

The Properties of P-Type Nanostructured Copper (I) Iodide (CuI) Thin Films Prepared by a Novel Mister Atomizer Technique for Dye-Sensitized Solar Cell (DSSC) Application

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Abstract— In this research, the nanostructured CuI thin film for the solid state dye-sensitized solar cells (SSDSSC) was produced by a spraying method which uses mister atomizer. The 0.05 mol of CuI solution was prepared at room temperature by mixing the CuI power with 50ml acetonitrile as solvent and doped with iodine. The CuI concentration was varied from 1 at % (atomic percent) until 5 at % of the iodine doping. Then the CuI thin films were deposited on a glass substrate. The electrical properties of CuI thin films were studied using current – voltage (I-V) solar simulator (CEP 2000) and the thickness of CuI thin films were measured using surface profile (VEECO DEKTAK 150). Then metal contacts have been deposited using sputter coater (EMITECH K550X). The best conductivity of the CuI thin film is at 4at% which is 6.94×10^{-1} S.cm in dark and 6.98×10^{-1} S.cm in illumination since it has less resistivity. The optical properties of CuI thin films were investigated by JASCO UV-VIS/NIR spectrophotometer. The result of the transmittance spectra is at high transparency which is at 71% - 90% nm. Then the surface morphology of the CuI thin films were characterized using field-emission scanning electron microscope (FESEM). The FESEM images show the CuI thin films were in nanoparticle size. The particle size evaluated from FESEM was at 25nm to 90 nm range. The electrical properties, optical properties and surface morphology of CuI thin film could be affected by changing the atomic percent (at%) of the doping concentration of iodine.

Keywords – copper (I) iodide; mister atomizer; FESEM; electrical properties; optical properties

I. INTRODUCTION

A solar cell also known as photovoltaic cell or photoelectric cell. In the solar cell the energy of light directly convert into electricity by the photovoltaic effect. The solar cells are used for powering small devices such as in electronic for example electronic calculators. The photovoltaic device is based on the concept of charge separation at an interface of two materials of different conduction mechanism [1]. The dye-sensitized solar cells (DSSC) provide a technically and economically credible alternative concept to present the p-n junction photovoltaic devices.

Dye-sensitized solar cells (DSSC) based on a semiconductor formed between a photo-sensitized anode and

an electrolyte, a photoelectrochemical system. These cells were invented by Michael Grätzel and Brian O'Regan and are also known as Grätzel cells. A dye-sensitized solar cell (DSSC) is a low-cost solar cell belonging to the group of thin film solar cell. Unfortunately, the liquid electrolyte presents several technological problems such as dye desorption, solvent evaporation and the leakage of the volatile solvents [2]. CuI use to overcome several problems in the dye-sensitized solar cells. Therefore, many efforts were made to replace the liquid electrolyte with solid or quasi-solid type hole transporting materials where is organic hole conductors and inorganic hole conductors. CuI is the p-type semiconductors that are suitable as hole conductors in all solid state dye-sensitized solar cells. CuI has a good conductivity and have a favorable valence band position which allow hole injection from oxidized or excited dye. Copper (I) iodide (CuI) is an inorganic compound with the highest bandgap material which is 3.1 eV [3].

Dye-sensitized solar cells have recently been under intensive investigation because of their low cost and reasonably high efficiency. Q.-B. Meng et. al, conducted studies examining on the fabrication of an efficient solid-state dye-sensitized solar cell. They found that the small size of these CuI crystals is a great advantage in filling the voids of TiO₂ porous films [9]. The electrical and optical properties of nanostructured Copper (I) Iodide thin film for DSSC also will be studied by M.N Amalina et. al [4]. They obtain, the nanostructured thin film using mister atomizer.

In this paper, the CuI thin films were deposited on a glass substrate by using the spraying technique. The system is called mister atomizer. Mister atomizer is one of several kind of the deposition technique. The technique is the similar concept with the spray pyrolysis. Spray pyrolysis is a process in which a thin film is deposited by spraying a solution on a heated surface, where the constituent react to form a chemical compound. The chemical reactants are selected such that the products other than the desired compound are volatile at the temperature of deposition. The process is particularly useful for the deposition of oxides [5].

