of γ -CuI thin films prepared by electron-beam and thermal evaporation method.

Sample name	Energy Bandgap (eV)
EB1	2.99
EB2	3.03
EB3	3.02
EB4	2.89
TE1	2.85
TE2	3.00
TE3	3.02
TE4	3.01

4.8 ELECTRICAL PROPERTIES: HALL MEASUREMENT SYSTEM AND FOUR POINT PROBE METHOD

The Hall Measurement System employs the Hall effect method. This system was used to determine the electrical parameters such as, mobility, bulk concentration and hall coefficient of γ -CuI thin films at room temperature. The four-point probe method was used to determine the conductivity and resistivity of the thin films at room temperature. Table 11 shows a summary of the electrical properties of the γ -CuI thin films at room temperature. The order of resistivity is decreasing with an increase in thickness for both deposition methods. For electron-beam deposited samples EB1, EB2 and EB4 have resistivity of order $10^{-2} \Omega\text{cm}$, EB3 had the lowest resistivity of order $10^{-3} \Omega\text{cm}$ among all the electron-beam deposited thin films. Samples TE1 and TE2 deposited by thermal evaporation method, have resistivity of order $10^{-2} \Omega\text{cm}$, while TE3 and TE4 have shown a resistivity of order $10^{-3} \Omega\text{cm}$. The increase in thickness may have reduced the dangling bonds and defects such as point defect cluster in the film structure, trapping centers of charge carriers and vacancy sites which could be caused by a decrease in the grain boundary scattering [161]. This causes the resistivity to decrease with an increase with thickness. The findings for all the resistivity values at lower thicknesses are in agreement with the low resistivity of $4.5 \times 10^{-2} \Omega\text{cm}$ for thickness in the range 200 nm to 300 nm obtained by Bädeker et al [80]. The low resistivity is associated to

a high carrier concentration at low temperatures [162]. Moreover, the values of the mobility for samples EB1, EB2 and EB3 increased with an increase in thickness from 17.5 cm²/Vs for EB1 to the highest mobility of 58.2 cm²/Vs for EB3. For the sample with the largest thickness (EB4) mobility decreased to 46.3 cm²/Vs. For thermally evaporated samples, TE1 has a mobility of 43.7 cm²/Vs and the highest mobility is obtained for TE3 at 83.5 cm²/Vs. Finally, a slight decrease as thickness increases is observed for TE4 which has a mobility of 74.5 cm²/Vs. Most of the values are significantly higher than the values reported by Yamada et al [47] who obtained mobility of 34 cm²/Vs using solution iodination approach but they are in agreement with the obtained mobility of bulk CuI (> 40 cm²/Vs) caused by the fairly small effective mass of 0.30m_e for the light holes [93, 49]. The values of mobility are much larger for samples deposited by thermal evaporation method compared to those for samples deposited by electron beam deposition method, this means that deposition method affects the electrical properties of materials. The positive values of the average Hall coefficient in Table 11 indicates that the majority of the charge carriers are *p*-type and that all the samples have a *p*-type conduction [92, 93, 163]. The Hall coefficient is found to increase with an increase in thickness.

Table 11: Electrical parameters of γ -CuI thin films for measurement at room temperature with variation to thickness.

Sample Name	Thickness (nm)	Resistivity (Ω .cm)	Mobility (cm ² /Vs)	Hall Coefficient (cm ³ /C)
EB1	219.7	1.69x10 ⁻²	1.75x10 ¹	5.80x10 ⁻³
EB2	268.0	1.20X10 ⁻²	3.16x10 ¹	4.32X10 ⁻¹
EB3	312.9	9.60x10 ⁻³	5.82x10 ¹	1.68x10 ¹
EB4	366.5	1.04x10 ⁻²	4.63x10 ¹	1.42x10 ¹
TE1	249.0	1.27x10 ⁻²	4.37x10 ¹	8.80x10 ⁻³
TE2	294.6	1.02X10 ⁻²	6.11x10 ¹	9.12X10 ⁻³
TE3	327.3	9.12x10 ⁻³	8.35x10 ¹	7.28x10 ⁻²
TE4	374.1	9.51x10 ⁻³	7.45x10 ¹	1.94x10 ¹

