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AN EFFECT OF MOLAR CONCENTRATION ON PROPERTIES OF SPRAY DEPOSITED COPPER OXIDE THIN FILMS

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Abstract- Copper(II) oxide thin films were deposited on the glass substrate by spray coating technique which simple and low-cost. We have investigated the effect of molar concentration on optical and structural properties of the films. For this reason, we used UV-Vis spectrophotometer and X-ray diffraction (XRD) spectroscopy techniques. The XRD measurement results confirmed that the deposited films are exhibited cupric oxide (CuO) phase in the monoclinic crystal structure. The optical transmittance spectra indicated that the films have high absorption in the 600-800 nm region. Band gap values of the films have been found that 1.86 eV and 1.76 eV for the 0.05 M and 0.1 M precursor concentration, respectively. The optical measurement results have showed that the band gap of CuO thin films decreased with the copper acetate concentration. It was understood from the present study that optical and structural properties of the copper oxide films can be easily controlled by the molarity of precursor solution. These results indicate that the CuO thin films can be used for photovoltaic applications.

Keywords: CuO, Thin Film, Spray Coating, Concentration, Copper Acetate.

I. INTRODUCTION

In modern material science, importance of thin films is very great. Today, thin film technology has a wide range of unique applications and thin film coating technology has been used in electronic and mechanical applications from the beginning of the 20th century to the present day [1, 2].

In recent years, metal oxide thin films with unique properties have attracted considerable attention [3, 4]. Copper Oxide is one of the first compounds as a semiconductor [5]. Silicon has begun to be used in semiconductor industry; the study on copper oxide has remained limited until the late 90's. From this date on, research and review studies have gained momentum and become a focus of interest in the world again [6]. Copper oxide thin films, especially as absorption layer for solar cells owing; to its material natural abundance, absence of toxicity and suitable semiconductor band gap characteristics [7].

Copper oxide thin films have many important applications such as photovoltaic [8-10], optoelectronic devices [11], thin film transistors [12], photo catalysts [13, 14], photo detectors [15], biosensor [16], gas sensors [17] etc. Especially, in spite of widespread use of copper oxide in heterojunction solar cells, photovoltaic performance is far from expected [18].

Copper oxide is a semiconductor formed in two basic phases: copper(I) oxide/Cu_2O and copper(II) oxide/CuO [19]. Cu_2O (cuprite or cuprous oxide); direct band gap, crystallized in cubic structure, band gap varying between 1.8-2.5 eV, mostly exhibits p-type semiconductor properties and widely used in solar cell structure due to its optical properties. CuO (Tenorite or Cupric Oxide); a semiconductor with indirect band gap, crystallized in a monoclinic structure and present p-type semiconductor behavior, with a forbidden energy gap ranged from 1.2 to 1.9 eV, close to the ideal energy range for solar cells. In recent years, CuO has so many applications in various fields such as solar cell, due to theoretical efficiency of about 20% [20, 21]. The characteristic properties of the thin films are directly dependent on the molar concentration of the precursor solution [22-24]. Therefore, in the present work, by considering applicability to solar cells, we investigated optical and structural characteristics of CuO thin films prepared with different molar concentration precursor solution.

II. MATERIAL AND METHOD

There are many methods used in thin film fabrication. Copper oxides can be prepared by many techniques, including, sol gel deposition [5, 10], Successive Ionic Layer Adsorption and Reaction (SILAR) [17], ion beam sputtering [21], spray pyrolysis [22], spin coating [25], radio frequency (RF) magnetron sputtering [26], etc. In this study, we used airbrush spraying method which is a method based on the spraying of the aqueous complex salt solution containing the atoms forming the desired compound (spray) and the precipitation of the chemical reactions on the heated substrate.

In this study, we deposited thin films by spraying a solution (the nozzle was a distance of 20-25 cm from the substrate during deposition) solution sprayed by means of a spray gun which is connected to a small compressor and called airbrush nozzle so that the solution atoms or molecules are deposited on the hot glass substrates. Compressed air was used as the carrier the pressure of gas should be 0.5 kg/cm^2. The deposited films were allowed to cool down to room temperature. In this way, many metal oxide semiconductor thin films can be formed.

In the spraying method, the solution containing the elements of the material to be obtained is sprayed on the heated substrates for a certain time by means of compressed air gas. The spraying method is the easiest and cheapest method of obtaining a thin film. In this method, setting the film thickness to the desired amount and selecting the correct starting solution are important factors. The physical properties of films obtained by this method depend on various parameters. These are the substrate temperature, the spraying speed, the distance between the substrate and the nozzle, the composition ratios of the solution (molar concentration), the spraying time and the amount of solution sprayed.

This method differs from other methods in that a large number of thin films can be prepared easily and inexpensively. But in many cases it is difficult to produce it as a quality film. On the other hand, depending on the solvent used, there are disadvantages such as quick clogging of the device needle and quick deterioration when the physical and chemical cleaning procedure is not done well.