This paper focuses on the properties of p-type nanostructured copper (I) iodide (CuI) thin films prepared by a novel mister atomizer technique for dye-sensitized solar cell (DSSC) application. The thin films were being characterized in the electrical, optical and structural properties of CuI thin films.

II. METHODOLOGY

In this experiment, the CuI solution was deposited on the glass substrate. The glass substrates were cleaned with acetone, ethanol and deionized water (DI). The cleaning processes use the ultrasonic cleaner by 10 minutes every stage at the 27°C. The CuI solution was prepared by mixing the Copper (I) iodide powder with acetonitrile as solvent and doped the solution with the iodine. 0.05M concentration of CuI was doped with the various atomic percent of iodine which is 1at%, 2 at%, 3 at%, 4 at% and 5at%. All the solution were stirred for 3 hours at the room temperature.

The CuI solution was deposited on the glass substrate using mister atomizer. By using Mister Atomizer, all the material is mixed together and was stirred using hot plate at 50°C for 3 hours to yield a clear solution. The glass substrates were preheated at the 50°C for 10 minutes before the deposition process. The solution was sprayed using argon gas with fine droplets on the glass substrate. The solution was sprayed with 50ml for the entire sample. The substrate temperature was use at the room temperature. After spraying the solution finished, the thin film was dried at 50°C for 30 minutes in the VT furnace. The flowchart of the experimental process was shown in Figure 1.

The current – voltage (I-V) measurement was conducted by using two points probe by using solar simulator (CEP 2000). Au was used as a metal contact for the I-V measurement and will deposit it using a sputter coater (EMITECH K550X). The optical measurement of the thin film was characterized using JASCO UV-VIS/NIR spectrophotometer. The wavelength of the optical measurement was measured at wavelength 300 nm – 900nm. Then the thickness of the thin film will measure using surface profile (VEECO DEKTAK 150+). The surface morphology of the thin film was measured using field-emission scanning electron microscope (FESEM) which is JOEL JSM 6701F. All the measurements were done in the room ambient.

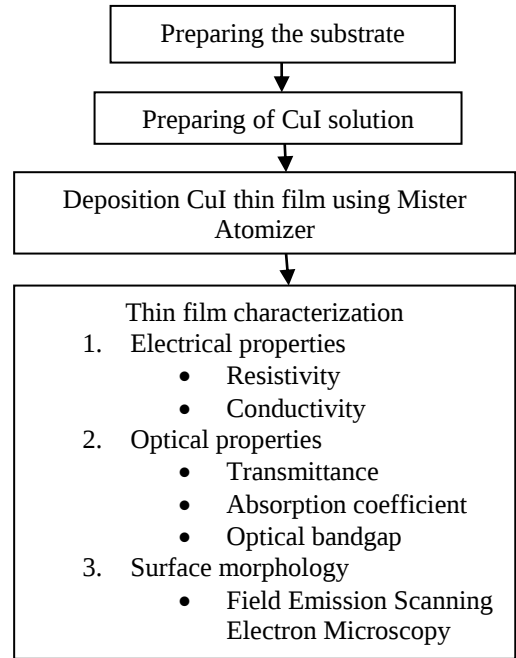


Fig. 1: Flowchart of the project development

III. RESULTS AND DISCUSSION

A. Electrical Properties

The electrical properties of CuI thin film were analyzed by I-V measurements performing of the thin films. In order to measure the I-V characteristics, metal contact was being deposited on CuI thin films. In this research, gold (Au) was used as the metal contact. The reason gold was used because gold is the standard metal contact used as finishing electrode on samples. This is due to it forms a good ohmic contact [8]. The I-V measurement was done using two points probe by using solar simulator (CEP 2000). The measurement was carried in two conditions which are dark and under illumination. From the I-V measurement, the entire samples exhibit an ohmic contact as linear curve is obtained in all the films. In the electrical properties, the resistivity and conductivity were obtained from the measurement of current. The thickness of the CuI with different doping concentration was shown in Figure 2. The thickness will decrease with the increasing doping concentration. The highest thickness 553.82 nm and decrease to 224.24nm. From the current measurement and thickness the resistivity (ρ) and conductivity (σ) of CuI thin films were calculated using this equation:

