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COPPER OXIDE THIN FILMS PREPARED BY SPRAY COATING TECHNIQUE AS A SOLAR CELL MATERIAL: INFLUENCE OF SUBSTRATE TEMPERATURE ON GROWTH AND CHARACTERIZATION

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Abstract- In this study, copper oxide thin films were produced by airbrush spraying method and their suitability for solar cell applications were investigated and compared with the studies in this subject. For this, copper oxide thin films were produced at different substrate temperatures using the spray method and the effect of temperature on the film characteristics was investigated. For this purpose, copper-II acetate $[(CH_3COO)_2Cu.H_2O]$ solution which has the same molarity was used at four different temperatures such as 250 ºC, 300 ºC, 350 ºC and 400 ºC. From transmittance measurements, optical band gap values of the films are found 1.95 eV, 1.76 eV, 1.84 eV and 1.76 eV for 250 ºC, 300 ºC, 350 ºC and 400 ºC, respectively at constant 0.05 M precursor concentration. Atomic force microscopic (AFM) imagines confirmed that the surface morphology of the film is roughness and agree with previous studies. X-ray diffraction (XRD) pattern of the film grown at 250 ºC has a monoclinic CuO phase. It is found that band gap values of the films decrease from 1.95 eV to 1.76 eV while increasing of substrate temperature from 250 ºC to 400 ºC. The forbidden energy gap values obtained for the copper oxide films correspond to intensive part of solar spectrum. These properties of copper oxide thin films render them attractive for photovoltaic device applications.

Keywords: Copper Oxide, Solar Cell, Spray Coating, Thin Film, XRD

I. INTRODUCTION

With the interest in renewable energy sources increases, interest in solar energy and especially solar cells is also increasing [1]. Efforts to reduce the cost of solar cells and research on semiconductors used in solar cell manufacturing have also increased. At this point it is very important to produce solar cells with new materials and to improve the performance of existing materials. In recent years, thin film materials used in solar cells have been investigated with great interest [2]. As a thin film layer, the performance of materials used in solar cells highly depends on the manufacturing conditions. Using of copper oxide as the active light absorbing layer in solar cells is quite old [3].

The semiconductor band gap of this material is within the ideal limits for making a good solar cell. In recent years, despite the considerable study on this material, the targeted performance has not been achieved. However, in the studies so far, the photovoltaic performance has not reached the desired level [4].

Copper oxide have two basic semiconductor phases are cuprous oxide(Cu_2O) and cupric oxide(CuO) of cubic and monoclinic structure with band gap values of 2.0-2.6 eV and 1.3-2.1 eV, respectively. The band gaps is well matched as an absorber for photovoltaic applications. Copper oxides are both promising material for photovoltaic materials due to its suitable optical properties and the theoretical power conversion efficiency in order of 20% [5-7]. Copper oxide thin films have many important applications such as photovoltaic and optoelectronic devices, thin film transistors, photo catalysts, photo detectors, biosensor, gas sensors [8-17]. Besides these, copper oxide is seen as a promising material in thin film solar cells [18]. Both oxides have been studied extensively due to their compatibility with photovoltaic applications [19].

A wide variety of techniques have been used for deposition of copper oxide thin films, such as sol-gel deposition, spin coating, radio frequency (RF) magnetron sputtering, ion beam sputtering [20-24]. In the process of copper oxide thin film fabrication, the substrate temperature is an important parameter that determines the quality and phase of film. Copper oxide thin films produced by thermal oxidation method are formed in Cu_2O phase at annealing temperature of 200 ºC and CuO phase at annealing temperatures exceeding 300 ºC [23]. In another study, copper oxide thin films produced by sol-gel dip coating method; pure cuprite (Cu_2O) phase were obtained at 200 ºC annealing temperature. Films were obtained in the cuprite (Cu_2O) and tenorite (CuO) phase combination when annealed at 300 ºC and in the pure tenorite (CuO) phase when annealed at 450 ºC [26].

In this study, copper oxide thin films were produced at different substrate temperatures by spray coating technique and optical and morphological properties of the films were investigated. Because, the substrate temperature is an important control parameter affecting the crystal properties of thin films and strongly affects film morphology [27].

II. EXPERIMENTAL DETAILS

A. Growth of Copper Oxide Films

Spray method is an aqueous-based method known as sol-gel. In this method, a solution is first prepared which will form a semiconductor thin film and the solution is coated on the desired substrate by spraying, dipping or spinning. In this study, we used the spray method known as spray coating. The starting material, copper acetate monohydrate as solid powder, was dissolved in de-ionized water. For this, about 0.5 g of copper acetate was added to 50 ml of water and stirred with magnetic stirrer and allowed to age for 2 hours.

