Preparation and Characterization of Post-Doped CuI:I Thin Films

Norhafizah Binti Abu Bakar
Faculty of Electrical Engineering
Universiti Teknologi MARA 40450
Shah Alam, Selangor
Email: norhafizah1506@gmail.com

Abstract— **The undoped and iodine doped CuI thin films with diffirent doping concentration were synthesized by using mister atomizer technique. The CuI solutions were prepared using CuI powder with acetonitrile as a solvent. The quantity of iodine was varied with 10, 20, 30, 40 and 50 mg. The results are observed on the properties of surface morphology, electrical and optical. The surface morphology characterized by FESEM revealed that the microstructure of CuI films depended on the relative amount of doping iodine in the solution. The surface morphology in the presence of iodine was closely packed spherical CuI grains. The resistivity of about 10^3 Ω cm^{-1} is observed in those CuI thin films. The optical transmittance was 0.2%-2.4% at various doping concentration. The result indicates that all CuI films exhibit low transmittance in the visible region than in the near infra- red region. The optical band gap was recorded between 2.14 eV to 2.96 eV. The PL intensity peaks was observed at 420 nm, between 680 to 685 nm and between 835 to 840 nm. The nature of the photoluminescence is discussed.**

Keywords: Copper (I) Iodide; Mister Atomizer; FESEM; Electrical; Optical

I. INTRODUCTION

Recently, CuI has been used to construct fully solid- state DSSC [1]. Tennakone et al. reported that CuI was used as a hole- collecting agent in a solid- state DSSC [2]. There are many reports regarding the preparation and characterization of CuI films with several deposition techniques. T. Tanaka et al. studied the electrical and optical properties of CuI thin films deposited by magnetron sputtering technique [3]. CuI films deposited by pulse laser have been studied by P. M. Sirimanne et al [4].

CuI has unique features such as larger band gap about 3.1eV with an exciting binding energy of 62mev which is larger than the mean thermal energy at room temperature of 25meV [5]. CuI is an inorganic p- type semiconductor material with has a negative spin orbit splitting, anomalous diamagnetism behavior, unusually large temperature dependency and new high pressure phases [6, 7]. Besides that, CuI also has a great potential for application in electronic devices [6, 8].

CuI is a water insoluble solid with three crystalline phases α, β and γ. The α phase is a cubic structure with high temperature of 392˚C while the β phase is an ionic conductor with temperature between 392˚C and 350˚C. The low temperature below 350˚C is a γ phase behaves as a p- type semiconductor with zinc blend cubic structure [6, 7]. Due to intense radiative recombination of excitons and its unique properties of γ phase, CuI is a promising material for the production of semiconductors lasers, light emitting diodes (LEDs) and field emission display [8, 9].

In this study, CuI thin films will be deposited by using spraying technique with a system called as mister atomizer. This technique is the same concept of spray pyrolysis which use atomizer to convert the liquid solution into the form of mist. This deposition method produce the uniform distribution of diameters and controllable and purity of the products produce is high [8, 10]. Meanwhile, the cost is inexpensive since no vacuum condition needed and able to give high production rates [8, 10]. The precursors for spraying technique that most commonly used for an inorganic compound are nitrates, carbonate, sulfate and chloride [11]. The significant parameters in the spraying technique are gas flow rate, doping concentration, deposition time and substrate temperature. Doping concentration is important as it influences the film morphology, electrical and optical properties.

Therefore, in this present work it will be focusing to investigate the doping concentration on the structural, electrical and optical properties of CuI thin films. CuI thin films were doped with iodine at concentrations of 10, 20, 30, 40 and 50 mg. Tennakone et al. reported that CuI doping with iodine show the excess iodine molecules present in CuI diffused to the CuI surface and created surface hole traps that mediated recombination [2]. Moreover, excess iodine in the CuI acts as an acceptor of electrons from the valence band to attributed p-type conductivity [2]. Meanwhile, the undoped CuI exhibits p-type conductivity since the dominant intrinsic defects are acceptor type copper vacancies that formed due to excess iodine in the crystal lattice [5].