$$\rho = \left(\frac{V}{I} \right) \frac{wt}{l} = \frac{1}{\sigma} \quad (1)$$

Where V is applied voltage, I is a current measurement, t is the thin film thickness, w is the electrode width and l is the length between electrodes.

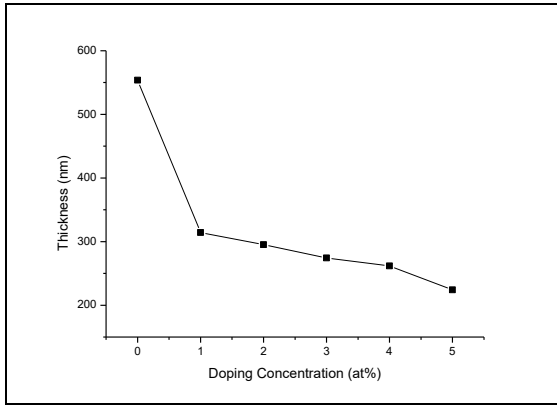


Fig 2: Thickness of CuI thin film with different doping concentration.

The thickness of the thin films can affect resistivity and conductivity. It is because the movements of the electron will be difficult if the thin film is too thick [6]. Figure 3 shows the resistivity of the CuI thin film with different doping concentration. The highest resistivity is at 3at% where are 1.03×10^3 cm in dark and 9.51×10^2 cm in the illumination. Then the lowest resistivity is at 4at% where 1.44cm in dark and 1.43cm in illumination. M.Z. Musa et.al conducted studies on examining the effects of cobalt doping concentration on the structural, electrical, and optical properties of titanium dioxide thin films. They found that the electrical resistivity of the thin films appears to be decreasing with the increase of doping concentration [11]. From the Figure 3 the best electrical resistivity is at 4 at%. It is believed that the introduction of iodine source into CuI will induced oxygen vacancies sites which are known to act as donor to increase the free electron concentration in the thin films.

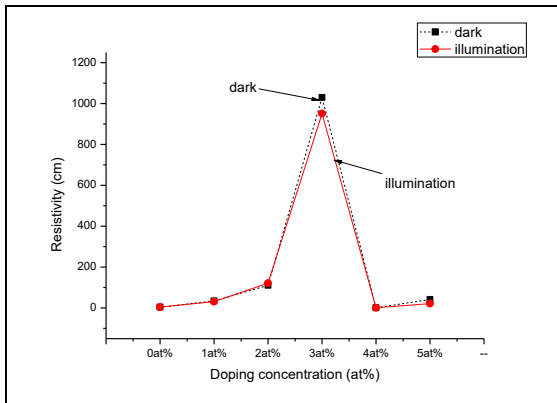


Fig 3: Resistivity of CuI thin film with different doping concentration in dark and illumination

Figure 4 shows the conductivity of CuI thin film with different doping concentration. The conductivity is inversely related to the resistivity. The best conductivity is at 4at% with 6.94×10^{-1} S.cm in dark and 6.98×10^{-1} S.cm in illumination since it has less resistivity. It means that at the doping concentration of 4at% is the best sample because when resistivity less, the defect is also less so that electron easy to move from the valence band to the conduction band. To

support this, the bandgap energy will be present in the optical properties section.