A. Growth of Copper Oxide Films

In this work, copper oxide thin films were prepared spray method by adding copper-II acetate monohydrate [$(CH_3COO)_2Cu$, H_2O] precursor to de-ionized water which are solvent.

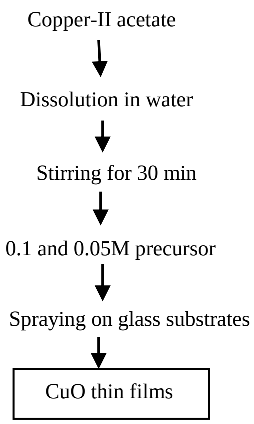

Figure 1. Diagram of experimental procedure

Firstly, the copper-II acetate monohydrate complex salt was added to de-ionized water to form 0.5 M and 1 M solution and stirred by a magnetic stirrer. Before all else, the glass substrates were cleaned in acetone and ethanol in a ultrasonic bath.

Then, the substrates rinsed de-ionized water and were dried with nitrogen atmosphere. The copper-II acetate solution of about 10 ml was transferred reservoir of airbrush spray apparatus and sprayed on microscope glasses with airbrush at constant temperatures of 250 ºC.

The solution flow rate was held 5 ml/min during spraying. As a result, brown-black color thin films were obtained. Diagram of experimental procedure is given in Figure 1.

B. Optical Properties of Copper Oxide Thin Films

Copper oxide films characterized using optical and structural techniques. In order to determine the optical properties of copper-oxide films; absorbance and transmission measurements were taken with UV-Vis spectrometry for determination of optical band-gap and semiconducting properties. X-ray diffraction studies were carried out by a Rigaku Ultima IV diffractometer to investigate the structural properties of the films. Transmission spectra were taken with a UV-Vis spectrophotometer for determination optical band gap of the films.

B.1. Transmittance Spectra of Copper Oxide Thin Films

Figure 2 shows transmittance (%T) plots of the films. According to these plots; transmittance increased exponentially from 300 nm and reached a maximum transmittance (48%) at around 900 nm wavelength. It appears that the transmittance of the films in the visible region increases while increasing wavelength of light, reaches the maximum level between 800 nm and 900 nm after dropping between 600 nm and 700 nm.

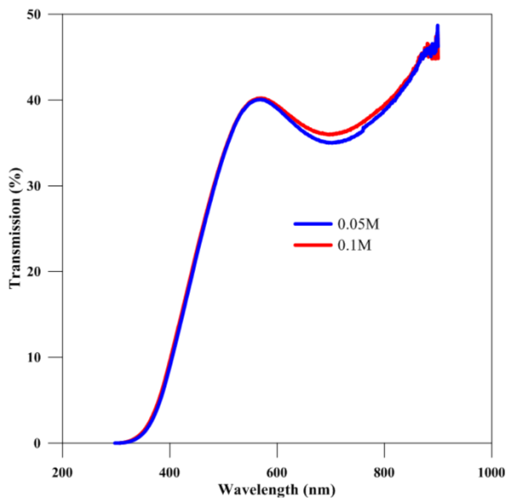

Figure 2. T (%) - λ (nm) plots of CuO thin films at different molarity

B.2. Characteristic $[\alpha(h\upsilon)]^{1/2}$-hν Plots of the Samples

The $[\alpha(h\nu)]^{1/2}$ vs $h\nu$ graphics of the thin films are given in Figure 3 for the samples prepared by 0.05 M and 0.1 M precursor concentration at constant temperature. From the plots; the optical band gap (E_g) of the films was calculated from the energy axis point of the linear portion of the curve with the help of Taue equation. According to this equation [1];

$$\alpha h\nu = \alpha_0 \left(h\nu - E_g\right)^n \quad (1)$$

where, α_0 is a constant, $h\nu$ is the photon energy, E_g is band gap energy of material and h is Planck constant. ($n = 1/2$ is the exponent for indirect allowed transition). The values are listed in the Table 1.

Table 1. Characteristics of the films with different molarity

Precursor concentration	Temperature	Maximum Transmittance	Band gap
0.1 M	250 ºC	47.8%	1.76 eV
0.05 M	250 ºC	48.6%	1.86 eV

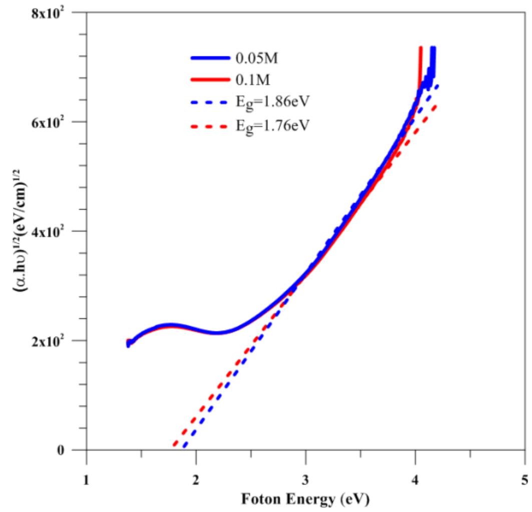

Figure 3. $[\alpha (h\upsilon)]^{1/2}$-$h\upsilon$ plots of CuO thin films at different molarity

C. X-Ray Diffraction (XRD) Analysis of Samples

The XRD structural analysis technique is based on the principle; if X-ray is sent on thin film it will reflect from characteristic lattice planes. Whether or not the thin films are in the crystal structure and the crystal orientations are determined in this way.

