

CuI Film Produced by Chemical Extraction Method in Different Media

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CuI crystalline thin films were produced on substrates (commercial glass) using chemical extraction method in different chemical bath media. In this study, their structural, optical and electrical properties were analyzed. Transmittance, absorption, optical band gap and refractive index of the films were examined by UV/VIS spectrum. XRD data showed that the film has a hexagonal structure for CuI. Surface and elemental (in terms of ratio) analysis of the films were performed via SEM and EDX analysis. The highest average grain size of CuI was observed for the film produced in aqueous media whereas the lowest average grain size was seen in chloroform bath. The curve formed by the number of crystallites per unit area (N) is different than the curves of dislocation density and average grain size. Number of crystallites per unit area has reached its maximum value in CCl₄ bath, but it has been decreased in chloroform bath. In addition, film thickness has varied between 1232 nm and 3624 nm according to the solvent of bath.

Keywords: *CuI films, Chrystal growth, Thin film, Optical properties*

1. Introduction

Copper iodine is a metal halide such as AgI, PbI₂, etc... Similar to AgI, Copper iodine has three crystalline phases α , β , γ ¹⁻⁴. In α -phase, CuI has a cubic structure and it is conductive because of copper ions¹. In β -phase, it has a hexagonal structure and ionic conductivity is observed, whereas in γ -phase, cubic structure with p-type semiconducting has been observed. These phases change with temperature; in the literature it has been stated that CuI is at α -phase up to 392° C, whereas it switches to the γ -phase at below 350° C. CuI shows P-type semi conductivity depending on the excess iodine in its structure and the band gap was determined as 3.1 eV²⁻⁴.

Copper iodine thin films are used in photovoltaic cells, cathodic dye-sensitization and electrolytic methods⁵⁻⁷. Researchers have worked on copper iodine by using different methods, both chemical (in water and ethanol) and physical⁸⁻¹⁰. But nobody has investigated CuI thin films produced via chemical extraction method up to now, so we are unaware of how the bath conditions will impact CuI film structure, as well as its optical and electrical properties. Producing CuI thin film via chemical bath deposition is quite difficult, because copper ions are reduced by iodine, consequently contamination of iodine decreases with the formation of copper iodine.

The aim of this paper is to produce CuI thin film via chemical extraction method and examine its structural and optical properties. In this study, we attempted to show that optical and structural properties of CuI could be controlled by changing the media in which CuI films are produced. Since no one has worked on CuI thin film produced via chemical extraction method, we were unaware of how different bath environment might affect CuI film structure and its optical properties.

2. Experimental

The components of bath were 1 % (w/v) nitric acid, 0.005 M copper nitrate hemi hydrate and 0.015 M potassium iodide. First, 100 mL 0.015 M potassium iodide was prepared as a stock solution using different solvents, namely water, ethanol, CCl₄ and chloroform; then 0.005 M copper ion stock solution was prepared. 10 ml 0.005 M copper nitrate hemi hydrate and 10 ml 0.015 M potassium iodide (each time prepared with different solvents) were put in the beakers. Iodide solutions used in chemical baths were prepared with different solvents. The deposition temperature of chemical baths was 50°C and the deposition time was 4 hours. After taking the films out of the bath, each of them was washed with the solvent forming the base of the iodine solution, in order to get rid of iodine ions that might have been adhered to the surface. Figure 1a shows the production of the films

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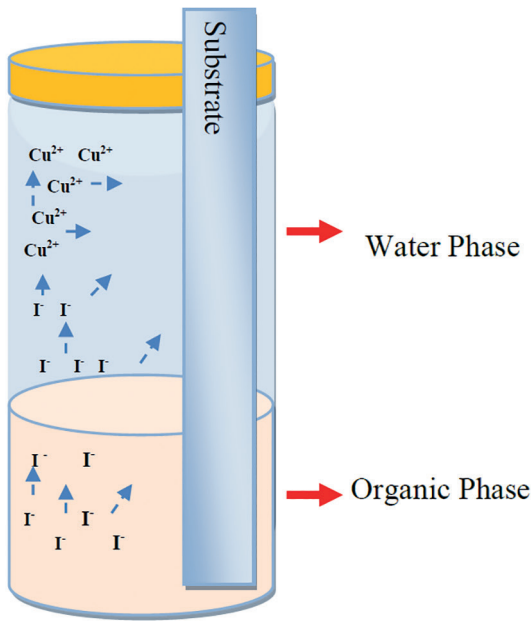


Fig 1. a.