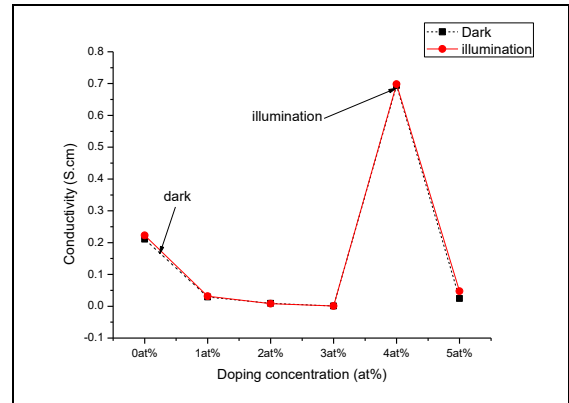


Fig 4: Conductivity of CuI thin film with different doping concentration in dark and illumination

B. Optical Properties

The glass substrate is preferred especially for the optical properties measurement because glass substrate is the good optical transmission. The measuring thickness and transmittance was a very important thing in the calculation of the bandgap energy (E_g) and absorption coefficient. So, in the optical properties the transmittance, absorption coefficient and bandgap energy were related together. Figure 5 and 6 show the transmittance of CuI thin film with different doping concentration of iodine. The graph will divide by two because the value of the range is not same. Graph 5 shows the transmittance of 1at%, 2at% and 3at%. Then graph 6 shows the CuI (0at %), 4at% and 5at%. The result of the transmittance spectra is at high transparency which is at 71% - 90% nm. The high transparency of the transmittance of the thin film is suitable for the electric device such as solar cell [4].

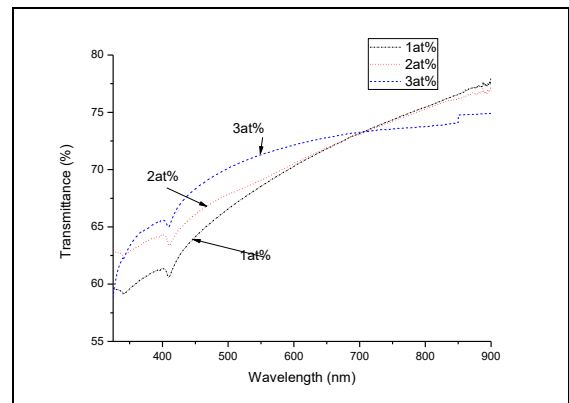


Fig 5: Transmittance spectra of CuI thin film at 1at%, 2at% and 3at%

From the measurement of the transmittance and thickness the absorption coefficient (α) will be defined using following formula:

$$\alpha = \frac{1}{t} \ln \frac{1}{T} \quad (2)$$

where t is the thin film thickness and T is the transmittance.

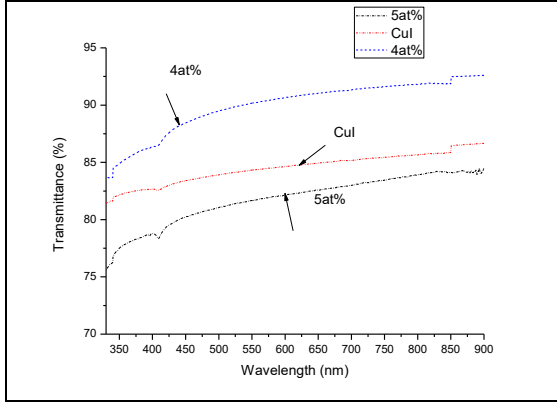


Fig 6: Transmittance spectra of CuI thin film at 4at%, 5at% and 0at% (CuI)

Figure 7 and figure 8 show the absorption coefficient, α that have a high absorption which is 10^6m^{-1} . The absorption coefficient exhibits that the measurement on how far the light can be penetrated inside the thin film before it was absorbed. The higher absorption coefficient is the better light that absorbed in the thin film. From the result, it can conclude that the higher transmittance is the lowest of the absorption coefficient. The result indicates that at the 410nm of the wavelength it is observed a hump. The hump was being observed may be due to excitation of electrons from sub bands in the valence band to the conduction band [6].

