Influence of Annealing Temperatures on Properties in Chelate Based CuI Thin Films

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Abstract— Copper(I) iodide (CuI) has received considerable scrutiny as a hole transport material in solid-state dye-sensitized solar cells (ss-DSSC), amidst challenging issues such as rapid crystallization, pore filing, and dye desorption. This paper would attempt to study the influence of heat on various properties of CuI thin film in the presence of chelating agent tetramethylethylenediamine (TMEDA) in the CuI precursor solution at fixed CuI:TMEDA molar ratio of 1:1. Although heat did not seem to alter the morphology of the thin film, slight broadening was observed in the diffractogram peaks which suggested reduction in particle size. Photoluminescence (PL) spectra for all the samples which were annealed below 80 $^{\circ}$C were red shifted which suggested than some of the absorbed energy has been lost most likely due to non-radiative emission usually caused by deep space traps. In other word, this finding also suggest that an optimum heating temperature would mend the material's internal structure leading to fewer formation of deep space traps normally associated with the presence of internal stress in the material. At an optimum annealing temperature of 80 $^{\circ}$C, thin film resistivity fell from 6.2 Ω.cm to 4.7 Ω.cm and achieved a remarkable conductivity of 165 S/cm^2. These remarkable findings seems to be in accord with our argument that CuI-TMEDA complex could find its application as a hole transport material (HTM) in ss-DSSC.

Keywords— dye-sensitized solar cells; tetramethylethylenediamine; copper(I) iodide; chelating; annealing

1. INTRODUCTION

Copper(I) iodide (CuI) which is also known as cuprous iodide is water insoluble, inorganic polymorph which normally assumes several crystalline structures depending on its temperature; α-CuI phase at temperatures above 392 $^{\circ}$C, β-CuI phase in the temperature range between 350 and 392 $^{\circ}$C, and γ-CuI phase at temperature below 350 $^{\circ}$C. The low-temperature (γ-CuI) phase adopts the zinc blend structure with four I$^-$ anions coordinated to the central Cu$^+$ cations in tetrahedral arrangements. This p-type semiconducting material has a wide band gap of 3.1 eV, and its conductivity came from excess iodine atoms which creates holes by accepting electron [1, 2]. This versatile material has find its use in various applications such as in the catalytic system for the synthesis of organic compunds [3], biological application [4, 5], construction of metal organic frameworks [6], as well as hole transport material (HTM) for use in solid-state dye-sensitized solar cells (ss-DSSC) [7, 8] which will be the subject of this study.

Among the challenges faced by previous researchers was the issue of rapid crystal formation in CuI during heat treatment. The formation of large CuI crystals would reduce the available surface area for dye attachment, and created microscopic voids or large empty pores which resulted in nonuniform dye coverage. In an effort to address this issue, ligand substitution have been attempted by reacting metal halide solution such as CuI with another complex substance acting as ligand donor complexes. This has been demonstrated with varying success though inadequately discussed in terms of coordination chemistry [9, 10]. Kumara et al. had demostrated that rapid crystallization in heated CuI sample could be quenched by adding molten salts which melted in room temperature such as 1-ethyl-3-methyl-imidazoliumthiocyanate (MEISCN) and triethylaminehydrothiocyanate (THT) into

the CuI precursor solution, which could effectively inhibit large crystal formation. The best efficiency of 3.75% had been reported for cell fabricated with CuI and THT [11, 12]. Despite this impressive results, slow decay in photocurrent and voltage were observed in both cases, which suggested the need to find a better alternative. Moreover, the synthesis of MEISCN would require complex purification process and higher cost. This paper will attempt to demonstrate the use of tetramethylethylenediamine (TMEDA) which would be introduced into the CuI precursor solution as chelating agent. Unlike other binding agents which usually form a single dentate ligand to metal halide compound, chelating agent binds to CuI through bidentate ligands to form a stable halogen dimer [13, 14].