4.8.1 Charge carrier concentration

The charge carrier concentration of γ -CuI thin films as a function of thickness was studied and the results are presented in Figure 28. Figure 28(a) and (b) reveals that the charge carrier concentration of the γ -CuI thin films, prepared by electron-beam and thermal deposition respectively, is of the order 10^{20} to 10^{21} cm^{-3} . In Figure 28(a) it can be seen that the carrier concentration increased with an increase in thickness from EB1 ($3.94 \times 10^{20} \text{ cm}^{-3}$) to EB3 ($1.02 \times 10^{21} \text{ cm}^{-3}$). With further increase of thickness (EB4) the carrier concentration starts to decrease slightly. Similar behavior is found for CuI thin films deposited by thermal evaporation deposition method. Figure 28(b) shows that the carrier concentration increased from TE1 ($5.45 \times 10^{20} \text{ cm}^{-3}$) to TE3 ($1.7 \times 10^{21} \text{ cm}^{-3}$), while for TE4 there was a slight decrease in the carrier concentration. The decrease in carrier concentration for samples with large thickness (EB4 and TE4) from both deposition methods, can be attributed to charge recombination. The increase of carrier concentration may be attributed to a decrease in trapping centers of charge carriers with thickness increase. According to that, the grain boundary scattering decreases and this restricts the hole mobility in thinner films due to improved film structure [161]. The carrier concentrations found in this study are in agreement with Wang et al. for a carrier concentration that ranges between 10^{17} to 10^{21} cm^{-3} [93].

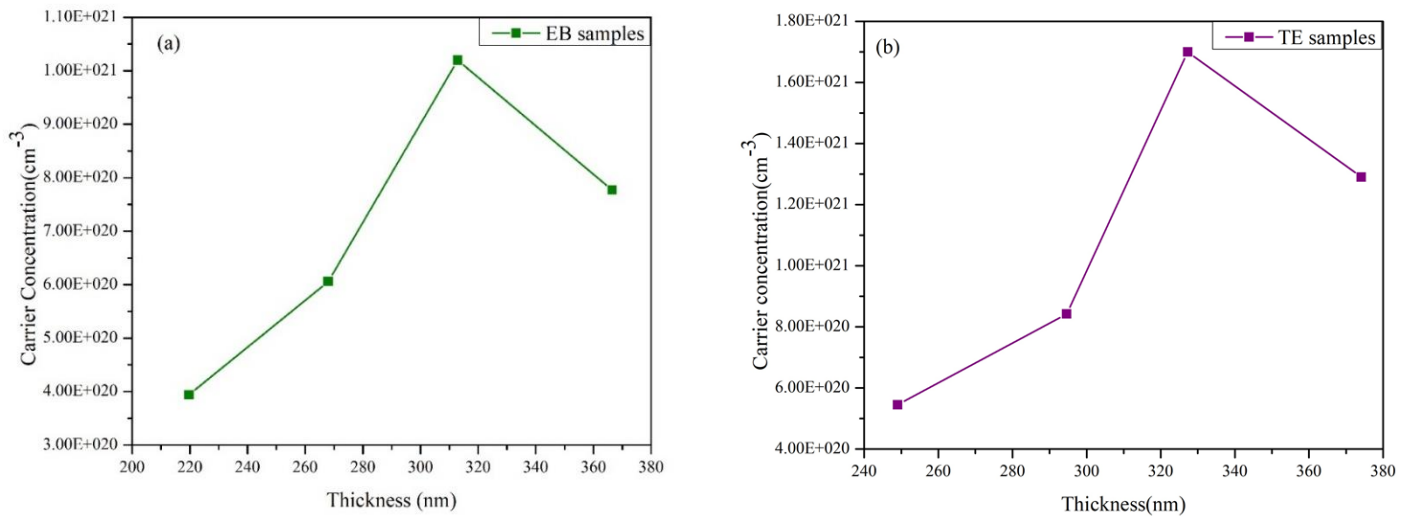


Figure 28: Carrier concentration as a function of thickness (a) electron-beam deposition method and (b) thermal evaporation deposition method.