After the precursor solution was prepared, the microscopic glass slides used as a substrate were chemically cleaned. After the slides were cleaned with isopropanol, they were rinsed with de-ionized water and dried with nitrogen gas. Substrate heater temperature was set at 250 ºC, 300 ºC, 350 ºC and 400 ºC. Approximately 5 ml of the solution was taken at each time to fill the solution reservoir of the airbrush atomizer. The spraying process was started by operating a small air compressor connected to the sprayer. This process was repeated four times to produce dark brown thin films shown in Figure 1.

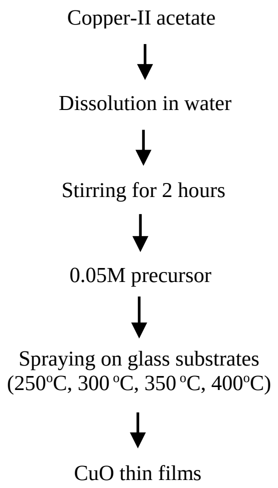

Figure 1. Experimental processing steps of copper oxide thin films

III. RESULTS AND DISCUSSION

A. UV-Visible Studies of the Copper Oxide Films

Optical transmission characteristics of copper oxide thin films deposited on glass substrate were studied by a UV-Vis spectrophotometer. Figure 2, shows the UV-Vis transmittance spectra of copper oxide films, deposited at 0.05 M constant copper acetate precursor concentration. The optical transmission of the copper oxide thin films decreases with increasing deposited temperatures. The transmittance spectra show that transmittance depends on substrate temperature and maximum transmittance is about 80%.

Optical absorption coefficient (α) was evaluated using the Beer-Lambert equation [27]:

$$\alpha = \ln T^{-1} / t \qquad (1)$$

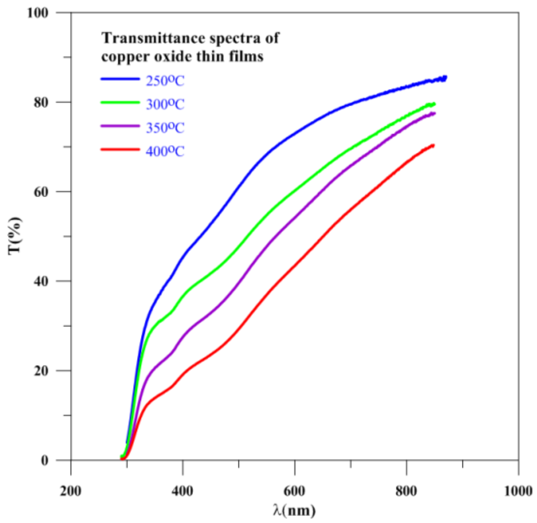

Figure 2. T(%)-λ(nm) plots of copper oxide films

where t is the film thickness and T is the optical transmittance. The optical band gap $(h\nu)$ of the material calculated with help of the Tauc's equation [28].

According to the equation; the relation, between absorption coefficient and incident photon energy can be written as

$$\alpha h\nu = \alpha_0 (h\nu - E_g)^n \qquad (2)$$

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).

According to this relation, from plot of $[\alpha(h\nu)]^{1/2}$ versus $h\nu$, the value of optical band gap (E_g) has been determined from the energy axis cutting point of the linear portion of the curve. $[\alpha(h\nu)]^{1/2}$ vs $h\nu$ graphics of the thin films are given in Figure 3.

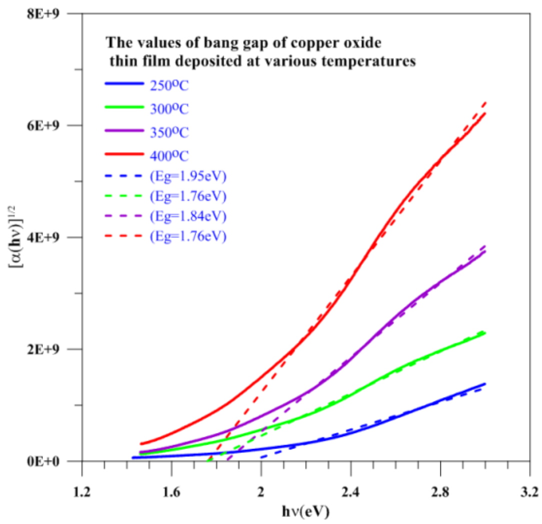

Figure 3. $[\alpha(h\nu)]^{1/2}$–$h\nu$] plots of copper oxide thin films

These measurement indicating that band gap values of the copper oxide films are in the range of 1.76-1.95 eV. Optimized deposition parameters given in Table 1.