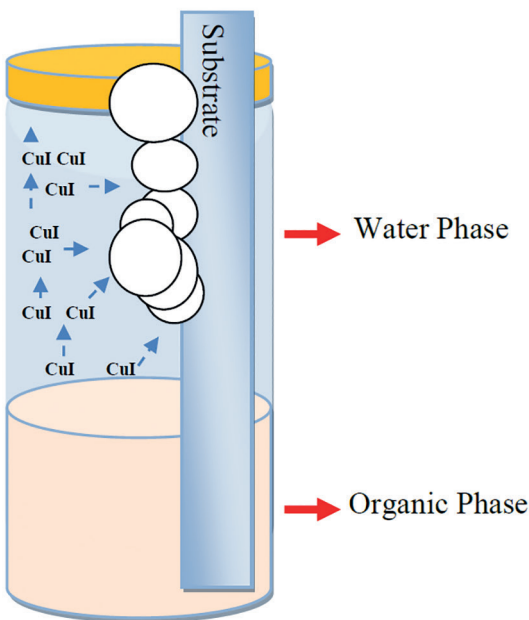


Fig 1. b.

Figure 1: Chemical Extraction Method and Chemical Bath Deposition

via Chemical Extraction Method with organic solvents whereas Figure 1b shows chemical extraction deposition resulted after this process.

The crystalline structure of CuI was confirmed by X-ray diffraction (XRD) with a $\text{CuK}\alpha_1$ radiation source (Rikagu RadB model, $\lambda=1.5406 \text{ \AA}$) over the range $10^\circ < 2\theta < 90^\circ$ at a speed of 3° min^{-1} with a step size of 0.02° . The

surface properties of the films were examined by using an EVO40-LEO computer controlled digital scanning electron microscope (SEM). Film thicknesses were measured with a Veeco Multi Mode AFM (Controller=NanoScope 3D). Thicknesses were measured in a $10 \times 10 \mu\text{m}$ area with tapping mode. The optical measurements were performed by Hach Lange DR 5000 Spectrophotometer at room temperature by placing an uncoated identical commercial glass substrate to the reference beam. The optical spectrum of thin films was recorded at the range of 300-1100 nm wavelength.

3. Results and Discussion

The chemical reactions regarding the deposition of copper iodine films, which occurred in the bath, are shown below. Copper ions (Cu^{+2}) are combined with iodine (I^-) in order to form the insoluble CuI in the bath.



The production of copper iodine was not similar to producing other metal halides, because, the solid iodide formed in the bath was giving a dark red color to the solution. Then, iodide should be separated from copper iodine thin film and should be purified. Accordingly, Iodine ions adhered to the surface of CuI has been removed and the amount of iodine ions was reduced. Thus, performing the production in aqueous media may not always be the right way for thin films where a very good purification is required, of course without damaging the film. We didn't even need to do it because excess iodine was not seen much in chloroform, carbon tetra chloride, and ethanol media. Iodine passes to aqueous media before the equilibrium is established. The main problem was that these solvents might also remove copper iodine thin film from the substrate. Thus, we should decide about which solvent is correct. In other words, the quality of CuI films depends on the media of chemical bath.