II. METHODOLOGY

A. Sample preparation

The glass substrate was cleaned by using acetone, methanol and deionized water in the ultrasonic cleaner. The cleaning process was done stage by stage at 10 minutes and the glass substrate was dried by using Argon gas. CuI solution is then were prepared by mixing CuI powder with acetonitrile as a solvent and the solution was stirred in 3 hours at room temperature. The glass was deposited with 50 ml of CuI solution. Argon gas was used as a carrier gas during deposition process. This process takes about 2 minutes for solution to complete sprayed. The film then is heated at 150˚C in 10 minutes to evaporate the solvent.

After that, CuI films were doped with iodine at doping concentration of 10mg, 20mg, 30mg, 40mg and 50mg by using Chemical Vapor Deposition (CVD) technique. The types of CVD was used is Atmospheric Pressure CVD (APCVD). In order to reduce the sample contamination, the CVD equipment should be cleaned with acetone before using it. There are two furnace namely furnace 1 and furnace 2. Iodine was placed at the furnace 1 while CuI sample was placed at furnace 2. Then, the process must wait within 5 minutes in order to make sure there is only an argon gas in the furnace. The heat of furnace 2 must switch on first until its temperature achieve at 150˚C. The heat of furnace 1 was switch on after heat of furnace 2 achieved that temperature. Then, the process must wait within 10 minutes when heat of furnace 1 was at 100˚C. After 10 minutes, both of furnaces were switch off.

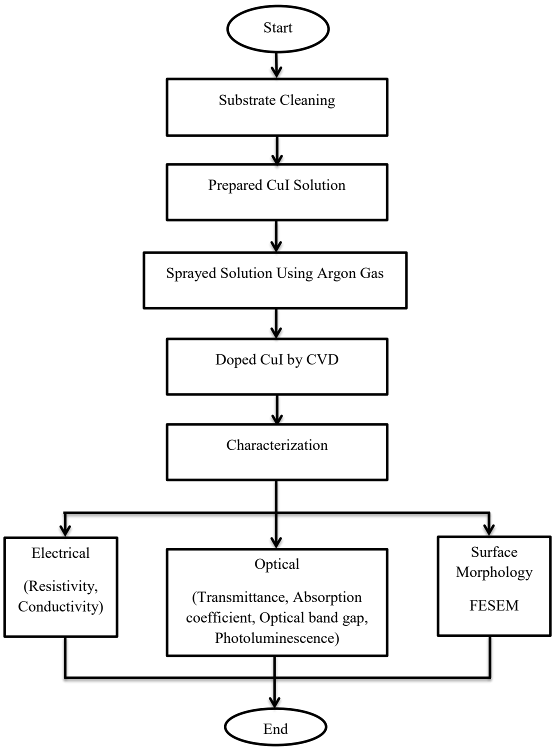

Figure 1. Flowchart of preparation CuI thin films

B. Characterization technique

The characterizations were done for its surface morphology, electrical and optical properties. Surface morphology was observed with a Field Emission Scanning Electron Microscope (JEOL JSM-7600F). The two point probes were used to measure the resistivity of the sample by using solar simulator. Gold was used as metal contact for I- V measurement and it was deposited by using sputter coater (EMITECH K550X). Meanwhile, the optical measurements of the films were characterized by JASCO UV- VIS- NIR spectrophotometer. The wavelength for the optical measurement was measured at wavelengths between 400nm until 1000nm. Apart from optical properties, photoluminescence also measured by using CDRH Microscope Enclosure (HORIBA JOBIN YVON). The photoluminescence was measured between the wavelengths 350nm until 900nm.