4.8.2 Varying thickness effect on conductivity

Next, the dependence of conductivity of the γ -CuI thin films on thickness was studied for both deposition methods at room temperature. Figure 29 reveals that the conductivity increases with an increase in thickness for samples with thicknesses of 300nm and below. For electron-beam samples EB1 has the lowest conductivity of 59.1 S/cm. The highest conductivity of 104.4 S/cm among all the samples is obtained for EB3. Looking at EB4, a further increase in thickness leads to a decrease of the conductivity to 96.3 S/cm. For thermally evaporated samples it is observed that at the lowest thickness (TE1) has the lowest conductivity of 79.0 S/cm. With further increase of the thickness, the highest conductivity of 110.2 S/cm is obtained for TE3. As the thickness increases further the conductivity decreases slightly to 105.3 S/cm. The results obtained are higher than the literature value of 75 S/cm [85] for samples deposited by thermal evaporation method. Moreover, the conductivity of thermally evaporated samples is higher than that of CuI thin films prepared by electron-beam deposition method as seen in Figure 29. This is in agreement with the carrier concentration values because as thickness increases it increases the number of carrier concentrations. From Figure 28(a) and (b) it can be seen that thermally evaporated samples have high carrier concentration values when compared electron-beam deposited thin films.

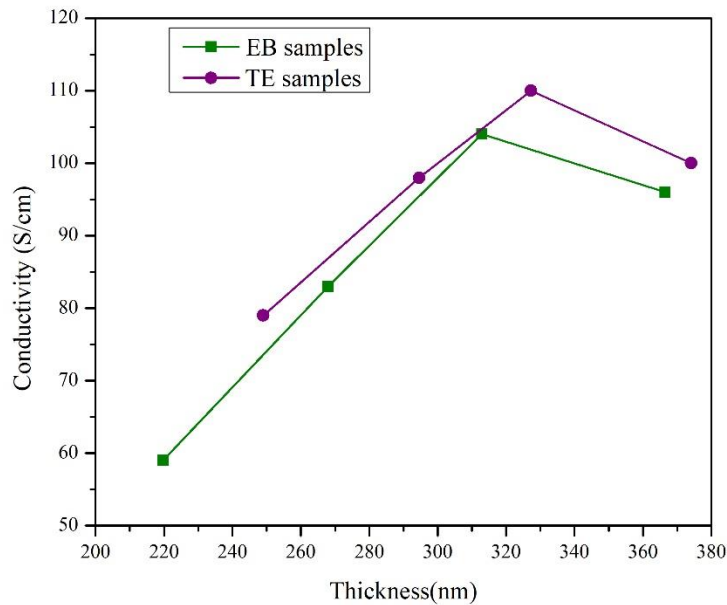


Figure 29: Conductivity of γ -CuI thin films as a function of thickness.

4.8.3 Varying temperature effect on conductivity

The temperature was varied from 295 K to 320 K and the conductivity as a function of temperature was studied for both deposition methods. Looking at Figure 30, the conductivity obtained for all the samples is in the range of the previously reported γ -CuI conductivity of 5-283 S/cm [85, 108, 111, 138, 150]. It can be observed that the conductivity for each sample increases with an increase in temperature. This may be because of free charge carrier generation due to thermal excitation [164]. We also found that thermal evaporation deposited samples have high conductivity when compared with the electron beam deposited samples. For both deposition methods EB3 and TE3 have the highest conductivities. That shows that the thickness of ~ 300 nm is optimal when compared to other thicknesses which is in agreement with Bädker [80].