XRD patterns of CuI films deposited via CBD in different bath media are presented in Figure 2 and hkl values are presented in Table 1. Structural properties were calculated by Scherrer formula with the following variables; grain size (D), dislocation density (δ), and number of crystallites per unit area (N). Lattice parameters along (220), (102), (200), (103) plane were calculated by using the formulas given below¹¹⁻¹⁵:

$$D = \frac{0.9\lambda}{B \cos \theta} \quad (3)$$

$$\delta = \frac{1}{D^2} \quad (4)$$

$$d^2 = \frac{1}{\frac{4(h^2 + hk + l^2)}{3a^2} + \frac{l^2}{c^2}} \quad (\text{Hexagonal Structure}) \quad (5)$$

$$N = \frac{t}{D^3} \quad (6)$$

Where t is film thickness, λ is wavelength of X-ray used (1.5406 Å), β is FWHM of the peak, θ is Bragg angle, δ is dislocation density which is defined as the length of dislocation lines per unit volume of the crystal, N is number of crystallites per unit area. Higher N value indicates an abundance of crystallization. Average grain size of CuI has varied according to the media of the bath. The change of dislocation density and number of crystallites per unit area for each bath media are displayed in Figure 3.

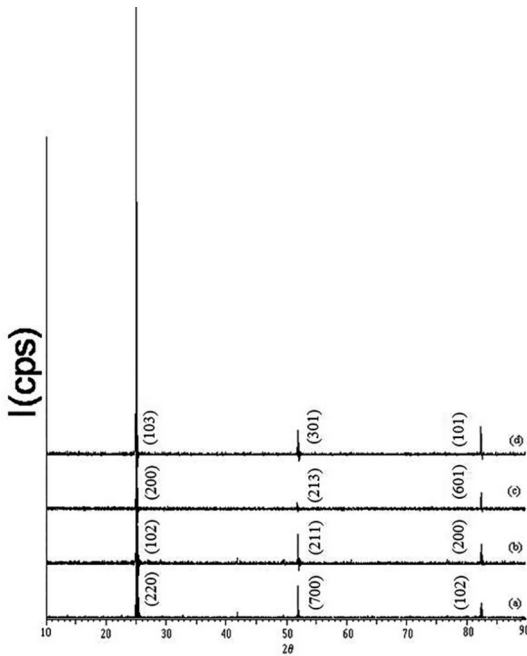


Figure 2: XRD patterns of CuI thin films formed in different media of chemical bath (a) water, (b) ethanol, (c) chloroform, (d) carbon tetrachloride

Maximum peaks of the films with γ -CuI structure, were observed at 24-25 2θ degree. Z. Zheng et al. produced CuI thin films via sonochemical method and they observed maximum peaks at 43.12-50.32 (θ) degree. They also observed peaks at 25.16-42.02 (θ) degree. K. Tennakone et al. also produced CuI films in aqueous media, on glass substrates. The film that they have produced had γ -CuI structure and they identified maximum peaks at 25.563 (θ) degrees⁸. In fact, all our peaks are compatible with ASTM data files; their structures could be easily elucidated by indexing via XRD EVA program. Actually, it is not possible to find CuI films produced via chemical extraction method, on amorphous glasses with so obvious and clearly marked XRD peaks in the literature.

Table 1: XRD patterns of CuI thin films formed in different chemical bath media.

Preparing Solutions	(hkl)	2θ (Observed)	2θ (Calculated)	I/I_0
Water	301	24.800	24.803	17.3
	220	25.060	25.021	100.0
	102	25.220	25.212	35.4
	700	51.920	51.917	12.4
	102	82.497	82.500	5.8
Ethanol	003	24.781	24.790	25.8
	102	25.060	25.074	100.0
	211	51.918	51.918	15.8
	200	82.440	82.439	10.5
CCl ₄	200	25.000	25.014	100.0
	111	25.120	25.123	13.2
	213	51.860	51.860	2.8
	601	82.440	82.439	6.8
Chloroform	004	24.740	24.742	8.8
	103	24.980	24.980	100.0
	301	51.896	51.896	5.4
	101	82.421	82.421	5.9

We even didn't need to clean the raw data that we have received from EVA program¹⁶. Of course, there is a difference between these degrees and the ones in the literature, which occurred because of different crystalline orientations formed due to different production methods. But, these values are not very big; these are the deviations acceptable by the international literature. These results were in agreement with the literature.