Table 1. Characteristics of copper oxide thin films with different temperatures

Precursor concentration	Substrate temperature	Band gap energy
0.05 M	250 °C	1.95 eV
0.05 M	300 °C	1.76 eV
0.05 M	350 °C	1.84 eV
0.05 M	400 °C	1.76 eV

B. X-Ray Diffraction (XRD) Studies of the Copper Oxide Films

The crystallographic properties of the produced copper oxide thin films were analyzed with X-ray diffraction studies. Figure 4, show the XRD spectrum of copper oxide thin film grown on glass substrate at temperature of 250 °C. In this graph, diffraction peaks were observed at 2θ=35.52 and 2θ=38.66 angles and from these peaks plane orientations of the atoms were obtained. These peaks corresponding to CuO are observed in thin films which consisted of monoclinic tenorite phase with lattice parameters of a=4.67 A°, b=3.43 A° and c=5.12 A°, β=99.53° (PDXL named program, COD file, 1011194 Quality: C card was used) [29].

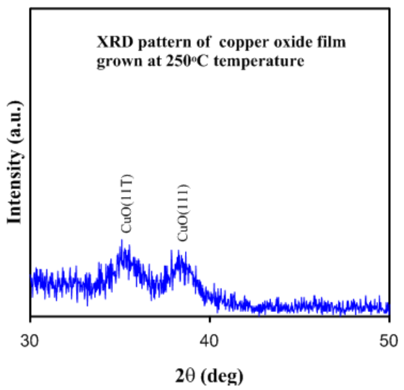

Figure 4. XRD pattern of copper oxide thin film produced on glass substrate at 250 °C

Table 2. The crystallite values of the copper oxide thin films

Molarity	Measured (2θ)	Density	h	k	l
0.05M	35.52	77.9	1	1	-1
0.05M	38.66	100	1	1	1

As seen from Table 2, the strongest peaks are appeared on the reflection planes of (11-1) and (111). Analysis of diffraction spectra indicates that the peak positions correspond to CuO phase for copper oxide films prepared at 250 °C and show (1 1 -1) and (1 1 1) planes.

C. Atomic Force Microscopy (AFM) Studies of the Copper Oxide Films

Surface morphologies of the films was characterized using atomic force microscopy (AFM). One of the AFM images of the films produced at 400 °C is shown in Figure 5. From the AFM imagine, surface morphology of the film reveal that grains have like spherical shapes. Generally, the films were homogenous and film thickness was measured to be approximately 100 nm per layer of coating.

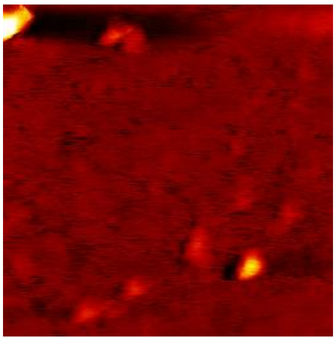

Figure 5. Morphology of copper oxide thin film produced at 400 °C

IV. CONCLUSIONS

In Summary, copper oxide thin films were prepared on microscopic glass substrate by airbrush spray coating technique at different substrate temperatures and their optical, morphological and structural properties were investigated. It was understood from the transmittance measurements that optical band gap of the copper oxide films has decreased with increasing temperature. That is, band gap values of the copper oxide films are 1.95 eV, 1.76 eV, 1.84 eV and 1.76 eV for the substrate temperature of 250 °C, 300 °C, 350 °C and 400 °C, respectively at constant 0.05M copper acetate monohidrate [$(CH_3COO)_2Cu.H_2O$] concentration. It is understood that values of the band gap energy of the films are very suitable for photovoltaic applications. As a result of the findings obtained in this study; Copper oxide thin films prepared by spray coating method at 250 °C, 300 °C, 350 °C and 400 °C substrate temperatures were found to crystallize in CuO tenorite phase. However, the films prepared more low baking temperatures are amorphous in nature. Atomic force microscopic (AFM) imagine confirmed that the surface morphology of the film is roughness and agree with previous studies.

NOMENCLATURES

CuO	Tenorite or Cupric Oxide
$CH_3COO)_2Cu.H_2O$	Copper-II acetate monohydrate
AFM	Atomic Force Microscope

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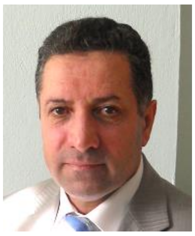

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