The use of TMEDA in CuI precursor solution was first demonstrated by Zainun et al. when they investigated the effect of chelation on size and conductivity of CuI particles [15]. To the best of author's knowledge, the effect of different heat treatment has never been discussed before. Therefore, it would be interesting to see the effect of different annealing temperature on structural, optical, and electrical properties of the CuI-TMEDA thin film.

2. EXPERIMENTAL PROCEDURE

A. Prepare CuI Precursor Solution

All the supplied chemicals were used as they were received without additional purification. The CuI and TMEDA concentrations were kept constant throughout the study. The study of the effect of different heat treatments on the properties of CuI-TMEDA complex (from here on referred as chelate complex) began with the synthesis of CuI particles from acetonitrile solution. Copper(I) iodide powder, white with slightly pale brown color (Sigma-Aldrich 98%) was dissolved in 50 ml acetonitrile solution to yield a concentration of 1.0 M and mechanically stirred without heating at 100 rpm initially, and the speed was gradually increased up to 450 rpm. Note that CuI only dissolve moderately in acetonitrile, so white solids of undissolved CuI would remain in the solution. After three hours of continous stirring, the solution turned from clear to pale-green and slightly yellow color and ready for chelation. The solution was poured into different container to separate the liquid from the undissolved solids, and left undisturbed for 30 min to let any remaining solids settled to the bottom.

B. Prepare Chelate Complex for Deposition

For the purpose of studying the effect of different annealing temperature on chelate samples, an equimolar amount of TMEDA (Sigma-Aldrich 99%) was added drop-wise fashion to the CuI precursor solution prepared as previously mentioned prior to drop coating. Upon addition of TMEDA, the CuI solution turned from yellow and pale-green to dark blue. The solution was stirred again for additional 15 min before deposition onto substrate. Prior to deposition, the ITO glass were cleaned in detergent solution followed by 15 min of ultrasonification in acetone and ethanol respectively before final rinsing with deionized water. The solution was administered using a micro pipet onto the ITO glass (Sigma-Aldrich) preheated to 50 ^{o}C, and air dried at room temperature for five minutes between each successive drops. Each drop contain approximately 0.05 mL of precursor solution, and the substrate would be ready for heating after 10 to 15 drops have been administered. The samples were then annealed in air at different temperatures (50 ^{o}C, 80 ^{o}C, and 110 ^{o}C) for 10 minutes, and subsequently cooled to room temperature.

C. Sample Characterizations

The sample's geometric structure and surface morphology were examined under X-Ray diffractometry (RIGAKU Miniflex II) and field emission scanning electron microscopy (FESEM) (ZEISS SUPRA 40VP). The sample's optical absorbance and emission characteristics were obtained using an ultra-violet visual near-infrared spectroscopy (UV-Vis-NIR) (Shimadzu UV-2600), and photoluminescence spectroscopy (PL) (Edinburgh Intruments). Finally, the electrical properties were measured using two-probe current-voltage (IV) measurement systems which were connected to a potentiostat (PARSAT 2273) and equipped with a solar simulator (ORIEL) as illumination source.

3. RESULTS AND DISCUSSIONS

A. Surface and Structural Characteristics

The field emission scanning electron microscopy (FESEM) image of the chelate sample suggested that chelating with TMEDA could reduce the particle size and prevented formation of large crystals. This was evident from image in Fig. 1(a-c) which showed the surface morphology of the chelate sample after being subjected to different annealing temperatures. All three images showed an almost identical surface structure regardless of the heating temperature which suggested that surface structure was not affected by the different heat treatment. The dense porous structures were uniform but agglomeration was evident from the image which could be caused by the presence of water in the acetonitrile solution which induced coalescence between CuI particles as a result of strong hydroxylic bond which occurred in the drying stage [16]. The tendency of nanoparticles to coalesce and agglomerates could be weaken if dehydrated organic solvents such as anhydrous acetonitrile solution were used instead. The high magnification image of the sample annealed at 80 ^{o}C showed a well interconnected spherical grains having particle sizes in the order of 1 μm.