The highest and sharpest peaks were observed in water and ethanol, and presented in Figure 1. Hexagonal structure was seen in all CuI thin films. The biggest average grain size of CuI was observed in the film formed in the water bath, as 64 nm while the smallest was observed as 33 nm in the film from the chloroform bath. This is because the solubility of Cu^{2+} and I^- ions is lower in water and alcohol, compared to chloroform. If CuI, which was formed in these phases, is not dissolved easily in the solvent, it precipitates fast and causes the crystal to overgrowth on the surface of the substrate. The solubility of ionic types and CuI is a bit higher in chloroform compared to the other phases, which resulted with the formation of smaller crystals. The lowest dislocation density (δ) of CuI was calculated for the film prepared in water bath, whereas the highest dislocation density (δ) was found for the one formed in chloroform bath, as presented in Figure 2. Number of crystallites per unit area (N) of CuI had a different curve than dislocation density and average grain size. Number of crystallites per unit area of CuI reached its maximum value in the film obtained from the CCl_4 bath, but decreased in the one obtained from the chloroform bath.

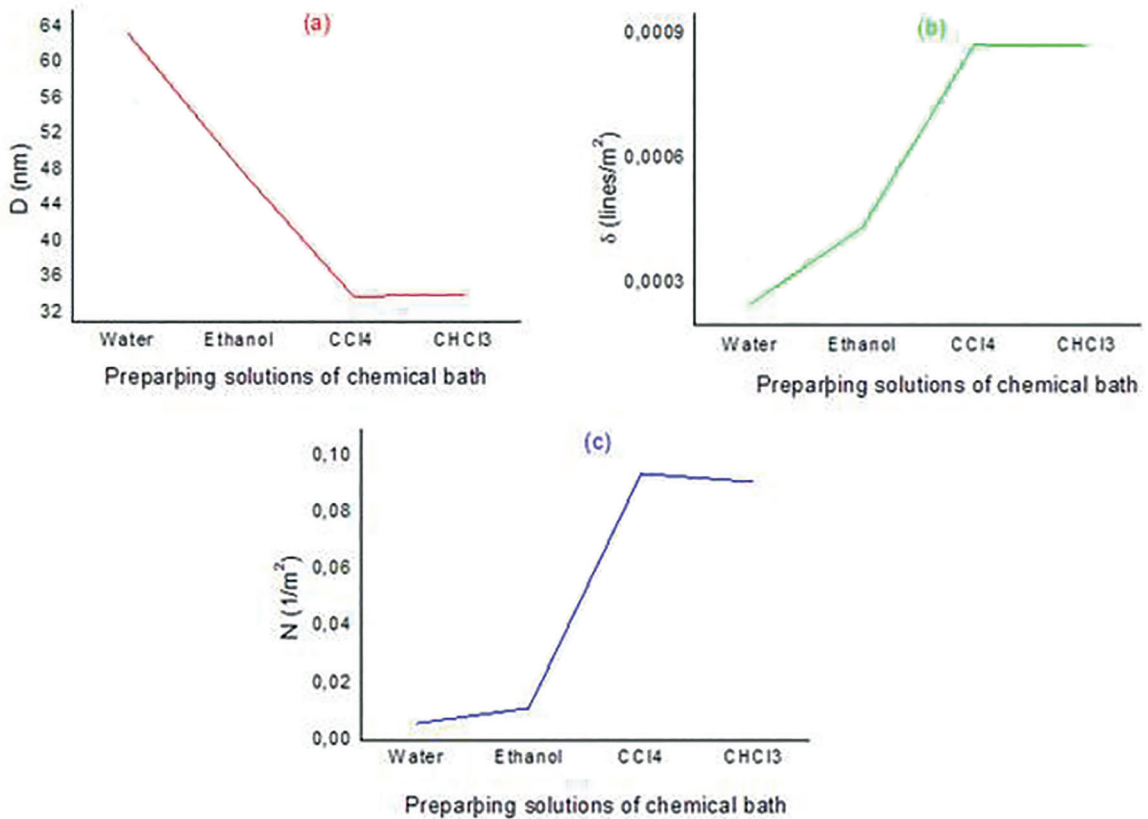


Figure 3: Average crystallite size (a), dislocation density (b), and number of crystallites per unit area (c) of CuI produced in different chemical bath media.