Figures 5 and 6 show the XRD spectrum of the thin films prepared at 0.1 and 0.05 M precursor concentration, grown at room temperature. Crystallographic properties of thin films prepared spray method at 0.05 and 0.1 M concentrations. XRD spectrum reveals that; both of the samples have polycrystalline CuO phase with a monoclinic crystal structure and with agree standard data. (PDXL named program, COD file 1011194 Quality: C card with a = 4.67 Aº, b = 3.43 Aº and c = 5.12 Aº).

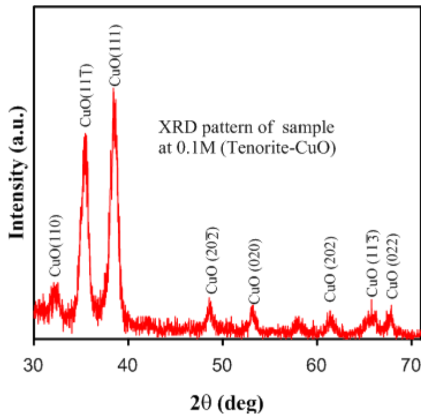

Figure 4. XRD pattern of CuO thin film synthesized at 0.1 M

Figure 4 shows XRD diffraction peaks of CuO film carried out room temperature at 0.1 M molar concentration. The XRD spectrum gave eight peaks, two of which were strong and the others are weak.

These peaks are given in Table 2 with the corresponding lattice planes in the range of 2θ angles from 30° to 70°. In the diffraction pattern of the film at 0.1 M concentration is shown in Figure 4 that the peaks are observed at 2θ = 35.44 and 2θ = 38.42 angles.

Table 2. The crystallite values of the CuO thin films

Molarity	Measured (2θ)	Density	h	k	l
0.05 M	35.52	77.9	1	1	-1
0.05 M	38.66	100	1	1	1
0.1 M	32.52	7.4	1	1	0
0.1 M	35.44	77.9	1	1	-1
0.1 M	38.42	100	1	1	1
0.1 M	48.74	29.0	2	0	-2
0.1 M	53.08	10.6	0	2	0
0.1 M	58.44	15.1	2	0	2
0.1 M	61.34	20.4	1	1	-3
0.1 M	65.76	16.3	0	2	2

In the diffraction pattern of the film at 0.05 molar concentration shown in Figure 5, peaks were observed at 2θ = 35.52 and 2θ = 38.66 angles. it is understood that these peaks belong to CuO crystal and that it is a crystal in monoclinic Tenorite phase. As seen from Table 2, the strongest peaks are appeared on the reflection planes of (11-1) and (111). (PDXL named program, COD file, 1011194 Quality: C card was used) [19, 27].

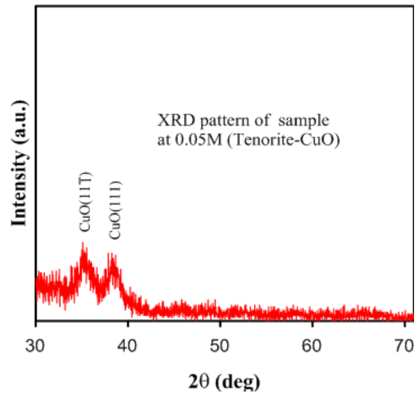

Figure 5. XRD pattern of CuO thin film synthesized at 0.05 M

III. CONCLUSIONS

CuO thin films were successfully grown onto microscope glass substrates by spray coating technique with different molar concentration and constant substrate temperature of 250 ºC. In general, the films produced with this technique are polycrystalline, stable and hard material. It was determined that the copper oxide films exhibited single-phase CuO polycrystalline property in the monoclinic crystal structure and agree with the standard data. Moreover, the change in the optical properties of the film was attributed to the increase in film thickness.

Band gap of the films 1.76 eV for 0.1 M concentration and 1.86 eV for 0.05 M precursor concentration were determined. The transmittance spectrum of CuO thin films shows a maximum transparency of near 50% in the visible region. These results indicate that the CuO thin films we produced, can be used for photovoltaic applications.

NOMENCLATURES

CuO: Tenorite or Cupric Oxide
Cu_2O: Cuprite or Cuprous Oxide
COD: Crystallography Open Database

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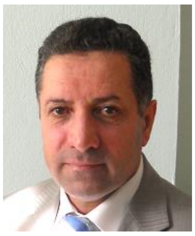

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