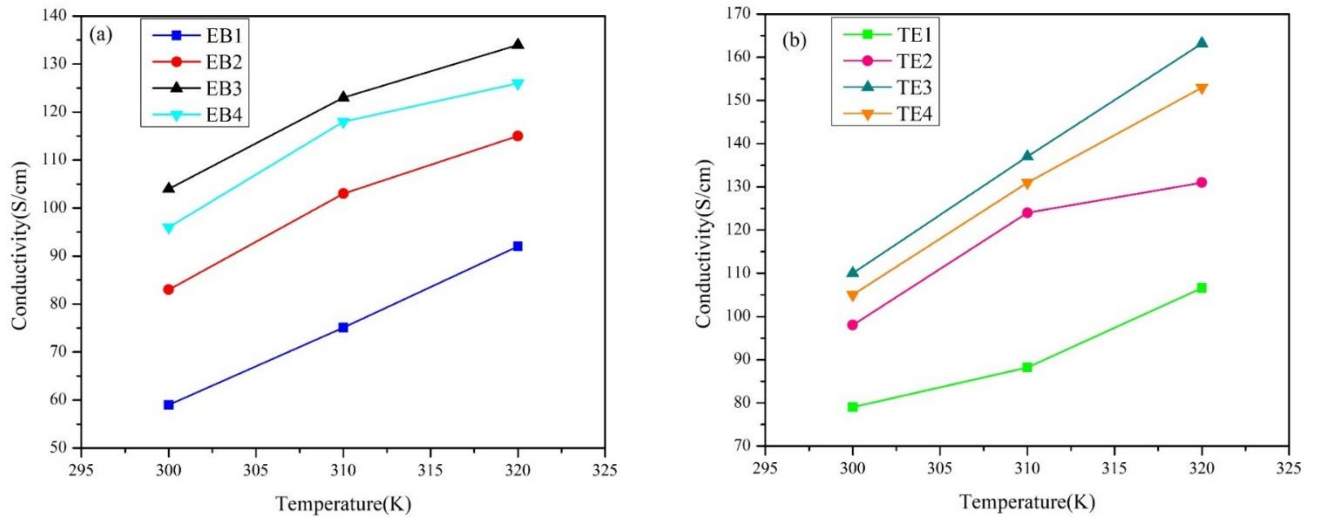


Figure 30: conductivity of γ -CuI thin films as a function of temperature (a) electron-beam deposition method and (b) thermal evaporation deposition method.

4.9 THERMOELECTRIC PERFORMANCE OF γ -CUI THIN FILMS

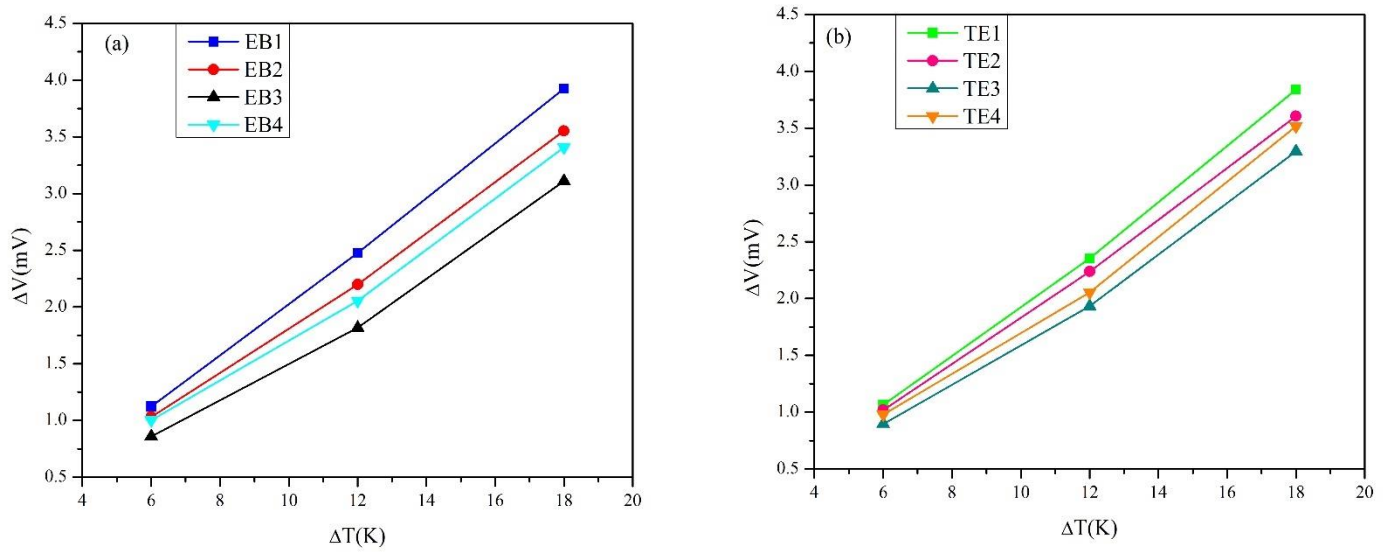


Figure 31: Graphs of Seebeck voltage vs temperature difference for (a) films deposited by electron-beam deposition method and (b) films deposited by thermal evaporation method.