This result showed that the film thickness has been increased in chloroform bath. Regarding the utilization of carbon tetra chloride and chloroform, since they are immiscible with water, copper ions stayed in the water whereas iodide ions stayed in the solvent. This fact let us reflect if the film can be produced on the surface via the extraction process, a method very well-known by chemists. Although copper ions cannot pass into carbon tetra chloride and chloroform media, the transition of iodine to another media, such as water or ethanol, is possible. So, we took iodine from the other solvents, and we performed a very different extraction process in the aqueous media enriched by CuI. Chloroform has a polar structure, whereas the structure of carbon tetra chloride is apolar. Thus, iodide ions in the chloroform pass to aqueous media better than iodide ions in carbon tetra chloride. Therefore, because of the increased concentration of iodine in the water, CuI precipitation has been formed. While the film is formed on the substrate's surface, the amount of CuI in the water decreases and a portion of it formed a precipitate. In this event, the increase of the amount of iodine in the aqueous media will affect the film thickness depending on the extraction process. This effect is shown in Figure 4. However, since the whole substrate would not be

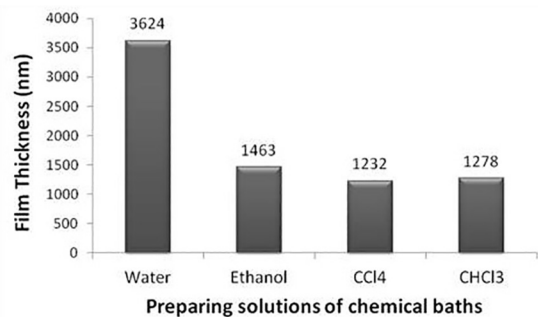


Figure 4: Film thickness of CuI thin films.

covered with the film, we had to cut a part of the substrate (the part stayed in the other solvent). But still, about half of the substrate was covered with the film.

The transmittance (T) for CuI thin film can be calculated by using reflectivity (R) and absorbance (A) spectra from the expression¹⁶:

$$T = (1 - R)^2 e^{-A} \quad (7)$$

Transmission and absorption were measured at room conditions, by scanning at the range of 300-1100 nm wavelength and the results are shown in Figure 5. Chemical

baths were prepared with different solvents. Therefore, transmissions of the films produced in different media have varied. Transmission of the film produced in chloroform bath was the highest whereas the one produced in water bath was the lowest. As mentioned above, the formation of smaller particles in chloroform media causes the films produced in this media to absorb the light less. The transmission of the materials, which absorb light less, is lower. As expected, reflectivity curves of CuI thin films were just opposite of the transmittance curves. Optical transmission of the film produced in water bath was 63 %, whereas optical transmission of the film produced in chloroform bath was 79 % (550 nm wavelengths). Reflectivity of the film produced in water bath was 12 %, whereas reflectivity of the film produced in chloroform bath was 6 % (550 nm wavelengths). Transmission increased with film thickness whereas reflection decreased with it.

Y. Yan et al. produced CuI via spraying method. They produced CuI having 35 nm grain sizes, with 65 % transmittance¹⁷. The results of the films obtained from chloroform and carbon tetra chloride baths were in accordance with the literature regarding grain size and transmittance.

Refractive index and extinction coefficient of the films are given by the following formulas¹⁶:

$$n = \frac{(1 + R)}{1 - R} + \sqrt{\frac{4R}{(1 - R)^2} - k^2} \quad (8)$$

$$k = \frac{\alpha\lambda}{4\pi} \quad (9)$$

Refractive index and extinction coefficient of CuI thin films are shown in Figure 6. Refractive index were 2.05, 2.02, 1.74 and 1.66, for the films produced in water, ethanol, carbon tetra chloride and chloroform solutions, and it is displayed in Figure 5 (550 nm wavelength). Similarly, the refractive index of the film produced in the chloroform bath, in which particle size was comparably smaller than the others, is lower. On the other hand, extinction coefficient behaved as refractive index and took values 0.014, 0.013, 0.008 and 0.007, for the films produced in the baths prepared with water, ethanol, carbon tetra chloride and chloroform, respectively (550 nm wavelength). Refractive index and extinction coefficient of CuI thin films were directly proportional to film thickness.