III. RESULTS AND DISCUSSION

A. Surface Morphology

The surface morphology of CuI films was observed using Field Emission Scanning Electron Microscopy (FESEM). All measurements were taken at 5 kV with 30K magnifications. Figure below shows the CuI films deposited on the glass substrate at (a) 0, (b) 10, (c) 20, (d) 30, (e) 40 and (f) 50 mg. From the figure, it can be seen that the morphology of CuI films with particles in nm size in the range between 96 to 198 nm.

From the Fig. 2, it could be understood that an addition of a trace amount of iodine significantly influences the shape of the CuI grains. Closely packed CuI grains are obtained in the presence of iodine in doping CuI thin film. The surface of undoped CuI film (Fig. 2a) is continuous with a uniform distribution of larger faceted grains. When doping concentration at 40 mg of iodine, the grain sizes apparently increase. However, at 50 mg of iodine, the grain size was slightly decreased.

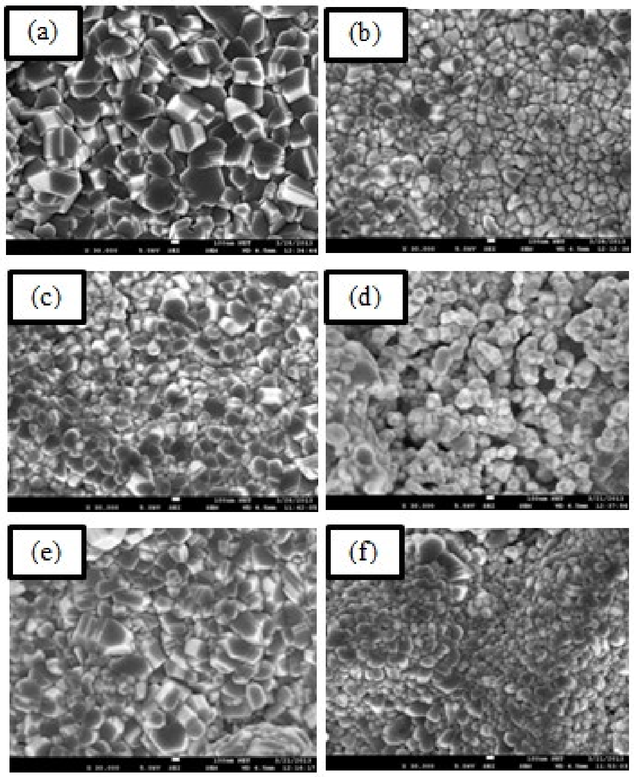

Figure 2. FESEM images of CuI thin films at (a) 0, (b) 10, (c) 20, (d) 30, (e) 40 and (f) 50 mg

B. Electrical Properties

The electrical properties was studied in this work are resistivity and conductivity of CuI thin films at different doping concentration by using mister atomizer deposition technique. The current voltage measurements (I-V measurements) of the CuI thin films at different doping concentration were measured under dark condition at a room temperature. The applied voltage was at -5V to 5V. The equation of the resistivity, ρ and conductivity, σ of CuI thin film is shown in equation (1):

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

Where V is supplied voltage, I is measured current, t is the film thickness, w is the electrode width and l is the length between electrodes. Fig. 3 showed the I-V curves of CuI films at various doping concentrations. The I-V curves show straight line characteristics and indicate that the contacts are ohmic between the semiconductor and the metal.

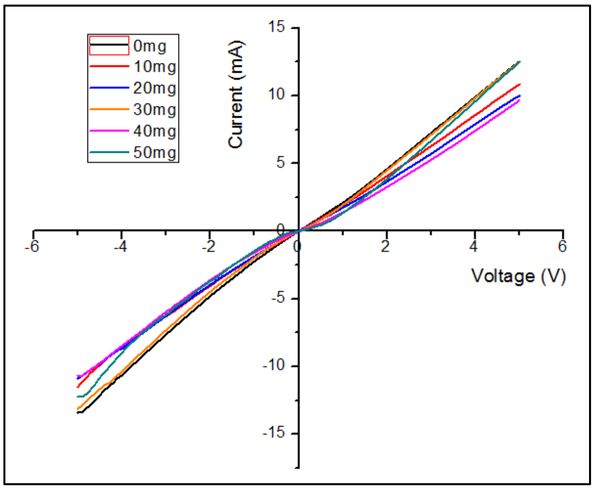

Figure 3. I-V curve of CuI films at various doping concentrations under dark condition