The home-made seebeck setup was used to measure the Seebeck voltage (ΔV) as a function of the temperature difference (ΔT) for an average temperature of 27 °C. For all the samples prepared by both deposition methods. It can be seen in Figure 31 (a) and (b) that the Seebeck voltage increases with an increase in the temperature difference. The Seebeck voltage ranges from 0.85 mV to 3.93 mV for films deposited by electron beam deposition method, while the Seebeck voltage ranged from 0.90 mV to 3.84 mV for thermally evaporated thin films. For both deposition methods EB1 and TE1 have the highest values of the Seebeck voltage when compared to other CuI thin film samples. While a low conductivity is attributed to a low carrier concentration (see Table 12), it can be observed that for both deposition methods the Seebeck coefficient decreases with increasing thickness. For electron beam deposited thin films, EB1 has the lowest conductivity and the highest Seebeck coefficient value of 203.8 $\mu\text{V/K}$. By contrast, EB3 has the highest conductivity and the lowest Seebeck coefficient value of 155 $\mu\text{V/K}$. For thermally evaporated thin films the same trend is observed, i.e., TE1 has the lowest value of conductivity and the highest Seebeck coefficient value of 195.7 $\mu\text{V/K}$. While TE3 has the lowest Seebeck coefficient value of 164.5 $\mu\text{V/K}$,

however, it has the highest conductivity. These results are in agreement with the results obtained in Figure 28(a) and (b). High carrier concentration values results in low Seebeck coefficient values [31]. The Seebeck coefficient results obtained in this work are slightly lower than the values obtained in literature [90, 165, 166].

Table 12: The average Seebeck coefficient and Power factor (PF) of films deposited by electron-beam and thermal evaporation deposition method.

Sample name	Conductivity, σ (S/cm)	Seebeck Coefficient, S ($\mu\text{V/K}$)	PF ($\mu\text{Wm}^{-1}\text{K}^{-2}$)
EB1	59.1	203.8	2.45
EB2	83.0	184.1	2.81
EB3	104.4	155.8	2.53
EB4	96.3	175.9	2.98
TE1	79.0	195.7	3.03
TE2	98.2	185.6	3.38
TE3	110.2	164.5	2.98
TE4	105.3	176.6	3.28

The Seebeck coefficient results obtained are positive revealing that this is a *p*-type material. This is in agreement with the Hall coefficient results obtained in Table 11. When comparing with the findings in Chapter 4.4 (see Table 7), the Seebeck coefficient *S* decreases for both deposition methods as the grain size increased. According to Zeng et.al [167] this is due to the decrease in the carrier mean free path or the decrease in the carrier scattering. The Power factor (PF) obtained in this work for both deposition methods is observed to be higher for thermally evaporated films ranging from $2.98 \mu\text{Wm}^{-1}\text{K}^{-2}$ to $3.38 \mu\text{Wm}^{-1}\text{K}^{-2}$ than for films deposited by electron beam deposition method as they had a power factor in the range of $2.45 \mu\text{Wm}^{-1}\text{K}^{-2}$ to $2.98 \mu\text{Wm}^{-1}\text{K}^{-2}$. Thermally evaporated films had a power factor higher than for films deposited by electron beam deposition method because since the power factor is calculated using electrical conductivity and

Seebeck coefficient, and both of these parameters are highly affected by the carrier concentration. Thermally evaporated films have a high carrier concentration as seen in Figure 28, which has increased the electrical conductivity obtained and has reduced the value of S . This impact of the carrier concentration on the electrical conductivity and the Seebeck coefficient was found in literature [65, 168] for pulsed laser deposition method (PLD). The obtained power factor values are lower than the literature values [90, 165, 166, 79] for sputtering, solid iodination, thermal evaporation deposition methods. The results in this study are close to the power factor values obtained by Faustino et al., [166]. Faustino et al. obtained values of order 10^{-5} to 10^{-6} for thermally evaporated thin films. This reveals that the deposition method has a crucial impact on the thermoelectric properties of a material.