Scanning electron microscopy (SEM) was used to examine the effect of the bath media on the properties of film surface, as the surface properties directly affected electrical and optical properties of the films. SEM images of CuI thin films produced in different baths are presented in Figure 7. SEM analysis provided more accurate information about grain structure. As can be seen in Figure 7a–d, the size of crystallites is smaller for the films produced in chloroform and carbon tetra chloride solutions. The biggest grains were observed for the film produced in water bath. All films had insular structure (island) and had strong adherence to substrates. It can be seen in Figure 7b and 7c that in some areas CuI nanoparticles were gathered together.

These surface properties have strong effects on the optical properties of the films, such as transmittance, absorbance and reflection. So, it is seen that surface properties of CuI

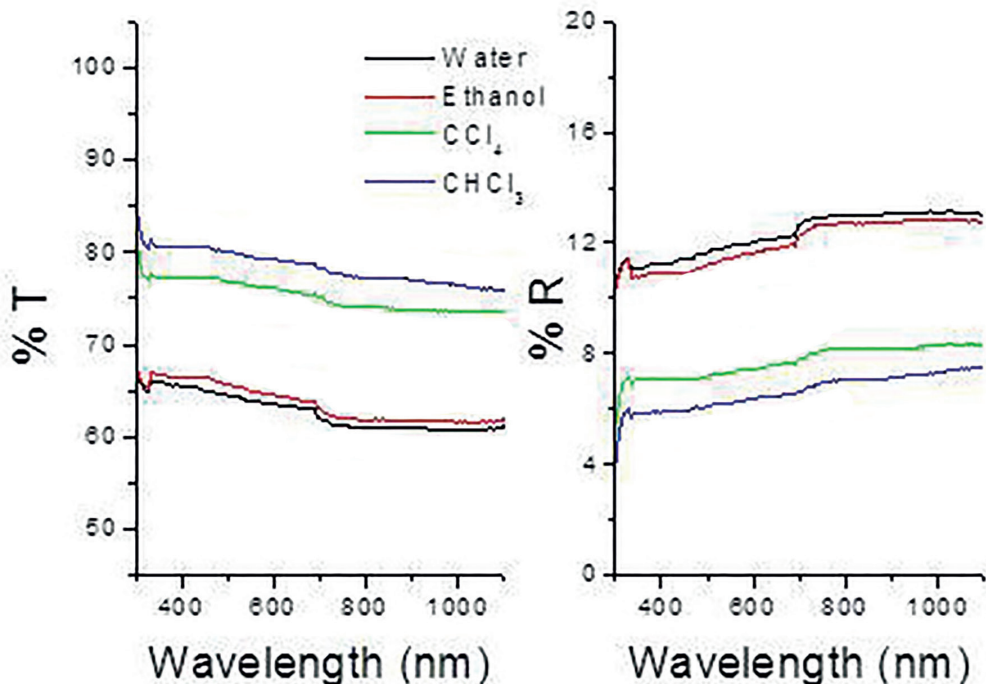


Figure 5: Transmittance (T) and reflectivity (R) of CuI thin films produced in different media.