The peak shifts in all annealed samples were evident in the XRD diffractogram shown in Fig. 2 and its associated crystal planes in Table 1. This strongly suggested that the lattice geometry of chelate samples changed at elevated temperatures. The XRD patterns in all chelate samples also conformed to the standard fcc structure regardless of annealing temperature. The peaks were identified as (111), (200), and (220) which matched well with the characteristic peak of crystalline γ-CuI [17]. This strongly suggested that chelation with TMEDA did not alter the internal geometry of CuI. The presence of other peaks were also identified which could indicate the presence of iodine, nitrogen, carbon, and hydrogen atoms in the organic complex. Broader peaks were observed in heated samples especially the chelated sample at an annealing temperature of 80 ^{0}C. This seemed to suggest that heat treatment toughened the thin films internally and helped to reduce the particle size as well. Further comparison between the XRD patterns of the annealed samples did not reveal any noticeable differences in the number of peaks, as well as large variation in grain sizes.
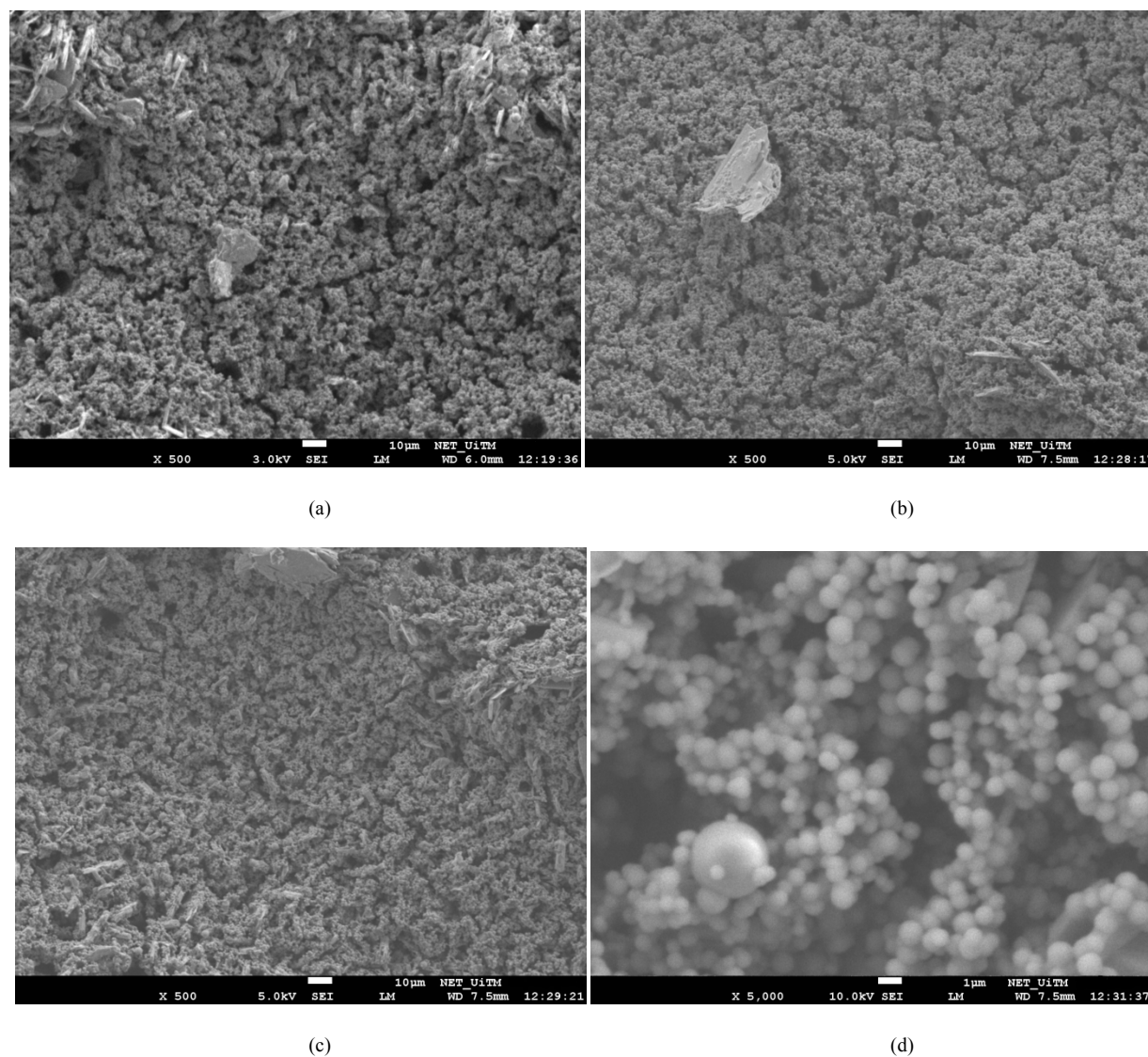
Figure 1: FESEM images of chelate sample at various heating temperature (a) room temperature (b) 50 ^{o}C (c) 80 ^{o}C (d) magnified image of 80 ^{o}C thermally annealed sample.