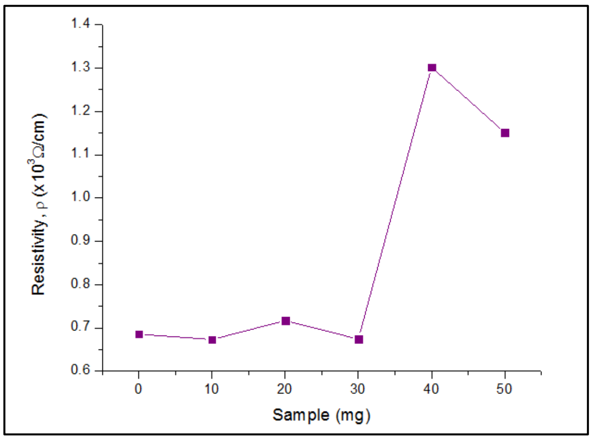

Figure 4. Resistivity of CuI thin films at various doping concentrations

Fig. 4 shows the resistivity of CuI films at various doping concentrations. The lowest resistivity is 6.73 x 10^2 Ωcm^{-1} at 10 mg of iodine doping concentrations and the highest resistivity is 1.3 x 10^3 Ωcm^{-1} at 40 mg of iodine doping concentrations. Basically, a high carrier concentration will result in lower resistivity but higher grain boundary scattering will cause higher resistivity [13]. When the grain boundary is increase, the carrier mobility is decrease. The low resistivity at 50mg of iodine may be due to the less carrier scattering attributed from less grain boundaries as shown by the FESEM image. Hence, the carrier mobility of CuI atoms was enhanced.

An excess of iodine concentrations in the lattice had created a charge trapping layer of electron. The low carrier mobility that contributed to the high of resistivity was caused by the surface traps in the lattice from the excess of iodine act as a recombination. Therefore, the increase of resistivity at 10mg to 40mg is probably caused by the lower carrier mobility which attribute by surface traps induced by iodine [12].

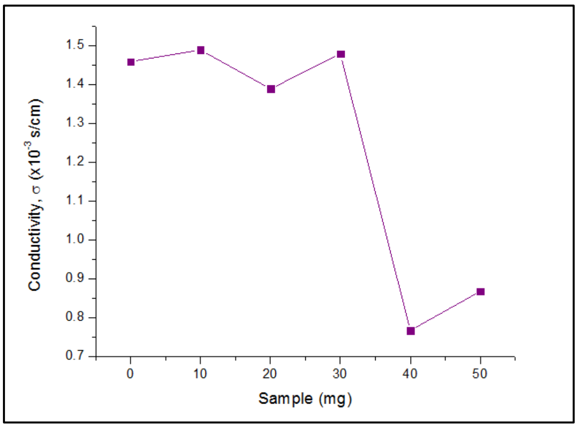

Figure 5. Conductivity of CuI thin films at various doping concentrations

Fig. 5 shows the conductivity of CuI films. At 40 mg of iodine concentrations, it can be seen that the conductivity is lower with the value of 7.68 x 10^{-4} Scm^{-1}. This lower conductivity may be due to the poor contact between the metal and the thin film which is caused by high surface roughness. [14].

C. Optical Properties

The effect of doping iodine concentrations on the optical transmittance of CuI thin films is presented in Fig. 6. The transmittance spectra were measured between the wavelengths of 350 to 1000 nm. The results indicates that all CuI thin films exhibit low transmittance in the visible region than in the near infra- red region (NIR).