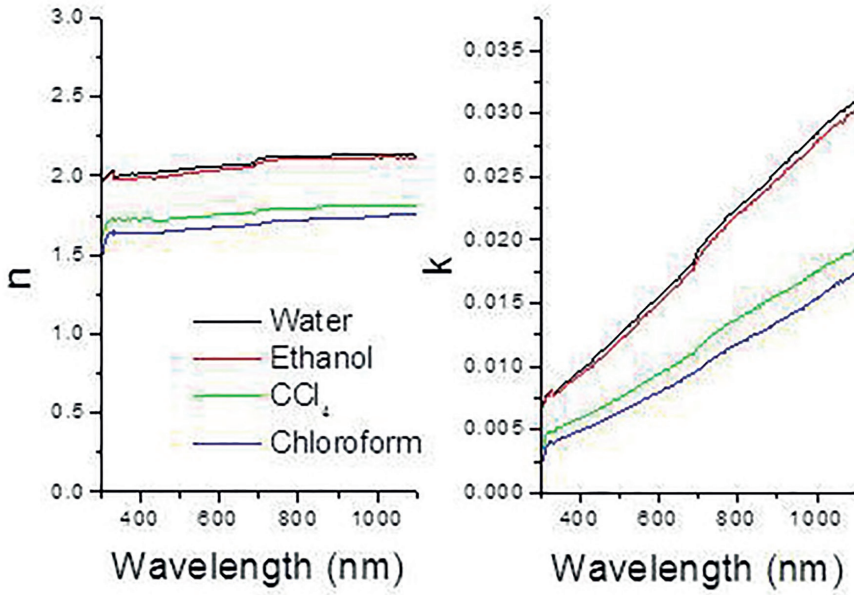


Figure 6: Refractive index (n) and extinction coefficient (k) of CuI thin films produced in different media.

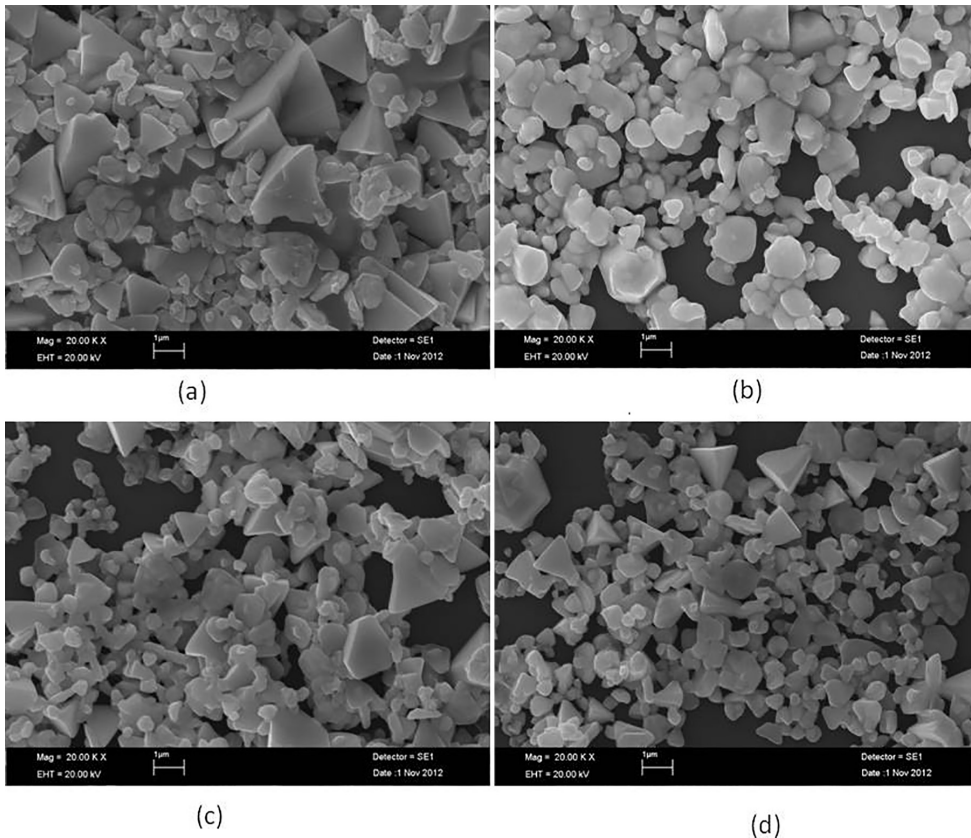


Figure 7: SEM images of CuI thin films.