CHAPTER 5: CONCLUSION AND RECOMMENDATIONS

5.1 CONCLUSION

The main aim of this work was to fabricate transparent thermoelectric γ -CuI thin films using both electron-beam deposition method and thermal evaporation deposition method based on different thicknesses. The γ -CuI thin films were successfully fabricated by varying their thicknesses on borosilicate glass substrates and their properties were studied. The structural characterization confirmed the formation of γ -CuI thin films on the borosilicate glass substrates. According to the XRD results, highly crystalline γ -CuI thin films were formed and the films were growing along the (111) plane for both deposition methods. The Raman results also confirmed the formation of γ -CuI thin films with an intense Raman peak at 122 cm^{-1} for films deposited by electron-beam deposition method, while the Raman peak is located at 124 cm^{-1} for thermally evaporated films. We found that the crystallinity was more dependent on the deposition method than on the thicknesses. γ -CuI thin films deposited by electron-beam deposition method have shown a high level of crystallinity. The crystallite size increased with an increase in thickness. The thermally evaporated thin films have shown a decrease in crystallinity and the crystallite size decreased with an increase in thickness. The morphological properties of the γ -CuI thin films were also studied and the SEM results revealed that the average grain size increased with an increase in the thickness for both deposition methods. Thermally evaporated thin films had a large grain size in the range of 20.5 nm to 25.1 nm when compared to the thin films fabricated by electron-beam deposition method which had a smaller grain size ranging from 12.1 nm to 18.2 nm. The AFM results confirmed these findings by showing a large surface roughness for thermally evaporated thin films with an increase in thickness when compared to electron-beam deposited thin films.

Furthermore, the optical properties of all the γ -CuI thin films were studied. Films deposited by electron-beam deposition method had a wide optical bandgap in the range of 2.89 eV to 3.03 eV. Thermally evaporated thin films had an optical bandgap ranging from 2.85 eV to 3.02 eV. All the γ -CuI thin films deposited by both electron-beam and thermal evaporation methods showed a high transparency of 60% to 90% in the visible range spectrum. The electrical conductivity of all the CuI thin films was ranging from 59 S/cm to 110 S/cm. At room temperature, the conductivity has

increased with an increase in thickness. In addition, when the temperature was varied from 300 K to 320 K the conductivity increased with increasing temperatures. The electrical resistivity showed a decrease with an increase in thickness for both deposition methods and the carrier concentration increased with an increase in the thickness. The Seebeck coefficient was ranging from 155.8 $\mu\text{V/K}$ to 203.8 $\mu\text{V/K}$ for all deposition methods and the power factor calculated for thermally evaporated films was ranging from 2.98 $\mu\text{Wm}^{-1}\text{K}^{-2}$ to 3.38 $\mu\text{Wm}^{-1}\text{K}^{-2}$. Films deposited by electron beam deposition method have shown a power factor in the range of 2.45 $\mu\text{Wm}^{-1}\text{K}^{-2}$ to 2.98 $\mu\text{Wm}^{-1}\text{K}^{-2}$. Finally, we found that thermally evaporated CuI thin films have a larger power factor compared to films deposited by electron beam deposition technique.

5.2 RECOMMENDATIONS

The objective of this work was successfully achieved, however, there is still a lot of interesting research work that needs to be done:

- (i) Further interesting measurements on the γ -CuI thin films such as;
 - Performing the X-ray Photoelectron Spectroscopy (XPS) measurements.
 - Study the photoluminescence (PL) of the thin films.
 - Study the thermal conductivity of the γ -CuI thin films and calculate the Figure of merit (ZT).
- (ii) Improvement of the γ -CuI thin films by doping or making hybrid systems (CuI with Pedot: PSS).

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