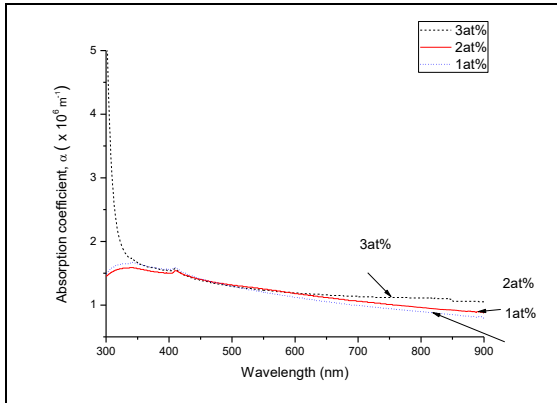


Fig 7: Absorption coefficient for 1at%, 2at% and 3 at%

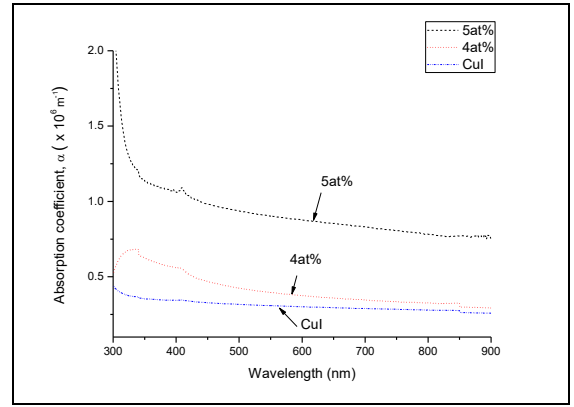


Fig 8: Absorption coefficient for 4at%, 5at% and CuI

The optical bandgap energy, E_g of CuI thin film was calculated from the optical absorption and transmittance studies. The relationship between absorption coefficient, α the indicate photon energy $h\nu$ is given by following formula:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (3)$$

where A is constant and E_g is the bandgap energy. The $(\alpha h\nu)^2$ vs photon energy for the CuI thin film with different doping concentration of iodine are presented in figure 9,10 and 11. The optical bandgap, E_g can be determined using Tauc's plot by extrapolating the linear curve to the photon energy axis [10].

The value of the optical bandgap varied between 2.55 and 2.73 eV shown in the Table 1 is taken from the linear portion of the curve. The optical bandgap of CuI slightly increase as atomic percent (at%) doping concentration of iodine increase to 3at% but it decreased after it. Mostly the reported bandgap energy of CuI thin film is 3.1 eV [3]. The energy bandgap was show lowest from 3.1 eV because the CuI was doped with the iodine. The doping concentration of iodine will affect the bandgap energy of the CuI thin film. However the different measured value of bandgap maybe because the thickness of the thin films that depends on the deposition process [6]. The small value of bandgap was good for a device such as a solar cell. It is because the surface energy of the thin film was high so that the electron easy to move.