It can be seen that the optical transmittance of CuI thin films decreases with increasing doping concentrations. The decrease of transmittance at higher doping level is probably attributed to the increased scattering of photons by the crystal defects created by doping [15]. The decreasing in the optical transmission of heavily doped films may also attributed by the free carrier of the photons [15]. The highest transmittance was recorded at 10 mg of doping concentrations and the lowest transmittance was recorded for CuI films with 40 mg of iodine concentrations. However, 40 mg of iodine concentrations was the highest absorption compared with 10mg of iodine concentrations.

The absorption coefficient can be determined by the measurement of the transmittance. Absorption coefficient equation obtain by using Lambert's law is shown in equation (2) where T is the optical transmittance and t is the film thickness.

$$\alpha = \ln(T)/t \qquad (2)$$

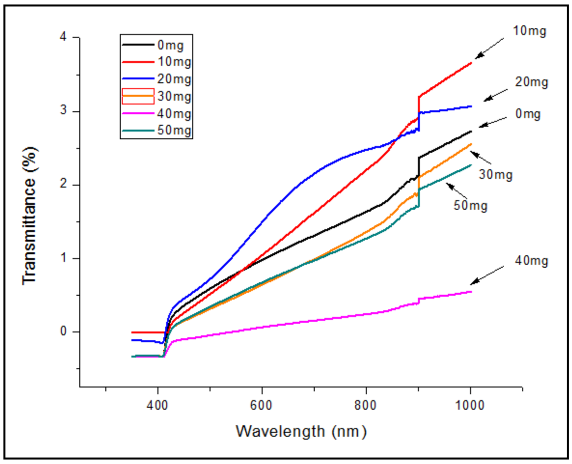

Figure 6. Transmittance spectra of CuI thin films at various doping concentrations

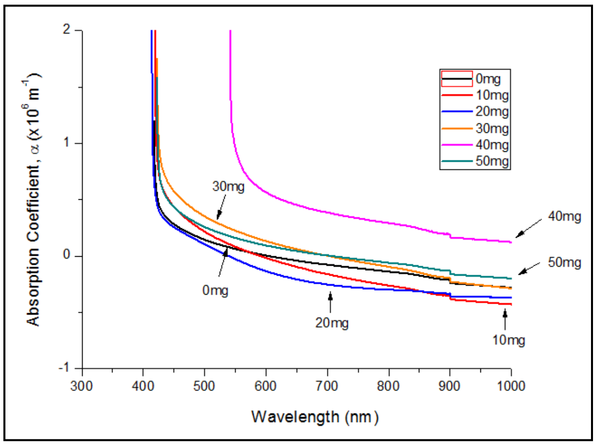

Figure 7. Absorbance coefficient of CuI thin films at various doping concentrations

TABLE I. BANDGAP ENERGY OF CUI THIN FILMS AT VARIOUS DOPING CONCENTRATIONS

Sample (mg)	Bandgap (eV)
0	2.92
10	2.96
20	2.94
30	2.88
40	2.14
50	2.92

The optical band gap can be determined by using Tauc's Plot. The relation of direct band gap energy with the absorption coefficient and photon energy is given by equation (3) where A is constant and $h\nu$ is the photon energy.

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

The direct band gap energy of the CuI films was recorded between 2.14eV to 2.96eV at various doping concentrations as shown in Table 1. It can be seen that the optical band gap energy was decreased as the dopant concentrations increased. The decreased in the band gap at 10 to 40 mg of iodine concentration may probably cause by the increasing in the grain size [12].

However, at 50 mg of iodine concentrations, the optical band gap was increased. The increased in optical band gap energy can be attributed in terms of Burstein- Moss effect where the increase in the carrier concentration affects considerably the low energy transitions [15, 16]. This gives rise to an increase of the Fermi level in the semiconductor conduction band leading to a widening of the optical band- gap [15, 16].