films were in line with their optical properties. The lowest transmittance, the highest refractive index, and regular grain structure of CuI thin films were observed in the films

produced in water and ethanol baths⁹. Kosta et al. have also identified pebble structure for CuI¹⁸. The quality of the films that we have produced on amorphous glass through a simple,

easy and cheap method is similar to the quality of the ones that Kosta et al. have produced through electrochemical method on a crystalline structure; a similar type of surface can be seen in Figure 7a. Grundman et al, who showed that they have produced the most regular structure through SEM images, have captured particle structures similar to triangular prism, as can be seen in our SEM images¹⁹. But all these researchers have attempted to growth crystalline film on crystal substrates using devices.

The EDX technique was used to estimate the composition of CuI thin films. Figure 8 shows the average elemental molar ratio of Cu/I as a factor of chemical bath solvents. It was seen that Cu/I ratio has been changed with chemical bath's solution. EDX results indicate that the average elemental molar ratio of Cu/I was nearly equal to its stoichiometric ratio in the ethanol solution (elemental molar ratio of Cu/I = 0.458 and elemental ratio of Cu/I 29.06% / 70.94% = 0.409). The theoretical elemental molar ratio of Cu/I is 0.459 and elemental ratio of Cu is 29.16% and I is 70.84%. The EDX results are in line with XRD and SEM measurements. Since the solubility of iodine and CuI is higher in chloroform and carbon tetra chloride, Cu²⁺ ions were stuck to the surface of the substrate with the film because of the incarceration mechanism.

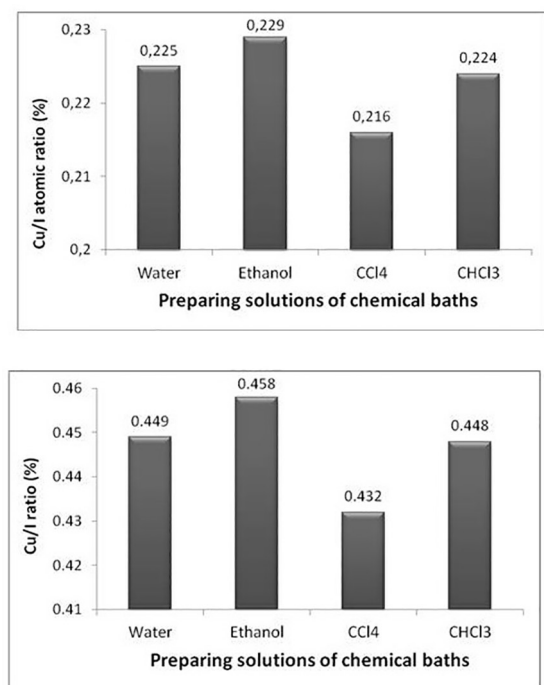


Figure 8: EDX analysis of CuI thin films produced in different media.

4. Conclusion

CuI thin film attracted the attention of the researchers because of its ionic conductivity, thus in this study we discussed what kind of CuI films we can produce using

extraction method, which is very often used by organic chemists. The aim of this study is to decide which media or solvent should be used in chemical bath for producing better CuI thin films. As a result, it has been found that CuI thin films produced in the water bath had the best crystalline form; their average grain size and film thickness were higher than the others according to XRD calculations and SEM images. Films produced in chloroform and carbon tetra chloride baths had the lowest film thickness; they were coated only on the half of the glass material. Although commercial glass is very cheap, ITO or FTO substrates are quite expensive. So, this method is not suitable for producing thin films on ITO or FTO. Finally, the film thickness and grain size can change with bath media and this is a very useful and cheap method for producing CuI in ethanol media. In addition, the ratio of Cu/I in ethanol media is almost equal to its theoretical ratio. At the same time, due to their spectroscopic properties, these films can also be used in scintillation applications. Thallium-activated NaI crystals are used to measure low-energy X- and gamma rays. CuI thin films can be used instead of it, which will be more handy and ergonomic.

5. Acknowledgement

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