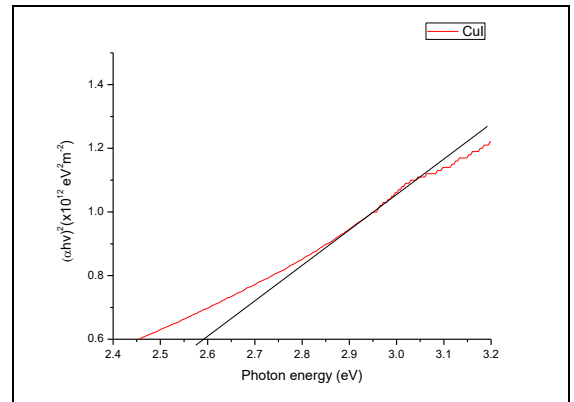


Fig 9: the optical bandgap of CuI as reference

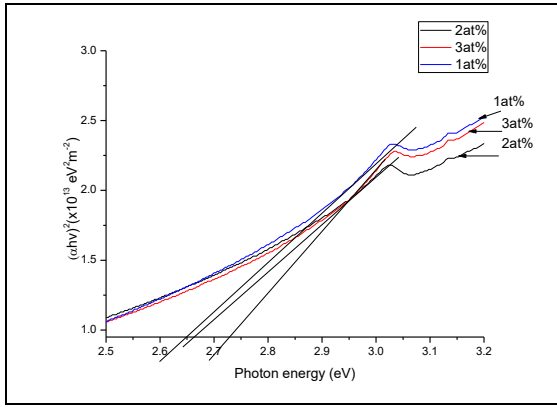


Fig 10: The optical bandgap of 1at%, 2at% and 3at%

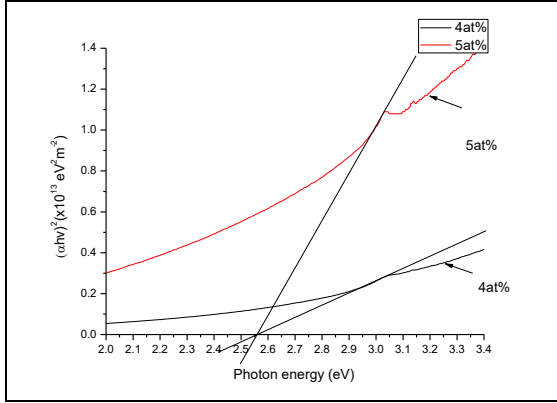


Fig 11: The optical bandgap of 4at% and 5at%

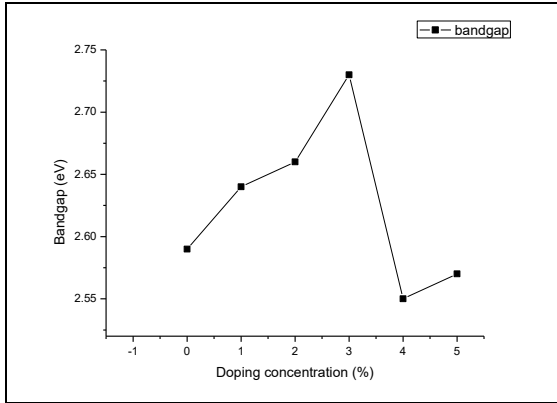


Fig 12: Optical band gap estimation of CuI thin film with different doping concentration of iodine using Tauc's plot

TABLE 1: BANDGAP ENERGY OF CUI THIN FILM WITH DIFFERENT DOPING CONCENTRATION OF IODINE

Atomic percent (at%)	Bandgap (ev)
CuI	2.59
1at%	2.64
2at%	2.66
3at%	2.73
4at%	2.55
5at%	2.56

C. Surface morphology

The surface morphology of the CuI thin film was observed by using Field Scanning Electron Microscopy (FESEM). Figure 13 shows the CuI thin film with different doping concentration were deposited on the glass substrate at (a) CuI 0at%, (b) 1at%, (c) 2at%, (d) 3at%, (e) 4at%, (f) 5at%. All the measurement is taken at 5kV with 100K magnification. The FESEM images show that the presence of CuI nanoparticles combined together and formed a thin film. FESEM image uses to analyze the surface morphology of the thin film and to determine the accurate size of the morphology that deposited on the thin film. From figure 13, it is noticed that the CuI thin film looks like particle with nm size. The particle size evaluated from FESEM was at 25nm to 90 nm range. From the FESEM image, it can be said that the particle size of CuI thin film was uniform deposited on the glass substrate. Uniformity of the particle size across the thin film is crucial since the particle size greatly affects the electrical conductivity of the film [7].

The elemental composition of CuI thin films as studied by energy dispersive X-ray (EDX) spectrum shown in figure 14 indicated that the thin film exhibit electron distribution of orbital state of copper and iodine.