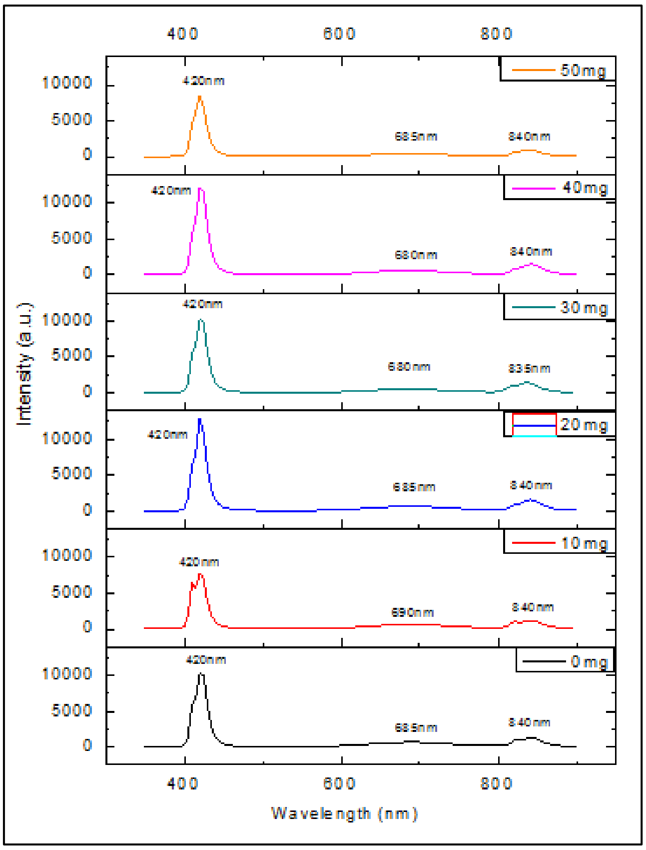

Figure 8. Photoluminescence of CuI thin films at various doping concentrations

Fig. 8 showed that the photoluminescence at various doping concentrations. The emission properties of CuI are strongly affected by the coordination environments, surface states and dopant substances [17]. There is an intensive emission at 420 nm, a broad emission between 680 to 690 nm and an additional weak emission between 835 to 840 nm. Perera and Tennakone reported that a CuI film exposed to iodine vapor shows a strong fluorescence when the film is irradiated with light of wavelength λ<CuI band gap radiation (~400 nm) [2]. In this result, the peak located at 420 nm (2.952eV) was attributed to the surfaces states associated with excessive iodine. On the other hand, various research groups have studied the luminescence of CuI. It was found that, the emission peak observed at 420 nm may be due to the recombination of electrons excited into the defect status below in the conduction band of CuI samples with holes in the valance band [4].

The broad emission between 680 to 690 nm is much lower than 420 nm emission peak due to the trapping of holes at CuI surface sites. This emission also cause of recombination for this film [18]. The weak emission located at near infra- red region which is between 835 to 840 nm may be due to the oxygen vacancies [19].

IV. CONCLUSION

The CuI:I were synthesized by using the mister atomizer technique at various doping concentration. The surface morphology characterized by FESEM revealed that the microstructure of CuI films depended on the relative amount of doping iodine in the solution. The CuI thin films show an ohmic behavior with gold as the metal contact. The highest resistivity was shown for films at 40mg doping concentration. This result is related with surface morphology where the grain scattering also cause the higher resistivity. However, the highest resistivity will cause the lowest conductivity. Then, for the optical properties, the band gap for CuI films was decreased as the dopant concentrations increased due to the grain size of particles. Then, the optical band gap was increased at 50mg of iodine concentration due to the Burstein-Moss effect. Photoluminescence was observed for undoped CuI and doped CuI thin films. The PL intensity of CuI was exhibited with three emission peaks at 420 nm, between 680 to 690 nm and between 835 to 840 nm, which cause by recombination and oxygen vacancies in the CuI sites.

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