Table 1: List of crystal planes for XRD diffractogram

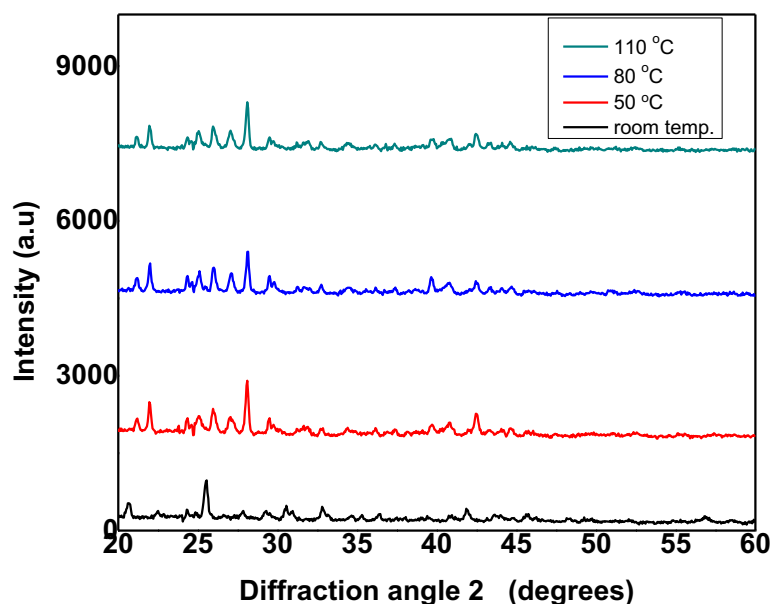| Temperature	2θ Angle, (Crystal Plane)			
room temperature	25.55, (111)	29.12, (200)	41.86, (220)	Others (element of I,N,C,H)
50 °C	24.98, (111)	29.39, (200)	42.47, (220)	Others (element of I,N,C,H)
80 °C	24.59, (111)	29.43, (200)	42.39, (220)	Others (element of I,N,C,H)
110 °C	24.97, (111)	29.40, (200)	41.98, (220)	Others (element of I,N,C,H)

Figure 2: XRD diffractogram (top) and peak listing (Table 1) for chelate samples under different heat treatment

B. Optical Properties

The photoluminescence (PL) action spectra shown in Fig. 3 for all the annealed samples were red shifted relative to the non-annealed sample. It appeared that heating resulted in emission at lower energy photons, which also implied lower bandgap energy. This could suggest that thermal annealing could improve the internal structure and relieve the internal stress and defects in the thin film, thereby reducing the energy required to promote an electron across the bandgap [18]. The PL spectra also showed that highest intensity was obtained for sample at annealing temperature of 80 °C, which suggested that insufficient heat treatment would result in formation of trap centers created possibly by solvents left behind as well as the presence of internal stress in the material, which were then manifested as lower intensity in the emission curves. Following heat treatment, more electrons could now return to the valence band upon excitation as a result of less impurities [1].