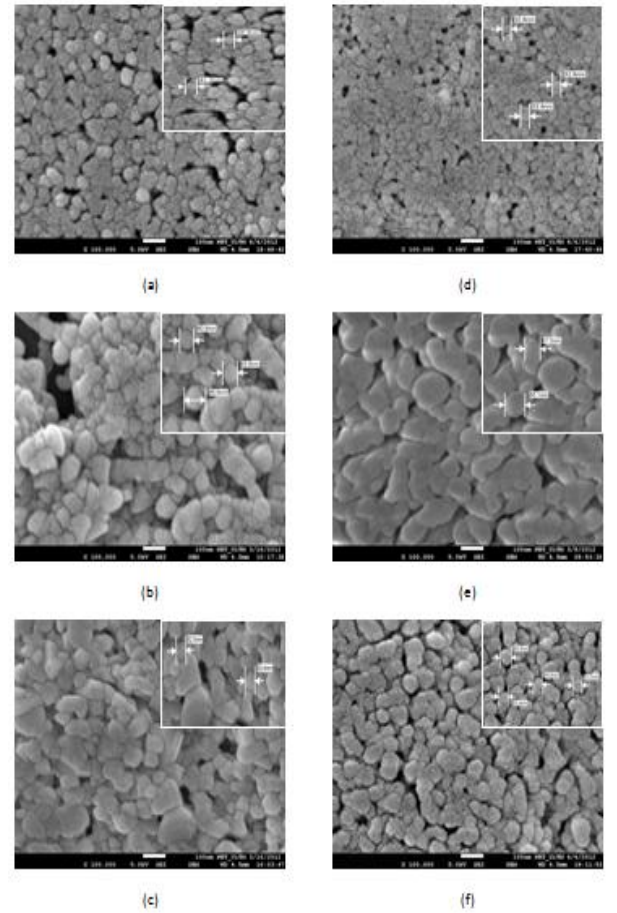


Fig 13: FESEM image of CuI thin film at (a) 0at%, (b) 1at%, (c) 2at%, (d) 3at%, (e) 4at%, (f) 5at%.

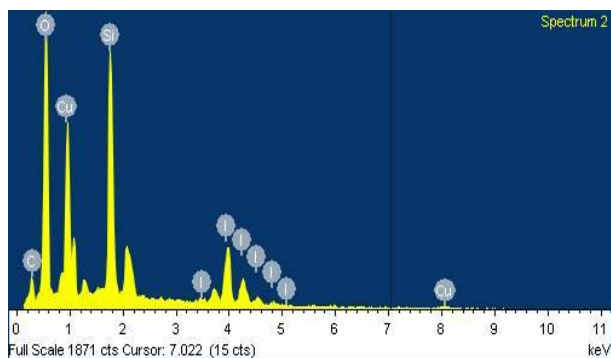


Fig 14: the EDX spectrum of CuI thin film

IV. CONCLUSION

CuI thin films have been successfully deposited by using mister atomizer and were doped with iodine at the different value of atomic percent. The thickness of CuI thin films deposited on glass substrates is about 553.82 nm and decrease to 224.24 nm. The I-V measurement shows the highest resistivity is at 3at% and the lowest resistivity is at 4at%. Then the best conductivity is at 4at%. The deposition CuI thin film exhibited optical transmittance is at 71% - 90% nm in the wavelength 300 – 900 nm. Then, the absorption coefficient (α) also has a high absorption which is 10^6m^{-1} . The optical bandgap of CuI thin film was measured is between 2.55- 2.73 eV. This result was supported by surface morphology of the film. Based on FESEM result, the CuI thin film showed in nanoparticle size. As a conclusion, the electrical properties, optical properties and surface morphology of CuI thin film could be affected by changing the atomic percent (at%) the doping concentration of iodine. In order to improve the capability and effectiveness of this research, this work can be extended by using other substrate such as silicon or Indium Tin-Oxide (ITO) instead of glass.

ACKNOWLEDGMENT

I would like to express my gratitude and appreciation to my co-supervisor Assoc. Prof. Eng. Dr. Mohamad Rusop and my supervisor Mrs. Norulhuda Abd Rasheid for all the guidance, support and advice provided to me throughout the study for the completion and success of this project. Then I also like to extend my gratitude and appreciation to Miss Amalina for her comment on this paper and also her idea to support me to finish this paper.

I would like to take this opportunity to express my appreciation to my family and friends for give a lot of support until finish my study. May ALLAH SWT bless all of you and thank you so much.

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