C. Electrical Properties

Another interesting observation was made in the CuI-chelate samples which were heated at different annealing temperatures. It appeared that heating had also lowered the resistivity of the CuI-chelate samples, and the lowest resistivity of 4.7 Ω.cm was obtained in sample heated at 80 °C which which was evident in Fig. 4. It was very likely that the improved internal structure and the relieved of the internal stress as a result of heat treatment had actually improved the electron and holes mobility inside the bulk material as well as across the heterojunctions.
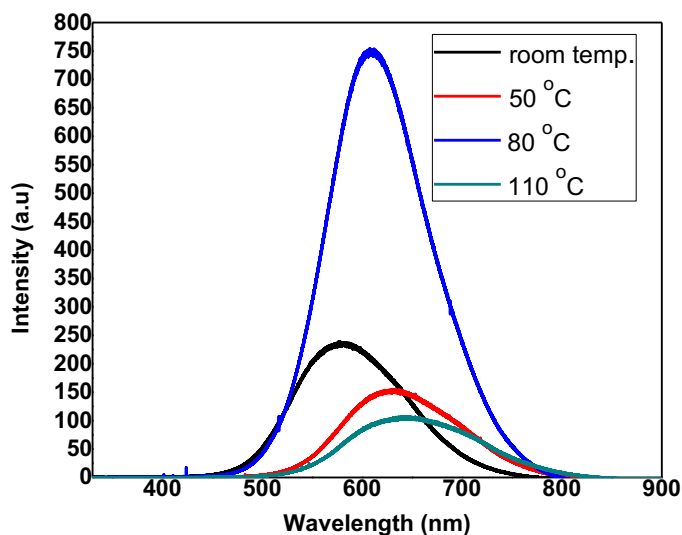
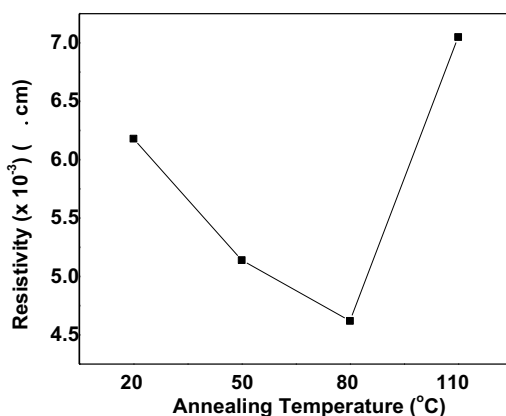Figure 3: Photoluminescence (PL) spectra chelate complex at different annealing temperatures.

Figure 4: Thin film resistivity of chelate samples at different annealing temperatures.

4. CONCLUSION AND RECOMMENDATION

The CuI chelate complex had been successfully prepared by adding TMEDA as chelating agent in the CuI precursor solution. TMEDA bound to CuI through bidentate ligand to form a chelate complex. The FESEM studied had verified that the particle size was in the order of 1 μm. The observed broadening in the XRD diffractogram was in aggreement with FESEM findings which suggested that particle size had been reduced. It appeared also that heating could actually lower the bulk resistance in the chelate sample. All these findings seemed to be in agreement with our argument that TMEDA could find its application as a chelating agent for CuI in the fabrication of an all solid-state dye-sensitized solar cells. Various techniques have been employed to fabricate CuI thin films on glass substrates such as chemical vapor deposition [19], pulsed laser deposition [20], and spin coating [2], but the complexity and cost associated with these techniques seemed to outweigh the benefit that these techniques delivered. This paper had demonstrate that drop coating technique was just as effective and offered a simplified and cost effective strategy when depositing CuI thin films at room temperature.

The CuI should be synthesized via chemical route in order to obtain a pure sample. The sample obtained commercially usually contain minute traces of iron which would affect the analysis to some extent. It would be interesting as well to examine the structural, electrical, and optical characteristics of TMEDA bound to other copper halide molecules such as copper bromide (CuBr).

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